2. The decomposition pressure of the anhydrous normal sulfate reaches one atmosphere at about 810°.

3. P_H measurements of indium sulfate solutions show that a considerable degree of hydrolysis occurs.

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Heat Capacity Curves of the Simpler Gases. III. Heat Capacity, Entropy and Free Energy of Neutral OH from Near Zero Absolute to 5000°K.

BY HERRICK L. JOHNSTON AND DAVID H. DAWSON[1]

One of the interesting developments in chemistry during the past decade has been the discovery of hitherto unsuspected, and even unorthodox, molecules which often play important roles during the intermediate stages of chemical reactions. Among the more important of these is the neutral OH molecule, present in flames and often formed in gaseous reactions in which hydrogen and oxygen are present in either the free or combined forms. The importance of this molecule, particularly in connection with reactions at high temperatures, warrants the computation of tables of its thermodynamic properties, for use in equilibrium calculations. Its spectrum, although complicated, has been satisfactorily worked out and so permits application of the accurate methods employed in earlier papers[2] of this series. Added interest is attached to the heat capacity curve at low temperatures due to the influence of an unusually large Λ type doubling. While no immediate practical importance attaches to this in connection with OH itself it typifies an effect sometimes present to a lesser degree in the heat capacity curves of other, more stable molecules.

In the following pages we make tabulations of heat capacity, entropy, "free energy" and "total" energy to a maximum temperature of 5000°K. For a description of the details of the methods which we have employed in our calculations and for the meanings of symbols which are employed in the following pages without redefinition the reader is referred to the paper by Johnston and Chapman.[2a]

Spectroscopic Interpretation of Neutral OH.—The ultraviolet "water vapor" bands were among the earliest molecular spectra to undergo examination,[3] and have been the subject of numerous subsequent investiga-

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(1) Du Pont Fellow in Chemistry, Academic Year 1932–1933.

(2) (a) Johnston and Chapman, THIS JOURNAL, **55**, 153 (1933); (b) Johnston and Walker, *ibid.*, **55**, 172, 187 (1933).

(3) Liveing and Dewar, *Proc. Roy. Soc.* (London), **30**, 498, 580 (1880); *ibid.*, **33**, 274 (1882); *Phil. Trans.*, **129**, 271 (1880); *cf.* also Deslandres, *Ann. chim. phys.*, **14**, 257 (1888); *Compt. rend.*, **100**, 854 (1888).

tions.[4,8] At one time assigned to H_2O, then to O_2,[5] the bands were eventually identified with the neutral OH molecule.[6] From the fact that the bands occur in absorption[7] it is evident that the ground state of the bands is the normal state of the molecule.

For a complete résumé of the band structure, and its interpretation, the reader is referred to Mulliken,[4] who has admirably summarized our knowledge of the rotational structure. We present here only those facts essential to the calculations in the present paper.

The ground state of neutral OH is an inverted $^2\Pi$ state with a doublet separation, at the origin, of 140.3 cm.$^{-1}$ (399 calories per mole). Johnston, Dawson and Walker[8] find that the vibrational energies, in either the $^2\Pi_{1/2}$ state or the $^2\Pi_{3/2}$ state, are closely reproduced by the formula

$$\tilde{\nu} = 3734.9\, v - 82.6\, (v^2 + v) \tag{1}$$

where $\tilde{\nu}$ refers to the energy (in wave number units) in excess of the "zero point" vibrational energy held in the ($v = 0$) level.

Kemble[9] gives two equations for the rotational energy. One, which empirically reproduces the levels, except for Λ type doubling, up to and including $K = 5$ but deviates rapidly at higher quantum numbers, is of the form

$$F(J) = B^*[(J + {}^1/_2)^2 - \Lambda_0^2] + D^*[(J + {}^1/_2)^2 - \Lambda_0^2] \tag{2}$$

while the other, which reproduces the data for the higher levels with a fair degree of accuracy but does not fit for low quantum numbers, may be put in the form

$$F(K) = B\left[(K + {}^1/_2)^2 - \Lambda^2 + \frac{D}{B}(K + {}^1/_2)^4 \pm \frac{P(P + 2\propto)S^3}{(K + {}^1/_2)}\right] \tag{3}$$

Here K. which may assume integral values from 1 to ∞, is the rotational quantum number and is equal to $(J + {}^1/_2)$ for the $^2\Pi_{1/2}$ state and to $(J - 1/2)$ for the $^2\Pi_{3/2}$ state, where J is the total angular momentum. The constants appropriate to these equations, for OH, are given by Kemble and are listed in Table I.

