ON THE THEORY OF THE TEMPERATURE VARIATION OF THE SPECIFIC HEAT OF HYDROGEN

By E. C. Kemble and J. H. Van Vleck

Abstract

Quantum theory of rotational and vibrational specific heats of an elastic, non-gyroscopic model of a diatomic gas.—To account for the abnormally large specific heat of hydrogen at high temperatures, the molecule is assumed to have an internal vibrational degree of freedom. Assuming a dumb-bell model and the following law of force $F = a(r - r_0)/r^3$, the energies of the stationary states are derived on the basis of the Bohr-Sommerfeld form of the quantum hypothesis, and an expression for the specific heat obtained. When suitable values of the two adjustable constants are chosen, satisfactory agreement is obtained with the experimental results for hydrogen throughout the entire range, to 1300° K.

Constants of the hydrogen molecule, computed from the empirical constants of the specific heat equation are: Nuclear spacing, 0.488×10^{-8} cm; moment of inertia, 1.975×10^{-41} gm cm^2; wave-length corresponding to normal vibration, 2.05 μ.

Specific heats of hydrogen and water vapor; new empirical formulas for temperatures between 300° and 2300° K derived from Pier's data, are given: For hydrogen: $c_v = 4.87 + 0.539 \times 10^{-3}t + 0.146 \times 10^{-6}t^2$; for water vapor: $c_v = 6.03 + 4.2 \times 10^{-3}t - 4.07 \times 10^{-6}t^2 + 1.95 \times 10^{-9}t^3$.

Introduction

THE problem of explaining the abnormal specific heat of hydrogen at low temperatures has engaged the attention of numerous investigators.[1] The theory most generally accepted at the present time was first formulated by one of the writers of this paper in an unpublished doctor's dissertation in 1917.[2] A brief account of the theory was given in a paper read before the American Physical Society in October, 1917.[3] This paper was unfortunately marred by an error made in an attempt to take into account the expansion of the molecule due to centrifugal force at the larger rotational speeds. The publication of the details of the theory was delayed by the war and in 1919 Reiche,[4] working independently, published a complete discussion of the problem based on a rigid model of the molecule and differing only in minor respects from that contained in the above-mentioned thesis.

---

[1] For a resumé of the results see F. Reiche, "Die Quantentheorie," Berlin, 1921.

[2] E. C. Kemble, "Studies in the Application of the Quantum Hypothesis to the Kinetic Theory of Gases and to the Theory of their Infra-red Absorption Bands," Harvard University, 1917.

[3] E. C. Kemble, Phys. Rev. **11**, p. 156, 1918 (abstract).

[4] F. Reiche, Ann. der Phys. **58**, p. 657, 1919.

The purpose of the present paper is to present a corrected calculation of the rotational and vibrational specific heat of an elastic model of a diatomic gas molecule. Such a calculation is desirable since the observed specific heat of hydrogen at high temperatures is appreciably greater than the limiting theoretical value for rigid molecules, $(5/2)R$ or 4.963 calories per mol. We cannot correct for the effect of elasticity simply by adding to the specific heat of a rigid molecule the vibrational specific heat of an ideal linear oscillator, for the expansion of the molecule by centrifugal force must be taken into account.[1] This expansion alters the energies of the stationary states corresponding to various values of the angular momentum and thus causes an increase in the rotational specific heat. The effect is largest for those molecules with the smallest moments of inertia and hence is particularly important for hydrogen.

In this connection it may be observed that the classical statistical mechanics does not demand a constant rotational specific heat as is commonly assumed. The equipartition law specifies the average kinetic energy of rotation for a diatomic gas to be RT. If the molecules are regarded as elastic a rotational potential energy must be added which is roughly proportional to the square of the kinetic energy. It follows that the complete rotational specific heat is an approximately linear function of T having the value R as a lower limit. Needless to say, the correction is small for most molecules at moderate temperatures.

DETERMINATION OF THE ENERGIES OF THE STATIONARY STATES

The first part of the problem of computing the specific heat for a model of a gas molecule consists in the application of the quantum conditions to the determination of the energies of the stationary states. In order to get a definite result we must introduce an assumption regarding the nature of the law of force binding the nuclei of the two atoms together. A good deal of information regarding the nature of the law for the HCl molecule can be obtained from the study of its infra-red band spectrum, but we have no sure hold, either experimental or theoretical, on the law for the hydrogen molecule. We know, however, that when the nuclei are close to their equilibrium positions the restoring force must be an approximately linear function of the displacement. For large displacements, on the other hand, the force must drop off as the inverse square of the distance between the nuclei, or more rapidly. These two requirements are conveniently met by the assumption that the force is of the form

$$F = a(r - r_0)/r^3. \tag{1}$$

---

[1] This expansion is the cause of the asymmetry of the infra-red absorption bands of polar diatomic gases.

