on absorption is available. For this reason we are postponing a discussion of the relation of our observations to the quantum theory until the completion of experimental and theoretical work now in progress on the absorption of organic vapors and liquids in the infra-red and ultraviolet regions of the spectrum.

Grateful acknowledgment is made to L. A. Yingling and O. R. Fouts for assistance in making observations.

Summary

1. The absorption spectra between 1 μ and 2.5 μ have been studied for a series of ethers, esters and related compounds.

2. The positions of the absorption bands found in these compounds do not change appreciably with molecular structure.

3. The decrease in the intensity of these absorption bands in such compounds as tetrachloro-ethane and trichloro-ethylene as compared with ethylene chloride and dichloro-ethylene, respectively, is probably due to the decrease in the number of hydrogen-carbon linkages in the molecule.

4. These absorption bands are characteristic of the hydrogen-carbon linkages and can be expressed approximately as a harmonic series.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 94]

THE SPECIFIC HEAT AND ENTROPY OF HYDROGEN CHLORIDE DERIVED FROM INFRA-RED BAND SPECTRA

BY HERVEY C. HICKS AND ALLAN C. G. MITCHELL

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I. Introduction

It is the purpose of the following paper to compute the rotational-oscillational specific heat of hydrogen chloride and its rotational-oscillational entropy, using the actual experimental energy levels for the different states of rotation and oscillation, which can be calculated from the interpretation of the absorption spectrum of hydrogen chloride in the near infrared. A number of previous investigators have calculated the specific heat and entropy of rotating or rotating-oscillating dipole molecules, but in general have assumed some simple dumbbell-like model for the molecule and have then theoretically calculated the different energy levels by quantizing the rotation and oscillation of their models. Many of these earlier calculations do not now seem applicable, since the rotation of the molecules was quantized using whole rather than half quantum numbers. Tolman,[1] however, has calculated a rotational specific-heat curve of hydrogen using

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[1] Tolman, *Phys. Rev.*, **22**, 470 (1923).

half quantum numbers, and Tolman and Badger,[2] using half quantum numbers, have calculated the rotational entropy of a number of gases at temperatures high enough so that the rotation may be regarded as fully excited. Our present calculations, however, differ from all previous work by going directly to the energy levels which can be obtained from the spectral data themselves using, nevertheless, the theory of half quantum numbers to determine the *a priori* probabilities of the different states.

The authors desire to express their thanks to Professor R. C. Tolman for suggesting this new method of treating the data, and for his interest in the calculations.

As data on the infra-red band spectra of hydrogen chloride we shall make use of the observations of Imes[3] and of Colby, Meyer and Bronk.[4] We shall first calculate directly from these data the energy levels for the different states of rotation and oscillation of the hydrogen chloride molecule; and then, by taking the *a priori* probabilities of successive rotational states to be 2, 4, 6, etc., as given by the theory of half quantum numbers,[5] we shall calculate the rotational-oscillational specific heat of hydrogen chloride at different temperatures. We shall then get the total specific heat by addition of the specific heat due to translational energy.

To calculate the entropy of hydrogen chloride at different temperatures, we shall assume that the total entropy of a diatomic gas may be obtained by adding the entropy given by the Sackur equation for the translational entropy to that due to other forms of energy. This hypothesis was used by Tolman[6] in calculating from the experimental rotational specific-heat curve the entropy of hydrogen, leading to a value agreeing approximately with the known entropy of that gas. An equivalent hypothesis was earlier employed by Langen[7] in the calculation of Nernst's chemical constants, using, however, the incorrect Einstein-Stern specific-heat curve. In accordance with this hypothesis we shall use for the total entropy of a diatomic gas the equation of Tolman and Badger[2]

$$S = 5/2\, R\, ln\, T - R\, ln\, p + 3/2\, R\, ln\, M + S_1 + \int_0^T C_R \frac{dT}{T} \qquad (1)$$

where T is the absolute temperature, p the pressure, M the molecular weight and S_1 the entropy constant for a monatomic gas as given by Tetrode[8] or Lewis.[9]

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[2] Tolman and Badger, This Journal, **45,** 2277 (1923).