Although these equations do not, in themselves, reproduce the experimental data to within the limits of accuracy of the latter, by means of a deviation plot which compared energies calculated by equations (2) and (3) with those obtained directly from the spectrum by appropriate combina-

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(4) Among the more notable of these are: Grebe and Holtz, *Ann. Physik*, **39**, 1243 (1913); Heurlinger, Dissertation, Lund (1918); Fortrat, *J. Phys. Radium*, **5**, 20 (1924); Watson, *Astrophys. J.*, **60**, 145 (1924); Dieke, *Proc. Acad. Sci. Amsterdam*, **28**, 174 (1925); Jack, *Proc. Roy. Soc.* (London), **A115**, 373 (1927); *ibid.*, **A118**, 647 (1928); Mulliken, *Phys. Rev.*, **32**, 388 (1928); Almy, *ibid.*, **35**, 1495 (1930).

(5) Steubing, *Ann. Physik*, **33**, 553 (1910); **39**, 1408 (1912); Reiss, *Z. physik. Chem.*, **88**, 513 (1914). See also Fortrat, Ref. 4.

(6) *Cf.* Watson, and Mulliken, Ref. 4, and also Bonhoeffer and Reichardt, *Z. physik. Chem.*, **139**, 75 (1929).

(7) Hulthen and Zumstein, *Phys. Rev.*, **28**, 13 (1926); E. D. Wilson, *J. Opt. Soc. Am.*, **17**, 37 (1918); and also *cf.* Bonhoeffer and Reichardt, Ref. 6.

(8) Johnston, Dawson and Walker, *Phys. Rev.*, **43**, 473 (1933).

(9) Kemble, *Phys. Rev.*, **30**, 387 (1927).

TABLE I

ROTATIONAL CONSTANTS FOR OH (KEMBLE'S EQUATIONS)

B^* (for $^2\Pi_{3/2}$ levels) $= 16.60$ B^* (for $^2\Pi_{1/2}$ levels) $= 20.565$
D^* (for $^2\Pi_{3/2}$ levels) $= 0.0129$ D^* (for $^2\Pi_{1/2}$ levels) $= -0.0237$
Λ_0 (for $^2\Pi_{3/2}$ levels) $= 3/2$ Λ_0 (for $^2\Pi_{1/2}$ levels) $= 1/2$
$B = 18.479$ $D = -0.0018$ $P = 7.595$
$\Lambda = 1$ $s = 1/2$ $\alpha = \Lambda/s = 2$

tions of the rotational lines we were able to obtain smoothed values of the latter and to extrapolate for the higher rotational levels without appreciable inaccuracy.[10]

The Λ type doubling of the rotational levels, in OH, is unusually large and cannot be disregarded in preparing the sums, as was the case in NO.[2a] However, the experimental values of the Λ separations are well reproduced by the equation of Mulliken[4]

$$F_A''(J) - F_B''(J) = CJ^2 \qquad (4)$$

where $C = 0.04$ cm.$^{-1}$ for the $^2\Pi_{3/2}$ levels and 0.03 for the $^2\Pi_{1/2}$ levels. Accordingly, we calculated the energies of the respective A and B sublevels by the respective addition, or subtraction, of one-half the amount calculated by equation (4),[11] to the rotational energies calculated with the aid of equations (2) and (3). This procedure was necessary since the rotational energy equations neglect the Λ doubling and lead to *average* rotational energies of the component levels.

It was found unnecessary to consider the excited $^2\Sigma$ state of OH since this electronic level makes no contribution to the specific heat below 5000°K. No other electronic levels are known for OH.

Statistical weights are given by $p_i = 2\,(2J + 1)$, where the factor 2 outside of the parenthesis arises from the $^1/_2$ unit of nuclear spin associated with the hydrogen nucleus. However, since it is convenient to exclude the nuclear spin contribution in carrying out thermodynamic calculations,[12] we made our computations with the aid of the relationship

$$p_i = (2J + 1) \qquad (5)$$

The Heat Capacities and Entropy.—Molar heat capacities of neutral OH in the hypothetical ideal gaseous state have been calculated with the aid of equation (2), and the entropies with the aid of equation (3), of the paper of Johnston and Chapman.[2a] Values of the heat capacities and of the entropies from 200 to 5000°K. are given in Table II.