Here r is the distance between the nuclei, r_0 the equilibrium value of r, and a is a constant, which may be adjusted to give the frequency of vibration any desired value. The equations of motion resulting from the law stated above are mathematically of the same general form as those which govern the motion of an electron around a single hydrogen nucleus when the relativity correction is taken into account. Consequently by postulating a force of the form given in (1) we can carry through the determination of the energies of the permitted motions without further approximations. Of course this law is not to be considered as actually correct, but fortunately auxiliary computations indicate that an accurate formula for large displacements is not needed over the range of temperatures considered in this article.

Let the angular and radial momenta be denoted by p_φ and p_r respectively. Denoting the masses of the nuclei by m_1 and m_2 and introducing the abbreviation $\mu = m_1m_2/(m_1 + m_2)$, we readily derive the following expression for the energy (Hamiltonian function):

$$W = \frac{p_\varphi^2}{2\mu r^2} + \frac{p_r^2}{2\mu} + \frac{a}{2r_0} - \frac{a}{r} + \frac{ar_0}{2r^2}. \qquad (2)$$

The application of the Wilson-Sommerfeld quantum conditions yields the relations[1]

$$p_\varphi = mh/2\pi, \qquad m = 0, 1, 2, 3, \cdots, \qquad (3)$$

and

$$\oint p_r dr = -2\pi\left[\sqrt{p_\varphi^2 + \mu a r_0} - \frac{\mu a}{\sqrt{2\mu(a/2r_0 - W)}}\right] = nh, \qquad (4)$$
$$n = 0, 1, 2, 3, \cdots.$$

Solving the above equations for the total energy W as a function of the quantum numbers m and n, we obtain

$$W = \frac{a}{2r_0}\left[1 - \frac{4\pi^2\mu a r_0}{h^2(n + \sqrt{m^2 + 4\pi^2\mu a r_0/h^2})^2}\right]. \qquad (5)$$

We denote by ν_0 the frequency of vibration of a non-rotating molecule with an infinitesimal amplitude. This may be proved to be

$$\nu_0 = (1/2\pi)\sqrt{a/\mu r_0^3}. \qquad (6)$$

From the definition of the angular momentum p_φ the following expression for the angular velocity is readily deduced:

$$\omega = p_\varphi/\mu r^2 = mh/2\pi\mu r^2.$$

---

[1] In the earlier work by Kemble the condition (3) was derived from Planck's cell theory by introducing the assumption that the permitted stationary states are those whose representative points lie on the cell boundaries. Cf. M. Planck, Verh. d. D. Phys. Ges. **17**, p. 407, 1915.

Hence, to a close approximation, the frequency of rotation of a non-vibrating molecule with a single unit of angular momentum is

$$\nu_1 = h/4\pi^2\mu r_0^2. \qquad (7)$$

The frequency of rotation for a rigid molecule would be an integral multiple of ν_1. With the aid of Eqs. (6) and (7) the expression for the energy can be thrown into the form

$$W_m{}^n = \frac{h\nu_1}{2}\left(\frac{\nu_0}{\nu_1}\right)^2\left[1 - \frac{1}{\{(\nu_1/\nu_0)n + \sqrt{1 + (\nu_1/\nu_0)^2 m^2}\}^2}\right]. \qquad (8)$$

In most applications of this theory the ratio ν_1/ν_0 will be a small number. The value derived from the infra-red band spectrum of HCl is 0.0076. In applying the above expression to hydrogen we may treat ν_1 and ν_0 as adjustable constants whose values may be chosen to fit the experimental specific heats. From the values of these constants used in obtaining the curves given later in this article and from the assumed law of force we may compute the energy required to break up the molecule.[1] This has the right order of magnitude, being about 40 per cent greater than the heat of dissociation as observed by Langmuir. No better agreement could be expected in view of the fact that our law of force makes no pretence at accuracy for large values of r.

