THE QUANTUM THEORY OF THE DIELECTRIC CONSTANT OF HYDROGEN CHLORIDE AND SIMILAR GASES

By Linus Pauling*

Gates Chemical Laboratory, California Institute of Technology

Under the influence of an electric field a gas whose molecules have a permanent electric moment and in addition can have a further moment induced in them by deformation becomes polarized in the direction of the field, the amount of polarization per unit volume being[1]

$$P = \frac{3}{4\pi} \frac{\epsilon - 1}{\epsilon + 2} F = N\mu \overline{\overline{\cos \theta}} + N\alpha F. \tag{1}$$

Here ϵ is the dielectric constant of the gas, F the strength of the applied field, N the number of molecules in unit volumes, μ the permanent electric moment of a molecule, and α the coefficient of induced polarization of a molecule; $\overline{\overline{\cos \theta}}$ is the average value of $\overline{\cos \theta}$ for all molecules in the gas, and $\overline{\cos \theta}$ is the time-average of $\cos \theta$ for one molecule in a given state of motion, θ being the angle between the dipole axis and the lines of force of the applied field.

On the basis of the classical theory it was shown by Debye[2] that $\overline{\overline{\cos \theta}}$ is given by the Langevin function

$$\overline{\overline{\cos \theta}} = \coth \frac{\mu F}{kT} - \frac{kT}{\mu F}. \tag{2}$$

This reduces, for values of μF small in comparison with kT, to

$$\overline{\overline{\cos \theta}} = \frac{1}{3} \frac{\mu F}{kT}. \tag{3}$$

This result must now, however, be replaced by one based upon the quantum theory. In this case a generally applicable expression cannot be obtained, and it is necessary to consider particular molecular models. W. Pauli, Jr.[3] has treated the diatomic dipole, which is of interest to us, and his treatment forms the basis of this discussion.

The Hamiltonian function for this dynamical problem, using polar coördinates with the polar axis in the direction of the lines of force, is

$$H = \frac{1}{2I} \left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2 \theta} \right) - \mu F \cos \theta. \tag{4}$$

In this expression p_θ and p_φ are the momenta corresponding to the coördinates θ and φ, and I is the moment of inertia of the rotator about

an axis through its center of mass and normal to the line joining the atomic nuclei. Applying the Wilson-Sommerfeld quantum conditions we write

$$\oint p_\theta \, d\theta + \oint p_\varphi \, d\varphi = mh, \Big\} \atop \oint p_\varphi \, d\varphi = 2\pi \, p_\varphi = nh. \Big\} \tag{5}$$

The time-average value of $\cos \theta$ for a given rotator characterized by the quantum numbers m and n is found to be, in case μF is small in comparison with the energy-constant W,

$$\overline{\cos \theta} = \frac{4\pi^2 \mu F I}{m^2 h^2} \left(\frac{3}{2} \frac{n^2}{m^2} - \frac{1}{2} \right). \tag{6}$$

Pauli assigned to m the values 1, 2, 3, ... ∞, and to n the values ± 1, ± 2, ± 3, ... $\pm m$. We shall give m the values $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, ... ∞, and n the value $\pm \frac{1}{2}$, $\pm \frac{3}{2}$, $\pm \frac{5}{2}$, ... $\pm m$; for these half-quantum numbers for m are indicated by the infra-red oscillation-rotation absorption spectrum[4] of hydrogen chloride and definitely required by the recently observed[5] pure rotation absorption spectrum, and it can be shown that similar values for n are reasonable. Assigning equal *a priori* probabilities to all of the possible quantum states characterized by half-integral values of m and n we have for the probability of a given state

$$w \, (m, n) = \frac{e^{-\frac{W}{kT}}}{\displaystyle\sum_{m=1/2}^{\infty} \sum_{n=\pm 1/2}^{\pm m} e^{-\frac{W}{kT}}} \tag{7}$$

Introducing the variable $\sigma = \dfrac{\theta}{T} = \dfrac{h^2}{8\pi^2 I k T}$ we obtain the following expression for $\overline{\cos \theta}$:

$$\overline{\cos \theta} = \frac{\mu F}{kT} \frac{1}{2\sigma} \frac{\displaystyle\sum_{m=1/2}^{\infty} \sum_{n=\pm 1/2}^{\pm m} \frac{1}{m^2} \left(\frac{3}{2} \frac{n^2}{m^2} - \frac{1}{2} \right) e^{-\sigma m^2}}{\displaystyle\sum_{m=1/2}^{\infty} \sum_{n=\pm 1/2}^{\pm m} e^{-\sigma m^2}}. \tag{8}$$

Pauli, who obtained a similar expression with whole quantum numbers, evaluated the sums by assuming σ to be very small. This is not justifiable, however, in cases of practical interest, for which σ has values near 0.05, for it then leads to results in error by 30% or more. Replacing m by $r - \frac{1}{2}$ and n by $s - \frac{1}{2}$ and summing for s one obtains

$$\overline{\cos \theta} = \frac{\mu F}{kT} C, \tag{9}$$

where

$$C = \frac{1}{4\sigma} \frac{\sum\limits_{r=1}^{\infty} \dfrac{r}{(r - \frac{1}{2})^3} e^{-\sigma(r - \frac{1}{2})^2}}{\sum\limits_{r=1}^{\infty} r\, e^{-\sigma(r - \frac{1}{2})^2}}. \tag{10}$$

C has been evaluated for a range of values of σ by direct substitution. The values obtained are given in table 1.

