PROC. N. A. S.

While these experiments were concerned largely with a determination of  $\phi_+$ , the equivalent voltage of the work function for the removal of a positive ion from the hot surface, other experiments with positive ions may be simplified by the use of this ion source.

In conclusion, the author wishes to express his appreciation for the interest shown in this work by the members of the Laboratory staff, and to Prof. K. T. Compton of Princeton for making the mass spectrograph analysis possible, and especially to Mr. R. A. Nelson for his careful work in the construction of the apparatus and assistance in the experimental work.

<sup>1</sup> Science, 62, 269 (1925); Physic. Rev., 25, 892 (1925).

<sup>2</sup> Physic. Rev., 27, 739 (1926).

<sup>8</sup> J. Phys. Chem., 30, 525 (1926).

<sup>4</sup> For an exact determination of  $\phi$ , a method similar to that used by Davisson and Germer (*Phys. Rev.*, 20, 300 (1922); 24, 666 (1924)) should be used. However, with the present method, a value of  $\phi_{-}$  for pure tungsten was obtained as 4.25 volts, where the value determined by Davisson and Germer with the same equation was 4.78 volts.

<sup>5</sup> Wychoff and Crittenden, J. Amer. Chem. Soc., 47, 2866 (1925).

<sup>6</sup> Geiss and Liempt, Z. Metallkunde, 16, 317 (1924).

<sup>7</sup> Davisson and Pidgeon, *Physic. Rev.*, 15, 553 (1920); Langmuir and Kingdon, *Science*, 57, 58 (1923); *Proc. Roy. Soc.*, A107, 61 (1925).

## THE DIELECTRIC CONSTANT AND DIAMAGNETISM OF HY-DROGEN AND HELIUM IN THE NEW QUANTUM MECHANICS

## BY J. H. VAN VLECK

#### DEPARTMENT OF PHYSICS, UNIVERSITY OF MINNESOTA

#### Communicated November 15, 1926

The new Heisenberg-Schrödinger quantum mechanics enables one to calculate exactly the diamagnetic and dielectric susceptibilities of hydrogenic atoms. We shall see that whenever the quantum numbers are small the numerical values obtained for these susceptibilities are considerably different from those of the old quantum theory, and usually in more convincing agreement with experiment.

Dielectric Constant of Atomic Hydrogen in the Normal State.—After application of a field F the energy of a state n is, in general, of the form

$$W_n = W_{0n} + a_1 F + \frac{1}{2} a_2 F^2 + \dots, \qquad (1)$$

where  $W_{0n}$  is the energy in the absence of the field. Waller<sup>1</sup> and Epstein<sup>2</sup> have independently recently shown that in a strong electric field F the coefficients  $a_1$  and  $a_2$  have the values

$$a_{1} = \frac{3h^{2}n(m_{1} - m_{2})}{8\pi^{2}\mu eZ}, \qquad a_{2} = -\frac{n^{4}h^{6}}{512\pi^{6}Z^{4}e^{6}\mu^{3}} [17n^{2} - 3(m_{1} - m_{2})^{2} - 9m_{3}^{2} + 19], \quad (2)$$

where Ze is the nuclear charge,  $\mu$  is the mass of an electron, and  $m_1, m_2, m_3$ are quantum numbers which can assume all values from 0 to n - 1. The principal quantum number n is  $m_1 + m_2 + m_3 + 1$ . The formula (2) differs from that of the old quantum theory only in the addition of the constant +19 in the bracketed factor of  $a_2$ , and in the fact that the equatorial quantum number  $m_3$  is uniformly one unit lower than previously.

Let us suppose that the hydrogen atoms are all in their lowest or normal state. Then n = 1, and the *m*'s all vanish, so that by (2)  $a_1 = 0$ . There is then no first order Stark effect, and if there are N atoms per cc., the dielectric constant  $\epsilon$  is given by

$$\epsilon - 1 = -4\pi N a_2 = 9N h^6 / 32\pi^5 Z^4 e^6 \mu^3, \qquad (3)$$

as it is easily shown that when  $a_1 = 0$  the polarization induced in an individual atom is  $-a_2E$ , equally well in the new or old mechanics. This fact has already been utilized by Waller<sup>1</sup> in an interesting calculation of the polarization of the inner orbit by the outer electron in excited helium, and the resulting contribution to the "quantum defect" in the Rydberg formula. If Z = 1, as in hydrogen, formula (3) gives  $\epsilon = 1.000229$  at 0°C. and atmospheric pressure. The old quantum theory would give  $\epsilon = 1.000051$ , as  $a_2$  is 4.5 times greater in the new than in the old theory when n = 1. Adequate experimental evidence on the dielectric constant of monatomic hydrogen is unfortunately not at present available due to the difficulty of dissociating hydrogen gas into the atomic form.\*

