THE ELECTRIC MOMENT OF GASEOUS MOLECULES OF HALOGEN HYDRIDES

By C. T. Zahn

Abstract

Dielectric constant of the hydrogen halides HCl, HBr and HI to 300°C.—An improved heterodyne null method of measurement was used in which the beats between two high frequency oscillations from separate electron tube generators are adjusted to the frequency of a tuning fork, the small change of capacity due to the introduction of the gas being compensated by a large change in a large capacity in series with the gas condenser. Measurements were made at atmospheric pressure, using carefully purified gases, over a range of nearly 400° from just above the liquefaction point. The results are well represented by the Debye equation $(\epsilon-1)vT=AT+B$, where v is the specific volume and T the absolute temperature. [The values found for A are .001040 (HCl), .001212 (HBr) and .001856 (HI); and for B are .895(HCl), .52(HBr) and .12 (HI)]. This agreement lends support to the *Debye classical theory* of electric polarization due to fixed moments in the molecule. The values obtained for the *electric moment of the molecules* are, in 10^{-18} c.g.s.u., 1.034(HCl), 0.79(HBr) and 0.38(HI). The *Pauli quantum theory* gives an equation of the same form as Debye's but leads to smaller values for the electric moment. The upper limit for the moment given by infra-red absorption data for HCl, however, is 6 times the classical value and 13 times the quantum value and hence does not decide between the two theories.

Dielectric constant for hydrogen, oxygen, nitrogen and air.—The values obtained for $(\epsilon-1)\times 10^6$ at 0°C and 760 mm pressure are 265, 518, 581 and 572 for H_2, O_2, N_2 and air, accurate probably to within 1/2 per cent.

Introduction

The primary object of this investigation was to determine the electric moment of the molecules of HCl and HBr in order to compare their effective dipole length with their nuclear separation as obtained by Kratzer[1] from infra-red absorption spectra. This comparison would give, on certain assumptions, an idea of the distortion of the electronic configuration of the molecules. Further it was hoped that it might be possible by the use of high frequency technique to develop a method of measurement of dielectric constants more accurate than had hitherto been attainable by the use of electrometer and bridge methods and high frequency methods of different character. Similar methods have been

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[1] Kratzer, Zeit. f. Phys. **3**, 389 (1920)

used by Whiddington[2] for the measurement of small displacements, by Herweg[3] for studies of the effect of field strength on the dielectric constant, by Belz[4] for the measurement of the magnetic susceptibilities of salts, and by others. An experimental value of the dipole length also offered a possibility of choosing between the Debye theory and a more recent theory by Pauli applicable to dipole gases and based on Sommerfeld's conditions of quantum mechanics.

Debye's equation is as follows:[5]

$$\frac{\epsilon-1}{\epsilon+2}=\frac{4\pi}{3}N\left\{\lambda e^2+\frac{\mu^2}{3RT}\right\}=N\left\{A+\frac{B}{T}\right\},$$

where ϵ is the dielectric constant, N the number of molecules per cubic centimeter, λ the constant of elastic binding of the "optical" electrons, e the electronic charge, μ the electric moment of the molecule, R the Boltzmann gas constant and T the absolute temperature. The Debye equation has been found satisfactorily to represent data obtained by Jona and by Bädeker on H_2O, NH_3, SO_2, CH_3OH, C_2H_5OH, CS_2, CO_2 and CO.[6,7,8] Both Bädeker and Jona worked at temperatures in the range from room temperature to about 180° C. From the Debye equation it will be seen that the greatest contribution of the doublets, and so the greatest anomaly in the behavior of the dielectric constant is to be expected at the lowest temperatures. A more accurate verification of the Debye equation becomes of more particular interest also in view of a theory proposed more recently by Lundblad,[9] who considers the mutual effect of electrons of the same molecule.

Experimental Method

The measurement of the dielectric constant of gases is rendered extraordinarily difficult by the calibration of the apparatus. In fact, a number of investigators, some of whose results are quoted in tables of constants, have relied upon previous measurements for this calibration. Relative values of $(\epsilon-1)$ can be obtained much more accurately than absolute values. Indeed, different investigators have differed by as much as ten per cent in the values of gases such as nitrogen, air and hydrogen, but

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[2] R Whiddington, Phil. Mag. **40**, 634 (1920)
[3] J Herweg, Zeit. f. Phys. **3**, 36 (1920)
[4] V. H Belz, Phil. Mag. **44**, 479 (1922)
[5] P. Debye, Phys. Zeit. **13**, 97 (1912)
[6] K. Bädeker, Zeit. f. Phys. Chem. **36**, 305 (1901)
[7] M. Jona, Phys. Zeit. **20**, 14 (1919)
[8] J J. Thomson, Phil. Mag. **27**, 757 (1914)
[9] R. Lundblad, Zeit. f. Phys. **5**, 349 (1921).

since the values for the different gases obtained by two observers usually bear a nearly constant ratio, the variations in the absolute values can be attributed to errors in the calibration of the apparatus. It is believed that the method herein described has reduced this difficulty of calibration of the apparatus and has accordingly given results less liable to such errors.

