solves, forming a violet colored solution of soluble complexes. The $Ni(enH_2)(P_2O_7)\cdot 4H_2O$ can be reprecipitated by adding dilute hydrochloric acid until all of the violet, then blue color is discharged.

Anal. Calcd. for $Ni(enH_2)(P_2O_7)\cdot 4H_2O$: Ni, 15.98; N, 7.63; P, 16.90; H_2O, 19.62. Found: Ni, 15.88; N, 7.58; P, 17.10; H_2O (145°), 19.77. The apple green crystals were obtained in the form of prismatic spherulites.

A Tetrametaphosphate

$Na_2(enH_2)(P_4O_{12})\cdot 2H_2O$.—Brief, exploratory reactions were carried out with the various divalent metal ions, ethylenediamine and several condensed phosphates. Most such reactions led to mixtures, or to salts that have been reported by previous workers. However, when the condensed phosphate was sodium tetrametaphosphate, one single product was consistently obtained. Reactions were performed by dropping dilute hydrochloric acid into a solution of the metal ion (0.8 *M*), until the *p*H reached 1.0 or less. A quantity of sodium tetrametaphosphate equimolar to the amount of metal salt present was then added, and ethylenediamine added slowly. A precipitate appears, and remains unchanged until the *p*H is raised to at least 6.0.

Anal. Calcd. for $Na_2(enH_2)(P_4O_{12})\cdot 2H_2O$: P, 27.10; N, 6.09. Found: P, 27.07; N, 6.04.

These prismatic crystals lose no weight at 105°. Dehydration of condensed phosphates by heat above this temperature are of questionable analytical value because hydrolysis of the phosphate by the water of hydration is quite possible.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LAVAL UNIVERSITY]

Recommended Values for the Thermodynamic Properties of Hydrogen and Deuterium Peroxides[1]

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Recent spectroscopic and calorimetric data on H_2O_2 have been used to recalculate the thermodynamic functions of that compound. The contribution of the internal rotation mode was estimated using an equivalent potential barrier height of 4.45 kcal. based on the third law entropy. Similar calculations were carried out for the isotopic molecules D_2O_2 and HDO_2. Various derived thermodynamic quantities of the peroxide molecules are tabulated for convenience. From these the dissociation energy *D*(HO–OH) is found to be 51 kcal. at 0°K.

A few years ago one of us calculated the thermodynamic functions for hydrogen peroxide and some of its most important reactions.[2] Since then new spectroscopic[3] and calorimeteric measurements[4,5] have been reported which justify revision of these quantities of fundamental interest. The major uncertainty in the previous values arose from the internal rotation mode about which little definite information was then available. Thanks to the recent determination of the calorimetric entropy[4] the uncertainty has now been reduced significantly. This was confirmed by treating the internal rotation by an alternate method, which gave very nearly the same values of the thermodynamic quantities for all temperatures up to 1500°K. Further improvements in the accuracy of these data will have to await more complete knowledge of the height and shape of the potential barriers restricting mutual rotation of the OH groups. Also, because the peroxide molecule is not a very rigid one, such terms as anharmonicity of vibrations and centrifugal stretching may become significant at high temperatures.

The same structural parameters were assumed for the three isotopic molecules,[3] namely: $r_{O-H} = r_{O-D} = 0.965$ Å.; $r_{O-O} = 1.49$ Å.; $\alpha_{OOH} = \alpha_{OOD} = 100°$; $\phi = 95°$. The calculated moments of inertia and the vibrational frequencies are listed in Table I. Obviously those for the hybrid molecule HDO_2 are less accurately known than for the other two. The external symmetry number of that molecule is only 1, and the reduced moment for internal rotation is given with sufficient accuracy by the expression

$$I_{\text{red.}} = \frac{I_A \times I_A'}{2(I_A + I_A')} \qquad (1)$$

where I_A and I_A' are the small moments of inertia of H_2O_2 and D_2O_2, respectively.