(10) The use of Hill and Van Vleck's quantum mechanically correct equation [*Phys. Rev.*, **32**, 250 (1928).] with the constants evaluated by Johnston, Dawson and Walker (Ref. 8) would have been preferable to the procedure which we employed both in point of convenience and of accuracy. However, the method which we followed yields the rotational energies with sufficient exactness to permit the calculation of heat capacities, free energies, etc., to within the limits of error imposed by other factors.

(11) As equation (4) is not applicable to the $^2\Pi_{1/2}$ levels below $J = 9/2$, these doublets were calculated directly from the experimental data.

(12) (a) Giauque and Johnston, *Phys. Rev.*, **36**, 1592 (1930); (b) Giauque, THIS JOURNAL, **52**, 4816 (1930).

TABLE II

HEAT CAPACITY AND ENTROPY OF NEUTRAL OH IN THE IDEAL GASEOUS STATE[13]

T, °K.	C_p°	S°	T, °K	C_p°	S°
250	7.195	42.644	1125	7.476	53.379
298.1	7.139	43.905	1250	7.613	54.174
350	7.098	45.048	1375	7.750	54.905
400	7.072	45.995	1500	7.881	55.860
500	7.047	47.569	1750	8.114	56.818
600	7.053	48.856	2000	8.311	57.915
700	7.087	49.943	2500	8.611	59.803
800	7.150	50.893	3000	8.844	61.396
900	7.236	51.740	4000	9.165	63.989
1000	7.336	52.508	5000	9.509	66.074

Values of heat capacity have also been calculated below 250°K. in order to ascertain the influences both of the Λ doubling, which produces a sharp maximum in the heat capacity curve at about 0.06°K., and of the spin doubling (the $^2\Pi$ doublet), which leads to a maximum at about 100°K. The effect of the Λ doubling is shown in Fig. 1. A similar effect in nitric oxide, leading to a maximum at very much lower temperatures than for OH, was predicted by Johnston and Chapman.[14] For nitric oxide this factor had already made its contribution of R ln 2 to the entropy of the gas at temperatures well below 0.01°K. while, for OH, the contribution from the Λ-type doubling is made, in its entirety, between about 0.01 and 1°K. Figure 2 shows the heat capacity curve from 1 to 250°K. The absorption of energy by molecules passing from the $^2\Pi_{3/2}$ levels into the $^2\Pi_{1/2}$ levels is clearly evident. The broken curve was calculated by arbitrarily omitting the contributions of the $^2\Pi_{1/2}$ levels from the sums in the heat capacity equation. Since higher vibrational levels are not yet effective over this range of temperature, the dotted curve represents the rotational specific heat of the molecule. As in hydrogen[15] this effect occurs in OH at comparatively high temperatures and the attainment of rotational equipartition

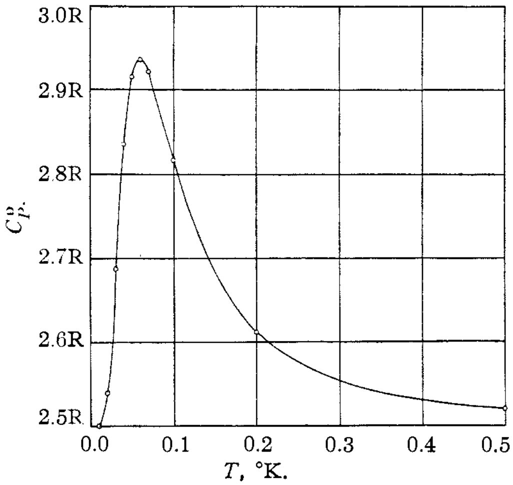

Fig. 1.—Heat capacity of OH, illustrating the effect of Λ type doubling.

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(13) These values include translation. The entropies are for a pressure of one atmosphere and the nuclear spin entropy is not included.

(14) *Cf.* Ref. 2a, p. 166.