Calculation of Specific Heat

Let N denote the number of molecules in a gram molecule and let $p_m{}^n$ denote the intrinsic probability of the stationary state mn. The rotational and vibrational energy E of a gram molecule of gas at the temperature T may be computed from Planck's formula [2]

$$E = N\frac{\sum\limits_n\sum\limits_m p_m{}^n W_m{}^n e^{-W_m{}^n/kT}}{\sum\limits_n\sum\limits_m p_m{}^n e^{-W_m{}^n/kT}}, \qquad (9)$$

in which the average energy of the molecules in the "region element" mn (Planck's second theory) is replaced by the energy $W_m{}^n$ of the molecules in the stationary state associated with this region element.[3]

The corresponding expression for the specific heat is obtained by differentiation with respect to T. It is

$$c = \frac{Nk}{J}\left[\frac{P_3}{P_1} - \left(\frac{P_2}{P_1}\right)^2\right] \qquad (10)$$

---

[1] The formula for energy of dissociation is $(h\nu_1/2)(\nu_0/\nu_1)^2$.

[2] Planck, Verh. d. D. Phys. Ges. 17, p. 412, 1915.

[3] Each of the quantum conditions defines a family of surfaces in the state-space of statistical mechanics. These surfaces divide this space into cells which may be identified with Planck's region elements.

where J = mechanical equivalent of heat; $P_1 = \sum_n \sum_m p_m{}^n e^{-\sigma_m{}^n}$; $P_2 = \sum_n \sum_m p_m{}^n \sigma_m{}^n e^{-\sigma_m{}^n}$; $P_3 = \sum_n \sum_m p_m{}^n (\sigma_m{}^n)^2 e^{-\sigma_m{}^n}$; $\sigma_m{}^n = W_m{}^n/kT$. In evaluating the above series, the stationary state ($m = 0$, $n = 0$) is assumed to have zero probability as indicated by the infra-red absorption bands of diatomic gases.[3] At the highest temperatures used the series need to be summed to 13 terms in m, and 3 terms in n. It is of interest to note that strictly speaking they are only semi-convergent since $W_m{}^n$ and the exponential factor approach finite limits as m and n become infinite.

It remains to discuss the formula to be used for the intrinsic probability $p_m{}^n$. Planck assumes that the probability of each cell is proportional to the volume of that cell as in the classical statistical mechanics, and we follow the line of least resistance in identifying the cell probability of his theory with the probability of the corresponding stationary state in the new theory. Since, however, the stationary state of zero energy ($m = 0$, $n = 0$) is arbitrarily ruled out, there is more than one way of assigning the remaining states to the cells, and consequently this point of view leads to an ambiguous set of values for the p's.

Reiche makes use of the fact that an external electric or magnetic field will break up each of the stationary states into new ones having (on the basis of Planck's hypothesis) unit intrinsic probability. He therefore identifies $p_m{}^n$ with the number of new states between which the molecules having m units of angular momentum are divided by the field.[1] The application of the quantum conditions to the angular coördinates in the presence of a magnetic field involves the use of two quantum numbers. One, which we denote by the symbol m_1, gives the number of units of angular momentum parallel to the field. If the stationary states corresponding to all values of both numbers are recognized as equally probable, the value of $p_m{}^n$ is easily shown to be $2m + 1$. On the other hand, if we rule out those states for which m_1 is zero, following an argument due to Bohr, $p_m{}^n$ works out to be $2m$. Specific heat calculations based on a rigid model of the hydrogen molecule favor the latter formula for $p_m{}^n$.

Comparison of Theoretical and Experimental Values

Hydrogen.—The form of the specific heat curve for hydrogen between 35° K and 350° K has been pretty well established by the experiments of

---

[1] Since Reiche deals with rigid molecules the quantum number n does not appear n his analysis.

Eucken,[1] Scheel and Heuse,[2] and Escher.[3] Less trustworthy determinations of the specific heat at higher temperatures have been made by Crofts [4] from observations of the ignition temperatures of adiabatically compressed mixtures of electrolytic gas and hydrogen, and by Pier [5] and others using the explosion method.

While the observations of Pier are the latest and apparently the best for very high temperatures, his formula does not agree at low temperatures with the well-established results of other investigators. We therefore attempted at first to fit our formula at high temperatures to a point taken from the work of Crofts.[6] The result of these initial calculations was unsatisfactory. Whether the intrinsic probability $p_m{}^n$ is set equal to $2m$ (curve B' in the accompanying graph) or to $2m + 1$ (curve B), it is impossible to pass a curve through the Crofts point which will also fit the observations near 300° K.