At this point the question naturally arises whether the dielectric constant in weak fields may not differ from the value we have given because the relativity corrections are neglected in (2), whereas actually in very weak fields in ordinary mechanics the relativity precession may be larger than the change in frequency produced by the electric field. In the old quantum theory such a suggestion has been made by Miss Aylesworth.<sup>3</sup> However, in the new quantum mechanics the analog of the relativity precession frequency is the spectroscopic frequency emitted or absorbed when the azimuthal quantum number changes and the principal quantum number is unaltered. Such frequencies are not involved in the normal state of hydrogenic atoms, for this is a singlet level characterized by but one value of the azimuthal quantum number, and is not even split into component levels by an electric field. Therefore in the normal state there is no degeneracy introduced by omitting relativity corrections and external fields, and we do not need to consider the secular perturbations whose technique has been developed by Born, Heisenberg and Jordan,<sup>4</sup> and by

Schrödinger,<sup>5</sup> and which are the analog in the new mechanics of the "longperiod terms" of the old theory. Born, Heisenberg and Jordan's determinantal equation (25) (loc. cit.,<sup>4</sup> p. 589) is easily seen to reduce to a single element in the normal state and to be precisely the same as in the absence of the field. Thus there is no secular change in energy, and the quadratic Stark effect in the normal state arises entirely from amplitudes associated with transitions to the higher quantum states  $n = 2, 3, \ldots$ , and also to hyperbolic orbits of positive energy. This quadratic effect is of the nonsecular type which could be calculated directly from the Kramers' dispersion formula, or from the perturbation technique for non-degenerate systems if all the amplitudes were known, and such a computation would, of course, give the same result as (3). In weak fields the relativity corrections may materially modify the intensity of individual Stark effect components, but not their aggregate intensity, either parallel or perpendicular to the field, as in virtue of this "spectroscopic stability" the quadratic term of non-secular type is invariant with respect to any perturbations which produce energy changes small compared to those involved in the (Lyman) transitions to states having higher values of the principal quantum number.

The mathematical detail of the rather technical proof that this invariance follows from the spectroscopic stability characteristic of the new quantum mechanics will be deferred until a later paper. We may simply mention that in summing the polarization given by the Kramers' dispersion formula over the various fine-structure levels (or in averaging  $\rho^2$  over the various quantized orientations in the calculation of diamagnetism given below) we are led to an expression of the type form

#### $\Sigma_k \Sigma_l q(kl) q(lk)$

where q(kl) is a matrix element, and where we sum k over all the component states of one multiple level and l over all the states of another. The essence of the proof consists in showing this sum invariant under a contact transformation of the type involved in reducing the secular part of the perturbative potential to a diagonal element. In the case of spacial degeneracy such a transformation corresponds to changing the axis of quantization. Born, Heisenberg and Jordan,<sup>4</sup> prove the invariance of the sum in case only the k or l level is multiple, but the extension to the case where they are both multiple occasions no difficulty. This invariance led the writer to predict in a recent note to Nature<sup>6</sup> that there would be no variation of the dielectric or diamagnetic susceptibility with pressure or field strength.

Thus despite the relativity corrections the dielectric constant has the same value 1.000229 in strong and weak fields. Similarly  $\epsilon$  will be unchanged by other disturbances. We have not, for instance, mentioned the internal spins of the electron, but they respond to magnetic rather than electric fields. The "spin electron corrections" are thus mathematically coördinate with the numerically comparable relativity corrections, and without influence on the dielectric constant for the same reason. Furthermore, questions of spacial quantization do not enter, as the spectroscopic stability argument alluded to above shows that the dielectric constant for the same reason.

stant has the same value with random orientations as with the particular orientations allowed by the quantum conditions.

