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ON THE QUANTUM THEORY OF THE SPECIFIC HEAT OF HYDROGEN

PART I. RELATION TO THE NEW MECHANICS, BAND SPECTRA, AND CHEMICAL CONSTANTS

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Abstract

1. If in the new quantum mechanics the hydrogen molecule is treated as a simple rotating dipole like HCl, the a priori probability is $2m$, and the rotational quantum number assumes the values $m=\frac{1}{2}, \frac{3}{2}, \cdots$. This, however, gives the old Planck specific heat curve, which rises to a maximum above the equipartition value, contrary to experiment. The failure of the simple theory is doubtless due to the non-polar character of the hydrogen molecule and is probably intimately connected with the alternating intensities found in the band spectra of certain non-polar molecules.

2. The following ways of removing the specific heat dilemma are considered: (*a*) use of whole quanta, (*b*) exclusion of the state $m=\frac{1}{2}$, (*c*) exclusion of every other state in accord with the type of quantization for non-polar molecules proposed by Ehrenfest and Tolman, (*d*) "weak" quantization of every other state, (*e*) a gyroscopic molecule. Satisfactory curves are obtained with (*a*) and (*b*), but the theoretical basis on the new quantum mechanics is obscure. Hypothesis (*c*) probably gives too steep a curve and an excessively large moment of inertia, (*d*) is questionable, and (*e*) is incompatible with the diamagnetism of hydrogen. The Einstein-Bose statistics do not affect the rotational specific heat of hydrogen appreciably. Recent experimental work of Bartels and Eucken and of Schreiner shows the moments of inertia of N_2, O_2, and CO cannot be deduced from existing specific heat data and so obviates the necessity of the absurdly small moments of inertia previously required by Scheel and Heuse's measurements for these elements.

3. Recent theories of the hydrogen secondary spectrum give moments of inertia which are larger than the old values and which are hence more easily reconciled with specific heats. Ehrenfest and Tolman have suggested that the angular momentum of non-polar molecules equals only even multiples of $h/2\pi$, and according to Slater their proposal may be intimately related to the alternating intensities sometimes found in band spectra. It is shown that according to the correspondence principle the angular momentum can change by zero or $h/2\pi$ even in a non-polar molecule, provided there are simultaneous electron jumps. This fact partially destroys the quadrupolar symmetry and causes serious difficulties for their theory. The alternating intensities, however, seem difficult to explain otherwise, and may be related to the Heisenberg extension of the Pauli exclusion principle.

Croze and Dufour find that, unlike the non-magnetic Fulcher bands, certain other lines of the hydrogen secondary spectrum are resolved by a magnetic field into doublets whose displacement is comparable with the normal Lorentz value and so surprisingly large for a molecule. It is suggested that these peculiar Zeeman doublets, whose polarization is sometimes anomalous, are due to loose coupling of the spin axis of the valence electron in either the initial or final state, but not in both.

4. The Stern-Tetrode formula for chemical constants must be modified by including terms involving the a priori probability of the lowest state and the symmetry number. If the entropy of the solid phase vanishes at the absolute zero, observed vapor pressures apparently require a whole quantum specific heat curve for hydrogen and do not allow the specific heat curve (*b*); but if we abandon the Nernst heat theorem a more general interpretation of Simon's results is simply that in hydrogen the minimum a priori probability is the same in the gaseous and solid phases. The moment of inertia 10^{-41} gm. cm^2 often deduced for the hydrogen molecule from chemical constants is erroneous. Present data on chemical constants are chaotic and the theory is uncertain owing to inadequate knowledge of the a priori probability in the solid phase and of the rôle of the symmetry number. Possibly this number is required in the solid as well as in the gas or else in neither.

INTRODUCTION

IT IS well known that the behavior of the heat capacity of hydrogen at low temperatures, where the specific heat falls below the classical value $c_p=\frac{7}{2}R$ is explained by quantizing the rotational motion of the nuclei about the center of gravity. This has been done by Reiche and other writers mentioned later in the article, using a rigid model of the molecule. An elastic model must be employed at high temperatures, since there the specific heat exceeds $\frac{7}{2}R$ because of the acquisition of quanta of nuclear vibrational motion. The resulting rotational and vibrational specific heat has been considered jointly by E. C. Kemble and the writer, and the present article can in part be regarded as an extension and revision of their paper[1] in the light of recent experimental and theoretical developments. It is now clear that the quantum theory has been revolutionized by the new mechanics developed by Born, Heisenberg and Jordan, Dirac, and Schrödinger.[2] The bearing of the new mechanics on the specific heat of hydrogen is considered in Section 1. It is there shown the specific heat data proves that in the new mechanics the hydrogen molecule cannot be quantized in the same way as a simple rotating dipole such as HCl. The failure of the simple theory is doubtless due to the non-polarity of the hydrogen molecule. In the absence of an adequate quantum theory of non-polar molecules, several speculations are given in section 2 concerning the modifications in quantization necessary to give a satisfactory specific heat curve.

[1] E. C. Kemble and J. H. Van Vleck, Phys. Rev. **21**, 653 (1923).

[2] W. Heisenberg, Zeits. f. Physik, **33**, 879 (1925); M. Born and P. Jordan, *ibid.* **34**, 858 (1925); M. Born, W. Heisenberg, and P. Jordan, **35**, 557 (1926); P. A. M. Dirac, Proc. Roy. Soc. **109*A***, 642 (1925); **110A**, 561 (1926); E. Schrödinger, Ann. d. Physik, **79**, 361, 489, 734; **80**, 437 (1926); Phys. Rev. in press.

Sections 3 and 4 consist of a discussion of band spectrum theory and chemical constants, especially in relation to the specific heat of hydrogen. Existing theories of alternating intensities in the band spectra of non-polar molecules are considered at some length as this phenomenon is doubtless intimately related to the failure of the simple (HCl type) dipole theory in explaining the specific heat of hydrogen. A digression is made to consider the unexpectedly large Zeeman separations found in certain band spectra, which we attribute to the spinning electron. The discussion in Sections 2–4 is unfortunately rather void of many definite conclusions but nevertheless represents the result of considerable labor by the author in endeavoring to correlate and criticize existing evidence and theory. It is hoped that this will at least serve to acquaint some readers with the uncertain present status of many points connected with the theory of diatomic molecules, which makes dogmatic results impossible.

Graphs of the theoretical curves obtained under various assumptions discussed in Sections 1 and 2 are deferred to Part II, in which Dr. Hutchisson correlates existing experimental data on the specific heat of hydrogen and gives the numerical results of his calculations.

1. SPECIFIC HEAT OF HYDROGEN IN THE NEW MECHANICS

By a well-known formula[3] the rotational and vibrational specific heat per gram-mol. is

$$c = R\rho^2 d^2 \ln Q/d\rho^2, \tag{1}$$

where

$$\rho = 1/kT, \quad Q = \sum_n \sum_m p_m e^{-\rho W(m,n)} \tag{2}$$

We denote by $W(m, n)$ and p_m respectively the energy and a priori probability of the stationary state of rotational quantum number m and vibrational quantum number n. We use the notation p_m rather than $p(m, n)$ inasmuch as the value of n does not influence the a priori probability. As usual, R and k denote respectively the molar and molecular gas constants. The summation in (2) is to be taken over all possible values of the quantum numbers m and n.

Value of W(m, n). Throughout the article, unless otherwise stated, we shall utilize a non-gyroscopic model of the molecule, as this seems to be required by the diamagnetism of hydrogen. Up to room temperatures the specific heat can be approximately calculated with the further

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[3] Eq. (1) has been given for a rigid model by Planck,[18] Reiche,[21] Tolman,[14] and many others. It is easily seen to be equivalent to Kemble and Van Vleck's Eq. (10) or to Eq. (1) of Part II.

supposition that the model is rigid. The vibrational quantum number then does not enter,[4] and the energy is

$$W(m)=(m^2h^2/8\pi^2I)+A\,, \tag{3}$$

where I is the moment of inertia and A is a constant independent of m. According to the new quantum mechanics, the rotational quantum number m is to be given the values $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$ in contrast to the whole quantum values characteristic of the old quantum theory. In order to make a closer connection with band spectrum notation we employ a rotational quantum number m one-half unit larger than the number j sometimes employed so that $m^2-\frac{1}{4}$ occurs in place of $j(j+1)$. This is, of course only a difference in notation, and our procedure corresponds to the Landé rather than Sommerfeld usage. That Eq. (3), with half quanta, is the proper value for the energy of a rigid rotator in the new mechanics has been shown by Heisenberg,[2] Schrödinger,[5] Mensing,[6] Dennison,[7] and others.[8] According to Schrödinger[5] the additive constant A is $-h^2/32\pi^2I$, making $W=j(j+1)h^2/8\pi^2I$ in Sommerfeld's notation. Somewhat different values of A have been proposed by Dennison[7] and others, but such differences are of no concern to us, as by Eqs. (1, 2) the additive constant in the energy does not affect the specific heat in any way.

Above room temperatures we must consider the vibrational specific heat, and it is then necessary to employ an elastic model. Also at lower temperatures the centrifugal expansion influences the specific heat to a certain degree. With an elastic model the energy W cannot be evaluated numerically until we specify the nature of the restoring force $F(r)$ for the nuclear vibrations. We have in general no knowledge concerning the form of $F(r)$ except that it must vanish as $1/r^2$, or more rapidly, for large values of r, and must be an approximately linear function of r when the nuclear separation r is close to its equilibrium value r_0. As first noted by Kratzer,[9] these requirements are conveniently met by taking

$$F(r)=a(r-r_0)/r^3. \tag{4}$$

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[4] In the new mechanics there is a half quantum of vibratory energy even at the absolute zero, but, neglecting centrifugal expansion, this only adds a constant to the energy unless the temperature is so high that larger vibrational states are excited.

[5] E. Schrödinger, Ann. der Physik **79**, 489 (1926); Phys. Rev. (in press).

[6] Lucy Mensing, Zeits. f. Physik **36**, 814 (1926).

[7] D. M. Dennison, Phys. Rev. **28**, 318 (1926). Dennison's quantum numbers m, n are the same as $m-\frac{1}{2}, \sigma$ in our notation.

[8] L. Brillouin, Comptes Rendus **182**, 374 (1926); I. Tamm, Zeits. f. Physik, **37**, 685 (1926); O. Halpern, *ibid.* **38**, 8 (1926); J. R. Oppenheimer, Proc. Cambr. Phil. Soc. **23**, 327 (1926).

[9] A. Kratzer, Zeits. f. Physik **3**, 289 (1920).

This assumption, which was used in Kemble and Van Vleck's paper[1] on vibrational specific heats, greatly simplifies the calculation and enables one to determine the energy without resorting to series developments. We do not pretend that the approximation (4) is valid for large values of $r-r_0$ but this is unnecessary since an accurate formula for large displacements is not needed in our study of specific heats. Kratzer,[9] also independently Kemble and Van Vleck,[1]showed that with (4) the energy in the old quantum theory took the very simple form

$$W(m,n)=-\tfrac{1}{2}u^{-2}h\nu_1(un+\sqrt{1+u^2m^2})^{-2}+\text{constant}, \tag{5}$$

where u is the ratio ν_1/ν_0 of the lowest quantum rotational frequency $\nu_1=h/4\pi^2I_0$ to the frequency ν_0 of infinitesimal nuclear vibrations. It is easily shown that $I_0=Mr_0^2$ and $\nu_0^2=a/4\pi^2Mr_0{}^3$, where $M=m_1m_2/(m_1+m_2)$ and m_1, m_2 are the masses of the two nuclei in the diatomic molecule.

In the new quantum mechanics, too, the assumption (4) (r and r_0 now being matrices) greatly simplifies the calculation, for then the energy takes exactly the same form (5) as in the old theory, except that now the rotational and vibrational quantum numbers m and n are both to be given half instead of whole quantum values. This result was proved in a recent paper by Fues[10] and has also been obtained independently by the author. We may note that without going through Fues' detailed solution of the Schrödinger wave equation, the result (5) (with half quanta) can be derived in a very simple manner by comparison of the Hamiltonian function resulting from (4) with that of a hydrogen atom. As shown by Miss Mensing,[6] the calculation of W in a central field for a given value of m is reducible to a problem of one degree of freedom by substituting $(m^2-\frac{1}{4})h^2/4\pi^2$ for the square of the resultant angular momentum. With the simplification (4) the Hamiltonian function is then

$$\frac{1}{2M}\left(\boldsymbol{p}_r^2+\frac{(m^2-\frac{1}{4})\,h^2}{4\pi^2\boldsymbol{r}^2}\right)-\frac{a}{\boldsymbol{r}}+\frac{1}{2}\,\frac{a\boldsymbol{r}_0}{\boldsymbol{r}^2}+\frac{1}{2}\,\frac{a}{\boldsymbol{r}_0}=W, \tag{6}$$

where matrices are written in bold-face type. Neglecting the trivial additive constant $a/2\boldsymbol{r}_0$, Eq. (6) is like the Hamiltonian function for the hydrogen atom except in the numerical values of the coefficients of $1/\boldsymbol{r}$ and $1/\boldsymbol{r}^2$. On comparing coefficients with those for the hydrogen atom it is easily seen that the energy W for our problem can be obtained simply by substituting a for Ze^2 and $(m^2+4\pi^2ar_0Mh^{-2})^{\frac{1}{2}}$ for k

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[10] E. Fues, Ann. der Physik **80**, 367 (1926). Our Eq. (5) is equivalent to combination of his Eqs. (19) and (39).

in the energy-formula of the hydrogen atom. Eq. (5) then follows on remembering that in the new quantum mechanics the energy of an H atom is still the well-known Balmer expression $-2\pi^2 MZ^2e^4/(n+k)^2h^2$, except that now both the radial quantum number n and azimuthal quantum number k are half-integral.