(a) *The measuring circuits.* The method of measurement adopted involves the use of high frequency oscillations produced by electron tube generators. A diagram of the electric circuits is shown in Fig. 1. There are two separate generators; one operates steadily at a frequency of the order of a million per second; the other, at a frequency differing from this by an audible frequency of a thousand per second. These two generators are coupled electrostatically to a detector-amplifier circuit consisting of three stages as shown. A heterodyne note of frequency one thousand per second is heard from the telephone receiver *T*. This note is kept adjusted by the method of beats with a tuning fork operated by an auxiliary electron tube circuit. The variable generator contains a system of condensers one of which can be evacuated or filled with the gas to be

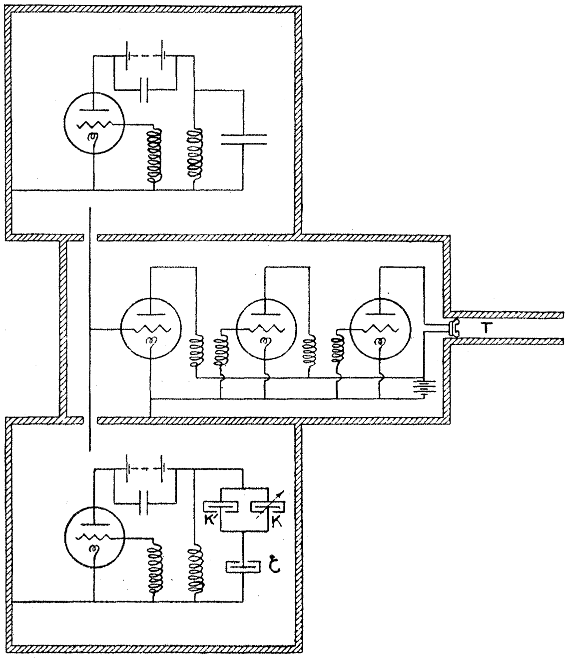


Fig. 1. Diagram of electric circuits.

studied. The procedure is as follows. With the gas condenser evacuated the variable generator is adjusted to the condition of zero beats between the notes from the tuning fork and the receiver T; then the gas is introduced into the condenser and a measurable compensation is made for the resulting change in capacity by means of a device to be explained later.

The various parts of the electrical apparatus are carefully shielded wherever necessary. The two generators and the detector-amplifier are separately enclosed in metal boxes. In order to avoid coupling between the two generators themselves, and thus to make the frequency of the generators independent of each other, the coupling to the amplifier is reduced to a minimum. It is found quite sufficient to use a "floating grid"; i. e. a wire connected to the grid of the detector tube and having two branches, one passing through a small hole in the shield of each generator. This wire receives sufficient charge, mainly by electric induction, to give a conveniently audible note in the receiver T. The receiver itself is completely shielded electrostatically, the sound being heard at the end of a metal tube enclosing it. All the variable condensers are operated by shafts running through the shielding boxes, and readings are made through small holes in the boxes.

All five electron tubes are Western Electric 203B tubes operated at 45 volts on the plate and about 3 volts on the filament. The four inductance coils of the two generators consist of about 20 turns of 10 cm radius. For coupling between the stages of the amplifier, ordinary telephone transformers are used. The plate batteries of the generators are shunted with telephone condensers in order to reduce the resistance of the circuits for high frequency currents. All connecting wires are made of solid brass or copper rod.

(b) *The compensation device.* The system of condensers used in the variable generator consists of the three condensers K, K', and C shown in Fig. 1. K' is a fixed condenser of about $10000\mu\mu$f and K is a variable precision condenser of about $1500\mu\mu$f maximum capacity. The precision condenser has a slow adjustment screw which permits readings of capacity to be taken to within $(1/20)\mu\mu$f. The capacity $(K+K')$ is connected in series with the gas condenser C. Compensations for changes in C by the variation of K can be measured accurately since it will be seen that they can be made as large as desired according to the value of the shunted capacity K'. It would, of course, be quite impossible to measure the small capacity changes due to the influx of the gas into the condenser by means of an ordinary condenser in parallel with C. The series arrangement of the condensers magnifies the effect to be measured. Since by the use of zero beats as a criterion of adjustment the total capacity of this combination is always kept constant it follows that for a compensation ΔK corresponding to a change ΔC produced by the influx of gas

$$\frac{1}{K+K'}+\frac{1}{C}=\frac{1}{K+K'+\Delta K}+\frac{1}{C+\Delta C}\ ,$$

or

$$\Delta C=-\left\{\frac{C^2}{(K+K'+C)\Delta K+(K+K')^2}\right\}\Delta K\ .$$

However, for the purpose of simplifying the calculations, a much more convenient form can be obtained for ΔC by the use of an approximate equation, which gives the same result as the latter equation to an accuracy within the limits of experimental error. For very small changes one could use the differential equation $dK/dC=d(K+K')/dC=-(K+K'/C)^2$, which, however, is not a sufficiently close approximation for the requirements of this problem. The next order of approximation consists in assuming that the differential coefficient dK/dC is a linear function of K. Then an average value of dK/dC can be used and for finite values of ΔC and ΔK

$$\Delta C=-\left\{\frac{C}{K+\frac{1}{2}\Delta K+K'}\right\}^2\Delta K\ .$$

For cases where measurements were to extend over a long period of time a special arrangement was used to eliminate errors due to gradual changes in the tube circuits external to the condenser system. This consists in having a standard condenser so arranged that it can be interchanged for the condenser system shown in Fig. 1. The interchange is made by a switch of special construction consisting of three equidistant mercury cups. Into one of these is inserted a vertical wire free to turn about the vertical axis and having attached a hozirontal wire which makes contact in turn with the mercury meniscus of either of the other two cups In order to compensate for possible changes in the circuits with time the distributed capacity of one of the generator circuits is varied by means of a threaded brass rod with a small brass disk attached to it on the inside of the shield. Small changes in frequency can be obtained by turning this rod and thus varying the distance of the small disk from the generator circuit.