Dielectric Constant of Excited Hydrogen Atoms.-If the hydrogenic atoms are all in one particular excited state; i.e., all have some given value of  $n \neq 1$ , the part of the dielectric constant which is independent of the temperature may be determined from (2) by averaging over all the various allowed integral values of  $m_1$ ,  $m_2$ ,  $m_3$  which are consistent with the given n. Each value of  $m_3 \neq 0$  is to be counted twice because of the possibility of both left- and right-handed rotations about the axis of the field. Because of the relativity corrections which in weak fields introduce small frequencies in the denominator except when n = 1, the numerical magnitude of  $a_2$ will be much greater than (2) when the field is very weak. It may, however, be proved that our average value of  $a_2$  is invariant of the field strength, and can be calculated from (2) even in weak fields. The proof consists in noting that the non-secular part of  $\overline{a_2}$  is invariant in virtue of the general spectroscopic stability argument alluded to above, while the secular part can be shown invariant by using the same method as that employed by Heisenberg and Jordan in proving the permanence of g-sums in the anomalous Zeeman effect (see especially the paragraph containing equation 17 on p. 269 of their article in Zeits. f. Physik, 37, 269). In addition to the term proportional to  $\overline{a_2}$ , there will be another term in the dielectric constant arising from the fact that the Boltzmann temperature factor has different magnitudes for different component states. This second term is important only if the field is strong enough to produce a linear Stark effect. The complete dielectric constant is thus readily found to be

$$\epsilon - 1 = -4\pi N\overline{a_2} + \frac{4\pi Na_1^2}{kT} = \frac{Nh^6(15n^6 + 21n^4)}{128\pi^5 Z^4 e^6 \mu^3} + \frac{3Nh^4(n^4 - n^2)f(F)}{32\pi^3 Z^2 e^2 \mu^2 kT}$$

where f(F) equals unity in strong fields, but vanishes in weak fields, in which always  $a_1 = 0$ .

Diamagnetic Susceptibility.—By a fundamental formula developed by Pauli,<sup>7</sup> the diamagnetic susceptibility per gram mol. is

$$X_M = -(e^2 L/4\mu c^2) \Sigma \ \overline{\rho^2} \tag{4}$$

where L is the Avogadro-Loschmidt number. We note by  $\rho$ , z,  $\varphi$  the cylindrical coördinates of an electron, with the magnetic field H as the z-direction. The summation in (4) extends over all the electrons in the atom or molecule. Equation (4) differs by a factor 2 from the original Langevin-Weber formula, as noted by Glaser<sup>8</sup> and Barnett,<sup>9</sup> and is much more satisfactory since Pauli assumes real electronic motions rather than hypothetical particles which can rotate only in one particular plane. The impression is usually conveyed that Larmor's theorem is basic to the derivation of (4), as it was so stated in Pauli's original paper. In reality the

assumption of Larmor's theorem is unnecessary, as (4) can be deduced from the very general dynamical principle that in a magnetic field the generalized momentum  $p_{\varphi}$  conjugate to  $\varphi$  must be defined<sup>10</sup> as  $p_{\varphi} = \mu \rho^2 \dot{\varphi} - (He\rho^2/2c)$  in order to preserve the Hamiltonian form of the equations of motion. The diamagnetic moment is simply a correction term resulting from the fact that the magnetic moment of an electron about the axis of the field is proportional to the ordinary angular momentum  $\mu \rho^2 \dot{\varphi}$  rather than to the generalized momentum  $p_{\varphi}$  given above which is canonically conjugate with respect to  $\varphi$ . For let M be the axial component of the part of the magnetic moment of an individual atom or molecule which arises from the orbital angular momentum of the electrons. Then  $M = -1/2 \Sigma e \rho^2 \dot{\varphi}/c$  as  $-e/2\mu c$  is the ordinary ratio of orbital magnetic moment to angular momentum. If we make the substitution  $\mu \rho^2 \dot{\varphi} = p_{\varphi} + (He\rho^2/2c)$  then

$$M = -(e/2\mu c)\Sigma p_{\omega} - (e^2/4\mu c^2)\Sigma \rho^2 H.$$

The first term is simply the contribution of the orbital angular momentum of the electrons to the paramagnetic moment. The second term gives our equation (4) on multiplying by the Avogadro number and averaging over all atoms or molecules.

From this general mode of derivation it is seen that Pauli's formula can be applied to molecules as well as atoms, since on account of the factor  $1/\mu$  we may neglect the contribution of the heavy nuclei to the diamagnetic moment. Furthermore the advent of the spin electron does not destroy the applicability of (4). There is, to be sure, a distinction between the ordinary definition of the angular momentum associated with the internal spins and the Hamiltonian definition in a magnetic field (a distinction similar to the orbital one described above, but with an internal dimension entering in place of  $\rho$ , etc.); nevertheless the resulting contribution to the diamagnetism is a mere nothing since the internal radius of the electron is extremely small. It is, of course, to be understood that the internal spin may give a large contribution to paramagnetism. It is, in fact, responsible for all the paramagnetism of normal hydrogen atoms, but we are concerned with the diamagnetic effects which always remain as residuals even in compounds (such as  $H_2$ ) where the paramagnetic effects of individual electrons neutralize each other. To summarize, equation (4) applies far more generally than Larmor's theorem, but the literature is nevertheless honeycombed with misleading statements and formulas. may note in particular a recent paper by Tartakowsky<sup>11</sup> which attempts to introduce the Landé g-factor into diamagnetism. This procedure appears erroneous to the writer because the general argument given above shows (4) holds even with anomalous precessions due to internal spins.