Value of p_m. For a long time there was considerable uncertainty as to whether p_m should have the value $2m$ or $2m+1$, but the new quantum mechanics indicates very definitely that the value $2m$ ($2j+1$ in the Sommerfeld notation) is correct,[11] since in an external field with axial symmetry the axial component of angular momentum can assume the $2m$ values $-(m-\frac{1}{2}), \cdots, (m-\frac{1}{2})$. This result is required by the new mechanics for molecules (at least if polar) as well as atoms. In HCl an independent experimental proof of the a priori probability $2m$ is furnished by Bourgin and Kemble's[12] recent data on absorption intensities, and here also the half quantum numbers $m=\frac{1}{2}, \frac{3}{2}, \cdots$ are directly confirmed by Czerny's[13] measurements of frequencies in the "pure rotation" infra-red spectrum.

Failure of the simple theory. Unfortunately an impossible specific heat curve is obtained if we use the a priori probability $p_m=2m$ and half quanta[14] $m=\frac{1}{2}, \frac{3}{2}, \cdots$ to be expected from the simple theory of the rotator in the new mechanics. It is easily seen, as noted by various writers,[15,16,17] that these assumptions concerning p_m and m lead to a curve of the same type as that derived by Planck[18] with the old cell ("second") form of the quantum theory. Instead of rising gradually to the equipartition value R, the rotational specific heat with this curve ascends to a maximum about 10 percent above R and then gradually descend to the latter. No such effect is observed in hydrogen.[19] If the moment of inertia is adjusted to yield agreement

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[11] The objection cited by Pauling (Phys. Rev. **27**, 568, 1926) that an a priori probability $2m$ gives the wrong sign to the temperature coefficient of the dielectric constant in HCl etc., disappears if the calculations are made by the new rather than old quantum mechanics. This has recently (Aug. 1926) been shown independently by Mensing and Pauli (Phys. Zeits. **27**,509);Kronig (Proc. Nat. Acad. **12**, 488);and Van Vleck (Nature **118**, 226).

[12] D. G. Bourgin and E. C. Kemble, Phys. Rev. **27**, 802A (1926).

[13] M. Czerny, Zeits. f. Physik **34**, 227 (1925).

[14] The possibility of these half quanta in hydrogen was first suggested by Tolman (Phys. Rev. **22**, 470, 1923), but his calculations stressed the a priori probability $2m+1$.

[15] E. Hutchisson and J. H. Van Vleck, Phys. Rev. **25**, 243A (1925).

[16] G. H. Dieke, Physica, **5**, 412 (1925); also Phys. Rev. **27**, 639A (1926).

[17] H. Lessheim, Zeits. f. Physik, **35**, 831 (1926).

[18] M. Planck, Verh. d. D. Phys. Ges. **17**, 407 (1915).

[19] It would be interesting if measurements could be conducted at sufficiently low temperatures to see whether the anomalous maximum is found in the specific heat of

at low temperatures, the maximum would come at about 250°K whereas the specific heat observed for hydrogen is still below the equipartition value at this temperature.

2. EMPIRICAL WAYS OF ESCAPING THE SPECIFIC HEAT DILEMMA

We are thus confronted with a serious difficulty. Since we have abundant evidence for the new mechanics, the failure of the simple theory is probably because the H_2 molecule is non-polar and so cannot be quantized in the same way as a simple rotating dipole such as HCl. Just what modifications should be made is, of course, uncertain in the absence of a detailed quantum-mechanical analysis of the electron orbits in non-polar molecules. We shall list below several specific ways of crawling out of the specific heat dilemma by assuming more or less empirically a different quantization than in the simple polar rotator. Most of the suggestions appear rather artificial and are frankly only conjectures, but one must at the same time realize that observed specific heats furnish fairly definite evidence as to what a priori probabilities and ranges of quantum numbers are legitimate. For this reason it does not appear altogether unlikely that the true specific heat curve is of the form (*b*) given below.

(*a*) *Whole quanta.* The most obvious possibility is that we still have $p_m = 2m$ but that the rotational quantum number assumes the integral values $m = 1, 2, \cdots$ instead of $\frac{1}{2}, \frac{3}{2}, \cdots$. We then get a specific heat curve calculated for a rigid molecule by Bohr[20] as early as 1916, and also independently by several other writers.[21] The computations were extended to the elastic model by Kemble and Van Vleck.[1] They show that quite satisfactory agreement can then be obtained with observed specific heats up to 2000°K provided the moment of inertia and nuclear vibration frequency are arbitrarily assigned the proper values.[22]

HCl, for we have abundant spectroscopic evidence that the simple rotator theory can be applied to HCl even though it fails in H_2. Such measurements, however, would be difficult, if not impossible, as the maximum in HCl comes at about 12°K.

H. C. Hicks and A. C. G. Mitchell have recently made an interesting attempt to calculate the specific heat of HCl from spectroscopic energy levels, but unfortunately use an a priori probability $2m+1$, Journ. Amer. Chem. Soc. **48**, 1520 (1926).

[20] N. Bohr, Abhandlungen über Atombau aus den Jahren 1913–1916. (Vieweg, 1921).

[21] E. C. Kemble, Doctor's Dissertation, Harvard University, 1917 (unpublished); F. Reiche, Ann. der Physik, **58**, 657 (1919); S. Rotszajn, *ibid.* **57**, 81 (1918).

[22] Kemble and Van Vleck used integral values for the vibrational quantum number, but Hutchisson shows in Part II of the present paper that the introduction of the half-integral vibrational quantum numbers characteristic of the new mechanics (cf. Section 1) does not alter the specific heat curves materially.

The great difficulty with the introduction of these whole quanta is that it is very doubtful whether they are allowable in the new quantum mechanics for a non-gyroscopic rotator, although Born, Heisenberg, and Jordan[2] have shown that in general the resultant angular momentum of an isolated dynamical system can be either a half or whole multiple of $h/2\pi$. By examination of the characteristic values of his partial differential equation, which is allied to the matrix theory, Schrödinger[5] is lead unambiguously to half quanta for the rotating dipole in three dimensions. Also Dennison claims that with whole quanta the transition probabilities do not fulfill the proper boundary conditions, i. e., do not vanish when the final state is impossible.[23] At the same time we must keep in mind that the hydrogen molecule is non-polar and that the low frequency part of its electrical field is that of a quadrupole rather than of a dipole (see Section 3) so that the amplitudes of the type considered by Dennison and others do not enter in radiation. It is barely possible that a quantization of a non-polar molecule with the same amount of electronic symmetry as hydrogen will yield whole quanta when the internal degrees of freedom are carefully considered. Against this possibility is the general rule advanced by band-spectrum spectroscopists[24] that whole or half quanta are to be used according as the number of electrons is odd or even.

(*b*) *Exclusion of the state* $m=\frac{1}{2}$. Another possibility is that the a priori probability is $2m$, but that the rotational quantum number m only assumes the values $\frac{3}{2}, \frac{5}{2}, \cdots$. We then get a specific heat curve of the type calculated independently by various authors[15,16,17] for the rigid molecule, and extended to the elastic model by Hutchisson. This curve is in quite satisfactory agreement with observed data. Graphs of the curves obtained for the elastic model under the assumptions (*a*) and (*b*) are given by Hutchisson in Part II, to which the reader is referred for detailed comparison of the theoretical curves and experimental values. Hutchisson shows the preference between the curves for cases (*a*) and (*b*) depends largely upon what experimental data are accepted as most accurate.

We shall see in Section 3 that some plausibility is lent to the suggestion (*b*) from a study of the Fulcher bands of hydrogen, but on the other hand it will be shown in Section 4 that the observed chemical constant of hydrogen is hard to reconcile with the idea that the hydrogen molecule has an a priori probability 3 (i. e., three different positions)

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[23] Dennison, l.c. 7, p. 326.

[24] R. S. Mulliken, Proc. Nat. Acad. **12,** 148 (1926).

in its state of lowest energy. It is hard to imagine any theoretical basis for the complete exclusion of the state $m=\frac{1}{2}$ without diminishing or otherwise affecting the a priori probabilities of the remaining states, though it is barely possible that some such surprising result may ensue when a detailed analysis of electron orbits in non-polar molecules is made with the new quantum mechanics and especially with the extension of the Pauli exclusion principle which is used by Heisenberg in explaining the helium spectrum, etc., and which will be briefly described on p. 1003. Use of the a priori probability $2m-1$ instead of $2m$ would automatically exclude the state $m=\frac{1}{2}$, but Hutchisson shows in Part II that the resulting specific heat curve is unsatisfactory.

(*c*) *Exclusion of every other state.* Ehrenfest and Tolman[25] have shown that in a non-polar molecule the rotational quantum number can change only infrequently and only by even multiples of $h/2\pi$, unless there are simultaneous electron jumps. For this resaon they suggest that every other value of the rotational quantum number must be excluded in a non-polar molecule. The discussion of the theory for such a procedure will be deferred until section 3, where it will be shown that the necessity of including electronic as well as nuclear transitions raises some serious difficulties, but that there is nevertheless quite possibly some analogy to the Pauli-Heisenberg exclusion principle. Irrespective of the theory we must note with Mecke[26] that there is some very strong experimental evidence in the helium band spectrum for successions of states in which every other value of the rotational quantum number is wanting, for otherwise it would be necessary to introduce the unreasonable "quarter quanta," which will be criticized in Section 3 in connection with the hydrogen and helium band spectra.

If we assume that m has the values $\frac{1}{2}, \frac{5}{2}, \frac{9}{2}, \cdots$ we are led to an impossible specific heat curve, as this supposition gives a ratio 1 : 5 between the probabilities of the two lowest state, whereas Schrödinger[27] has shown that observed specific heats demand this ratio to be about 1 : 2. Better results are obtained with $m=\frac{3}{2}, \frac{7}{2}, \frac{11}{2}, \cdots$ but even then the curve is probably too steep, as it is easily shown to be intermediate in form between the impossible Planck curve and the curve obtained under assumption (*a*), and Hutchisson shows that even the latter is rather too high at room temperatures. If we use only alternate values of m it is very likely that the state $m=\frac{1}{2}$ is wanting, as it is not found in the Curtis classification of the helium band spectrum or the

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[25] P. Ehrenfest and R. C. Tolman, Phys. Rev. **24,** 287 (1924).

[26] R. Mecke, Phys. Zeits. **26,** 217 (1925); Zeits. f. Physik, **31,** 709; **32,** 823 (1925).

[27] E. Schrödinger, Zeits. f. Physik, **30,** 341 (1924).

Takahashi-Dieke interpretation of the hydrogen Fulcher bands (see section 3). We might therefore try taking $m=\frac{5}{2}, \frac{9}{2}, \frac{13}{2}, \cdots$, although this would not appear as likely as $m=\frac{3}{2}, \frac{7}{2}, \frac{11}{2}, \cdots$. With $p_m=2m$ we would then get a very good specific heat curve, as it is not difficult to show that it would be intermediate in form between the curves obtained under the assumptions (*a*) and (*b*) and these curves fall on opposite sides of some of the experimental values (see Part II). The a priori probability $2m-1$ would have the advantage of automatically excluding the state $m=\frac{1}{2}$, but the corresponding curve would probably be too steep.

If we exclude alternate values of the rotational quantum number it is necessary to employ rather large moments of intertia, viz., about[28] 7×10^{-41} gm. cm^2 with $m=\frac{3}{2}, \frac{7}{2}, \cdots$ and 9×10^{-41} with $m=\frac{5}{2}, \frac{9}{2}, \cdots$. These values appear rather large; the latter, especially is larger even than the moments of inertia deduced spectroscopically by Dieke for excited hydrogen molecules (Section 3). Also the difficulty with chemical constants mentioned under (*b*) still must be considered.

(*d*) *Diminished a priori probability for every other state.* We shall see in Section 3 with Slater[29] that the alternating intensities found in the hydrogen band spectrum furnish some evidence that every other state has a diminished a priori probability (to be contrasted with the complete exclusion of every other state under assumption *c*). Schrödinger[27] has shown that with the half quanta $m=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$, a satisfactory specific heat curve can be obtained by assuming the a priori probabilities of the three lowest states to be in the ratio 4 : 7 : 17 (or possibly 1 : 2 : 4) instead of the theoretical ratio 4 : 12 : 20 for the HCl-type rotator. Schrödinger's probabilities seem to have no theoretical justification, but his curves will not be very materially modified is we assume the ratio to be 4 : 7 : 20 (or 4 : 8 : 20). This might be interpreted to mean that the states $m=\frac{3}{2}, \frac{7}{2}, \cdots$ had an a priori probability $2am$ differing by a factor $a=\frac{7}{12}$ (or $\frac{2}{3}$) from those of the remaining states. This, however, does not appear likely as we have already noted that the state $m=\frac{1}{2}$ is usually wanting in the bands with alternating intensities. Another, more likely possibility, suggested to the writer by Dr. Mulliken, is the complete exclusion of the state $m=\frac{1}{2}$, and diminished a priori probabilities for $m=\frac{5}{2}, \frac{9}{2}, \cdots$.

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[28] Without calculating the specific heat curves in detail we can deduce the approximate moments of inertia because observed specific heat data fix quite definitely the difference in energy between the two lowest permissible states. See Schrödinger.[27] If we excluded alternate states this energy difference would be increased unless we made an offsetting increase in the moment of inertia.

[29] J. C. Slater, Nature, April 17, 1926.

We should then have virtually a combination of (*b*) and (*d*). A satisfactory specific heat with this hypothesis does not appear altogether impossible, but calculations have not been attempted since they would be extremely arbitrary without anything to guide us on the numerical values of the ratios in the alternating sequence of probabilities. Theoretical difficulties connected with the weak quantization of every other state will be mentioned in Section 3.