TABLE I

MOLECULAR DATA FOR THE THREE ISOTOPIC PEROXIDES

Vibrational frequencies, cm.$^{-1}$

	H_2O_2	D_2O_2		HDO_2
ν_1	3610	2660	ν_{OH}	3610
ν_2	1350	1015	ν_{OD}	2660
ν_3	880	880	δ_{OH}	1310
ν_4	520	400 (?)	δ_{OD}	980
ν_5	3610	2660	ν_{OO}	880
ν_6	1266	947	δ_{torsion}	450 (?)

Moments of inertia (in 10^{-40} g. cm.^{2})

	H_2O_2	D_2O_2	HDO_2
I_A	2.785	5.14	3.98
I_B	34.0	38.3	35.9
I_C	33.8	37.9	36.6
$I_{\text{red.}}$	0.696	1.29	0.90

The question of internal rotation was dealt with by the method of Pitzer[6] for unsymmetrical tops attached to a rigid frame. According to that treatment the OH group is classified among those with a relatively small "off balance" factor. Such simplification is justified in the case of H_2O_2 (and to a slightly lesser extent for D_2O_2) as confirmed by the moderate change in the over-all moments of inertia with internal rotation.[7] Although the potential

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[1] This work was supported by the U. S. Air Force, through the Office of Scientific Research of the Air Research Development Command.

[2] P. A. Giguère, *Can. J. Research*, **B28**, 485 (1950).

[3] (a) P. A. Giguère and O. Bain, *J. Phys. Chem.*, **56**, 340 (1952); (b) O. Bain and P. A. Giguère, *Can. J. Chem.*, **33**, 527 (1955).

[4] P. A. Giguère, I. D. Liu, J. S. Dugdale and J. A. Morrison, *ibid.*, **32**, 117 (1954).

[5] P. A. Giguère, B. G. Morisette, A. W. Olmos and O. Knop, *ibid.*, **33**, 804 (1955).

[6] K. S. Pitzer, *J. Chem. Phys.*, **14**, 239 (1946).

[7] P. A. Giguère, *ibid.*, **18**, 88 (1950).

TABLE II

RECOMMENDED VALUES FOR THE THERMODYNAMIC FUNCTIONS OF GASEOUS HYDROGEN AND DEUTERIUM PEROXIDES AT 1 ATM.

Temp., °K.	$-\frac{(F^0 - H_0^0)}{T}$, cal./deg. mole			$-\frac{H^0 - H_0^0}{T}$, cal./deg.mole			S^0, cal./deg. mole			C_p^0, cal./deg. mole		
	H_2O_2	HDO_2	D_2O_2	H_2O_2	HDO_2	D_2O_2	H_2O_2	HDO_2	D_2O_2	H_2O_2	HDO_2	D_2O_2
298.16	46.95	48.98	48.18	8.70	8.87	9.09	55.66	57.86	57.28	10.31	10.68	11.14
300	47.00	49.04	48.24	8.74	8.88	9.10	55.72	57.92	57.35	10.33	10.71	11.17
350	48.36	50.44	48.66	8.99	9.19	9.45	57.35	59.63	59.13	10.98	11.40	11.91
400	49.59	51.67	50.97	9.28	9.51	9.80	58.87	61.19	60.76	11.58	12.01	12.56
500	51.72	53.87	53.21	9.84	10.11	10.46	61.51	63.99	63.68	12.56	13.03	13.59
600	53.56	55.76	55.15	10.36	10.67	11.05	63.91	66.43	66.23	13.31	13.78	14.34
700	55.20	57.44	56.91	10.83	11.15	11.56	66.02	68.60	68.48	13.86	14.35	14.92
800	56.66	58.96	58.49	11.24	11.55	12.01	67.91	70.45	70.51	14.30	14.82	15.40
900	57.90	60.34	59.92	11.60	11.97	12.41	69.61	72.32	72.35	14.69	15.22	15.81
1000	59.15	61.63	61.25	11.92	12.31	12.76	71.17	73.94	74.03	15.02	15.57	16.14
1100	60.31	62.43	62.49	12.22	12.62	13.09	72.62	75.44	75.59	15.33	15.88	16.45
1200	61.40	63.93	63.64	12.49	12.90	13.38	73.96	76.83	77.03	15.61	16.15	16.72
1300	62.41	64.97	64.72	12.74	13.16	13.64	75.23	78.13	78.37	15.87	16.40	16.94
1400	63.40	65.96	65.74	12.97	13.40	13.89	76.43	79.36	79.64	16.11	16.62	17.14
1500	64.28	66.89	66.70	13.19	13.61	14.11	77.53	80.51	80.83	16.33	16.80	17.31