(c) *The gas condenser.* The condenser C is a cylindrical condenser of about 4 cm diameter, 13 cm length and 0.5 mm separation between cylinders. Fig. 2 shows the main features. The two cylinders are held together and insulated by two quartz disks Q, which give a minimum of insulating dielectric to be corrected for in the calibration of the apparatus.

In order to prevent chemical action the cylinders themselves were made of an alloy of gold with small quantities of palladium and platinum. A gold plated brass condenser was first tried, but the distillation of zinc contaminated the gold plate at the higher temperatures. Around the outside cylinder is wound a platinum resistance thermometer *P*, insulated by a sheet of mica *M* wrapped around the condenser. The condenser is mounted in a Pyrex tube and held in position by tungsten wires fastened at the top and bottom of the gold cylinder. (These are not shown.) The two gold leads *L* and the two platinum leads *P* are first welded to tungsten wires *T* and then the seals in the glass tube are made at the top with the tungsten wires. A capillary tube is led from the tube to the vacuum and gas system. The Pyrex tube is then mounted in a small shielding cylinder of brass (plated with nickel to prevent corrosion by liquid air). This shielded condenser is then mounted in a large shielded box to permit the application of cooling baths and of the electric furnace without introducing capacity effects with the rest of the apparatus.

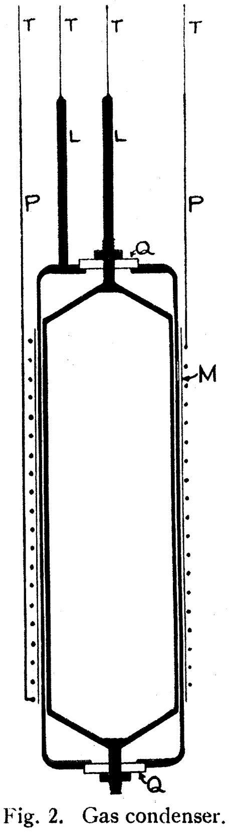


Fig. 2. Gas condenser.

The resistance thermometer consists of about 15 ohms of platinum wire wound around the condenser as loosely as is compatible with its staying in position. By means of a Wheatstone bridge the resistance can be measured to an accuracy of 0.001 ohm which corresponds to 0.02°C. The thermometer was calibrated under the experimental conditions to be used by means of three fixed points; the freezing and boiling points of water and the equilibrium point of a mixture of carbon dioxide snow and ether. In consideration of possible errors due to the calibration it is believed that this thermometer records temperatures accurate to at least 0.1 degree.

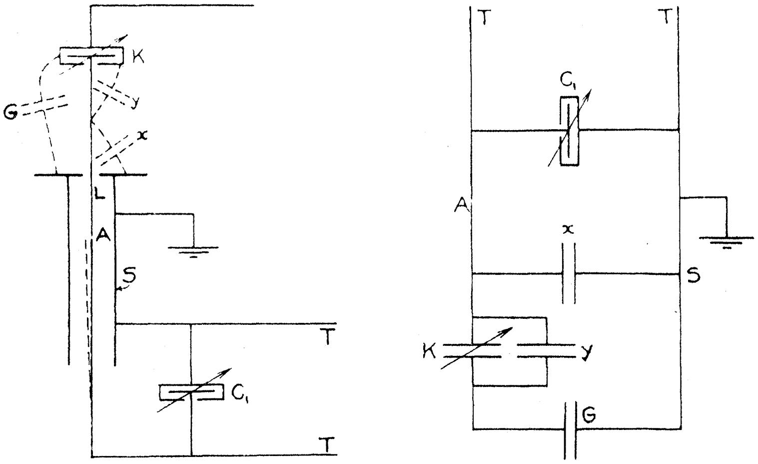
(d) *The calibration of the condenser system.* It will be noted that this is a null method and it depends in no way upon either the electron tube constants or the distributed capacity of the coils, etc., provided these do not change erratically. Actually, the limit of accuracy of the method depends upon the calibration of the condenser system. To make this as accurate as possible, the condenser system was so constructed that the whole calibration could be made in terms of one single condenser, the precision condenser K. The latter was calibrated by the Bureau of Standards in terms of the standard air condensers of the Radio Section. The capacity K' consists of three fixed mica condensers arranged so that they can be inserted in parallel with K by means of mercury cup contacts. These capacities K' were such values that they could be calibrated in terms of K by the method of substitution. This has the advantage of preventing errors which might result from the dependence of the capacity of the fixed mica condensers upon the frequency. Here they are calibrated at precisely the frequency at which they are to be used. The capacity C is determined by shortcircuiting K and K' by amalgamated contacts and tuning the fixed generator to zero beats. Then C is shortcircuited and K is substituted and tuned thus giving a measure of C. With this arrangement an error of the unit in the calibration of K would produce no error in e so long as relative values of K are correct. To check the calibration of K a small fixed mica condenser was constructed and differences on K were checked with satisfactory agreement, so that settings on K are good to at least $\frac{1}{2}\mu\mu$f.