(*e*) *Gyroscopic molecule.* If the molecule is gyroscopic due to an electronic angular momentum $\sigma h/2\pi$ about the axis of figure, then, as shown in fine print below, a formula for the specific heat is obtained which is the same as for a non-gyroscopic model of like moment of inertia and elasticity, except that in summing over the various states in Eq. (2) the rotational quantum number m must be given the values $\sigma+\frac{1}{2}, \sigma+\frac{3}{2}, \cdots$, instead of $\frac{1}{2}, \frac{3}{2}, \cdots$. That this is the proper range of values for m can be seen from examination of the Hönl-London amplitudes[30] for gyroscopic molecules or more directly from Dennison's matrix calculations[7] for the rigid gyroscopic molecule (his "symmetrical rotator"). The minimum value of m is greater than in the non-gyroscopic case, of course, simply because the resultant angular momentum cannot be less than the axial component thereof. It is immediately seen that a simple and tempting explanation of the ranges of values of m used in (*a*) and (*b*) is obtained if $\sigma=\frac{1}{2}$ in case (*a*) or $\sigma=1$ in (*b*), but unfortunately this is probably not the solution of the specific heat dilemma, as a gyroscopic molecule is incompatible with the diamagnetism[31] of hydrogen or with the absence of an appreciable Zeeman effect in the Fulcher bands. The latter, in fact, are not ordinarily susceptible to magnetic fields, despite the fact that according to Takahashi or Dieke (Section 3) their minimum m-value is probably $\frac{3}{2}$, indicating that the absence of the state $m=\frac{1}{2}$ is not due to the existence of a $\sigma>0$. Of course, as long as the ratio of magnetic moment to angular momentum for the internal spins of the electrons is twice the corresponding ratio for the orbital motions,[32] it is possible to have a zero magnetic moment without the logical necessity of a vanishing resultant electronic angular momentum, but a study of atomic Zeeman effect levels indicates that this situation is altogether unlikely in hydrogen. Irrespective of the diamagnetism, strong

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[30] H. Hönl and F. London, Zeits. f. Physik, **33**, 803 (1925).

[31] Hydrogen is about twice as diamagnetic as helium. Cf. A. P. Wills, and L. G. Hector, Phys. Rev. **23**, 209 (1924); L. G. Hector, *ibid.* **24**, 418 (1924).

[32] E. H. Kennard, Phys. Rev. **19**, 420A (1922); also especially Uhlenbeck and Goudsmit, Naturwissenschaften **13**, 953 (1925); Nature **117**, 264 (1926).

evidence that the hydrogen molecule is non-gyroscopic is furnished by analogy with atomic spectral terms. There is increasing evidence that there is a considerable similarity in the structure of spectra of atoms and molecules with equal numbers of valence electrons.[33] Since the hydrogen molecule contains two electrons, its spectral terms should thus show some resemblance to those of alkaline earth atoms,[34] and the normal states of the latter are always S-terms without either magnetic moment or angular momentum.

Theory of specific heat of gyroscopic molecule. For a *rigid* model the equivalence of the specific heat of a gyroscopic molecule to that of a non-gyroscopic one in which the rotational quantum number is given artificially by the values $\sigma+\frac{1}{2}$, $\sigma+\frac{3}{2}$, $\cdots$ (instead of $\frac{1}{2}$, $\frac{3}{2}$, $\cdots$) is obvious. For in the new[7] as well as the old quantum mechanics the rigid gyroscopic rotator has an energy of the form $B(m^2-\sigma^2)+C$, where B and C are constants. In specific heat calculations we are interested only in the minimum value of σ and need not sum over states with larger σ since they are occupied by only a negligible fraction of the molecules at ordinary temperatures. Because σ can thus be treated as fixed, the gyroscopic effect in a rigid molecule, besides increasing the minimum value of m, only introduces an additive constant $-B\sigma^2$ in the energy, and such a constant has no influence on the specific heat.

In the case of *elastic* molecules the equivalence mentioned in the preceding paragraph can be easily established by a simple calculation. Since the exact orbits of the electrons are unknown we may allow for their gyroscopic effect by imagining a fly-wheel to be mounted on the axis joining the nuclei. If we neglect terms involving the ratio of electronic to nuclear mass no particular difficulty is introduced if we assume the moment of inertia A of the fly-wheel to be a function of r, in accordance with the fact that the size of the electron orbits doubtless depends on the nuclear separation. The nuclear restoring force is then the r-derivative of $V(r)+\sigma^2h^2/8\pi^2A(r)$ rather than of the ordinary potential energy $V(r)$, and our model of the molecule may be characterized as an elastic top with masses m_1 and m_2 at the two ends and with variable moment of inertia $A(r)$. It is found that in either the new or old quantum mechanics the energy formula is of the same form as for a non-gyroscopic model with similar radial force, except that m^2 must be replaced by $m^2-\sigma^2$. We omit the details of the calculations inasmuch as the hydrogen molecule is probably non-gyroscopic. If in particular we make the simplifying assumption (4), the expression for the energy still takes the form (5), except that the constant under the radical is $1-\sigma^2u^2$ instead of 1. This alteration is inconsequential since the energy can still be thrown into the form (5) by replacing u by $u'=u/(1-\sigma^2u^2)^{\frac{1}{2}}$ and ν_1 by $\nu_1'=\nu_1/(1-\sigma^2u^2)^2$. Such a change in the constants is of no importance for specific heats as here u and ν_1 are regarded as perfectly arbitrary. Also the difference between u, ν_1 and u', ν_1' is negligible since u^2 is the square of the ratio of the lowest rotational to the vibrational frequency, and hence $1-\sigma^2u^2$ is nearly unity.

It is interesting to note that in the ordinary mechanics the elastic gyroscopic molecule is a problem which can be treated by separation of variables, even when the moment of inertia $A(r)$ of the fly-wheel is constrained to vary with r, provided we neglect terms

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[33] R. T. Birge, Nature, **117**, 300 (1926); F. Hund, Zeits. f. Physik, **36**, 657 (1926); R. Mecke, *ibid.* **28**, 261 (1924); Naturwissenschaften, **13**, 698, 755 (1925); R. S. Mulliken, Phys. Rev. **26**, 1, 561 (1925); Proc. Nat. Acad. **12**, 144 (1926); J. W. Nicholson, Phil. Mag. **50**, 650 (1925).

[34] Cf. Mulliken, Proc. Nat. Acad. **12**, 338 (1926).

[35] M. Born, die Naturwissenschaften, **10**, 677 (1922).

involving the ratio of the electronic to nuclear mass. The coordinates to be used are the nuclear separation r and a set of Eulerian angles θ, φ, ψ giving the position of the axis of figure and amount of rotation of the fly-wheel about same. By setting up the Lagrangian function one finds that the angular momentum $p_\psi = A(\dot{\psi}+\dot{\varphi}\cos\theta) = \sigma h/2\pi$ of the fly-wheel is constant. Because of this and the fact that the angular momentum of the nuclei is perpendicular to that of the fly-wheel, the interesting result is obtained that the axis of figure precesses regularly about the invariable axis of angular momentum and there is no nutation despite the oscillations in the nuclear separation and radius of the fly-wheel. This is also true in the new mechanics.

The crossed-orbit model of the hydrogen molecule. At this point we may note that in the old quantum theory we would have $\sigma = 1$ if we assumed a model of the hydrogen molecule proposed by Born[35] which is the natural analog of the Bohr-Kemble crossed-orbit model of the normal helium atom (to be contrasted with the early Bohr circle model which had $\sigma = 2$). This crossed-orbit model[36] has a good deal of dynamical simplicity and symmetry, but is incompatible with the diamagnetism of hydrogen.[37] A calculation of the energy and moment of inertia of the crossed-orbit model of the hydrogen molecule has been made by E. Hutchisson with the old quantum theory and will be published in the PHYSICAL REVIEW. His calculations yield a much greater work of ionization than is observed, and a moment of inertia 4.9×10^{-41} gm cm^2 which is larger than the estimates 1.98×10^{-41} and 2.99×10^{-41} deduced from specific heat curves with assumptions (*a*) and (*b*) respectively. These discrepancies are, of course, not surprising since the results with the new mechanics are doubtless different. We had originally intended to make the crossed-orbit model the central point of the discussion in the present article but have now relegated it to a subordinate position since in the new mechanics the normal hydrogen molecule is probably non-gyroscopic, although in other respects it may show a limited amount of resemblance to the crossed-orbit model of the old theory.

Einstein-Bose statistics immaterial. In a conversation with the writer, Dr. Kramers raised the question whether the rotational specific heat might not be modified at low temperatures by employing the Einstein-Bose statistics,[38] for which the evidence is accumulating. It is well known that according to this new statistics the Maxwell distribution of translational velocities is modified at very low temperatures, and Jordan[39] has indicated that there is a corresponding departure from the Boltzmann distribution formula for determining the distribution of atoms or molecules among a discrete succession of quantized states, as a factor $1/(e^{A+W/kT}-1)$ occurs in place of $e^{-A-W/kT}$. The specific heat equation (1) based on the Boltzmann distribution formula is then no longer applicable. This fact, however, cannot be the solution of the specific heat difficulty, for the corrections to (1) are entirely insigni-

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[36] For further description and discussion of this model, with references, see J. H. Van Vleck, "Quantum Principles and Line Spectra" (Bull. Nat. Research Council No. 54), Chap. VII, especially p. 90.

[37] Cf. Van Vleck, l.c.,[36] p. 99.

[38] We shall not attempt to explain the theory of the new statistics. See N. Bose, Zeits. f. Physik **26**, 178 (1925); A. Einstein, Berlin Acad., 1924, 261; 1925, 3, 18; also summary in A. Landé, "Die Neuere Entwicklung der Quantentheorie," 2nd Ed., p. 126.

[39] P. Jordan, Zeits. f. Physik **33**, 649 (1925).

ficant except at temperatures which are so low that the rotational specific heat has dropped to practically nil in hydrogen. The reason why the ordinary statistics can be employed in calculating specific heats is simply that the temperature and pressure range is such that two or more molecules seldom crowd into the same cell of the phase space, so that the Einstein-Bose interference effcts do not enter appreciably. A simple calculation [40] indicates that the modifications will first become appreciable when the quantity $\chi = (2\pi mkT)^{3/2}V/h^3N$ (which is of the order of magnitude of e^A unless A is very small) is comparable with unity. Here m is the mass of the molecule, and N/V is the no./cc. Now even at a temperature as low as 30°K, at atmospheric pressure we still have $\chi > 10^2$ so that the modifications are very small. This as what we should expect since no large "degeneration" of any gas has yet been observed experimentally.

Specific Heats of N_2,O_2,CO. We now digress to revise a previous attempt of Kemble and Van Vleck [1] to calculate the moments of inertia of N_2,O_2, and CO from specific heat data. In Scheel and Heuse's original paper the conclusion was reached that the specific heats of these gases fell appreciably below the equipartition value $c_p = \frac{7}{2}R$ at 92°K. Kemble and Van Vleck found that absurdly low moments of inertia were necessary to explain this result. Consequently they suggested as one possibility that the values given by Scheel and Heuse [41] for specific heats in the ideal gas condition might be too low because of an incorrect reduction to zero pressure of the measurements made at one atmosphere. Investigations of Bartels and Eucken [42] on the equation of state of nitrogen at low temperatures, of which Kemble and Van Vleck were not aware, indicate that this is indeed the case. Bartels and Eucken find the Berthelot equation of state employed by Scheel and Heuse is inaccurate at low temperatures, and they conclude that the specific heats of N_2,O_2, and CO are probably normal at 92°K. This is substantiated by recent experiments of Schreiner [43] who finds that

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[40] Cf., for instance, Landé, l.c.,[38] p. 132. Because the internal vibrational and rotational degrees of freedom must be added to those of translation, our phase space is 12 instead of 6-dimensional. However at low temperatures and also in calculating the order of e^A at higher temperatures, we may consider all molecules to be in their lowest rotational and vibrational state. We then have virtually a 6-dimensional problem, except that the a priori probability of the lowest state and Ehrenfest-Trkal symmetry number will enter as factors (cf. §4) but these factors will clearly not change orders of magnitude.

[41] Scheel and Heuse, Ann. der. Physik **40,** 473 (1913).

[42] R. Bartels and A. Eucken, Zeits. f. Phys. Chem. **98,** 70 (1921).

[43] E. Schreiner, *ibid.* **112,** 1 (1924).

the specific heats of these gases conform to the classical theory even at 60°K. The moments of inertia of N_2,O_2, and CO thus cannot be calculated from existing specific heat data.

3. RELATION TO BAND SPECTRA

It is essential that the theoretical interpretation of the specific heat of hydrogen be consistent with that of its band (secondary) spectrum. This requirement of consistency may furnish some light on what values for the moment of inertia and nuclear vibration frequency can legitimately be assumed in calculating specific heats and also whether half or whole quanta should be employed.

Moments of inertia. Here we must remember that excited states have larger orbits and hence ordinarily greater moments of inertia that normal states. Consequently we may expect the analysis of visible band spectra to set only an upper limit to the moment of inertia which it is permissible to use in specific heats.

Whole quanta were employed in Lenz's[44] early interpretation of the Fulcher bands of hydrogen, yielding a moment of inertia about 1.85×10^{-41} gm. cm.^{2}. After the advent of half quanta it was shown by Allen[45] and Curtis[46] that better results could be obtained if the rotational quantum number m were also given the values $\frac{1}{2}, \frac{3}{2}, \cdots$. In consequence of this and especially of the well-known success of half quanta in HCl it has been commonly supposed that the values $\frac{1}{2}$, $\frac{3}{2}, \cdots$ should be used in the specific heat of hydrogen, but we have seen that this is not consistent with experimental data unless we assume the rather unlikely a priori probabilities given in (*d*), Section 2. Irrespective of this fact, another difficulty confronting the Allen-Curtis interpretation of the Fulcher bands is that it gives a smaller moment of inertia than does specific heats. The moment of inertia 1.4×10^{-41} deduced from specific heats by Tolman[14] and Schrödinger[27] under the assumption $m=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$ is considerably smaller than the value 1.98×10^{-41} obtained with whole quanta (case *a*, Section 2) or 2.99×10^{-41} obtained with exclusion of $m=\frac{1}{2}$ (*b*, Section 2). This fact has frequently been cited [47] as an argument favoring the half-quanta $m=\frac{1}{2}, \frac{3}{2}, \cdots$ in specific heats, but even the value 1.4×10^{-41} is larger than one of

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[44] W. Lenz, Verh. d. D. Phys. Ges. **21**, 632 (1919). See also M. Kiuti, Proc. Phys.-Math. Soc. Japan (3) **5**, 9 (1923).