curve undoubtedly contains a high (*cis-*) and a low (*trans-*) maxima, the presence of two equal minima is of greater significance for the thermodynamic properties, so that a symmetry member $n_m = 2$ is a satisfactory approximation.

The barrier height for H_2O_2 was obtained from Table IV of Pitzer and Gwinn.[8] Thus from the third law entropy value, 55.66 cal./deg. mole,[4,9] we get for the entropy decrease from free rotation (S_f — S) = 57.20 − 55.66 = 1.54 cal./deg. mole, which corresponds to 4.45 kcal. for the height of an hypothetical twofold barrier. As a first approximation the same quantity was used for the three isotopic molecules.

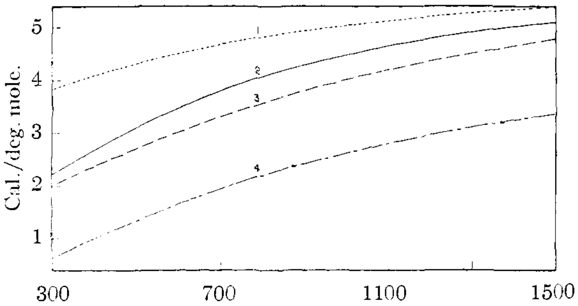

Fig. 1.—Contribution of the internal rotation mode to the entropy of gaseous hydrogen peroxide assuming: 1, free rotation; 2, hindered rotation; 3, double minimum oscillation; 4, torsional vibration.

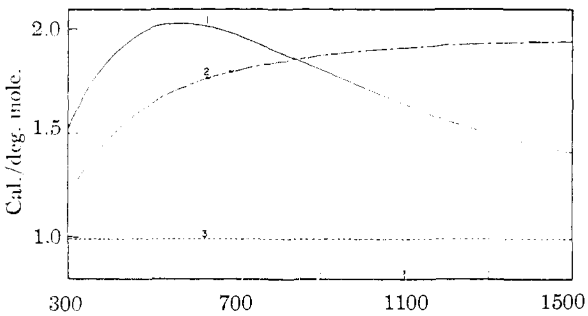

Fig. 2.—Contribution of the internal rotation mode to the heat capacity of gaseous hydrogen peroxide on the assumption of: 1, hindered rotation; 2, double minimum oscillation; 3, free rotation.

To check the adequacy of this treatment the internal mode was next considered as a double minimum oscillation[10] with a frequency of 520 cm.$^{-1}$, the average value found experimentally for the doublet of ν_4. According to this second method the standard entropy is 55.42 cal./deg. mole, and the other thermodynamic functions agree quite closely with the present values, the greatest deviation (of the order of 3%) occurring for the specific heat. An idea of the relative importance of the internal rotation may be had from Figs. 1 and 2 where the contributions to entropy and heat capacity are illustrated for various cases. It may be mentioned here that the use of a symmetrical potential function with a single minimum as was done before[4] is not particularly suitable here as indicated by a too high value of the specific heat, 11 cal./deg. mole at 25°. No direct determination of this property has been reported yet for H_2O_2 but various estimates, based either on heat of vaporization[5,11] or vapor pressure data,[12] point to 9.5–10 at ordinary temperature.[13] The two equations

$$C_p\,(H_2O_2) = 12.471 + 2.746 \times 10^{-3}T - 0.2818 \times 10^6T^{-2} \quad (2)$$

and

$$C_p\,(D_2O_2) = 13.698 + 2.634 \times 10^{-3}T - 0.3130 \times 10^6T^{-2} \quad (3)$$

fit the data in Table II to within 2%.