In the calibration of the condenser system the greatest possibility of error resides in the determination of the portion of the capacity C which is not altered by the influx of the gas. This is in part due to the quartz disks and in part to the capacity with ground of the lead passing from C to $(K+K')$. The inductance of this lead, even if appreciable, behaves just as though it were outside the system and in series with it and does not come into consideration. This lead will possibly have a small specific inductive capacity relative to the shield KK' and also with the grounded shield of C and other grounded apparatus such as the large shielding box enclosing the whole generator circuit. The former capacity is negligible as determined by both experiment and approximate calculation. The latter capacity is not negligible; it consists chiefly of the capacity of two wires about 15 cm long and 2 cm apart. These capacities were determined by a rather laborious process to be described below, by constructing a set of leads to imitate the actual leads to be used on the condenser tube and making measurements on these placed in position within the shields mentioned above. The lead capacity was thus found to be $5.5\mu\mu$f. To obtain the alterable capacity this must be subtracted from the total capacity $C = 204.5\mu\mu$f, and in addition there must be subtracted the capacity due to the portion of the dielectric space occupied by the quartz disks. A calculation for this latter capacity gives $0.5\mu\mu$f. Hence the final value for the alterable capacity, which may be called $C_0 = 204.5 - 5.5 - .5 = 198.5\mu\mu$f. The total correction for the lead and the quartz disk is less than three per cent of the total capacity C. A fair estimate of the greatest possible error in this determination would be about $1\mu\mu$f or 1/2 per cent.

The final equation for the dielectric constant is then:

$$\epsilon-1=\frac{\Delta C}{C_0}=\frac{C^2}{C_0}\frac{\Delta K}{\{K+\frac{1}{2}\Delta K+K'\}^2}=210.6\frac{\Delta K}{\{K+\frac{1}{2}\Delta K+K'\}^2}$$

The method of determining the lead capacity will now be considered in detail. The condensers K' were disconnected and condenser C was not yet mounted in its position in the shield S in Fig. 3a. L represents the immitation lead, at the end of which is connected by an amalgamated contact A another wire which passes out through the opening made by taking off the bottom of the shield S. The contact A is made or broken by a sidewise displacement of the lower wire. G is the ground capacity of the shield of K; and x and y, the lead capacities mentioned. C_1 is another precision condenser calibrated in terms of K; and T, the terminals of the coil of a high frequency generator which produces beats with the fixed generator. In Fig. 3b this condenser group is redrawn symbolically for the sake of clarity. Now if the circuit is broken at A and a compensation Δ_1C is made in C with the capacity K set at a particular value



(a) (b)

Fig. 3. Connections used in determining lead capacity.

$$\Delta_1C=x+G(y+K)/(G+y+K)$$

where x, y, and G are unknown and Δ_1C and K are obtained from condenser readings. By taking values of Δ_1C for three settings of K there are obtained sufficient equations to solve for the three unknowns. A simpler and more accurate method is to use one equation of the latter type and two other equations corresponding to the compensations $\Delta_2 C$ and $\Delta_3 C$ when G and $(K+y)$ are shortcircuited respectively. Then the following three much simpler equations are obtained

$$\Delta_1 C = x + G(K+y)/(G+K+y)$$
$$\Delta_2 C = x + K + y$$
$$\Delta_3 C = x + G.$$

The values of K, x, and y were obtained in this way and the method was checked by using different settings of K. It was in that way that y was found to be negligible.

(e) *The vacuum and gas system.* By the use of a diffusion pump the gas condenser could be evacuated within three minutes to a pressure as low as 10^{-3}mm Hg, which is far beyond the requirements of these experiments. The use of such a good pump is however important in ridding the system of water vapor, which is particularly necessary in the study of acids because of catalytic action. Before making a series of measurements the tube was first baked for several hours at a temperature of 300°C and evacuated to a pressure of 10^{-4} mm Hg or better. By taking this precaution and using P_2O_5 and a liquid air trap no difficulties were encountered such as prevented Bädeker from making a satisfactory study of HCl gas. Special arrangements were made for the generation and purification of each gas. These will be described in connection with the data on the individual gases.

MEASUREMENTS ON AIR, NITROGEN, HYDROGEN, AND OXYGEN

In order to test the behavior of the circuits, and to obtain data for comparison with those of other observers, measurements were made at room temperature on air, nitrogen, hydrogen, and oxygen. The air was passed through a P_2O_5 tube to absorb water vapor and through a liquid air trap to freeze out the CO_2. The nitrogen was prepared by heating sodium nitrite and ammonium chloride solutions together and freed from oxygen by storing it in a reservoir containing yellow phosphorous. It was then passed through a P_2O_5 tube with a liquid air trap. The same process of purification was used for hydrogen, which was prepared electrolytically. The oxygen also was prepared electrolytically and then passed through a P_2O_5 tube for drying.