[3] Imes, *Astrophys. J.*, **50,** 251 (1919).

[4] Colby, Meyer and Bronk, *ibid.*, **57,** 7 (1923).

[5] See Tolman, Ref. 1, p. 473.

[6] Tolman, This Journal, **42,** 1185 (1920).

[7] Langen, *Z. Elektrochem.*, **25,** 25 (1919).

[8] Tetrode, *Ann. Physik*, **38,** 434 (1912).

[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923,** p. 457.

II. Manipulation of Data

Imes, and later Colby, Meyer and Bronk, made a study of the infrared absorption bands of hydrogen chloride and measured the principal bands at 3.4μ and 1.76μ corresponding to oscillational quantum jumps 0–1, 0–2, respectively. Their measurements give frequencies corresponding to 39 rotational quantum transitions for the band at 3.4μ and nine for the band at 1.76μ. Their data are given in wave numbers.

Our problem is to calculate the energy corresponding to the various quantum levels from the above data. The energy of any given level we shall designate by $\epsilon_{m,n}$ where m and n are the rotational and oscillational quantum numbers, respectively. "m" may acquire values $^1/_2$, $^3/_2$, $^5/_2$, etc., and may change by one unit, and "n" assumes the values 0, 1, 2, etc. When the oscillational and rotational quantum numbers suffer changes simultaneously certain frequencies will be absorbed. If, for example, the oscillational quantum number changes from 0 to 1 and at the same time the rotational quantum number changes from $^1/_2$ to $^3/_2$, $^3/_2$ to $^5/_2$, etc., or from $^5/_2$ to $^3/_2$, $^3/_2$ to $^1/_2$, etc., a band will occur with its center at 3.4μ. Similarly for changes of the oscillational quantum number from 0 to 2 and corresponding rotational numbers we will have a band at 1.76μ. If, now, we select some state of the molecule as having zero energy, we may associate the energies of all the other quantum states with frequencies corresponding to the lines of the absorption spectrum. Since $\Delta\epsilon = h\nu$, we have only to multiply these frequencies by Planck's constant h to have the desired energies. This state of zero energy will be chosen as that in which the rotational quantum number is $^1/_2$ and the oscillational quantum number is 0.

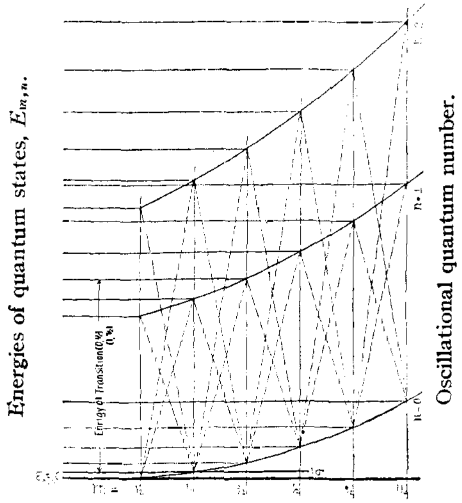

Fig. 1.—Rotational quantum number.

To compute the relative energy of the different states expressed in waves per centimeter from the data given, we shall make use of the diagram, see Fig. 1. Since the data represent an increase in oscillational quantum number combined with either a decrease or increase of rotational quantum number of one unit we may associate pairs of transitions having the same final state and having initial states of the same oscillational quantum number but differing by two rotational quantum numbers. The differences of members of each pair give the difference of energy between two states having the same oscillational quantum number and rotational quantum numbers differing by two.

Let us now assume that the $({}^{1}/_{2}, 0)$ state of the molecule has an energy zero and that the $({}^{3}/_{2}, 0)$ has an energy σ. By successively adding to the energy of the $({}^{1}/_{2}, 0)$ state alternate values of the differences just derived (1st and 3rd, etc.), and to the energy of the $({}^{3}/_{2}, 0)$ state the other alternate values (2nd, 4th, etc.) we obtain the energies of the states with zero oscillational quantum number except that alternate values depend on σ. Finally, by continuity properties σ is easily determined.