The method of deriving (4) shows that it will continue to hold in the new

667

quantum mechanics, as no non-commutative multiplications are involved. There is, however, the following marked superiority of the new dynamics. In the old quantum theory we could replace the average of  $\rho^2 = x^2 + y^2$  over all atoms by two-thirds the time average of  $r^2 = x^2 + y^2 + z^2$  for a single atom only if we assume a random spacial distribution of orbits, which makes the mean squares of x, y, z equal by symmetry; with spacial quantization the results would be different, as emphasized by Debye.<sup>12</sup> The spectroscopic stability characteristic of the new quantum mechanics (see a preceding paragraph in fine print) shows that we may replace  $\overline{\rho^2}$  by  $2/3 \overline{r^2}$  not only when there is random orientation, but also when there is spacial quantization relative to the axis of the magnetic field, or even relative to any other axis of reference. This explains why recent experimenters find no "Glaser effect" (variation of susceptibility with pressure). It is indeed most comforting that in the new theory we can always write (4) in the form

$$X_M = -(e^2 L/6\,\mu c^2) \Sigma \,\overline{r^2} = -2.85 \cdot 10^{10} \Sigma \,\overline{r^2}$$
(5)

where it is clearly to be understood that the bar in (5) denotes a time average for an individual atom (or molecule) whereas in (4) the bar denotes an average over the different allowed orientations. We have tacitly supposed that all the atoms or molecules of the diamagnetic material have the same time average of  $r^2$ . This condition is clearly fulfilled by hydrogenic atoms in the normal state and also is satisfied by most other free atoms and approximately by molecules which are not unduly elastic. The excitation of states with different mean values of  $r^2$  may, however, possibly be the explanation of the temperature variation of the diamagnetism of certain solid elements.

The time average of  $r^2$  will be different for a hydrogenic atom in the new mechanics than in the old, and one of the main aims of the present paper is to communicate the new value. The requisite average value, which is, of course, a diagonal element of the matrix  $r^2$ , is readily calculated by methods due to Waller<sup>1</sup> (especially his Eqs. 35–37). We thus find

$$\overline{r^2} = a_0^2 n^2 [\frac{5}{2} n^2 - \frac{3}{2} k(k+1) + \frac{1}{2}]$$
(6)

where  $a_0$  equals  $h^2/4\pi^2\mu Ze^2$ , the radius of a one-quantum orbit in the old theory, and where the azimuthal quantum number k assumes the values  $0,1, \ldots, n-1$ . The old quantum theory would give

$$\overline{r^2} = a_0^2 n^2 [\frac{5}{2} n^2 - \frac{3}{2} k'^2]$$

where k' is one unit larger than the new k.

For hydrogen atoms in the normal state we have Z = 1, n = 1, k = 0 and equations (5, 6) then give  $X_M = -2.42 \times 10^{-6}$ , a value three times that given by the old quantum theory. The diamagnetic susceptibility 2.93  $\times 10^{-6}$  is deduced for atomic hydrogen by Pascal<sup>13</sup> from experimental data

on organic compounds. He assumes that their susceptibilities are the sum of those of the constituent atoms plus a constant characteristic of the type of chemical bond. Pascal's value is over 250% higher than that given by the old theory (assuming the field too weak for spacial quantization), but only 22% higher than that given by the new. This must be regarded as a decisive confirmation of the new mechanics at the expense of the old. The 22% discrepancy is not surprising since atomic susceptibilities clearly cannot be calculated accurately by applying the method of mixtures to molecular data.