[45] H. S. Allen, Proc. Roy. Soc. **106A**, 69 (1924).

[46] W. E. Curtis, *ibid.* **107A**, 570 (1925). Like Allen, Curtis uses both half and whole quanta. The main difference between their interpretations is that the half and whole quantum states are transposed.

[47] Cf., for instance, Tolman,[14] Schrödinger,[27] Lessheim.[17]

the moments of inertia 1.25×10^{-41} deduced from band spectra by Curtis[46].

An interpretation of the Fulcher bands totally different from that of Lenz, Kiuti, Allen and Curtis has been proposed by Takahashi[48] and also independently by Dieke.[49] With the latter authors the rôles of vibrational and rotational quantum numbers are interchanged, the latter being indentified with Allen's "vertical" rather than "horizontal" series. The most important bands become "Q" rather than "P" or "R" branches,[50] and the rotational quantum number is given only the values $\frac{3}{2}$, $\frac{5}{2}$, $\cdots$, excluding the state $m=\frac{1}{2}$ and suggesting possibility (*b*), Section 2. The interpretation proposed by Takahashi and Dieke is probably preferable to the other viewpoints mentioned in the preceding paragraph. In the first place it is most natural to identify successive rotational quantum numbers with the "vertical" series and vibrational quantum numbers with the "horizontal," rather than vice versa, for the frequency differences between successive terms of the vertical series are smaller than those of the horizontal. Also moments of inertia are obtained which are larger than the values used in specific heats, as should be the case. Dieke derives the moment of inertia 8.2×10^{-41} for some of the excited states, while Takahashi gets the even larger value 2×10^{-40}.

The classification of lines in the hydrogen secondary spectrum has been greatly extended through the researches of Richardson and Tanaka,[51] Sandemann,[52] and Curtis.[53] Most of the moments of inertia deduced by Richardson and Tanaka are smaller than the values required by (*a*) or (*b*), Section 2, and one, at least, of their moments of inertia is smaller even than that with (*d*), Section 2. This may be a serious difficulty, for Richardson's classification includes a large number of lines not comprised in the Fulcher bands and so not included in the ordinary Takahashi-Dieke scheme. Fortunately, however, Richardson has just published another paper[54] in which he gives a large numer of

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[48] Y. Takahashi, Jap. Journ. of Phys. **2,** 95 (1923).

[49] G. H. Dieke, Proc. Amsterdam Acad., **27,** 490 (1924). Dieke's interpretation of the relations between the constants in the band spectrum differs from Takahashi's in some respects.

[50] We use the terminology of band spectroscopists, who call a spectral series of the "P" or "R" type if the rotational quantum number increases or decreases by unity in emission, and of the "Q" type if it is unaltered.

[51] Richardson and Tanaka, Proc. Roy. Soc. **107A,** 602 (1925); also Richardson, *ibid.* **108A,** 553; **109A,** 35, 239 (1925).

[52] I. Sandemann, *ibid.* **108A,** 607 (1925); **110A,** 326 (1926).

[53] W. E. Curtis, Phil. Mag. **1,** 695 (1926).

[54] O. W. Richardson, Proc. Roy. Soc. **111A,** 714 (1926); Nature, **118,** 116 (1926).

important new series relations which are intimately related to those of Takahashi and Dieke, and which can, in fact, partly be regarded as extensions of the latter. Previously missing P and R branches are supplied, etc. Richardson gives a new method of estimating the moment of inertia which is perhaps more accurate than those of Takahashi or Dieke. It gives moments of inertia mostly between 3×10^{-41} and 4×10^{-41}, or larger than any of the values deduced from specific heats in Section 2 except in case (*c*), in which every other rotational state is excluded. These recent developments are perhaps especially favorable to a curve of the type (*b*), Section 2, which yields a moment of inertia 2.99×10^{-41}. The new Richardson series relations seem to require at least a partial abandonment of some of the rotational classifications given in previous articles by Richardson[51] and Tanaka,[51] and possibly the revision is so complete that the difficulty of low moments of inertia is entirely avoided. At any rate the hydrogen secondary spectrum is so complicated and difficult to interpret that it does not as yet appear to furnish any conclusive evidence against any of the various specific heat curves enumerated in Section 2 except that case (*c*) probably requires an excessively large moment of inertia.

Nuclear vibration frequency. It is quite probable, however, that spectroscopists of the ultra-violet will soon be able to supply the moment of inertia of the normal state of the hydrogen molecule and so definitely determine the correct value for use in calculating specific heats. Ultraviolet measurements made by Witmer[55] have already furnished the value 1.277×10^{14} sec^{-1} for the normal nuclear vibration frequency which agrees almost exactly with that used in curve (*b*). The relation of this value to that deduced from specific heats is discussed by Hutchisson in Part II.

Alternating intensities and the correspondence principle. A curious phenomenon encountered in the band spectra of non-polar molecules is that consecutive lines of series generated by varying the rotational quantum number are sometimes alternately weak and strong in intensity. Such anomalies are apparently found in the "vertical" series of the Fulcher bands. As noted by Dieke,[56] this fact must be regarded as a strong argument for the Takahashi-Dieke interpretation of these bands, since the alternations in intensities are always a rotational rather than vibrational effect. An adequate theoretical explanation of the alternating intensities has yet to be given. Very likely, as suggested by Slater,[29] this phenomenon is ultimately ascribable to the fact that

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[55] E. E. Witmer, Proc. Nat. Acad. **12,** 238 (1926).

[56] G. H. Dieke, Zeits. f. Physik **32,** 180 (1925); Phil. Mag. **50,** 173 (1925).

nuclei in non-polar molecules radiate like a quadrupole rather than a dipole. Slater's suggestion is intimately related to a modification in the quantum conditions for non-polar molecules suggested by Ehrenfest and Tolman,[25] whose theory is based on the correspondence principle and is explained in the following paragraph.

In the classical theory the electric field at a large distance R from the molecule is shown by Page[57] and others to be

$$\boldsymbol{E}=\frac{1}{Rc^2}\left[\left\{\frac{d}{dt}\left(\sum q\mathrm{v}\right)+\frac{1}{c}\frac{d^2}{dt^2}\sum(q\boldsymbol{r}\cdot\boldsymbol{M}\,\mathrm{v})+\cdots\right\}\times\boldsymbol{M}\right]\times\boldsymbol{M} \qquad (7)$$

where $\boldsymbol{M}$ is a unit vector in the direction of the radius R and where $\boldsymbol{r}$ and v are respectively the position and velocity vectors of the charge q. The summation is to be taken over all the charges in the system. If we wish to consider only the rotational motion of the electrons and do not attempt to analyze the motion of the electrons, we may use the so-called "dumb-bell" model of the molecule, which consists of two rigidly-connected point charges rotating in a common plane about their center of gravity. The summation $\sum$ in (7) then consists of only two terms. In polar molecules, such as HCl, the two ends of the dumb-bell are different. The first order term $\sum q\mathrm{v}$ then does not vanish and has the same frequency ω_m as a rotation of the molecule or dipole through 360°. In a non-polar molecule, however, the two ends of the dumb-bell are identical and the two nuclei make equal and opposite contributions to $\sum q\mathrm{v}$. The molecule may then be termed a "quadrupole" and a rotation through 180° will give a configuration indistinguishable from the initial one. Since $\sum q\mathrm{v}$ vanishes, the nuclear radiation is to a first approximation zero in a non-polar molecule. If, however, we consider terms in $\boldsymbol{E}$ of the order $1/c^3$, there will be a small amount of radiation whose frequency is that of a rotation through 180°. This follows since in the symmetric dumb-bell the term $\sum(q\boldsymbol{r}\cdot\boldsymbol{M}\,\mathrm{v})$ does not vanish and is easily seen to have the frequency $2\omega_m$. Consequently the effective frequency is twice that for the polarized molecule and identified with a change in angular momentum of amount h/π rather than $h/2\pi$, since by the correspondence principle the octave of a frequency is associated with a change of two units in the corresponding quantum number. Therefore Ehrenfest and Tolman tentatively suggest that in a non-polar molecule the fundamental period is $1/2\omega_m$, and that correspondingly the proper quantized values for the angular momentum are 0, h/π, $2h/\pi$, $3h/\pi$ instead of 0, $h/2\pi$, h/π, $\cdots$ so that compared with a polar molecule every other rotational state is

[57] L. Page, Phys. Rev. **20**, 18 (1922).

missing.[58] Here and elsewhere in the following discussion we assume for brevity that the lowest allowed value of the angular momentum is zero. Actually because of the half quanta characteristic of the new quantum mechanics it is likely either $\frac{1}{2}h/2\pi$ or $\frac{3}{2}h/2\pi$ (in the Landé notation), but can fictitiously be made zero through changing the origin for measuring angular momentum. This is legitimate for our purposes as the inclusion in the angular momentum of an additive term $\frac{1}{2}h/2\pi$ or $\frac{3}{2}h/2\pi$ common to all stationary states does not affect the essential nature of our conclusions.

Miscellaneous considerations relating to Ehrenfest and Tolman's suggestion. In order for the nuclear radiation to vanish to a first approximation, it is essential that the two nuclei have equal masses as well as equal charges, for otherwise the center of rotation is not equidistant from both nuclei. Hence we may have a pure rotation spectrum emitted by a non-polar molecule whose two nuclei are different isotopes of the same element. Such a spectrum, however, would obviously be faint even though it arises from the first order terms in (7).

In Ehrenfest and Tolman's paper it is assumed that the nuclei rotate in one and the same plane. This assumption is not valid in a gyroscopic molecule, for here the invariable axis of angular momentum is no longer normal to the line joining the nuclei. Hence a rotation through an angle 360° rather than 180° about the invariable axis is required to bring the nuclei back to a configuration indistinguishable from the initial one. So we see that in the second order radiation from a gyroscopic molecule the angular momentum can change by $h/2\pi$ as well as h/π. In fact, it is not difficult to work out the Fourier expansion of the nuclear part of the second term of (7) for gyroscopic molecules. It contains trigonometric terms in both $2\pi\omega_m t$ and $4\pi\omega_m t$ and of comparable amplitude for low values of the rotational quantum number m. For high temperatures and large values of m the invariable axis is nearly normal to the line joining the nuclei. Then the term in $4\pi\omega_m t$ has much the larger amplitude and changes in angular momentum of amount h/π should be more common than those of amount $h/2\pi$. In this connection it may be noted that every other state appears to be wanting in certain series of the oxygen band spectrum,[26] though the experimental evidence is somewhat uncertain. In view of the above, this result is rather surprising, for the oxygen molecule is paramagnetic and so likely gyroscopic. Alternations might, however, arise from the low amplitude rather than complete absence of the terms in $2\pi\omega_m t$.

It may be noted that when the angular momentum changes by h/π due to second-order effects, the radiated wave-train cannot have the ordinary circularly-polarized structure associated with radiation from a rotating Hertzian dipole. In fact Rubinowitz and Bohr have shown that the angular momentum of any ordinary elliptically polarized spherical wave-train of energy $h\nu$ cannot exceed $h/2\pi$ (Cf. Sommerfeld, Atombau, Eng. Ed., App. 9). Instead we have a spherical wave of an entirely different type whose structure can be worked out with classical electrodynamics from the second term in (7).

The writer believes that a serious objection to the above conclusions of Ehrenfest and Tolman is the fact that they do not consider the effect

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[58] We assume a diatomic molecule throughout the discussion. Ehrenfest and Tolman show that in the more general case of any polyatomic molecule the analogous proposition is that the angular momentum changes by $\sigma h/2\pi$ and equals only integral multiples of $\sigma h/2\pi$, where σ is the Ehrenfest-Trkal symmetry number to be explained in Section 4.

of the electronic motions on the multiple Fourier expansion of the electrical moment of the atom. Although the electrical moment of a symmetric molecule is zero when averaged over the periods of the electrons, it is not instantaneously zero. It may, for instance, happen that one electron rotates about the axis joining the nuclei in a larger orbit than the "inner electrons", which presumably form some sort of "closed configuration".[59] There is then an instantaneous electrical moment which rotates rapidly about the line joining the nuclei. In fact we may expect that in general the multiple Fourier expansion of the electrical moment $p=\sum q\mathbf{r}$ of a diatomic molecule is of the form

$$\begin{aligned} p_x+ip_y &= \sum A\,(\tau_1,\,\cdots,\,\tau_f,\,\tau)\,\exp.\,2\pi i\,(\tau_1\,\omega_1+\,\cdots\,+\tau_f\omega_f+\tau\omega_n+\omega_m)t, \\ p_z &= \sum B\,(\tau_1,\,\cdots,\,\tau_f,\,\tau)\,\exp.\,2\pi i\,(\tau_1\omega_1+\,\cdots\,+\tau_f\omega_f+\tau\omega_n)t, \end{aligned} \tag{8}$$

where $\omega_1, \cdots, \omega_f$ are the electronic frequencies, ω_n is the frequency of vibration along the line connecting them, and ω_m is the frequency of a complete (360°) rotation of the molecule about its axis of resultant angular momentum, which we take as the z-axis. We shall denote by $n_1, \cdots, n_f, n, m$ the quantum numbers associated respectively with the frequencies $\omega_1, \cdots, \omega_f, \omega_n, \omega_m$. The summation in (8) is with respect to the integers $\tau_1, \cdots, \tau_f, \tau$ and extends in general from $-\infty$ to $+\infty$ for each integer. In non-polar molecules the terms are to be excluded for which $\tau_1=\tau_2=\cdots=\tau_f=0$, for in such molecules the average electrical moment in any direction is zero on averaging over the electronic periods. Hence in non-polar molecules there cannot be an appreciable vibrational or pure rotational spectrum in which the electronic quantum numbers $n_1, \cdots, n_f$ are unaltered, though there is, of course, still the second-order quadrupolar radiation discussed in the preceding paragraph. The amplitudes in (8) associated with combination overtones involving the electronic frequencies need not, however, vanish, and therefore there can be an "electronic spectrum" due to alterations in the electronic quantum numbers $n_1, \cdots, n_f$ along with which there may be a change in the vibrational quantum number n and a zero or unit change in the rotational quantum number m. Hence *even in a non-polar molecule the angular momentum may change by either* 0 *or* $h/2\pi$ *provided there are simultaneous changes in the electronic quantum numbers.* This point has been mentioned in connection with