(15) Eucken, *Sitzb. preuss. Akad. Wiss.*, 144 (1912); *Ber. deut. physik. Ges.*, **18**, 4 (1916).

covers a large interval of temperature. As the curves show, the growth of the rotational specific heat occurs almost simultaneously with the spin coupling contribution, in this instance.

We extended our calculations of the hypothetical pure rotation curve to 5000°K. by purposely omitting from the sums the contributions of all levels except the rotational levels of the normal vibrational state of the $^2\Pi_{3/2}$ molecule. As in nitric oxide and in oxygen[2] this led to values in excess of the rotational equipartition, at the higher temperatures, due to molecular stretching. For OH, the pure rotation curve exceeds rotational equipartition at about 1200 and at 5000°K., the sketching contribution amounts to 0.18 calorie. The vibrational contribution at 5000° exceeds that calculated from the Planck–Einstein equation by 0.52 calorie. This is considerably larger than the corresponding effect in either nitric oxide or oxygen, in spite of the fact that the vibrational contributions enter at higher temperatures for OH, and is a consequence of the fact that the OH molecule is farther removed from the ideal harmonic oscillator than is either NO or O_2.

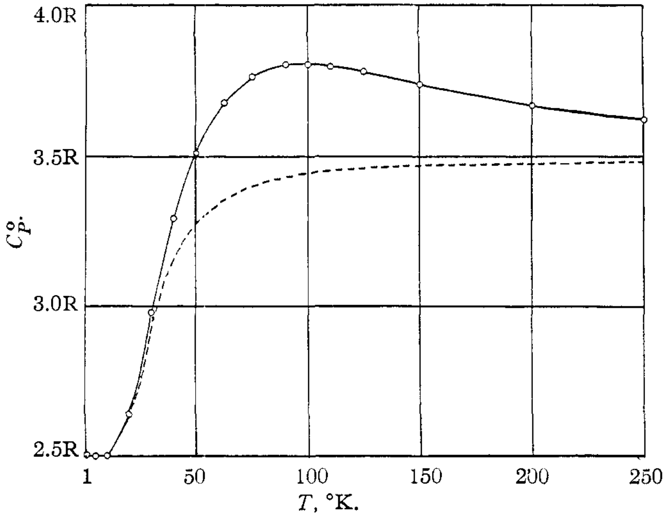

Fig. 2.—Heat capacity of OH: ———, total heat capacity; – – – —, rotational heat capacity.

Villars[16] calculated the entropy of OH by what is substantially the Sackur–Tetrode equation for a rigid rotator, with terms added for vibrational entropy and for entropy arising from the multiple character of the normal electronic state. Unfortunately, the electronic entropy was incorrectly evaluated through an error in the statistical weights of the respective electronic levels. Thus, at 298.1°K., Villars' value of the entropy

[16] Villars, *Proc. Nat. Acad. Sci.*, **15**, 705 (1929); **16**, 396 (1930).

(with nuclear spin entropy removed) differs from the accurate value in Table II by 0.6 of an entropy unit. Since there has been frequent misunderstanding with regard to the proper evaluation of electronic entropy, in cases similar to the present, it appears worth while to devote a brief consideration to this topic and to apply it to the present case. While the treatment by the extended Sackur–Tetrode equation for a diatomic molecule is never quite exact, at sufficiently high temperatures it is capable of yielding values which are correct to within a few hundredths of an entropy unit,[17] and its comparative ease of solution renders it a great time saver in problems in which no great accuracy is required.

The general, and exact, expression for entropy arising from *all* degrees of freedom other than translation is given by the final, bracketed, term of equation (3) of Johnston and Chapman.[2a] For an ideal molecule in which the rotational and vibrational energies may be regarded as independent of the electronic state of the molecule, the electronic contribution to entropy can be expressed by a precisely analogous expression in which electronic levels alone are included in forming the sums and in which all electronic energies are given as relative to the most stable level. For OH, the $^2\Pi_{3/2}$ configuration is the most stable and the $^2\Pi_{1/2}$ component is the only higher electronic level which influences the sums below 5000°K. At temperatures not too low the electronic entropy of OH can then be evaluated by the equation[18]

$$S^\circ_{\mathrm{E}} = R\left[\ln\,(2e^{0/RT} + 2e^{399/RT} + \ldots) + \frac{1}{kT}\left(\frac{0 + 798e^{399/RT} + \ldots}{2e^{0/RT} + 2e^{399/RT} + \ldots}\right)^2\right] \qquad (6)$$