A considerable number of readings was taken for these gases as shown in Table I. For all these individual readings the deviation from the mean is not greater than 1/2 per cent of the value of $(\epsilon-1)$ and the probable error of the observations is of the order of 1/10 per cent. The average value of the series capacity $(K+K')$ is $10000\mu\mu$f which gives a magnification of 2500 in ΔC. The measured capacity ΔK is about $200\mu\mu$f. All of the measurements were taken at room temperature and approximately room pressure. Then the values were reduced to 0°C and 760 mm Hg by the use of the perfect gas law $pv = RT$. This latter procedure is justified by the fact that these gases are known to show no anomalous behavior of the dielectric constant.

TABLE I

Results for air, N_2, H_2 and O_2

Gas	No. of readings	$(\epsilon-1)$ reduced
Air	39	.000572
N_2	41	.000581
H_2	19	.000265
O_2	9	.000518

It is intended to give in the future a discussion of these data as related to the values of other investigators and to data on the refractive index in view of the Maxwellian relation. Suffice it to say here that these values agree with those of other investigators as well as the latter agree among themselves.[10] It is, however, believed that, in consideration of the improved method previously described, these values are reliable to within one per cent.

MEASUREMENTS ON HCl, HBr, AND HI

After the preliminary measurements had been completed a series of observations were made on the gases HCl, HBr, and HI. The first method of procedure tried with HCl was unsatisfactory. The gas was let in after cooling the apparatus almost to the liquefaction point of HCl. Then readings were taken on the condenser K as the apparatus approached room temperature. This required several hours and it was found after-

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[10] In anticipation of later comment, it seems desirable to call attention to a recent paper by Fritts (Phys. Rev. **23**, 345, 1924) which gives data on the dielectric constants of oxygen, nitrogen and air differing by several per cent from those of the present paper, although claiming about the same accuracy. Fritts used a very ingenious method of recording the beats, so that his actual observations are certainly very accurate. His precautions regarding purity of gas and calibration of apparatus do not seem to be equally trustworthy, as judged by experience during the present investigation. We found the step-by-step calibration, in addition to the Bureau of Standards calibration, necessary in order to realize the possibilities of the method. We also found the method so sensitive as to detect impurities left in the gases after ordinary chemical methods of purification, so that unusual methods were employed to advantage. The correction for lead capacity is also important and difficult to be sure of. Since the present apparatus was designed primarily to permit convenient temperature adjustments, a new apparatus is being used to investigate further the sources of error in *absolute* values. For this reason further discussion of absolute values is deferred until a later communication.

ward that the gas had become contaminated, either as a result of chemical action or by gases occluded in the condenser tube. It was therefore found necessary to use another method of procedure, wherein after each gas reading a vacuum reading was taken and impurities in the gas were removed by a method described below. Formerly another source of error was found in the fact that whenever the temperature of the condenser was changing rapidly, the temperature of the inner cylinder would lag behind that of the outer, particularly when the condenser was evacuated, because of the extremely good heat insulation provided by the quartz disks; for this reason it was found necessary to take observations after steady temperatures had been reached or under conditions of slowly varying temperature. Further by the first method it was necessary to make an experimental run with the condenser evacuated in order to determine the change in K due to the thermal expansion of the gas condenser. By the second method of procedure the importance of this temperature effect is eliminated since now the effect appears only as a change in C and C_0, whereas before it appeared also as a correction in ΔK, a quantity of the same order of magnitude as the correction. In C there is produced thereby a change of the order of 1/10 per cent, which is neglected in the computations.

The preparation and purification of the three gases was achieved in the following manner. HCl was generated by dropping concentrated H_2SO_4 slowly onto concentrated HCl. The gas thus generated was passed consecutively through concentrated H_2SO_4, a P_2O_5 tube, and a liquid air trap where it was frozen. Then the liquid air trap was evacuated over the frozen HCl to remove any non-condensible gases such as air and hydrogen. Before letting the gas into the condenser tube a portion of it was boiled off and removed in order to eliminate possible impurities of lower boiling than that of HCl. Then the HCl was allowed to boil and to pass into the condenser until atmospheric pressure was reached, the stopcock to the generator was opened, and the surplus gas was allowed to bubble away through a trap of concentrated H_2SO_4. Other possible impurities would boil off last and have little chance of diffusing through the capillary tube running to the condenser. In this way the same gas could be used again and again. It may be noted that on renewing the gas no change in ϵ occurred.

For the generation of HBr bromine was dropped slowly into a moist mixture of sand and red phosphorous, and the gas evolved was passed through a tube of red phosphorous to remove free bromine vapor and to the P_2O_5 tube and the liquid air trap where it was distilled as was the HCl. The surplus gas was bubbled through concentrated HBr.

HI was generated similarly by dropping a thin mixture of water and red phosphorous onto moist iodine. It was bubbled through concentrated HI to remove free iodine vapor and then dried and frozen as was done for the other two gases.