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[59] Several examples of "one-valence-electron emitters of band spectra" have been given by R. S. Mulliken, Phys. Rev. **26**, 561 (1925).

the hydrogen molecule-ion by Niessen[60] and Pauli,[61] neither of whom, however, introduce the Ehrenfest-Tolman type of quantization.[62]

It is seen that Ehrenfest and Tolman's suggestion that the angular momentum be only even multiples of $h/2\pi$ can be accepted as valid only if the second-order nuclear transitions have a much more important effect on the quantization that the first order electronic transitions. We call the transition of the first or second order according as it results from the first or second term in (7). It is obviously impossible for all electronic levels to have angular momenta which are even multiples of h/π, for the rotational quantum number can change by unity in the emission or absorption of electronic spectra. It is, however, conceivable that certain electron levels might have only even angular momenta, others odd angular momenta and still others perhaps both even and odd angular momenta. Here for brevity we measure the angular momentum in multiples of the quantum unit $h/2\pi$. We would then have only "P" and "R" branches connecting even and odd levels, and only a "Q" branch connecting two even or two odd levels.[50] In passing from an initial state with both even and odd angular momenta to an even final state, the "Q" and "P, R" lines would alternate as the initial rotational quantum number becomes progressively even and odd.

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[60] K. F. Niessen, Zur Quantentheorie des Wasserstoffmolekul-Ions (Dissertation Utrecht, 1922).

[61] W. Pauli, Jr., Ann. der Physik **68,** 238 (1922).

[62] Our discussion is based on the multiple Fourier series of the classical theory rather than the matrices of the new quantum mechanics because this is simpler and does not affect the general trend of our conclusions if we use the correspondence principle as our guide. However, we must note that sometimes the electrons in the molecule might classically be so symmetrical that all the amplitudes in (8) vanish, making the electrical moment even instantaneously zero. This situation would be particularly likely to occur in the normal state. A simple example is furnished by the old Bohr circle model of the helium atom, in which the two electrons are at opposite extremities of a diameter. At first thought we might think that there would then be no electronic combination overtones to complicate the Ehrenfest-Tolman method of quantization, but we must take into account the fact that in employing the correspondence principle we must consider both the initial and final states (as well as intermediate orbits) and excited orbits will in general be less symmetric than the normal one. It is thus probably legitimate in the old quantum theory to take the electronic angular momentum of the crossed-orbit model of the hydrogen molecule or helium atom to be $h/2\pi$ rather than an even multiple of $h/2\pi$ despite the fact that in these models a rotation of the two electrons through only 180° about the axis of symmetry brings the system back to a configuration indistinguishable from the initial one.

In the new quantum mechanics it is still more apparent that the electron transitions will disturb the quadrupolar symmetry even in the most symmetric models. For when matrices are employed there will always be terms (matrix elements) of finite amplitude involving zero or unit changes in the rotational quantum number since there are always possible transitions to excited electron states.

This seems decidedly hard to reconcile with the correspondence principle, as with any simple application of the latter the "P", "Q", and "R" branches should by (8) occur simultaneously, whereas with the scheme just indicated it has been necessary to rule out either "P" and "R" or "Q" branches to avoid transitions to non-existent states. Nevertheless we shall see that the helium band spectrum furnishes evidence for this peculiar type of structure in which alternate rotational states are missing. Similarly the oscillatory intensities found in certain band spectra can be heuristically explained by assuming that because of the Ehrenfest-Tolman effect the statistical weights or a priori probabilities of even states are less than those of the odd, or vice versa. This is the essence of the suggestion recently made by Slater.[29] How this procedure is to be reconciled with the correspondence principle is not clear because of the considerations mentioned above, and Slater's idea would scarcely appear probable were not the experimental evidence so difficult to explain otherwise. As mentioned to the writer by Professor Bohr, a serious difficulty is the fact that if initial even and odd states are equally probable, but if the final even and odd states are of unequal weight, then the transition probabilities would have to be alternately large and small, scarcely in line with the simple correspondence principle.

At the absolute zero all the molecules may be assumed to have zero angular momentum (with our normalization of additive constants). As the temperature is increased states of larger angular momentum can be reached by (*a*) collisions with other molecules or atoms, (*b*) second order absorption of pure rotational quanta, or (*c*) first order absorption of electronic quanta, followed by a similar emission in which the change of angular momentum is not the reverse of that in absorption. Here the quanta associated with the frequency ω_m in (8) are termed "pure rotational", while the quantum numbers associated with $\omega_1, \cdots, \omega_f$ are termed "electronic". The mechanism (*a*) is probably the most important at ordinary pressures, for here collisions between molecules are frequent compared to the average time intervals between the absorption of quanta of radiation. Ehrenfest and Tolman suggest the mechanism (*b*), whereby molecules can reach only states whose angular momenta are even multiples of $h/2\pi$. A simple calculation may be made to estimate the relative importance of (*b*) and (*c*). This shows[63] that the second order rotational transitions are about

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[63] The calculation is considerably simplified by Tolman's observation (Phys. Rev. **26**, 431, 1925) that absorption probability coefficients are approximately determined by the size of the orbit rather than the frequency, and so have approximately the same

$v^2\rho(\nu_m)/c^2\rho(\nu_e)$ as probable as first order electronic transitions, where v is the nuclear velocity, $\rho(\nu)$ is the energy density, and ρ_m, ρ_e are respectively the frequencies associated with the rotational and electronic transitions. Using the Planck value of $\rho(\nu)$, and taking the moment of inertia $I = 2 \times 10^{-41}$ gm. cm^2 and $h\nu_e = 11.1$ volts, one of the resonance potentials in molecular hydrogen, we readily find that a temperature of about 3,000 degrees must be reached before the number of first order electronic transitions (*c*) is comparable to that of second order rotational transitions (*b*), while at a temperature of 100° K, such as enters in the study of specific heats, the process (*b*) is 10^{500} more probable than (*c*). The relative preponderance of the second order rotational transitions suggests that they exert the dominating influence on the quantization at low temperatures, where it might be asumed that the electron transitions are ineffective in so far as the quantum conditions are concerned. We might then have a case of "weak quantization"[64] whereby the a priori probability of the states of odd rotational quantum number is diminished at low temperatures. This, however, is questionable. We have seen in (*d*), Section 2 that the complete exclusion of every other state probably does not give a good specific heat curve and requires an excessively high moment of inertia. Also an a priori probability invariant of the temperature is basic to the Einstein derivation of the Planck radiation formula, and if there were a variation of the a priori probability, there would have to be a change of the transition probability coefficients with temperature, which is hard to reconcile with the correspondence principle. In bands with alternating intensities, the intensity ratio of the strong to the weak lines is found experimentally to be a small number (always less than ten), whereas with the weak quantization hypothesis in its most naïve form one would presumably expect this number to very large (or infinite in case alternate terms are entirely excluded). Nevertheless there seems to be experimental evidence that the oscillating intensities are due to (I) alternations in statistical weights, for otherwise it would be necessary to attribute them to (II) alternations in transition probabilities or to (III) overlapping of two distinct bands which give respectively the weak and strong lines. Against the possibility (II) Slater[29] notes

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value for first order rotational transitions (when present) and first order electronic transitions. The factor v^2/c^2 results from the fact that the second order transitions are of this order compared to the first order ones, while the factor $\rho(\nu_m)/\rho(\nu_e)$ comes from the fact absorption is proportional to the energy density.

[64] For theoretical discussions of "weak quantization," see ref. 25; also Ehrenfest and Breit, Zeits. f. Physik, **9**, 207 (1922); J. C. Slater, Phys. Rev. **26**, 419 (1925).

that lines with a common initial state are either all weak or all strong, presumably indicating that paucity of molecules in the original state (i.e. low statistical weight) rather than low transition probabilities are the cause of weakness, unless one makes the hypothesis that *all* transition probabilities associated with certain initial states are weakened. The hypothesis (III) has been made by Bury[65] in the Fulcher bands of hydrogen, but appears objectionable because it leads to quarter quanta in the helium band spectrum, which we shall see are untenable.

Relation to the Pauli-Heisenberg exclusion principle. It appears quite certain that the oscillations in intensity are somehow ascribable to the quadrupolar symmetry of non-polar molecules. Definite experimental evidence is furnished by the often-noted fact that the alternating intensities are found only in non-polar molecules. Slater's suggestion must thus be regarded as correct in a general way, even though we have seen that there can scarcely be a "weak and strong" quantization of the ordinary type proposed by various authors in the old quantum theory. As suggested to the writer by Professors Bohr, Kramers, and Born, and also by Heisenberg himself, it appears likely that the alternating intensities are in some way connected with the extension of the Pauli exclusion principle which has recently been developed by Heisenberg in applying the new quantum mechanics to the spectrum of neutral helium and to the differences between singlet and triplet spectra. Pauli[66] showed that it is necessary to exclude stationary states in which two or more electrons have identical sets of quantum numbers. Heisenberg[67] finds it is also necessary to exclude all stationary states which can combine spectroscopically with those excluded by Pauli. Heisenberg's extension of the Pauli rule debars complete spectral systems, as for instance a parhelium triplet system and orthohelium singlet system, neither of which have ever been observed. Possibly application of the Heisenberg procedure to non-polar molecules will exclude alternate rotational states in the cases (such as the helium band spectrum) where every other line is observed to be missing. At any rate one may tentatively assume that anomalous intensities are found in non-polar molecules because their high degree of symmetry

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[65] C. R. Bury, Phil. Mag. **50**, 1139 (1925). Bury uses whole quanta, whereas the half quanta used by Takahashi and Dieke are probably more satisfactory. The half quanta appear to remove the oscillating deviations in frequency noted by Bury and so may destroy perhaps the main argument for the hypothesis (III).

[66] W. Pauli, Jr., Zeits. f. Physik, **31**, 765 (1925).

[67] W. Heisenberg, *ibid.* **38**, 411 (1926).

necessitates exclusions by the Pauli-Heisenberg rule. It is to be hoped that the exclusion principle will lessen the intensity of every other line, rather than obliterate it entirely, in the more common instances where alternate lines are found experimentally to be weak instead of entirely missing. It is not clear whether this effect is more likely to result through the exclusion principle cutting down the statistical weight of every other state or through its diminishing the transition probabilities of all lines having a common origin at such a state. Definite answers cannot, of course, be given until a method is found for applying the new quantum mechanics to the general non-polar molecule.

Quarter quanta and the Kramers-Pauli Model. A quite different attempt to explain alternating intensities is found in the quarter quanta hypothesis of Dieke.[68] It is based on the formula $(m\pm\epsilon)^2h^2/8\pi^2I$ which Kratzer[69] and also Kramers and Pauli[70] have derived for the energy of a molecule possessing an electronic angular momentum $\epsilon h/2\pi$ normal to the axis of figure. The sequence of energy levels for the ordinary rotator with $\epsilon=0$ and half integral values of the rotational quantum number is obviously the same as that given by the Kramers-Pauli formula when in the latter we take ϵ to be $\frac{1}{4}$, m to be integral, and the moment of inertia I to be one fourth as large as in the simple rotator. The effective quantum number $m\pm\epsilon$ is then a "quarter integer." The values $\frac{3}{4}, \frac{7}{4}, \cdots$, correspond to parallel nuclear and electronic angular momenta, and $\frac{1}{4}, \frac{5}{4}, \cdots$, to anti-parallel. The alternating intensities are attributed by Dieke to the fact that the statistical weights are different in the parallel and anti-parallel cases, but this effect probably does not give as pronounced alterations as are observed experimentally.[71]

It is altogether probable that quarter quanta must be discarded for a variety of reasons. In the first place it requires half rather than whole unit changes in the effective quantum number $m\pm\epsilon$ in the emission of the "P" and "R" branches, and this is hard to reconcile with the correspondence principle.[26] Another difficulty is that Kramers and Pauli[70] have shown the motion is unstable in the anti-parallel case.

There are, furthermore, serious dynamical objections to the Kramers-Pauli model with $\epsilon\neq 0$. In such a model it is assumed that when the nuclei are at rest there is a stationary component $\epsilon h/2\pi$ of electronic

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[68] G. H. Dieke, Zeits. f. Physik **31,** 326 (1925).

[69] A. Kratzer, Münchener Akad. p. 107 (1922).

[70] H. A. Kramers, Zeits. f. Physik **13,** 343 (1923); H. A. Kramers and W. Pauli, Jr., *ibid.*, **13,** 351.