The double statistical weights which attach to each of the $^2\Pi$ levels are a consequence of Λ type doubling (*i. e.*, each of these $^2\Pi$ levels is in reality two levels, an A level and a B level). It appears that Villars overlooked the influence of Λ type doubling and, further, made the mistake of weighting the respective $^2\Pi$ levels in accordance with the statistical weights of the *lowest rotational* level in each configuration (4 and 2, respectively). Villars thus obtained an electronic entropy contribution of 3.5 entropy units, at 298°, whereas the contribution calculated by equation (6) is 2.7 entropy units at 298.1° and cannot exceed 2.8 entropy units at the limiting infinite temperature.

A still simpler method to evaluate the electronic contribution to the entropy, and one which is perhaps less subject to chance errors in usage, is by a procedure which is analogous to that by which Giauque and Johnston[19]

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(17) *Cf.* p. 2317 of Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

(18) This equation for the electronic entropy is correct only at temperatures sufficiently high (in the limit, at infinite temperature) that molecules are evenly distributed between the A and B sublevels which result from Λ type doubling, and between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states. The latter stipulation is equivalent to the condition that molecules are distributed through a very large number of rotational states since the statistical weights appropriate to the individual rotational levels are, respectively, (4, 6, 8, 10, 12, . . .) and (2, 4, 6, 8, 10, . . .) for the $^2\Pi_{3/2}$ and the $^2\Pi_{1/2}$ states and their ratio approaches unity for high rotational quantum numbers.

(19) Giauque and Johnston, THIS JOURNAL, **50**, 3221 (1928); *Phys. Rev.*, **36**, 1592 (1930).

correctly calculated the "ortho-para" contribution to the entropy of hydrogen. This consists in evaluating the entropy effect which would accompany the process of forming the actual mixture of molecules, considered only as to their electronic states, out of the requisite amounts of the pure electronic forms. For such a process, as for the formation of any perfect solution

$$\Delta S = -R\,(N_1 \ln N_1 + N_2 \ln N_2 + \ldots) \qquad (7)$$

where N_1, N_2, ... represent the mole fractions of the respective electronic forms in the final mixture. Applied to the specific case in question we would need to consider only four electronic species, the $^2\Pi_{3/2}$ (A), the $^2\Pi_{3/2}$ (B), the $^2\Pi_{1/2}$ (A) and the $^2\Pi_{1/2}$ (B) where the A's and B's refer to the Λ type component levels. The mole fraction of the $^2\Pi_{1/2}$ (A) electronic state, for instance, would be $1e^{-399/RT}/(1e^0 + 1e^0 + 1e^{-399/RT} + 1e^{-399/RT}$ and equation (7) would become

$$S^\circ_{\mathrm{E}} = -R\left[\frac{1}{(1+e^{-399/RT})}\ln\frac{1}{2(1+e^{-399/RT})} + \frac{e^{-399/RT}}{(1+e^{-399/RT})}\ln\frac{1e^{-399/RT}}{2(1+e^{-399/RT})}\right] \qquad (8)$$

Equation (8) can be shown to be mathematically identical with equation (6). For OH these equations do not give quite the correct value for S° at 298.1°K. since the conditions with respect to the distribution among the higher rotational levels[18] are not met until somewhat higher temperatures. From our accurate sums, which we evaluated in obtaining Table II, we find that the electronic contribution to the entropy is 2.52 entropy units at 298.1°K.

The Energy Content of Hydroxyl.—Table III gives the energy content of OH (excluding translation), calculated from the relationship

$$E^\circ - E^\circ_0 = N\Sigma B/\Sigma A \qquad (9)$$

TABLE III

ENERGY OF GASEOUS OH WITH REFERENCE TO THE ZERO STATE (TRANSLATIONAL ENERGY IS NOT INCLUDED)

T, °K.	Cal./mole	T, °K.	Cal./mole	T, °K.	Cal./mole
298.1	624.9	900	1906.6	2500	6783
400	842.3	1000	2138.2	3000	8667
500	1051.3	1250	2764.8	4000	12721
600	1259.8	1500	3460.2	5000	17103
700	1469.2	1750	4218.7		
800	1684.0	2000	5030		

These figures refer to the energy in excess of that due to translation and in excess of energy held at the absolute zero.