Table II shows the experimental and calculated data for these three gases. Each value $(\epsilon-1)$ represents the mean of from 5 to 10 or more readings taken at the given temperature. In the third column is given the value $T/273$, which is the specific volume relative to 0°C and 760mm Hg and calculated according to the perfect gas law. The fourth column gives the correction to be applied to this value of v as obtained from the constants of the van der Waals equation; and the fifth column, the corrected value of v. In the sixth column is given the value of $(\epsilon-1)$ reduced by a slight correction for pressure made on the simple gas law. The next column shows $(\epsilon-1)v$, which is the value of $(\epsilon-1)$ reduced to constant density by use of the Clausius-Mossotti relation $(\epsilon-1)v=\text{const.}$ for a given temperature. These values of $(\epsilon-1)$ for constant pressure and for constant density are shown in Fig. 4 to give an idea of the order of magnitude of the variations occurring throughout the range of temperature studied.

TABLE II

Gas	$T°\,K$	$\frac{T}{273}$	Correction to v	v	$(\epsilon-1)_{760}$	$(\epsilon-1)v$	$(\epsilon-1)vT$
HCl	201.4	.7375	−.60%	.733	.007452	.005462	1.110
	260.1	.953	−.07	.9527	.004716	.004494	1.169
	294.2	1.078	+.08	1.079	.003792	.004092	1.205
	359.2	1.316	+.22	1.319	.002672	.003524	1.266
	433.9	1.590	+.23	1.594	.001948	.003104	1.347
	503.9	1.847	+.23	1.851	.001526	.002823	1.423
	588.8	2.157	+.27	2.162	.001182	.002555	1.505
HBr	217.5	.7968	+.45	.7925	.004545	.003602	.7835
	269.0	.985	−.01	.985	.003209	.003160	.8501
	294.4	1.079	+.08	1.080	.002796	.003020	.8840
	338.9	1.241	+.36	1.245	.002228	.002773	.9400
	478.5	1.753	+.54	1.762	.001303	.002295	1.098
	599.1	2.194	+.59	2.208	.000943	.002081	1.248
HI	244.5	.8955	*		.002687	.002402†	.5885
	295.1	1.081			.002123	.002296	.6776
	345.9	1.267			.001760	.002231	.7713
	474.6	1.738			.001239	.002153	1.022
	612.2	2.243			.0009706	.002177	1.334

* No values of the van der Waals constants are available for this correction.
† The uncorrected value of v is used here.

The values in the last column of Table II serve as a test of the Debye equation as follows. This equation can be written as

$$(\epsilon-1)vT=AT+B$$

which shows that if the values of the last column be plotted against the absolute temperature there should be obtained a straight line with intercept B determined by μ, the electric moment, and with slope A depending upon the contribution of the elastic electrons to the polarization.

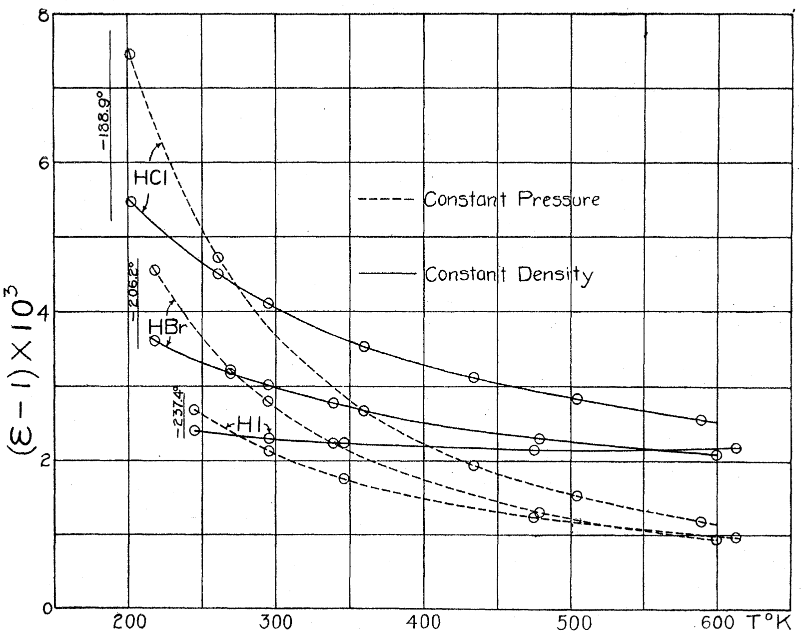

Fig. 4

These points are plotted in Fig. 5. For HCl and HBr straight lines could be drawn so that none of the points deviate by more than 1/2 per cent of $(\epsilon-1)$, even at temperatures near the liquefaction point. This agreement cannot be shown adequately by the necessarily small scale drawing of Fig. 5. For HI two sources of difficulty arise. At high temperatures this gas dissociates to a marked degree. In Gmelin and Kraut[11] the equilibrium degree of dissociation of HI is given as about 3 per cent at 0°C and 18 per cent at 300°C. In the experiments described this degree of dissociation was probably not reached at the moderately high temperatures on account of the slowness of the reaction velocity at such temperatures. (Any dissociated gas was removed after each reading by the purifying process so that no accumulation of dissociated gases could take place.) Since the number of molecules does not change in the dissociation, except possibly by a slight amount due to condensa-

[11] Gmelin und Kraut, Handbuch der anorganischen Chemie **1**, (2), p. 321.

tion of the iodine on the walls of the tube, this consideration becomes less important. Also from data on the refraction indices of HI, H_2, and I it is seen that the refractivity of HI is about ten per cent greater than would be expected on the principle of additivity of refractivities. Hence in dissociation the effect of the destruction of the moment would in part be compensated for by the increase in the contribution from the elastic electrons. However, the experimental values of $(\epsilon-1)$ give a much better straight line than might have been hoped for. With the above considerations in view a straight line was drawn through the lower three points, where very probably the above mentioned errors are only very small; the fourth point is fairly good but the last point is considerably off the straight line. Another difficulty in the case of HI is that no data are available on the constants of the van der Waals equation. The uncorrected values of v were used here. This introduces a possible error of about 1/2 per cent.