[71] This is noted by Dieke himself in connection with Hulthen's data in nitrogen (Zeits. f. Physik **33,** 167, 1925, footnote).

angular momentum which is normal to the axis of figure. Miss Mensing[72] shows that actually, except with unlikely special orbital arrangements, the forces exerted by the nuclei will cause the normal component of angular momentum to precess[73] rapidly about the axis of figure. There is, in fact, a rough similarity to the familiar precession of a gyroscope in a gravitational field. Owing to the precession, the average electronic angular momentum in any direction normal to the axis of figure vanishes on the average, and from this it is easily shown that, neglecting additive constants, the energy due to nuclear rotation is very approximately $m^2h^2/8\pi^2I$ instead of $(m\pm\epsilon)^2h^2/8\pi^2I$. Miss Mensing used the conventional mechanics, and Hund[33] states that in the new quantum dynamics there are not even special solutions in which $\epsilon\neq 0$. Consequently in the discussion of quantization and specific heats in Sections 1 and 2 we have not introduced an electronic angular momentum $\epsilon h/2\pi$ normal to the axis of figure, even though such an addition obviously introduces no particular difficulty in the calculation, at least with a rigid model. Dieke[16] has already calculated a specific heat curve with quarter quanta, but this is not as satisfactory as some of the other curves.

Until recently half as well as quarter quanta were often ascribed to the existence of an $\epsilon\neq 0$, for in the absence of a basis for half quanta in the old quantum theory it was commonly supposed that m was integral and that $\epsilon=\frac{1}{2}$. This was done even in bands not susceptible to magnetic fields, regardless of the fact that with an $\epsilon\neq 0$ there should be an observable Zeeman effect (of the order $1/m$ times the normal separation). Fortunately the new quantum mechanics has furnished a natural basis for half quanta (cf. section 1) and thus made unnecessary the assumption $\epsilon=\frac{1}{2}$ in most cases. As noted to the writer by Dr. Mulliken, the facts of band spectra still sometimes demand an $\epsilon\neq 0$, but this effect is probably not due to a rigidly fastened electronic angular momentum of the Kramers-Pauli type, but rather to loose coupling of the spin axis of the electron, which makes this axis orient itself relative to the combined nuclear and orbital angular momentum rather than relative to the orbital alone. We then have coupling of Hund's[33] type (*b*), which

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[72] Lucy Mensing, Zeits. f. Physik, **34**, 602 (1926). Miss Mensing also shows that in any case it is impossible to have simultaneously a stationary normal component $\epsilon h/2\pi$ of angular momentum and a component $\sigma h/2\pi$ parallel to the axis of figure. She does not consider explicitly angular momentum due to internal spins of the electrons, but it is not likely that its inclusion will modify the conclusions.

[73] This precession is intimately connected with the existence of doublets in band spectra. See O. Klein, Phys. Rev. **25**, 109A (1925); also Hund, l.c.[33]

gives an expression for the energy in some ways analogous to the Kratzer or Kramers and Pauli formula.

In an important recent paper Curtis and Long[74] have classified a large number of lines in the helium band spectrum with the aid of quarter quanta. The initial states for a given branch are represented either by the series of numbers $\frac{3}{4}, \frac{7}{4}, \cdots$, or else by $\frac{5}{4}, \frac{9}{4}, \cdots$, but not by both series simultaneously. Because of the difficulties mentioned above, it is probable that the quarter quanta should be replaced by half quanta, as suggested by Mecke.[26] This has just been done in Mulliken's significant new analysis[75] of the electronic states and band spectrum of the helium molecule. In each band initial (or final) states are then wanting for every other value of the rotational quantum number, as $\frac{3}{4}, \frac{7}{4}, \cdots$, is replaced by $\frac{3}{2}, \frac{7}{2}, \cdots$, etc. We thus get a limiting case of alternating intensities, in which now every other line is completely missing. Some of the rotational quantum numbers required for the numerical representation of observed spectral terms are not exactly half integers, as ϵ is not always $\frac{1}{4}$ in the Curtis-Long formulae, but the slight deviations are probably due to loose coupling of the spin axes of the electrons relative to the rest of the molecule (cf. Hund[33]).

Owing to centrifugal expansion the rotational energy is not given accurately by the formula (3) based on a rigid model, but instead can be developed as a power series in m^2. The main correction term to Eq. (3) is thus of the form αm^4. It can be shown that theoretically[76] $\alpha = -h^4/128\pi^6 I^3 \nu_0^2$, and hence the nuclear vibration frequency can be deduced from observed values of the coefficient α if the moment of inertia I is known. The value thus obtained for ν_0 is twice as large with quarter as with half quanta since I and m^2 are four times as large with the latter as with the former. Mecke[26] notes that for this reason the use of quarter quanta destroys the regularity in his correlation of vibration frequency with moment of inertia. More specifically, Birge[77] finds that in nitrogen the vibration frequency deduced from α with quarter quanta is twice too large to be reconciled with estimates by other methods. Birge observes that this fact must be regarded as a conclusive argument against quarter quanta.

Zeeman effect. We shall now digress to consider the Zeeman effect

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[74] W. E. Curtis and R. G. Long, Proc. Roy. Soc. **108A**, 513 (1925).

[75] R. S. Mulliken, Proc. Nat. Acad. **12**, 158 (1926); also especially Phys. Rev., Dec., 1926.

[76] This is a well-known result in the old quantum theory, and the work of Fues or series expansion of (5) shows that it also holds in the new quantum mechanics.

[77] R. T. Birge, Phys. Rev. **27**, 107 (1926).

of molecules, especially hydrogen, as this subject is of some interest itself and also may throw some light on the structure of excited states.

If there is "rigid coupling" of the spin electrons, the change in energy produced by a magnetic field is

$$-\frac{\mu\sigma n_{\mathrm{H}}}{(m^2-\frac{1}{4})}H \tag{9}$$

where μ is the magnetic moment of the molecule in the direction of the axis of figure, $\sigma h/2\pi$ is the combined spin and orbital electronic angular momentum in this direction, and n_H is the magnetic quantum number, which is proportional to the component of total angular momentum in the direction of the external field. By "rigid coupling" we mean that the spin axes are so firmly bound that their orientations relative to the orbital angular momentum or axis of figure are uninfluenced by the nuclear rotation or by the applied magnetic field. Our formula (9) differs from those given by Kramers and Pauli,[70] Kemble,[78] and others in having $(m^2-\frac{1}{4})$ in place of m^2. That this is the modification required by the new quantum mechanics can be seen from the amplitude matrices for gyroscopic molecules given by Dennison.[7] In Eq. (9) we have, following Hund,[33] included only the contribution of the magnetic moment parallel to the axis of figure, because the normal component will doubtless precess very rapidly about this axis and make only a negligible contribution to the Zeeman separation, unless perchance there is a stationary angular momentum $\epsilon h/2\pi$ normal to the axis of figure. The existence of an $\epsilon \neq 0$ is very unlikely because of dynamical difficulties previously mentioned, but would give rise to a term in the energy proportional to $\epsilon H n_H/(m^2-\frac{1}{4})^{1/2}$ (if[72] $\sigma=0$) and a Zeeman separation of the order $1/m$ instead of $1/m^2$ times the normal separation.

Since by the selection principle m and n_H cannot change by more than one unit, it follows that according to (9) the spacing of Zeeman components should be of the order $1/m^2$ times the normal separation. The number of components should increase and their spacing decrease with increasing values of the rotational quantum number. Actually no Zeeman effect is observed by either Dufour[79] or Croze[80] in the Fulcher bands of hydrogen. This can only mean that the excited states involved in the emission of these bands have no magnetic moment; i.e., are non-gyroscopic. The question, of course arises whether the theoretical separation might be too small to be observable since it is

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[78] E. C. Kemble, Phys. Rev. **27**, 799A (1926).

[79] A. Dufour, Ann. de Chim. et Physique **9**, 361 (1906); J. de Physique, **8**, 258 (1909).

[80] F. Croze, Ann. d. Phys. **1**, 63 (1913).

of the order $1/m^2$ times the normal. The experimental error in Croze's experiments, however, is only about 1/50 of the normal separation, and so a magnetic moment could perhaps be detected unless m exceeded about 7, whereas actually m is smaller for most lines observed in the Fulcher bands. Richardson notes[54] that the central line of one of the bands shows traces of a slight effect.

In contrast to the Fulcher bands, certain other lines emitted by the hydrogen molecule have a pronounced Zeeman separation of a quite remarkable type.[79, 80] In such lines the Zeeman pattern sometimes consists of a doublet whose width is approximately (to 25% or so) equal to the distance between the outer components in the normal Lorentz triplet. The two components of the doublet are circularly polarized, but occasionally the sense of the polarization is the reverse of the usual, giving a positive apparent value of e/m. Lines of a similar Zeeman structure have also been observed for a few other molecules, notably BaCl, CaF, etc.[79] As mentioned by Kramers and Pauli,[70] a Zeeman pattern of this character must be due to loose coupling,[81] for we have seen in the preceding paragraph that with rigid coupling there would be more components and smaller separations. Until the advent of the spin electron, it was hard to see how there could be the proper loose coupling, since electron orbits would have to be enormously large compared to the nuclear separation in order to orient themselves freely in magnetic fields, and even then it would be difficult to account for the peculiar type of pattern and polarization. It is now, however, quite certain that the electron has an internal degree of freedom, probably due to spinning, as proposed by Compton[82] and by Uhlenbeck and Goudsmit.[32] Consequently we suggest that the peculiar Zeeman doublets found in molecular spectra are to be attributed to loose coupling of the axes of spin rather than of the orbits themselves, since spectroscopic data shows that the intra-molecular forces which orient the spin axes are much weaker than those which orient the orbit. The loose coupling may be expected only in excited states, for the force orienting the spin axes varies as the inverse cube of the radius of the orbit.[83]

Let us assume the molecule has one valence electron with an orbit so large that its spin axis is negligibly coupled to the molecule and so

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[81] J. W. Nicholson has recently discussed the pronounced Zeeman effect in some hydrogen lines and also notes that it indicates a quite different type of structure or coupling than in the Fulcher bands. Monthly Notices, R.A.S. **85**, 449, 656 (1925).

[82] A. H. Compton, J. Frankl. Inst. **192**, 145 (1921).

[83] Cf. L. H. Thomas, Nature **117**, 514 (1926); F. R. Bichowsky and H. C. Urey, Proc. Nat. Acad. **12**, 80 (1926); J. Frenkel, Zeits. f. Physik **37**, 243 (1926).

orients itself freely in a magnetic field. The theory of the anomalous Zeeman effect[84] shows that there are then two possible orientations for the spin axis, viz., parallel or anti-parallel to the field, and that the energy is

$$W=W_0+2P_r h\omega_H, \tag{10}$$

where ω_H is the normal Lorentz Zeeman separation, W is the energy in the absence of the field, and $P_r=\pm\frac{1}{2}$ is the axial component of the valence electron's spin angular momentum, measured in multiples of the quantum unit $h/2\pi$. The factor 2 in (10) arises from the doubly large ratio[32] of magnetic moment to angular momentum for internal spins. We have omitted the term contributed by the part of the magnetic moment which is rigidly coupled to the axis of figure and which arises from the orbital motion of the valence electron and from the spin and orbital motions of the other, firmly bound electrons. This neglected term is of the form (9) and hence much less than the contribution $2P_r h\omega_H$ of the spin of the valence electron unless the rotational quantum number m is small.

If there is loose coupling in both the initial and final states, then by (10) the frequency should be approximately the same as without the field, ar else displaced by twice the normal Lorentz value, according as ΔP_r is 0 or ± 1. The unit changes in P_r involve a semi-somersault of the spin axis, and do not appear to be found experimentally, as in atomic spectra a doubly large Zeeman displacement is not found in the Paschen-Back effect, where the spin axis is oriented relative to the applied field. This is probably because radiation is from the orbital rather than spinning motion, and the precession frequency $2\omega_H$ of the spin axis does not appear in the Fourier development of the orbital motions if the coupling between the spin and orbital motion is negligible.[85] It is thus probable that we can only have $\Delta P_r=0$ and if this is the case there is only a small Zeeman separation of the order ω_H/m^2, even with the loose coupling in both the initial and final states.

To avoid this difficulty the writer wishes to suggest that there is loose coupling in the initial state, but not in the final, or vice versa, so that the term $2P_r h\omega_H=\pm h\omega_H$ in (10) is absent for one of the two states. This hypothesis is attractive, as it gives a Zeeman displacement having the normal Lorentz value ω_H, and with the central undisplaced

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[84] We are concerned with the theory for strong rather than weak fields. For summary, cf., for instance, J. H. Van Vleck, l.c.,[36] p. 241. Effects previously attributed to the atom-core are now to be ascribed to internal spins.

[85] This is probably the solution of the difficulty mentioned in note 370 of the writer's Bulletin.[36]

component entirely wanting, as it is experimentally in Dufour's measurements on the fluorides of the alkaline earths. The observed displacements in the doublets are not exactly ω_H and in certain molecules the doublets are resolvable into quartets, but departures from the value ω_H must be expected because there may be a rigidly coupled magnetic moment in addition to the loosely bound spin moment, and also especially because we cannot neglect entirely the coupling between the spin of the valence electron and the remainder of the molecule. A mathematical theory of this interaction will be necessary to ascertain whether the suggestion of a loosely coupled spin in one state will explain the anomalous polarization of some of the lines and the exact quantitative values of the doublet separations. Our suggestion is only tentative. It assumes one loosely coupled electron, and so appears more likely for the bands emitted by the halides of the alkaline earths than for those of molecular hydrogen. The hydrogen molecule contains an even number of electrons, whereas Mulliken[33] ascribes the alkaline earth halide bands to odd, one-valence-electron molecules of the type BaCl, CaF, etc., instead of to the common even structures $BaCl_2$, CaF_2, etc.

If the spin axis is so loosely coupled that it can orient itself freely in an applied magnetic field of ordinary magnitude, it is probable that in the absence of the field its orientation is influenced by the nuclear rotation. We then may have coupling of a type considered by Hund[33] (case b, p. 662 of his article) in which the spin axis is quantized relative to the combined angular momenta of the nuclei and orbit rather than relative to the orbital angular momentum alone. A sufficiently weak field, would not, of course, be adequate to destroy this coupling and the Zeeman separation in such a field has been calculated by Hund.[33] He finds the spacing of components to then be of the order $1/m$ times the normal Lorentz separation or considerably smaller than the distance between the doublet components observed by Croze and Dufour. There must therefore be a sort of Paschen-Back effect whereby the internal coupling is overpowered and the closely spaced components merged into a wide doublet. This transition has apparently not been observed experimentally, but as noted by Hund, may be difficult to detect since the internal coupling may be so weak that it breaks down completely in any field strong enough to give a measurable Zeeman effect.