TABLE 1

σ	C	σ	C
0.20	2.848	0.04	3.690
0.10	3.264	0.03	3.796
0.07	3.445	0.02	3.929
0.05	3.599	0	4.570

In order to apply the results of the theory in the interpretation of the experimental measurements on hydrogen chloride, made by Zahn,[6] it is necessary to know Θ for this substance. Czerny[5] gives for $\dfrac{hc}{8\pi^2 I}$ the value 10.397, which leads to a value of 14.9° for Θ. It is found that Zahn's experimental results conform reasonably well with the theoretical curve corresponding to a value of 0.3316×10^{-18} c.g.s.u. for μ and 0.00077 for $4\pi N_0 \alpha$, with N_0 the number of molecules per cc. at standard conditions. These values differ considerably from those obtained from the same data with the classical theory, 1.034×10^{-18} and 0.00104.

The experimental points, which surprisingly enough lie very close to a curve of the type required by the classical theory, show deviations as large as 2% from the best quantum theory curve. Nevertheless it is not easy to reject the straight-forward and well-grounded quantum theory calculations given in this paper; possibly the discrepancies can be attributed to errors in the experimental measurements. Further measurements testing this point are needed.

The quantum theory value for $4\pi N_0 \alpha$ is confirmed by independent evidence; for it conforms with Maxwell's relation $4\pi N_0 \alpha = n_0^2 - 1$, in which n_0 is the index of refraction of the gas at standard conditions for light of frequency far from any frequency characteristic of the molecule. It is known that n as determined with light of ordinary wave-length is larger than n_0; hence the observed value 0.000888 for $n^2 - 1$ for hydrogen chloride with the sodium D-lines cannot be reconciled with the classical value 0.00104 for $4\pi N_0 \alpha$, but supports the quantum theory value 0.00077.

Similar calculations for hydrogen bromide lead to the values 0.252×10^{-18} for μ and 0.00102 for $4\pi N_0 \alpha$. The data for hydrogen iodide are inaccurate because of dissociation, and cannot be used.

The electric moment found for hydrogen chloride is equal to that of a dipole composed of a proton and an electron 0.0694 Å apart; for hydrogen bromide the equivalent distance is 0.0528 Å.

A more extensive account of these calculations will be presented to the *Physical Review* for publication.

* NATIONAL RESEARCH FELLOW IN CHEMISTRY.

[1] See, for example, Debye in Marx "Handbuch der Radiologie," Leipzig Akademische Verlagsgesellschaft, 1925, V. 6, p. 619.

[2] P. Debye, *Physik. Zeit.*, **13**, 97 (1912).

[3] W. Pauli, Jr., *Z. Physik*, **6**, 319 (1921).

[4] Colby, *Astrophys. J.*, **58**, 303 (1923).

[5] Czerny, *Z. Physik*, **34**, 227 (1925).

[6] Zahn, *Physic. Rev.*, **24**, 400 (1924).

THE MOBILITY OF GASEOUS IONS IN HCl GAS AND HCl AIR MIXTURES

BY L. B. LOEB

PHYSICAL LABORATORY, UNIVERSITY OF CALIFORNIA

Introduction.—In a further endeavor to answer the question as to the nature of the gaseous ion the writer undertook measurements of the mobilities of positive and negative ions in mixtures of HCl gas and air of varying composition. Practically no systematic measurements of mobilities in mixtures of varying concentrations of different gases have been made. Those of Blanc[1] in mixtures of H_2, CO_2 and air and those of Loeb and Ashley[2] on mixtures of NH_3 and air constitute the only ones up to the present. Certain differences between the results of Blanc on the mixtures of the less reactive gases and those of the writer and Miss Ashley on mixtures in NH_3 and air made it seem of importance to continue the investigation with other gases of dissimilar nature. The particular differences observed for NH_3 and air mixtures and their theoretical interpretation will form the subject of another paper.

The only mobility measurements made on HCl are those made by Rutherford[3] in 1897 who found that the sum of the positive and negative mobilities in HCl was in the neighborhood of 1.27 cm./sec. The results of the measurements of mobilities in pure HCl as well as in mixtures of HCl and air yielded such curious results that it seemed of importance to publish a preliminary account of them in this article.

Experimental Procedure.—The measurements were made by the Franck[4] modification of the Rutherford alternating current method, used by