Application to Helium and Molecular Hydrogen.—Since direct measurements have apparently to date been prevented by the difficulty of obtaining pure monatomic hydrogen, perhaps the best experimental method of testing the theoretical susceptibilities is by the data for helium and molecu-We shall assume that each helium atom or hydrogen lar hydrogen. molecule has the same susceptibility, energy, etc., as two hydrogenic atoms in the state n = 1 and with the effective nuclear charge Z. The theoretical energy, dielectric constant and diamagnetic susceptibility are then, respectively,<sup>14</sup>  $W = 27.1 \cdot Z^2$  volts,  $\epsilon = 1 + 0.000458Z^{-4}$ ,  $X_M = -4.84 \times$  $10^{-6}Z^{-2}$ . The experimental values are: for He, W = 78.8,  $\epsilon = 1.0000693$ ,  $X_M = -1.88 \times 10^{-6}$ ; for H<sub>2</sub>, W = 31.3,  $\epsilon = 1.000273$ ,  $X_M = -3.94 \times 10^{-6}$ . On equating the theoretical and experimental values of W,  $\epsilon$  and  $X_M$ , respectively, we have three independent estimates of the effective nuclear charge, and the good agreement between the three is a confirmation of the theory. The results are given in the following table:

	Effective	NUCLEAR CHARGE Z	
FROM	ENERGY	DIELECTRIC CONSTANT	DIAMAGNETISM
He	Z = 1.71 (1.71)	Z = 1.603 (1.10)	$Z = 1.607 \ (0.93^{-15})$
$H_2$	Z = 1.08 (1.08)	Z = 1.14 (0.78)	$Z = 1.11  (0.64^{-15})$

The values of Z which would have been obtained had the susceptibilities been calculated with the old quantum theory are included in parenthesis after the new values. The results obtained with the new theory are obviously vastly more consistent and reasonable than those with the old, and this gratifying fact must be added to the many other successes of the Heisenberg-Schrödinger Exact agreement between the various estimates of Z is not mechanics. to be expected, since introduction of a screening constant is clearly but a crude representation of the interplay between the two electrons. The closer agreement of Z calculated from the dielectric constant with that calculated from diamagnetism than with that calculated from energy is to be expected, as  $W, X_M$  and  $\epsilon$  are all quadratic in the amplitudes but involve the frequencies to the powers +2, 0 and -1, respectively, and so any divergence of frequencies from hydrogenic values will cause more spread between values of Z calculated from  $\epsilon$  and W than from  $\epsilon$  and  $X_M$ . It is thus tempting to calculate diamagnetic susceptibilities with the

values of Z deduced from dielectric constants. The values  $1.88 \times 10^{-6}$ and  $3.74 \times 10^{-6}$  are then obtained for the diamagnetic susceptibilities of He and H<sub>5</sub>, respectively, in remarkably close agreement with the experimental values  $1.88 \times 10^{-6}$  and  $3.94 \times 10^{-6}$  quoted above. The discrepancy may, however, be greater than apparent at first sight because the experimental values of X<sub>M</sub> which we employ may be in error, especially in H<sub>2</sub>. We have assumed Hector and Wills' values, <sup>16</sup> which are the only reliable data at present available for He, and which in the case of H<sub>2</sub> reassuringly agree within 2 per cent with an independent determination by Soné.<sup>17</sup> On the other hand tentative measurements by Lehrer<sup>18</sup> on hydrogen, which he states may be inaccurate, give  $X_M = -5.1 \times 10^{-6}$ which requires Z = 0.98, while an even greater diamagnetic susceptibility for H<sub>2</sub> is reported in a preliminary communication by Hammar.<sup>19</sup> The low value of Z required by the newer measurements on hydrogen is possibly an argument against them.

We shall not attempt in the present paper to extend the numerical calculation of susceptibilities to atoms or molecules with more than two electrons. Such computations of dielectric constants would show a certain amount of resemblance to those of J. H. Jones<sup>20</sup> in the old quantum theory. The results would perhaps be less significant than those for H<sub>2</sub> and He because the difference between the new and old mechanics is less for large quantum numbers and also because complicated atoms approximate less closely to hydrogenic conditions.

\* Note Added in Proof. Last month's issue of these PROCEEDINGS, 12, 639, contains an experimental determination of the dielectric constant of atomic hydrogen by R. M. Langer, who finds  $\epsilon - 1$  to have half the value for molecular hydrogen. This gives  $\epsilon = 1.000136$  for atomic hydrogen, which does not agree with the theoretical value 1.000229 within his tentative estimate  $\pm 0.000034$  of the experimental error. The directness and unambiguity with which the quantum mechanics give  $\epsilon = 1.000229$ suggest that the error in the very difficult experiment undertaken by Dr. Langer is larger than his estimate, possibly due to a smaller concentration of atomic hydrogen than ordinarily anticipated. Dr. Langer also includes an interesting second paper (Ibid., 12, 644) in which he endeavors to calculate the dielectric constant of atomic hydrogen with the new quantum mechanics by summing the various terms in the Kramers' dispersion formula. The theoretical value  $\epsilon = 1.000338$  which he obtains appears to the writer clearly erroneous because it assumes that all of the dispersion comes from the absorption band beyond the head of this series. Hence the Kramers' dispersion formula should be integrated over the continuous spectrum as well as summed over the monochromatic part, but this would be a more laborious way of getting the same result as obtained above directly from the quadratic Stark effect.