We have accordingly made a study of Pier's data which shows that the discrepancy between his formula (see Eq. (14) below) and the well-established points in the neighborhood of 300° K is not inherent in his observations. By combining the value of the specific heat at 289° K given by Scheel and Heuse with Pier's data we have derived a new empirical formula which fits the latter set of points better than the original one. Pier determined the average specific heats at constant volume of various mixtures of water vapor, argon, and hydrogen between 17° C and temperatures ranging from 1400° C to 2350° C. We have assumed the specific heat of argon to be 2.98 calories per mol and have set the specific heats of water vapor and hydrogen at 17° C equal to 6.1 [7] and 4.88 (Scheel and Heuse) respectively. The following formulas were then deduced by a semigraphical method which need not be described in detail: For water vapor, $0 < t < 2300°$ C,

$$C_v = 6.03 + 4.2 \times 10^{-3}t - 4.07 \times 10^{-6}t^2 + 1.95 \times 10^{-9}t^3, \qquad (11)$$

For hydrogen, $0 < t < 2300°$ C,

$$C_v = 4.87 + 0.539 \times 10^{-3}t + 0.146 \times 10^{-6}t^2, \qquad (12)$$

---

[1] A. Eucken, Sitz. d. Kon. Preus. Akad. d. Wis. **1**, p. 141, 1912.

[2] K. Scheel u. W. Heuse, Ann. der Phys. (4) **40**, p. 473, 1913.

[3] W. Escher, Ann. der Phys. (4) **42**, p. 761, 1913.

[4] J. M. Crofts, J. Chem. Soc. **107**, p. 290, 1915.

[5] M. Pier, Zeits. f. Elektrochemie, **15**, p. 356, 1909.

[6] Crofts gives 5.10 calories per mol as the mean specific heat between 15° C and 532° C. We have assumed that this value can be used for the specific heat at the average temperature 273° C, or 546° K.

[7] Cf. H. Levy, Verh. d. D. Phys. Ges. **11**, p. 331, 1909. All specific heats are for the ideal gas condition.

Pier's own formulas are,[1] for water vapor

$$C_v = 6.065 + 1.0 \times 10^{-3}t + 0.8 \times 10^{-6}t^3 \tag{13}$$

and for hydrogen

$$C_v = 4.70 + 0.9 \times 10^{-3}t. \tag{14}$$

There is apparently a misprint in Pier's published record of his 134th experiment, for we cannot check his calculation for that point. Discarding this one observation, we find that the sum of the squares of the residual errors is reduced 48 per cent by the changes we have introduced in the formulas.

Curve *a*, Fig. 1, is plotted from Pier's formula (14). Curve *b* is a plot of (12), which we believe to be the best available empirical estimate of the high temperature specific heat of hydrogen. Taking the point at 1350° K on this curve as standard for fixing an approximate value of ν_0, we have plotted the theoretical curve C' from our formulas (8) and (10), giving $p_m{}^n$ the value $2m$. It will be seen that the agreement between this last curve and the measured specific heats is quite satisfactory. A calculation for 2006° K, which does not appear on the graph, shows a discrepancy of 0.27 cal/mol, between the theoretical curve C' and the empirical curve *b*. In view of the fact that an error in the assumed form of the law of force would begin to make itself felt at such a high temperature as this, and considering the experimental uncertainty involved, the discrepancy is small. We thus obtain a simultaneous confirmation of our theory and of the Pier measurements of the specific

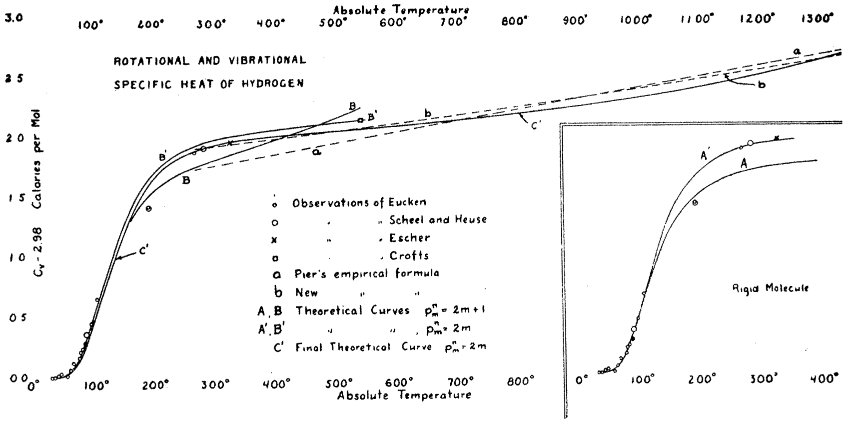

Fig. 1. Rotational and vibrational specific heat of hydrogen.

---

[1] Pier gives the formulas for the mean specific heats only. Eqs. (13) and (14) are the corresponding expressions for the instantaneous specific heats.

heat at high temperatures.[1] The formula for $p_m{}^n$ used in calculating the theoretical specific heats confirms the conclusion of Reiche but conflicts with the result previously obtained by Kemble.