4. ABSOLUTE ENTROPIES AND CHEMICAL CONSTANTS

The theory of specific heats is intimately related to that of chemical constants, as both must involve the same a priori probability, moment of inertia, etc.

Chemical constant of a thermally monatomic gas. The formula for the entropy of a gram-mol of thermally monatomic gas is

$$S=\tfrac{5}{2}R\ln T-R\ln p+\tfrac{5}{2}R+CR\ln 10, \qquad (11)$$

where R is the gas constant and C is the so-called "chemical constant" which appears in the vapor-pressure equation and which determines the absolute value of the entropy. We denote natural and common logarithms throughout by ln and log respectively. By a "thermally monatomic" gas we mean one whose specific heat c_p at constant pressure has the classical equipartition value $\tfrac{5}{2}R$ for a perfect monatomic gas. Here and elsewhere we neglect the possibility of a "degeneration" of c_p below the value $\tfrac{5}{2}R$, as this can take place only under extreme conditions (cf. end of Section 2). The theoretical value of C determined from quantum statistics is

$$C=\log\left[(2\pi m)^{3/2}k^{5/2}/h^3P\right]+\log p_0-\log\sigma=-1.587+\log(M^{3/2}p_0/\sigma) \qquad (12)$$

where m is the mass of a molecule, M is the molecular weight and $P=1.0132\times 10^6$ is the value of atmospheric pressure in dynes/cm². The factor P^{-1} is included in order that the pressure p in (11) may be expressed in atmospheres. p_0 denotes the a priori probability of the stationary state of lowest energy. In a monatomic molecule (atom) this state is simply the spectroscopic normal state, while in a diatomic molecule it is the state of minimum rotational quantum number, which is occupied by practically all molecules near the absolute zero. σ is the Ehrenfest-Trkal symmetry number, defined as the "number of orientations in space in which the molecule is statistically equivalent", and is not to be confused with the spin quantum number for gyroscopic molecules used in Section 2, which was also denoted by σ. In monatomic molcules we may neglect the term $-\log\sigma$, as here $\sigma=1$. For a "non-polar", symmetrical diatomic molecules such as H_2, the value of σ is 2, while $\sigma=1$ in polar, asymmetric molecules such as HCl.

Our expression (12) for the chemical constant differs from the ordinary Stern-Tetrode[87] formula by the presence of the additional terms $\log p_0$ and $-\log\sigma$. These terms are not usually included, but seem to be demanded with any rational application of quantum statistics. The theoretical necessity of adding the term $\log p_0$ appears to have been first suggested by Shottky[88] and especially R. H. Fowler,[89] and its

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[87] H. Tetrode, Ann. der Phys. **38**, 434 (1912); O. Stern, Phys. Zeits. **14**, 629 (1913).

[88] W. Schottky, Phys. Zeits. **22**, 1 (1921); Ann. der Physik, **68**, 481 (1922); also particularly Phys. Zeits. **23**, 9 (1922).

[89] R. H. Fowler, Phil. Mag. **45**, 32 (1923); **1**, 845 (1926).

possible utility in explaining experimental results has recently been stressed by Simon,[90] Eucken and Fried,[91] and others. This term is probably required even in the Einstein-Bose[38] statistics, although it has ordinarily been omitted in the latter. If the temperatures are so low that practically all atoms are in the lowest quantum state, we need consider only the translational degrees of freedom, but the number of cells between two given values of the translational energy is presumably p_0 times that assumed by Einstein (if $\sigma=1$) and the application of the Einstein-Bose theory with this modification yields the extra term $\log p_0$. The Einstein-Bose gas degeneration then does not make the entropy of a monatomic gas vanish at the absolute zero, as ordinarily stated. Instead the degraded value of the entropy becomes $R\ln p_0$ at $T=0$ in the absence of external fields. The Nernst heat theorem would thus not be applicable even to a monatomic gas (where $\sigma=1$) except for the fact that sufficiently near $T=0$ the application of an infinitesimal external field makes practically all the molecules select the one particular orientation of minimum energy, rather than all p_0 orientations, so that the effective a priori probability might then be 1 instead of p_0. The term due to the symmetry number σ is less easily deduced than $\log p_0$, but its necessity can be seen from the statistical work[92] of Ehrenfest and Trkal, Partington, and R. H. Fowler.

In monatomic gases there is as yet no exact quantitative experimental evidence for the additive term $\log \cdot p_0$ in (12). For discussion of the data, and references, the reader is referred to a very complete recent paper by Simon.[90] Some of the most satisfactory data confirming the Stern-Tetrode formula is for He, A, and Hg,[93] and here the additive term vanishes since the normal states of these atoms are S-terms with $p_0=1$. This perhaps explains why the Stern-Tetrode formula is so often given and accepted in unmodified form. In the alkalis there are two orientations for the normal state in a magnetic field, so that the additive term has the value $\log 2=.3$. Simon[90] shows that revised

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[90] F. Simon, Zeits. f. Phys. Chem. **110**, 572 (1924).

[91] A. Eucken and Fried, Zeits. f. Physik **29**, 36 (1924).

[92] P. Ehrenfest and V. Trkal, Proc. Amsterdam Acad. **23**, 162 (1921); J. R. Partington, Phil. Mag. **44**, 988 (1922); **46**, 329 (1923); R. H. Fowler, *ibid.* **45**, 1 (1923), especially p. 32.

These writers do not express their results in the form (12). Instead they deduce Eq. (15), but (12) is easily derived from (15), as we show after (15).

[93] The values for Hg, however, are rather high, as Simon (Zeits. f. Phys. Chem. **107**, 279, 1923) finds C to be .08 larger than required by theory and Rodebush and Dixon (Phys. Rev. **26**, 851, 1925) find C to be .19 larger. The latter state the discrepancy is within the experimental error but Simon claims an error of only .06.

data of Ladenburg and Minkowski for Na and K and of Scott for Rb and Cs give chemical constants very nearly .3 in excess of the Stern-Tetrode value. On the other hand Rodebush and Devries[94] recently find a constant for Na only .08 in excess, and estimate their experimental error to be but .1. Simon shows that the chemical constants for several other elements, notably Wohl's values for Cl, Br, and I, are .5 or more higher than the Stern-Tetrode values, indicating a $p_0 \neq 1$ in these substances, but the data are scarcely adequate for quantitative inferences concerning the magnitude of p_0.

Chemical constant of hydrogen at low temperatures. Eqs. (11) and (12) can be applied to a diatomic gas only if the temperature is so low that rotational quanta are not excited. This condition is realized experimentally only in hydrogen. Here the most accurate experimental value of C is probably that of Simon,[95] who finds $C = -1.11 \pm .03$, which agrees[96] within the limits of error with the unmodified Stern-Tetrode value $-1.59 + \frac{3}{2} \log 2.016 = -1.13$. This is consistent with (12) only if the terms $\log p_0$ and $-\log \sigma$ cancel. Since $\sigma = 2$ in H_2, such a cancellation would require that the a priori probability of the lowest rotational state be 2, as emphasized by Fowler.[89] Also as the a priori probability is in general $2m$, the whole quantum values $1, 2, \cdots$ would needs be assigned the rotational quantum number m, yielding a specific heat curve of the type (a) discussed in Section 2. Unfortunately we have seen in Sections 1 and 2 that it is doubtful whether such whole quanta are allowable in the new quantum mechanics. It is notable that the Nernst heat theorem applies if we use whole quanta in non-polar molecules and half quanta in polar, as then $p_0 = \sigma = 2$ in the former and $p_0 = \sigma = 1$ in the latter, so that in either case the additive term $\log (p_0/\sigma)$ vanishes but this may well be only a spurious argument for the whole quanta. If in hydrogen we assumed the half quanta $m = \frac{1}{2}, \frac{3}{2}, \cdots$ (case d, Section 2) we would have $p_0/\sigma = \frac{1}{2}$ and $C = -1.43$ if the symmetry number σ is retained,[97] while with half-quanta commencing at $m = \frac{3}{2}$ (cases b and c, Section 2),

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[94] W. H. Rodebush and T. Devries, J. Amer. Chem. Soc. **47**, 2493 (1925).

[95] F. Simon, Zeits. f. Physik, **15**, 307 (1923).

[96] Eucken, Karwat, and Fried,[107] on recalculating Simon's data and using somewhat different heats of vaporization find $C = -1.09 \pm .02$ which does not agree with the Stern-Tetrode value -1.13 within their estimate of the experimental error. There has been considerable controversy between these writers and Simon[99] regarding whose value of C is more accurate. In his last paper Simon claims to find a numerical error in Eucken's calculations.[97]

[97] F. Simon, Zeits. f. Physik **33**, 946 (1925).

p_0 becomes 3 and $C=-.95$. Neither of these values for C agrees at all with Simon's.[98]

At this point it must be emphasized that the experimental value $C=-1.11$ is deduced from vapor pressure measurements on the assumption that the Planck extension of the Nernst heat theorem can be applied to the solid phase, so that the entropy of the latter can be taken to be zero at $T=0$. This assumption is, however, scarcely more or less admissible than the unmodified Stern-Tetrode formula for the gaseous phase. Instead, it appears more satisfactory to assume that at $T=0$ the entropy of the solid phase is

$$S=R\ln p_s-R\ln\sigma_s \tag{13}$$

where p_s is the a priori probability associated with the normal state in the solid. The need of the term $R\ln p_s$ was first suggested by Shottky[88] and has also been mentioned by Simon,[90], Eucken and Fried,[91] and others. None of these writers introduce a symmetry number σ_s for the solid phase, but I see no reason why there may not be such a number for solids as well as gases, since solid molecules subject to inter-molecular forces can probably to some extent, at least, be regarded as limiting cases of gas molecules subject to strong external fields. Of course there can be no free rotations in a true solid, but nevertheless there may be degrees of freedom and quantum numbers corresponding to those associated with rotations in a gas.

If we admit (13), the effective chemical constant appearing in the vapor pressure equation is not the constant C appearing in the absolute entropy of the gas according to (11, 12), but instead can be shown to be $C_{\text{eff}}=C-\log(p_s/\sigma_s)$. Then according to Simon's data C_{eff}, not C, has the Stern-Tetrode value in hydrogen, and this simply means that the symmetry number and minimum a priori probability have the

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[98] On the basis of his theory of ultimate rational units, G. N. Lewis has proposed the value

$$C=\log[k^{5/2}m^{3/2}8\pi^5/15h^3e^{5/2}P]=-1.66+\log M^{3/2} \tag{12'}$$

for the chemical constant. (See, for instance, Lewis and Randall, Thermodynamics, p. 456. Lewis does not give his result in the form (12′), but (12′) is readily deduced from his expression for the absolute entropy and his relation connecting ϵ, h, and c. Cf. Dushman, Phys. Rev. **21**, 623, 1923. We here denote the electronic charge by ϵ, not e, as $e=2.718$ in 12′.) In hydrogen Eq. (12′) gives $C=-1.20$ which does not agree with experiment nearly as well as the Stern-Tetrode value -1.13. In getting (12′), Lewis assumes that an undetermined numerical factor has the value unity. He mentions that this factor might possibly be some other "simple number." If his theory is to be reconciled with (12), this number must be $15p_0e^{5/2}/2^{3/2}\pi^{7/2}\sigma$, which is not particularly simple but is nearly unity if $p_0/\sigma=1$. This coincidence perhaps explains why (12′) is often in approximate accord with experiment.

same ratio in the gaseous and solid phases, making C_{eff} equal the first log in (12). Since it is not unlikely that in hydrogen $\sigma = \sigma_s = 2$, we can thus have $p_0 = 1$ (case *d*, Section 2) without contradicting vapor pressure measurements if also $p_s = 1$. Similarly the effective chemical constant C_{eff} of sodium might have the unmodified Stern-Tetrode value if there are two equally probable orientations for atoms in the solid state, but this seems unlikely in view of the magnetic moment or polarity of alkali atoms.

We have seen in Section 2, cases *b* and *c*, that there is some evidence for half quanta in hydrogen commencing with the value $\frac{3}{2}$. According to the above, this is consistent with Simon's data if $p_s = 3$. It is easy to grant two configurations of equal energy in solid hydrogen, as configurations obtained from each other by rotation through 180° are statistically equivalent owing to non-polarity. It is, however, hard to imagine the three positions of sensibly equal energy which are required if $p_s = 3$. Their energies would have to agree to within less than 10^{-3} volt to secure virtually equal probabilities at Simon's lowest measured temperature $T = 11°$. Only one or two configurations might be occupied at the absolute zero, and, as noted by Simon,[99] there would then be an unobserved anomaly in the specific heat of the solid between the $T = 0$ and $T = 11°$, since the specific heat would show a sharp maximum at the temperature of transition from one or two to three configurations. In support of the possibility $p_s = 3$, we may cite a very interesting recent paper by Pauling and Tolman,[100] in which several orientations of equal energy are considered possible in a supercooled liquid but not in a crystalline solid, in accord with Lewis and Gibson's[101] observation of larger entropies for the former than the latter. On the other hand the solid hydrogen produced experimentally is probably to some extent crystalline, and Professors Darwin and Fowler inform the writer that for the crystal as a whole the symmetry number is unity. Of course it may be different for a single molecule, but it is uncertain how far individual molecules can be quantized in a crystal. Unit symmetry number in the solid would destroy all agreement with experiment if $p_0 = 3$ unless the symmetry number is omitted in the gaseous phase. It is, however, not certain how far symmetry numbers should be employed in statistical problems, although in some cases their necessity is unavoidable. We have already in Section 2 seen the difficulties connected with Ehrenfest and Tolman's attempt

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[99] F. Simon, Zeits. f. Physik, **31**, 224; **33**, 946 (1925).