The Free Energy.—In Table IV we give values of $-(F^\circ - E^\circ_0)/T$ for OH in the hypothetical ideal gaseous state at one atmosphere. Underscored values were calculated from the spectroscopic data by equation (4) of Johnston and Chapman.[2a] The remainder were interpolated by a sensitive graphical method.

TABLE IV

"FREE ENERGY" OF GASEOUS OH

T, °K.	$-\frac{F^\circ - E_0^\circ}{T}$	T, °K.	$\frac{F^\circ - E_0^\circ}{T}$	T, °K.	$\frac{F^\circ - E_0^\circ}{T}$
298.1	*36.842*	1250	*46.995*	3200	54.050
300	36.877	1300	47.276	3300	54.297
		1375	*47.681*		
350	*37.977*	1400	47.812	3400	54.532
400	*38.922*	1500	*48.312*	3500	54.763
450	39.754	1600	48.783	3600	54.989
500	*40.500*	1700	49.277	3700	55.209
		1750	*49.441*		
550	41.173	1800	49.650	3800	55.425
600	*41.789*	1900	50.051	3900	55.638
650	42.354	2000	*50.432*	4000	*55.842*
700	*42.877*	2100	50.773	4100	56.045
750	43.374	2200	51.154	4200	56.240
800	*43.821*	2300	51.487	4300	56.434
850	44.249	2400	51.812	4400	56.625
900	*44.654*	2500	*52.123*	4500	56.809
950	45.038	2600	52.426	4600	56.992
1000	*45.402*	2700	52.719	4700	57.170
1050	45.749	2800	53.001	4800	57.345
1100	46.080	2900	53.274	4900	57.518
1125	*46.241*				
1150	46.398	3000	*53.540*	5000	*57.687*
1200	46.702	3100	53.799		

Combined with similar tables for the other reactants and with reliable heats of reaction at the absolute zero, this table permits very accurate evaluation of the equilibrium constants in reactions which involve gaseous OH, even to 5000°K.

Evaluation of the Limits of Error.—Below 2000°K. substantially all of the terms needed in evaluating accurately the several sums lie within the range of energies covered by the spectroscopic observations. Even at 5000°K. the influence of the extrapolations on either the free energy or the entropy is very small and the influence on the heat capacity and total energy is not sufficient to introduce a serious source of error. For the rotational terms this is shown by Table V, which gives: (1) the total number of rotational terms summed in the $^2\Pi_{3/2}$ ($v = 0$) vibrational level, and (2) the number of those terms, starting with the ($J = 3/2$) term, which contributed 90% of the totals to the respective sums. The actual spectroscopic data available when the calculations were made covered the first forty-two terms (each Λ component is treated as a separate term).

TABLE V

THE NUMBERS OF ROTATIONAL TERMS WHICH CONTRIBUTED APPRECIABLY TO THE ROTATIONAL SUMS OF THE $^2\Pi_{3/2}$ ($v = 0$) STATE

T, °K.	Total (all sums)	Terms contributing 90% of the respective sums ΣA	 ΣB	 ΣC
1000	54	16	22	27
2000	84	25	33	39
5000	110	41	56	67

Table VI shows the percentage distribution of molecules among the vibrational levels as a function of the temperature. The $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ levels are combined in this tabulation.

TABLE VI

PERCENTAGE DISTRIBUTIONS OF MOLECULES AMONG THE VIBRATIONAL LEVELS

	T, °K.							
v	500	1000	1500	2000	2500	3000	4000	5000
0	99.996	99.37	96.54	91.83	86.31	80.67	70.18	61.26
1	0.004	0.62	3.32	7.42	11.62	15.28	20.36	22.95
2		.01	0.13	0.67	1.72	3.13	6.27	9.01
3			.01	.07	0.28	0.69	2.05	3.71
4				.01	.05	.17	0.71	1.60
Higher					.02	.06	.43	1.47

In spite of the fact that only the three lowest vibrational levels ($v = 0, 1, 2$) are represented in the experimental data, 93.2% of ΣA, 81.3% of ΣB and 67.6% of ΣC are contributed by the experimentally observed levels, even at 5000°K.