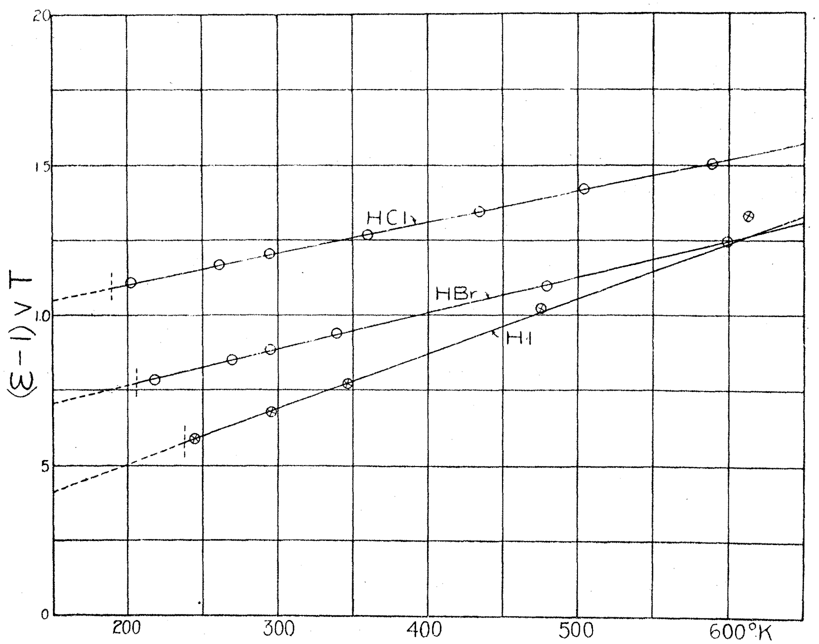

Fig. 5

Table III gives the results obtained from the lines of Fig. 5. The second column under $(\epsilon-1)_0$ gives the contribution of the elastic electrons to $(\epsilon-1)$; and the third column, values of (n^2-1) for the Na D line, since (n^2-1) for long wave-lengths is not known. These two columns should be identical if the values of the refractive index were given for long wavelength instead of for the Na D line. The last column gives the values of the electric moment as calculated from the intercept of the lines of Fig. 5.

$$B=(4\pi/3)(N_0\mu^2/3R), \quad (\text{using } \epsilon+2=3)$$

or

$$\mu^2=(3\times 1.36\times 10^{-16}/4\pi\times 2.71\times 10^{19})B=1.198\times 10^{-36}\,B$$

TABLE III

Results for HCl, HBr and HI₂

Gas	$(\epsilon-1)_0$	(n^2-1)	$\mu\times 10^{18}$
HCl	.001040	.000888	1.034
HBr	.001212	.001140	.788
HI	.001856	.001812	.382

DISCUSSION OF DATA

Of the three dipole gases here studied only HCl has been worked upon before so far as is known by the author. Bädeker[6] attempted to study HCl over a considerable range of temperature but was prevented by chemical action which he attributed to moisture. However, his values of $(\epsilon-1)$ for 84.4° and 106.6°C, .000269 and .000256 show very good agreement with the corresponding values from Fig. 4, .000270 and .000247, better than might be expected considering the fact that Bädeker did not put much confidence in his values. These values for HCl do not extend over a sufficiently large temperature range to allow the calculation of the electric moment with any degree of certainty.

It should be mentioned here that recently Falkenhagen[12] has published a value of the electric moment of HCl, $\mu=2.15\times 10^{-18}$ c.g.s.u., obtained from dielectric constant measurements. This is about twice the value given in Table III. Since no values of ϵ are given and only a brief description of the method, it is impossible to arrive at an explanation of the discrepancy. A calculation has been made of the contribution of the doublets alone to $(\epsilon-1)$ using the value given by Falkenhagen for the moment. This gives $B=\mu^2\times 10^{36}/1.198=3.86$; hence $B/T=3.86/373=.0104$ for 100°C. Thus it is seen that Falkenhagen's value of the moment leads to a value of electric polarization about four times the total value observed by the author and also by Bädeker. Hence the value given by Falkenhagen would seem to be impossibly large.

Frivold and Hassel[13] have made a determination of the dipole length of the HCl molecule by means of electrostriction. They give for the value of the dipole length 0.31×10^{-8} cm. This corresponds to a value of

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[12] H. Falkenhagen, Phys. Zeit. **23,** 87 (1922).

[13] O. E. Frivold und Odd Hassel, Phys. Zeit. **24,** 82 (1923)

$\mu = 1.48 \times 10^{-18}$ c.g.s.u., which is considerably less than the value of Falkenhagen. These electrostriction measurements are of very limited accuracy.