- <sup>1</sup> I. Waller, Zeits. f. Physik, 38, 635, 1926.
- <sup>2</sup> P. S. Epstein, Physic. Rev., 28, 695, 1926.
- <sup>8</sup> Evelyn Aylesworth, Physic. Rev., 28, 847A, 1926.
- <sup>4</sup> Born, Heisenberg and Jordan, Zeits. f. Physik, 35, 589-590, 1926.
- <sup>5</sup> E. Schrödinger, Ann. d. Physik, 80, 446, 1926.
- <sup>6</sup> J. H. Van Vleck, Nature, 118, 226, 1926.
- <sup>7</sup> W. Pauli, Jr., Zeits. f. Physik, 2, 201, 1920.

<sup>8</sup> A. Glaser, Dissertation, Münich, 1924.

<sup>9</sup> S. J. Barnett, Physic. Rev., 25, 835, 1925.

<sup>10</sup> This can, for instance, be seen from Darwin's Lagrangian and Hamiltonian functions for atoms in magnetic fields, *Phil. Mag.*, **39**, 537, 1920.

<sup>11</sup> P. Tartakowsky, Zeits. f. Physik, 34, 216, 1925.

<sup>12</sup> P. Debye, Physic. Rev., 25, 586A, 1925.

<sup>13</sup> A. Pascal, numerous references listed in Jahr. d. Rad. and Elektr., 17, 184, 1920.

<sup>14</sup> The value  $\epsilon = 1.0000693$  for He is that obtained by Herzfeld and Wolf, Ann. d. Physik, 76, 71 and 567, 1925, by extrapolating refractive indices to infinite wave-length, and is probably more accurate than direct determinations. The value  $\epsilon = 1.000273$  for H<sub>2</sub> is that obtained directly by Tangl. This value apparently is for 0°C. rather than 20°C., contrary to the statement in the Landolt-Bornstein tables (5th ed., p. 1041) and so is in good agreement with dispersion data.

<sup>15</sup> If the field were strong enough for spacial quantization, the values of Z obtained from diamagnetism with the old quantum theory would be 1.14 and 0.78 instead of 0.93 and 0.64. We suppose the electric but not the magnetic field adequate for spacial quantization in the old theory.

<sup>16</sup> Wills and Hector, Physic. Rev., 23, 209, 1926; Hector, Ibid., 24, 418.

<sup>17</sup> Soné, Phil. Mag., 39, 305, 1920.

<sup>18</sup> E. Lehrer, Ann. Physik, 81, 229, 1926.

<sup>19</sup> C. W. Hammar, Proc. Nat. Acad. Sci., 12, 594 and 597, 1926.

<sup>20</sup> J. H. Jones, Proc. Roy. Soc., 105A, 650, 1924.

# ON THE EQUILIBRIUM BETWEEN RADIATION AND MATTER

## By Richard C. Tolman

NORMAN BRIDGE LABORATORY OF PHYSICS, CALIFORNIA INSTITUTE OF TECHNOLOGY

#### Communicated October 27, 1926

1. Introduction.—The theories of stellar evolution of Eddington, Jeans and Russell apparently necessitate the transformation of matter into radiation in order to account for the great life span of the sun and other stars. Such a process, however, immediately implies the existence of the reverse change of radiation into matter, and thus leads to the possibility of an equilibrium between these two forms of energy under suitable conditions of concentration and temperature.

By applying the laws of thermodynamics to an equilibrium mixture of radiation and matter Stern<sup>1</sup> has attacked this problem in a very stimulating and original manner, and derived an expression for the concentration of perfect gas which would be in equilibrium with radiation at any given temperature. He obtains the surprising result that, even at a temperature of one hundred million degrees, only one electron per cubic centimeter could be present at equilibrium. For a mixture containing equal numbers of electrons and protons, such as would presumably have to form from radiation in order to maintain electrical neutrality, the equilibrium concentrations would be even enormously lower. This result seems somewhat