Reasonable limits of error, based on a consideration of the extent to which the spectroscopically derived energies are subject to uncertainty, have been determined by the use of the method employed by Johnston and Chapman.[2a] In applying this method we have been unnecessarily conservative. For instance, in making an estimate of the extent to which the energies of the respective rotational levels of the ($v = 0$) vibrational state may be in error we have: (1) computed the separations between successive pairs of rotational levels by the separate application of the Combination Principle to the data of Grebe and Holtz[4] on λ 3064, the data of Watson[4] on λ 2811, and that of Jack[4] on λ 2608; (2) regarded the possible error in any successive pair of levels as equal to the greatest divergence between the three independent sets of data, even though we actually employed weighted averages of these in computing the tables of energies employed in our calculations, and (3) taken the possible error in any one rotational level as equal to the full sum of the errors in all of the intervals which have been added to evaluate it. This leads to a possible error of about 10 wave numbers in the ($K = 21$) pairs of levels and is, obviously, a rather extreme treatment. In considering possible errors in the vibrational energies we assumed a possible error of ± 0.7 cm.$^{-1}$ in the 3734.9 constant of equation (1) and an error of ± 0.2 cm.$^{-1}$ in the 82.6 constant of the same equation. These figures correspond, as in the rotational case, to the maximum deviations between the several values obtained from the data. For the contributions from extrapolated vibrational levels we doubled the figures referred to above.

With this extreme treatment regarding the spectroscopic data we obtain the following figures for the limits of error at 5000°K.: $(F° - E_0°)/T$, 0.01 cal./mole/degree; $S°$, 0.02 cal./mole/degree; $C_p°$, 0.07 cal./mole/degree and $(E° - E_0°)$, 30 cal./mole. Values of the natural physical constants used in these calculations were taken from the "International Critical Tables." Uncertainties in these, which are introduced principally through the molar gas constant R, would influence the entropy and the free energy values to the extent of about an additional 0.01 calorie, which is nearly independent of the temperature.

We wish to acknowledge a grant from the National Research Council which provided an electric computing machine which was used in making these calculations.

Summary

The spectroscopic interpretation of the neutral OH molecule has been briefly summarized.

The heat capacity of OH in the ideal gaseous state has been calculated for the temperature range 0.01 to 5000°K. The heat capacity curve shows a sharp maximum at about 0.06°K., which is due to the existence of an unusually large Λ-type doubling in the normal electronic term; a second broad maximum at about 90°K. which results from excitation to the upper level of the inverted $^2\Pi$ electronic state of the normal molecule; and a vibrational component which starts at about 600°K. and attains the equipartition value at about 3500°K. The rotational specific heat enters at about 15°K. and approaches rotational equipartition at about room temperature. At 5000°K. the rotational stretching contributes about 0.18 cal. to the molal heat capacity and the anharmonic character of the oscillations contributes about 0.5 cal.

Accurate values of the entropy and of the "free energy function," suitable for accurate equilibrium computations, have been calculated and tabulated. A table of total energies (in excess of translation) is also included.

A table is included which shows the percentage distribution of OH molecules among the various vibrational levels, as a function of the temperature.

The limits of error of the heat capacity, entropy, free energy and total energy calculation have been determined. At 5000°K. these are: 0.07 cal./mole/degree, 0.02 cal./mole/degree, 0.01 cal./mole/degree and 30 cal./mole, respectively.

The approximate calculation of electronic entropy, for use with the Sackur–Tetrode equation, has been discussed and has been applied to OH at 298.1°K.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Thermal Reaction between Acetaldehyde Vapor and Oxygen

BY ROBERT N. PEASE

Some disagreement exists as to the nature of the reaction between acetaldehyde vapor and oxygen. According to Bodenstein,[1] the reaction is homogeneous, and yields mainly per-acetic acid. Hatcher, Steacie, and Howland,[2] on the other hand, find that the rate is increased by a glass packing (indicating wall reaction), and a complex mixture of products is obtained. Both are inclined to regard the reaction as of the chain type but for different reasons. Under these circumstances a re-investigation of the reaction has seemed to be in order. The reaction is of special

(1) Bodenstein, *Sitzber. preuss Akad. Phys.-Math.*, III, 1 (1931).

(2) Hatcher, Steacie and Howland, *Can. J. Research*, **7**, 149 (1932).