From the calculated thermodynamic functions and the pertinent data in the compilation of the National Bureau of Standards[14] the heat, free energy and equilibrium constants for the formation,

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[8] K. S. Pitzer and W. D Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

[9] P. A. Giguère, *Can. J. Chem.*, **32**, 1161 (1954).

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[13] I. D. Liu, Ph.D. Thesis, Laval University, 1954.

[14] F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular No. 500, Washington 1952.

the decomposition into water vapor and oxygen and the dissociation into radicals, of gaseous hydrogen peroxide were calculated for temperatures up to 1500°K. The basis for such calculations is, obviously, the measured heat of decomposition of the pure liquid peroxide, 23.44 ± 0.02 kcal./mole at 25°, according to the most recent determination.[5] This, combined with the heat of vaporization of the liquid, 12.34 ± 0.03 kcal./mole, led to the various quantities in Tables III, IV and V. Thus, the heat of dissociation into OH radicals is found to be 51 kcal. at 0°K. and 52.6 at 25°. A variety of values ranging from 46.3[15] up to 55.6[16] have been published before based either on somewhat less accurate calorimetric data for H_2O_2 or on different estimates of the dissociation energy of OH.

TABLE III

HEAT, FREE ENERGY AND EQUILIBRIUM CONSTANT FOR THE FORMATION OF GASEOUS HYDROGEN AND DEUTERIUM PEROXIDES

T, °K.	ΔH^0, kcal./mole		ΔF^0, kcal./mole		$\log_{10}K$	
	H_2O_2	D_2O_2	H_2O_2	D_2O_2	H_2O_2	D_2O_2
0	−31.04	−33.05	−31.04	−33.05		
298.16	−32.53	−34.45	−25.20	−26.59	18.47	19.49
300	−32.53	−34.45	−25.16	−26.54	18.33	19.34
400	−32.84	−34.67	−22.66	−23.87	12.38	13.04
500	−33.06	−34.79	−20.06	−21.15	8.98	9.24
600	−33.22	−34.85	−17.46	−18.42	6.36	6.71
700	−33.34	−34.88	−14.83	−15.68	4.63	4.90
800	−33.43	−34.90	−12.10	−12.96	3.33	3.54
900	−33.51	−34.88	− 9.52	−10.19	2.31	2.47
1000	−33.58	−34.85	− 6.85	− 7.46	1.49	1.63
1100	−33.62	−34.84	− 4.18	− 4.71	0.82	0.94
1200	−33.65	−34.80	− 1.49	− 2.11	0.27	0.38
1300	−33.68	−34.77	1.28	0.74	−0.22	−0.12
1400	−33.70	−34.74	3.84	3.45	−0.61	−0.54
1500	−33.71	−34.67	6.55	6.21	−0.96	−0.90