In support of the value obtained by this investigation Smyth[14] has calculated the electric moment of HCl by a simplified use [15] of an equation developed by Gans.[16] This equation applies to both the gaseous and the liquid states and is developed on the dipole assumption taking into account the intermolecular forces. By Smyth's method the electric moment can be calculated approximately from a knowledge of the indices of refraction at two different wave-lengths, the corresponding density, the dielectric constant at one temperature, the density at this temperature, the molecular diameter, and certain universal constants. For the value of the dielectric constant he used Bädeker's two values for the gaseous state and Schlundt's value for the liquid state at 27.7° C and obtained for $\mu \times 10^{18}$ at these three values, 1.096, 1.054, and 1.075 c.g.s.u. respectively. The mean of these three values, 1.075, agrees with the value of Table III, 1.034, better than could be hoped for taking into consideration possible errors in the calculations and in the experimental values involved.

A further argument in favor of the value 1.034 is the fact that $(\epsilon - 1)_0$ in Table III agrees fairly closely with the refractive index data.

Relation to Infra-Red Spectra

Values of the electric moment of the halogen hydrides are of particular interest for two reasons; first their structure is perhaps the simplest dipole structure because of the simple hydrogen atoms, and second their nuclear separation (except for HI) has been determined from infra-red absorption data.[17] Now it will be noted that once the nuclear separation is known a knowledge of the average position of the electronic configuration obtained from the value of the electric moment would be of considerable importance in the study of the structure of the halogen hydrides. Suppose that in the formation of the HCl molecule, for example, the electron from the hydrogen atom combines with the seven outer electrons of the chlorine atom to form a group similar to the outer group of the argon atom. If this argon group be assumed to be symmetrical and not appreciably distorted by the presence of the hydrogen nucleus, then the

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[14] This work is not yet published.

[15] C. P. Smyth, Phil. Mag. **45**, 850 (1923).

[16] R. Gans, Ann. der Phys. (4) **44**, 481 (1921);
H. Isnardi and R. Gans, Phys. Zeit. **22**, 230 (1921).

[17] See A. Kratzer, Zeit. f. Phys., **3**, 305 (1920);
Herbert Bell, Phil. Mag. p. 549, March 1924

chlorine atom plus its acquired electron would be equivalent to a single negative charge at the chlorine nucleus. This latter charge combined with the hydrogen nucleus gives an effective moment of HCl such that its dipole-length is equal to its nuclear separation. But one would expect the hydrogen nucleus to distort the electronic orbits in such a way as to decrease the dipole-length. Hence it seems reasonable to regard the nuclear separation as an upper limit to the dipole-length as pointed out by Pauli. C. P. Smyth[18] has made a calculation for the effect on the electric moment of the HCl molecule due to the distortion by the hydrogen nucleus. For this purpose a statical structure of the Langmuir type was assumed and the distortion of the individual electrons was calculated from the coefficient of elastic binding given by the refractive index of the substance. These calculations give the proper order of magnitude for this distortion. From the point of view of the Bohr theory one would not expect a calculation based upon the above assumptions to give a better agreement.

Such a consideration is of interest in connection with the quantum theory of dielectric polarization developed recently by Pauli.[19] Whereas Debye and Thomson used in the development of their formulas classical mechanics, Pauli has derived for the case of dipole gases a formula based on Sommerfeld's quantum conditions. The latter theory leads to an equation of the same form as that of Debye, differing only in the numerical factor which appears in the doublet term after integration.

$$\frac{\epsilon-1}{\epsilon+2}=(4\pi/3)\ N\left\{\lambda e^2+1.5367\ \mu^2/RT\right\}\ .$$

Thus so far as moments are concerned the two theories would give different values for the electric moment calculated from data on the dielectric constant, such that:

$$\mu\ (\text{classical})=2.15\ \mu\ (\text{quantum}).$$

The measurement of the dielectric constant of dipole gases at different temperatures offered a possibility of distinguishing between the two theories, should the classical theory lead to a value of the dipole-length greater than the nuclear separation.

In Table IV are given the results of some calculations relating to the above mentioned quantities. d is the dipole-length calculated on the classical theory, and r_0 is the nuclear separation obtained from the infra-red data. D is the distance of the center of gravity of the electronic configura-

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[18] C. P. Smyth, Phil. Mag., **47**, March 1924

[19] W. Pauli, Jr., Zeits. f. Phys. **4**, 319 (1921)

tion from the halogen nucleus; this may be regarded as a measure of the distortion caused by the hydrogen nucleus. A simple calculation gives $D=(r_0-d)/(N+1)$, where N is the atomic number of the halogen atom. Since the value of the dipole-length is about one-sixth the value of the nuclear separation it is impossible to choose between the quantum theory and the classical theory.

TABLE IV

Comparison of calculated dipole length d with nuclear separation r_0 from infra-red data.

Gas	$\mu\times10^{18}$	$d=\frac{\mu}{e}$	$r_0\times10^8$	$D=\frac{r_0-d}{N+1}$
HCl	1.034	.217	1.27	.0618
HBr	.788	.165	1.37	.0343
HI	.382	.080	....	.....

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PRINCETON UNIVERSITY,
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