To get the energy levels in the first oscillational state we have merely to add to the various zero oscillational-state energies, starting with $({}^{3}/_{2}, 0)$ the values of the transitions in which the rotational quantum number decreases by one while the oscillational quantum number increases by one. Thus we have determined the energies of all the states in which the oscillational quantum number is zero or one, and the rotational quantum number ranges from ${}^{1}/_{2}$ to 41/2. By exactly similar procedure, using the data for the band at 1.76μ, we derive the energies of the states in which the oscillational quantum number is two and the rotational quantum number ranges from ${}^{1}/_{2}$ to ${}^{15}/_{2}$.

TABLE I

VALUES OF THE ENERGY $\epsilon_{m,n}$ IN WAVE NUMBERS (cm^{-1})

m	p_m	$n = 0$	1	2
1/2	1	0	2886	5667
3/2	2	21	2907	5687
5/2	3	63	2948	5727
7/2	4	126	3009	5786
9/2	5	210	3090	5865
11/2	6	315	3192	5964
13/2	7	440	3314	6082
15/2	8	586	3456	6220
17/2	9	752	3617	(6376)
19/2	10	938	3798	. .
21/2	11	1145	3998	. .
23/2	12	1372	4218	. .
25/2	13	1619	4458	. .
27/2	14	1886	4717	. .
29/2	15	2173	4995	. .
31/2	16	2479	5293	. .
33/2	17	2805	5609	. .
35/2	18	3150	5944	. .
37/2	19	3514	6298	. .
39/2	20	3897	6669	. .
41/2	21	4298	7058	. .
43/2	22	4717	. .	. .
45/2	23	5154	. .	Extrapolated values
47/2	24	5609	. .	. .
49/2	25	6082	. .	. .

The results obtained are given in Table I. In those cases where the data of more than one investigation could have been used, the average was taken.[10] The accuracy of the values in the table is as good as the number of figures printed, except for those values which are denoted as extrapolated. The extrapolation was done by the method of differences and the values derived are probably accurate to three significant figures.

III. Method of Calculation of Energy and Specific Heat

We now proceed to find the total rotational-oscillational energy of one mole of the gas (N molecules) at various temperatures by combining the above data. To find this we make use, therefore, of the quantum form of the Maxwell-Boltzmann distribution law which gives:

$$E_R = \frac{N\,\Sigma m\,\Sigma n\,p_m\,e^{-\frac{\epsilon_{m,n}}{kT}}\,\epsilon_{m,n}}{\Sigma m\,\Sigma n\,p_m\,e^{-\frac{\epsilon_{m,n}}{kT}}} \tag{2}$$

where E_R is the rotational-oscillational energy per mole, $\epsilon_{m,n}$ the energy of one molecule in the state (m, n), p_m the *a priori* probability of a given quantum state, T the temperature, and k Boltzmann's constant.

If, now, we differentiate this energy with respect to the temperature, we obtain the rotational-oscillational specific heat at constant volume, thus:

$$C_R = \frac{\mathrm{d}E_R}{\mathrm{d}T} = \frac{\mathrm{N}}{kT^2}\left[\frac{\Sigma m\,\Sigma n\,p_m\,\epsilon^2_{m,n}\,e^{-\frac{\epsilon_{m,n}}{kT}}}{\Sigma m\,\Sigma n\,p_m\,e^{-\frac{\epsilon_{m,n}}{kT}}} - \left(\frac{\Sigma m\,\Sigma n\,p_m\,\epsilon_{m,n}\,e^{-\frac{\epsilon_{m,n}}{kT}}}{\Sigma m\,\Sigma n\,p_m\,e^{-\frac{\epsilon_{m,n}}{kT}}}\right)^2\right] \tag{3}$$

which for computing purposes can be arranged in the following form where, by a proper choice of constants, $\epsilon_{m,n}$ may be introduced in wave numbers and the resulting C_R given in calories per degree.