Table I. gives the numerical values from which the graph was plotted.

TABLE I.

Rotational and vibrational specific heat of hydrogen

Absolute temp.	A	A'	B	B'	C'	Observed	Source
60°					.020	.01	(1)
65	.060	.052	.059			.06	(1)
80	.183	.167	.182		.133	.16	(1)
100	.441	.441	.441	.44	.404	.44	(1)
110	.590	.599	.588		.521	.64	(1)
145		1.147			1.058		
149	1.098		1.109				
196.5	1.449	1.622	1.488		1.584	1.41	(1)
196.5						1.401	(2)
273		1.858	1.741	1.91	1.872	1.86	(1)
289			1.77	1.94	1.898	1.897	(2)
333	1.72	1.92	1.84	1.99	1.948	1.935	(3)
450			2.03	2.07			
546			2.22	2.12		2.124?	(4)
625					2.07	2.10	(5)
1000					2.28	2.36	(5)
1349					2.66	2.64	(5)
2005.6					3.532	3.263	(5)

Sources: (1) Eucken; (2) Scheel and Heuse; (3) Escher, mean value 293°–373°; (4) Crofts, mean value 288°–805°; (5) Empirical equation (12) from Pier's data.

From the values of the constants used in adjusting the curve C' we deduce the following *magnitudes for the hydrogen molecule:*

λ_0 = wave-length corresponding to the normal vibration frequency of the H_2 molecule = $2.05\ \mu$;

L_0 = normal moment of inertia of H_2 molecule = 1.975×10^{-41} gm cm^2;

r_0 = normal nuclear spacing = 0.488×10^{-8} cm.

Reiche's value for L_0 is 2.095×10^{-41} gm cm^2.

It is worthy of note that up to 1350°, at least, the rotational specific heat exceeds the limiting value for a rigid molecule (1.985 cal/mol) by more than the corresponding vibrational specific heat. This shows the impossibility of calculating high temperature specific heats of gases by

---

[1] Pier's work has been criticized by Bjerrum because of his failure to take into account the heat lost to the walls of the calorimeter before the pressure maximum, but the hypothesis that this loss is small is supported by Siegel in a later paper. The experiments of Womersley also seem to indicate that the heat loss to the walls is small, though his report is so brief that it is obscure. Cf. N. Bjerrum, Zeits. f. Elektrochem. **17**, 731 (1911); W. Siegel, Zeits. f. Phys. Chemie, **87**, 641 (1914); W. D. Womersley, Proc. Roy. Soc. A. 100, p. 483 (1922).

simply adding the specific heat of one or more ideal linear oscillators of suitable frequencies to the classical specific heat for a rigid molecule of the type in question.

Other diatomic gases.—While we have much less complete data on other diatomic gases than hydrogen, abnormally low specific heats have been calculated by Scheel and Heuse from their observations on nitrogen, oxygen, and carbon monoxide in the neighborhood of 92° K. Assuming that the Reiche formula for the specific heat of a rigid molecule ($p_m = 2m$) can be applied to these gases we may calculate the moments of inertia and nuclear separation from the observations in question. Table II. shows the result of such a calculation. The values of the distance between the atomic nuclei are absurdly small in comparison with the nuclear spacing for H_2 or with estimates of the radii of the atoms of oxygen, nitrogen, and carbon made in other ways. They force the conclusion that either the assumed specific heats are wrong, or that the theory is not applicable to these gases.

TABLE II.

Gas	t	c_{v0} calculated by Scheel and Heuse cal/mol	Rotational sp. heat cal/mol	Moment of inertia J 10^{-41} gm cm^2	Nuclear spacing 10^{-9} cm
N_2	−181° C	4.733	1.755	5.16	2.1
O_2	−181	4.91	1.93	8.11	2.47
CO	−180	4.758	1.780	5.3	2.16

It hardly seems probable that there can have been any considerable error in the observations of Scheel and Heuse, which were made on c_p at atmospheric pressure. The calculation of the specific heat at constant volume in the ideal gas condition involves a considerable correction for pressure, however, which may be inaccurate.

As regards the applicability of the theory to these gases it should be observed that we have assumed our molecular model to be non-gyroscopic. The positive magnetic susceptibilities of O_2 and N_2 suggest that these gases do not fall in the non-gyroscopic class and it is possible that carbon monoxide does not lie within the scope of the present theory for the same reason.

Our thanks are due to Mr. K. C. Mazumder for his assistance in working up Pier's data.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
December 13, 1922