[100] L. Pauling and R. C. Tolman, Journ. Amer. Chem. Soc. **47**, 2148 (1925).

[101] Lewis and Gibson, *ibid.* **42**, 1529 (1920).

to introduce the symmetry number into the quantization. At any rate any inferences about the chemical constants of gases made from vapor pressures seem rather uncertain until we have a clearer insight into the exact significance of symmetry numbers or a more complete statistical theory of the a priori probabilities of molecules in solids. On the whole, the most conservative interpretation of the experimental situation in hydrogen is probably simply that the minimum a priori probability is the same in the solid and gaseous phases.

Chemical constant for diatomic gases at high temperatures. If the temperature is high enough so that the rotational, but not the vibrational, degrees of freedom are excited, the specific heat of a perfect diatomic gas is $c_p=\frac{7}{2}R$ and its entropy per gram mol is

$$S=\tfrac{7}{2}R\ln T-R\ln p+\tfrac{7}{2}R+C'R\ln 10. \tag{14}$$

The corresponding chemical constant C is

$$C'=\log\left[(2\pi m)^{3/2}k^{7/2}8\pi^2 I/h^5 P\sigma\right]=36.81+\log(M^{3/2}I/\sigma) \tag{15}$$

where I is the moment of inertia. Eq. (15) was obtained independently by various authors, and differs from an early formula of Sackur[102] in the inclusion of the symmetry number. Eqs. (14) and (15) may be obtained in a simple manner from (11) and (12), or vice versa, by noting that the total entropy (14) is the sum of the entropy (11) for a thermally monatomic gas and the rotational entropy

$$S_r=\int_0^T c_r d\ln T. \tag{16}$$

This integral is easily evaluated by a method given by Tolman and Badger.[103] We shall assume a rigid molecule so that the specific heat given by Eq. (1) is all rotational. We substitute in (16) the value (1) for c_r, change the variable of integration from T to $\rho=1/kT$, and integrate by parts. Thus it is easily found that

$$S_r=R(\ln Q-\rho d\ln Q/d\rho)_0^T \tag{17}$$

At the lower limit the expression in parentheses is simply [104] $R\ln p_0$, while at sufficiently high temperatures we may find the value at the

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[102] O. Sackur, Ann. der Physik, **40**, 67 (1913).

[103] R. C. Tolman and R. M. Badger, J. Amer. Chem. Soc. **45**, 2277 (1923). A somewhat similar procedure has also been given in papers by Planck, (Verhd. d. D. Phys. Ges. **17**, 418, 1915) and Rotszajn.[21]

[104] The calculation is most simply made by assuming the additive constant in the energy to be so normalized that the energy vanishes at $T=0$. This is legitimate as we have seen in Section 1 that this constant does not affect the rotational specific heat.

upper limit by replacing the summation in (2) by an integral in a well-known way. Under very general assumptions[105] this procedure gives

$$Q(T)=8\pi^2IkT/h^2, \qquad S_r/R=1+\ln(8\pi^2IkT/h^2p_0) \tag{18}$$

from which (14) and (15) readily follow. Special instances of the formula for S_r have been given by Tolman and Badger and others.

Chemical constant of hydrogen at high temperatures. Vapor pressure measurements cannot be employed to test directly the validity of Eq. (15) for hydrogen, as rotational quanta are adequately excited only far above its critical point. The value of

$$C'-C=(S_r-R-R\ln T)/R\ln 10$$

can be calculated from observed specific heat data by graphical evaluation of the integral in (16) with Eucken's values of c_r. This has been done by Eastman[106] and by Eucken, Karwat, and Fried,[107] who thus find $C'-C=-2.60$. On the other hand the theoretical value of $C'-C$ is

$$C'-C=\log(8\pi^2Ik/h^2p_0)=38.40+\log(I/p_0), \tag{19}$$

as is seen on subtracting (12) from (15). Substitution of the value $C'-C=-2.60$ in (19) gives $I=1.0p_0\times10^{-41}$ gm. cm.^{2} Unfortunately in comparing theoretical and experimental values of $C'-C$, Eucken, Karwat, and Fried use the Sackur formula[102] for C' and the unmodified Stern-Tetrode formula for C. They thus get $I=1.0\times10^{-41}$. This value of I is quoted by Schrödinger[27] in support of his type of specific heat formula (*d*, Section 2) which yields a lower moment of inertia 1.4×10^{-41} than most of the other theoretical specific heat curves. The value $I=1.0\times10^{-41}$ appears to me clearly erroneous because the factor p_0 is omitted. The theoretical calculation of C or C' involves some rather abstruse statistical questions, but the determination of $C'-C$ is relatively simple for it involves only the evaluation of (17) with Q defined by (2). The result is (19) regardless of whether whole or half quanta are used, provided only the molecule be considered rigid. Lessheim[17] suggests that there is an uncertainty log 2 in the theoretical

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[105] The asymptotic formula (18) for $Q(T)$ is valid equally well with whole or half quanta and either with or without exclusion of the state $m=0$ or $m=\frac{1}{2}$. It holds with any a priori probability of the form $2m+a$, where a is any number independent of the rotational quantum number m. In the new quantum mechanics a is zero at least in polar molecules such as HCl, but the value of a is immaterial as regards $Q(T)$ since it gives[103] only a term proportional to $T^{1/2}$ which can be omitted. If every other state is excluded (case *c*, Section 2) our formulas, however, must be modified, as a term $-R\ln 2$ must then be added to S_r and $-\log 2$ to C'.

[106] Eastman, J. Amer. Chem. Soc. **44**, 1008 (1922).

[107] Eucken, Karwat, and Fried, Zeits. f. Physik, **29**, 1 (1924); **32**, 150 (1925).

formula for $C'-C$, but with this I cannot agree, as Eq. (19) is based only on simple specific heat theory and so the question of a symmetry number, etc., cannot enter. The comparison of theoretical and experimental values of $C'-C$ in hydrogen consequently does not furnish any new criterion for determining the moment of intertia other than that already found in specific heats.[108] With whole quanta the minimum a priori probability is 2 and then the moment of interia deduced from $C'-C$ is 2.0×10^{-41} gm. cm^2 (not 1.0×10^{-41} as usually stated), which agrees closely with Reiche's value 2.10×10^{-41} or Kemble and Van Vleck's value 1.98×10^{-41} deduced from a specific heat curve of type (*a*), Section 2. With the half quanta $m=\frac{3}{2}, \frac{5}{2}, \cdots$ (case *b*, Section 2), we have $p_0=3$ and Eucken's value of $C'-C$ then gives $I=3.0\times10^{-41}$, while Hutchisson finds that $I=2.99\times10^{-41}$ gives the best specific heat curve of type (*b*). The agreement of the two methods of estimating I is not a particularly crucial test, as the ability to give the proper value of $C'-C$ and hence the integral in (16), i. e., the proper area under a curve, is not nearly as exacting a test as the representation of the specific heat curve itself.

In distinction from the above considerations, accurate measurements of the dissociation equilibrium of hydrogen would furnish an independent method of determining C' and hence the moment of intertia. Existing dissociation data does not appear adequate to warrant any definite conclusions, although Simon[90] has discussed some of Wohl's explosion experiments in a preliminary way.

Chemical constants of other diatomic gases. Except for hydrogen, the specific heat of a diatomic gas is generally $\frac{7}{2}R$, or more, even below the critical point, and Eq. (15) can then be tested directly by vapor pressure measurements in cases where the vibrational specific heat is negligible. Comparisons of the theoretical values of the chemical constant or of absolute entropies with experiment have recently been given for several gases by Urey,[108] by Tolman and Badger,[103] by Cox,[109] and by Eucken, Karwat, and Fried,[107] all using in the theory the moments of intertia deduced from band spectra. The paper by Eucken and colleagues in particular surveys the experimental data very carefully. We shall not discuss the numerical results, for they do not yield any definite conclusions, except that Eq. (15) does not hold if solid phases are assumed to have zero entropies at $T=0$. As emphasized by Cox, the one case of really satisfactory agreement is that of nitrogen. Eucken and colleagues conclude that the best experimental value

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[108] This is also noted by Urey, J. Amer. Chem. Soc. **45**, 1445 (1923).

[109] R. R. S. Cox, Proc. Cambr. Phil. Soc. **21**, 541 (1923); **22**, 491 (1923).

of C' for nitrogen is $-.11\pm.05$, while Cox, on making an independent calculation from Eucken's data concludes that experimentally $C'=-.15$. Assuming that nitrogen has the moment of inertia 14.2×10^{-40} deduced from band spectra, the theoretical value of C' given by (15) is $-.16$. Omission of the symmetry number $\sigma=2$ would entirely destroy this excellent agreement.

It may perhaps be well to call attention to minor revisions in the calculations of the various authors which are necessary if we accept the statistical theory of Ehrenfest and Trkal, Partington, and R. H. Fowler, all[92] of whom agree on the value (15) for the chemical constant.

Urey, also Badger and Tolman assume that at very low temperatures the chemical constants of diatomic gases conform to a formula[98] of Lewis which is nearly the same as the unmodified Stern-Tetrode formula, instead of to (12). The main revision for their calculated entropies is thus the addition of the term $R\ln(p_0/\sigma)$. From this it can be shown that Urey's entropies S_{298}, also those calculated by Tolman and Badger for their cases V and VI must be increased by $R\ln2+.3=1.7$ for polar molecules but by only .3 for non-polar molecules. Here the term .3 is merely the difference between the Lewis and Stern-Tetrode absolute entropies. Tolman and Badger endeavor to draw conclusions concerning the form of the a priori probability p_m in (2) from a study of chemical constants at temperatures at which rotations are fully excited. According to the statistical theory of Ehrenfest, etc., this cannot be done, as p_0 does not enter in Eq. (15). If their calculations for their cases I and III are given the proper corrections, the numerical results are the same as for their cases V and VI, modified as above. Cases II and IV are probably untenable.

Eucken, Karwat, and Fried use the Sackur formula for C' in which the symmetry number is absent, although they mention the possibility that such a number should be included. Consequently according to Ehrenfest, etc., the logarithms of moments of inertia calculated from chemical constants on p. 34 of their paper should be increased by $\log 2=.3$ for non-polar molecules. This is indicated in their discussion, where it is noted that the symmetry number does not in general improve the agreement with experiment.

Cox's treatment is based on Fowler's statistical theory, and so contains a full allowance for symmetry numbers, etc.

A difficulty perhaps even more serious than the conflict between moments of inertia deduced from chemical constants and those deduced from band spectra is the fact that chemical constants calculated from vapor pressure measurements do not agree with those calculated from dissociation equilibrium. This has been particularly emphasized in a recent paper by Eucken and Fried,[91] as well as in the article by Cox. To avoid this disagreement Eucken and Fried suggest that the Nernst heat theorem is not of universal validity and that at $T=0$ the entropy of a solid may equal $R\ln p_s$ instead of zero (cf. Eq. (13)). Here, as previously, p_s denotes the a priori probability of the normal state in the solid phase. The experimental values of the chemical constants C' or C for the corresponding gaseous phases are then to be increased by $\log p_s$ in order to leave unaltered the effective chemical constant appearing in the vapor pressure equation. We have already briefly discussed on p. 1014 the possible theoretical justification for such a procedure. Eucken and Fried find that most of the discrepancy between vapor pressure and dissociation measurements can be removed by assuming that $p_s=2$ for H_2, N_2, I_2, NO, CO, CH_4, but that $p_s=1$ for O_2, HCl, HBr, HI, CO_2, H_2O, NH_3. They also indicate one or two other possible schemes. These empirical values for p_s yet await an adequate theoretical justification, as there is no obvious reason why some of the gases belong to the category $p_s=2$ and others to $p_s=1$. Also Eucken and Fried's conclusions have been questioned by Simon[99] on the ground that the experimental evidence is inadequate. We may, however, note that most of the gases for which they suggest $p_s=2$ are of a non-polar character, and this may possibly have something to do with the fact repeatedly emphasized in Section 2 that the simple rotator theory used in HCl, etc., cannot be applied to non-polar molecules. We have seen that there is some evidence that in such molecules the minimum value of the rotational quantum number is $\frac{3}{2}$ instead of $\frac{1}{2}$, and this might imply a larger value of p_s, possibly $p_s=3$. Also Pauling and Tolman[100] have noted that in supercooled liquids there may be several configurations of sensibly equal energy, giving a large p_s, and we may add that more configurations might perhaps be expected with non-polar molecules because the orientation has less influence on the energy. If a symmetry number $\sigma_s=2$ is introduced for non-polar molecules in the solid phase, the larger a priori probability would in part be offset by the term $-R \ln 2$ (cf. Eq. 13) and we would then require $p_s=4$ instead of $p_s=2$ to make $S_0=R \ln 2$ for H_2, N_2, etc. as in Eucken and Fried's scheme given above. According to this scheme we would have for hydrogen gas $C=-1.11+\log 2=-.81$. This can be reconciled with Eq. (12) only if the minimum a priori probability p_0 for the gas is 4, or if the symmetry number σ is omitted. The value $p_0=4$ is scarcely conceivable (much less so than $p_s=4$) and the omission of the symmetry number in the gas is questionable since the statistical theory for this number is much more firmly founded in gases than solids. We have seen in Section 2 that there is some evidence for $p_0=3$, but this would increase C by $\log \frac{3}{2}=.18$ instead of by .3 as proposed by Eucken and Fried. Their increased value of C' for nitrogen is consistent with (15) only if the symmetry number σ is omitted or if the moment of inertia be given an unlikely value considerably greater than that obtained from band spectra, whereas we have seen that without Eucken and Fried's modification there was excellent agreement in this particular case. In short the correlation of experimental and theoretical chemical constants is at present in a decidedly chaotic state.

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