$$C_R\,(T) = \frac{b_1}{T^2}\left[\frac{\Sigma_2}{\Sigma_0} - \left(\frac{\Sigma_1}{\Sigma_0}\right)^2\right] \tag{4}$$

where

$$\Sigma_r = \Sigma m\,\Sigma n\,p_m \left\{10^{b_2\frac{\epsilon_{m,n}}{kT}}\right\}\{\epsilon_{m,n}\}^r$$

and $p_m = m + \frac{1}{2}$

$$b_1 = \frac{c^2h^2\mathrm{N}}{kJ} = 4.080; \quad b_2 = -\frac{c\,h}{k}\log_{10} e = -0.622$$

c is the velocity of light (2.999×10^{10}), h Planck's constant (6.554×10^{-27}), k Boltzmann's constant (1.372×10^{-16}), N Avogadro's number (6.06×10^{23}), J the mechanical equivalent of heat (4.182×10^{7}), $\epsilon_{m,n}$

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[10] The first average was taken at that point in the calculation at which the energies of the states having zero oscillation quantum number and various rotational quantum numbers had been derived. Up to this point the data of the investigators had been handled separately. In the next step—determining the levels of the oscillational state of quantum number 1—the average of the energies in the two data lists for each transition was used. The average was unweighted.

energy in waves per centimeter relative to $\epsilon_{1/2,0}$ T the temperature in degrees absolute, m rotational quantum number, and n the oscillational quantum number.

The results of the computations are given in Table II. For temperatures between 50°K. and 400°K. the values of the specific heat are good to four significant figures, while outside of this range they are good to three. For high temperatures the neglected terms in the summation would amount to an inaccuracy in the fourth place. On the other hand for low temperatures the accuracy cannot be greater than that of determining σ since the first terms of the series become very large compared to the others. Fig. 2 shows the relation between C_R and T.

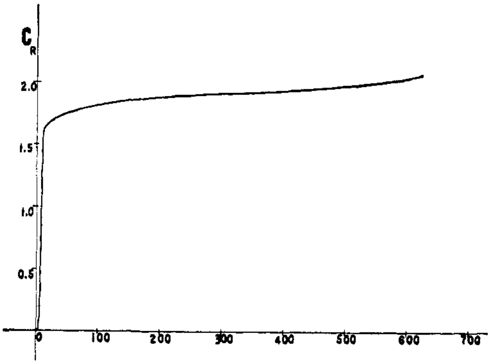

Fig. 2.—Variation of rotational specific heat with temperature.

TABLE II

VALUES OF C_R, C_R/T AND C_v IN TERMS OF T°K.

T	C_R	C_R/T	C_v
600	2.040	0.00340	7.011
500	1.967	.00392	6.938
400	1.929	.00482	6.900
300	1.906	.00635	6.877
298.1	1.905	.00638	6.876
200	1.881	.00940	6.852
120	1.832	.01527	6.803
60	1.766	.0294	6.737
30	1.706	.0569	6.677
12	1.626	.1355	6.597
10	1.541	.1541	6.512
8	1.207	.151	6.178
6	0.639	.1065	5.610
5	.332	.0664	5.303
4	.103	.0258	5.074
3	.018	.0060	4.989
2	.0002	.0001	4.9714
1	.00000	.00000	4.9712

IV. The Entropy

The entropy is calculated by means of Equation 1, using for S_1 each of the values (—2.30) as given by Tetrode and (—2.63) as given by Lewis.