TABLE IV

HEAT, FREE ENERGY AND EQUILIBRIUM CONSTANT FOR THE DECOMPOSITION OF GASEOUS HYDROGEN AND DEUTERIUM PEROXIDES

T, °K.	ΔH^0, kcal./mole		ΔF^0, kcal./mole		$\log_{10}K$	
	H_2O_2	D_2O_2	H_2O_2	D_2O_2	H_2O_2	D_2O_2
0	−26.07	−25.81	−26.07	−25.81		
298.16	−25.27	−25.10	−29.42	−29.46	21.56	21.59
300	−25.27	−25.10	−29.45	−29.48	21.46	21.48
400	−25.19	−25.10	−30.85	−30.95	16.85	16.91
500	−25.21	−25.18	−32.30	−32.40	14.11	14.16
600	−25.27	−25.29	−33.68	−33.83	12.27	12.32
700	−25.36	−25.42	−35.07	−35.28	10.95	11.01
800	−25.47	−25.54	−36.45	−36.64	9.95	10.01
900	−25.57	−25.67	−37.82	−38.03	9.18	9.23
1000	−25.66	−25.78	−39.18	−39.38	8.56	8.60
1100	−25.77	−25.90	−40.52	−40.85	8.06	8.11
1200	−25.86	−25.99	−41.87	−42.09	7.62	7.66
1300	−25.94	−26.08	−43.19	−43.42	7.26	7.30
1400	−26.03	−26.18	−44.48	−44.77	6.94	6.98
1500	−26.11	−26.25	−45.83	−46.09	6.67	6.71

TABLE V

HEAT, FREE ENERGY AND EQUILIBRIUM CONSTANT FOR THE DISSOCIATION OF GASEOUS HYDROGEN AND DEUTERIUM PEROXIDES INTO RADICALS

T, °K.	ΔH^0, kcal./mole		ΔF^0, kcal./mole		$\log_{10}K$	
	H_2O_2	D_2O_2	H_2O_2	D_2O_2	H_2O_2	D_2O_2
0	51.04	51.99	51.04	51.99		
298.16	52.65	53.56	43.07	43.63	−31.57	−31.98
300	52.65	53.56	43.00	43.55	−31.33	−31.72
400	52.98	53.81	39.74	40.20	−21.71	−21.96
500	53.18	53.92	36.38	36.78	−15.90	−16.07
600	53.29	53.95	33.04	33.35	−12.03	−12.14
700	53.34	53.93	29.66	29.91	− 9.26	− 9.34
800	53.35	53.88	26.28	26.49	− 7.18	− 7.23
900	53.35	53.82	22.89	23.06	− 5.55	− 5.60
1000	53.32	53.75	19.51	19.66	− 4.26	− 4.29
1100	53.28	53.67	16.13	16.25	− 3.20	− 3.22
1200	53.22	53.60	12.74	12.86	− 2.32	− 2.34
1300	53.18	53.53	9.39	9.46	− 1.57	− 1.59
1400	53.12	53.44	6.05	6.07	− 0.94	− 0.95
1500	53.05	53.36	2.66	2.68	− 0.38	− 0.39

For D_2O_2, no experimental determination of the heat of decomposition being available, a reliable estimate may be secured from consideration of the zero-point energy differences. On the assumption that the bond energies are the same for isotopic molecules the heat of formation of the two peroxides at 0°K. are related as

$$\Delta H^0_{0D_2O_2} = \Delta H^0_{0H_2O_2} + (\epsilon_{D_2O_2} - \epsilon_{H_2O_2}) - (\epsilon_{D_2} - \epsilon_{H_2}) \quad (4)$$

where the ϵ's are the zero-point energies. These quantities are known accurately for H_2 and D_2,[17] their difference amounting to 1.786 kcal./mole. For the peroxide molecules a satisfactory approximation (3.80 kcal.) is obtained from the half-sum of the frequencies of the first-order vibrations.[3] The error from neglecting the anharmonicity constant is, indeed, negligible since only the differences enter into the calculations. The heat of formation of D_2O_2 thus found, −33.05 kcal./mole, was combined with the recently calculated thermal properties for deuterium gas,[18] heavy water[19] and the OD radical[20] to arrive at the thermodynamic functions for the reactions of the isotopic peroxide (Tables III, IV and V).

Acknowledgment.—The authors are grateful to Dr. K. S. Pitzer for his enlightening comments on the question of internal rotation.

QUEBEC, CANADA

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