On substituting the values of T = 298.1°, p = 1 atm. and the values for the gas constant, molecular weight of hydrogen chloride and the value of the entropy constant, Equation 1 reduces to

$$S = 36.75 + \int_0^{298.1} C_R \, d \, ln \, T \quad \text{Tetrode constant} \qquad (5a)$$

$$S = 36.42 + \int_0^{298.1} C_R \, d \, ln \, T \quad \text{Lewis constant} \qquad (5b)$$

It is only necessary to integrate C_R with respect to $ln\ T$ from 0° to 298.1°K. and substitute the result in the above equations to get the entropy of hydrogen chloride in its standard state. Below 5°K. it is allowable to use a limiting form of Equation 4, since terms with $1/T$ in the exponent become small. This reduced formula is

$$C_R = \frac{3600}{T^2} 10^{-\frac{13.07}{T}} \left[1 - 4 \times 10^{-\frac{13.07}{T}}\right]$$

which can be integrated exactly. Above 5°K. we apply the method of graphical integration to a plot of C_R against $ln\ T$. The value of the integral $\int C_R \frac{dT}{T}$ between 0° and 298.1° is found to be 6.75. Substituting this value in Equation 5a or 5b above, we get for the entropy of hydrogen chloride from (5a) 43.40 and from (5b) 43.17.

V. Comparison with Other Values of the Entropy

In Table III the values of the entropy of hydrogen chloride as given theoretically by Tolman and Badger using half quantum numbers and a rigid dipole model, and by the authors, and the experimental values as given by Eastman[11] are given for reference.

TABLE III

COMPARISON OF VALUES OF ENTROPY

Author	Tolman and Badger	Hicks and Mitchell		Eastman
Values of entropy	42.9	43.40(a)	43.17(b)	43.3

It is evident that the experimental data now available are not sufficiently accurate to permit a decision between the Tetrode and Lewis values of the constant, although the Tetrode value gives a somewhat better check. It should be noted, however, that theoretical considerations[12] favor the Tetrode value.

VI. Summary of Results

1. A direct method has been given whereby the oscillational-rotational specific heat of hydrogen chloride may be calculated, and the curve showing the relation between specific heat and the temperature has been plotted.
2. By integrating under the curve C_R against $ln\ T$, the rotational-oscillational entropy has been calculated.

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[11] Eastman, THIS JOURNAL, **45,** 80 (1923).

[12] See, for example, Pauling and Tolman, *ibid.*, **47,** 2154 (1925).

3. By assuming that the additivity of entropy is due to translational and other forms of energy and by making use of the equation

$$S = 5/2\,R\,ln\,T - R\,ln\,p + 3/2\,R\,ln\,M + S_1 + \int_0^T C_R \frac{dT}{T}$$

the entropy of hydrogen chloride has been shown to be 43.40 using the Tetrode constant and 43.17 using the Lewis constant, in good agreement with the experimental value.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

THE POLYSULFIDES OF SODIUM AND POTASSIUM

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Introduction

During an investigation[1] of the reaction of sulfur with alkali hydroxides in boiling aqueous solution, it seemed desirable to determine with how many atoms of sulfur the free alkali metals tend most readily to unite in the formation of polysulfides. Although Locke and Austell[2] had sought an answer to this question by allowing a boiling solution of sulfur in toluene to react with molten sodium in toluene, the results of their experiments were not conclusive. In the two trials in which they used the most sulfur the percentages of sodium in their product lay between the values corresponding to the trisulfide and the tetrasulfide.

Experimental Part

The method of combining sulfur and an alkali metal employed by Locke and Austell was essentially modified, in that the metal was added to the solution of sulfur rather than the sulfur to the metal. Such an amount of recrystallized and dried sulfur as to be in large excess for the reaction was dissolved in toluene contained in the reaction flask. All the toluene used in this work had been twice distilled over metallic sodium and subsequently kept dry by storage over more of the same metal. In order to keep oxygen and moisture away from the reacting substances a vigorous stream of commercial hydrogen, purified by passage through alkaline pyrogallol and concd. sulfuric acid, was introduced above the surface of the toluene. The hydrogen escaped through a calcium chloride tube at the upper end of the reflux condenser with which the reaction flask was equipped. A cube of metallic sodium or potassium was weighed approximately, trimmed quickly under dry toluene and then dropped through a large hole in the fiber cork of the flask into the vigorously boiling solution

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[1] Tartar and Draves, THIS JOURNAL, **46**, 574 (1924).

[2] Locke and Austell, *Am. Chem. J.*, **20**, 592 (1898).