THE DIELECTRIC CONSTANTS OF AMMONIA, PHOSPHINE AND ARSINE[1]

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The dielectric constant of ammonia at various temperatures between 19° and 175° has been measured by Jona (*Physikal. Z.*, 1919, **20**, 14). Bädeker (*Z. physikal. Chem.*, 1901, **36**, 305) has also determined its value from 18° to 108°, and K. Wolf (*Physikal. Z.*, 1926, **27**, 588) has recently measured the rate of change of dielectric constant with pressure.

Jona showed that the change in dielectric constant with temperature could be represented by Debye's equation $\epsilon - 1 = N (A + B/T)$, and Zahn (*Physical Rev.*, 1924, **24**, 400) has shown that this relation also holds for the series of gases HCl, HBr, HI. It was considered of interest, therefore, to make similar measurements for the gases PH_3 and AsH_3, and to repeat the determinations for NH_3, in order to provide data for another series of gases in the periodic table. It has not been possible so far to examine SbH_3, as the rapid decomposition of this gas with the formation of a mirror would readily break down the insulation of a condenser of the ordinary type.

A brief perusal of the literature of dielectric constants is sufficient to show that, in spite of the extreme sensitiveness of methods depending upon the use of the thermionic valve, the results do not agree as closely as might be expected. In the present research special attention has been devoted to exploring sources of constant error and to obtaining absolute values for the dielectric constants.

EXPERIMENTAL.

Determinations of the dielectric constants were made at high frequency, the change in capacity with pressure of a condenser containing gas being compensated by a variable condenser in series so as to maintain the frequency of the system constant. An exact setting was obtained by the method of beats with a second oscillating system.

The general arrangement of the apparatus is shown in fig. 1, the actual position of the component parts being a matter of some importance. The main oscillating circuit consisted of a valve V, a low loss

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inductance C, reaction coil R, a variable condenser K, the gas condenser G, and a switch S. The whole system rested upon an earthed zinc sheet, from which it was very carefully insulated where

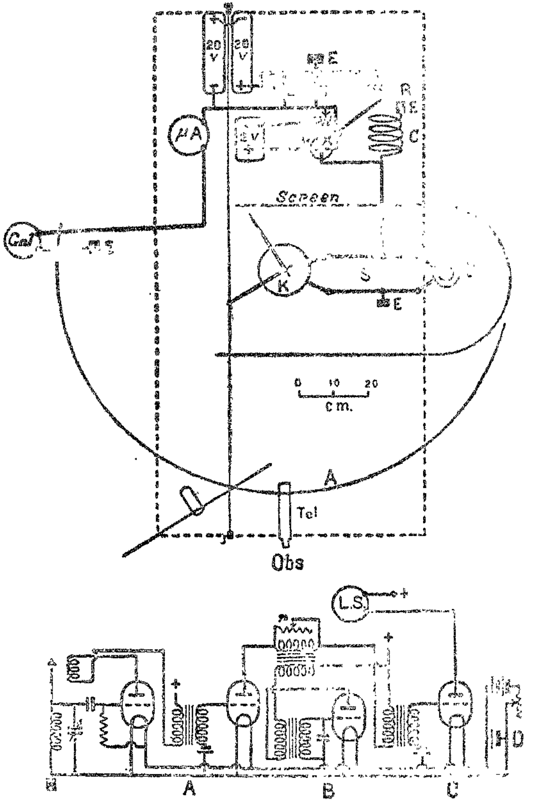

FIG. 1.

necessary, the batteries being supported on blocks of paraffin wax. The valve V was a cosmos S.P. 18 red spot, very much under-run (1·18 v. on the filament, as compared with the normal 1·8), and with only 40 volts on the plate. A microammeter (for rough settings) and a galvanometer were placed in series between the negative side of the filament and earth and measured the small grid current which was allowed to flow. In this way it was possible to adjust the voltage across the condensers and also to make calibration measurements, which did not require the extreme accuracy of setting given by the beat method, in the manner described by P. A. Cooper. (*J. Sci. Instrum.*, 1925, **2**, 342.) This author utilises the very sharp dip in grid current when the circuit is brought into resonance with an absorption wave meter. The frequency may be measured by this means, and small energy losses, such as those due to poor insulation, are readily detected. Owing to the special characteristic of the valve used, no grid bias battery was necessary, one possible source of error being thus eliminated. The method had, by numerous previous trials, been found very convenient and accurate provided the condensers were screened from the inductances.

All measurements were made when the grid current was 10μ A, corresponding with 2·85 volts r.m.s. as measured by means of a Moullin voltmeter. In the case of the series connection, the voltage across the gas condenser was about 8 per cent. lower than this. The valve characteristic under operating conditions was very straight, except just at the ends, and the harmonics could not be detected in the receiver used for the beat measurements. In any case, the presence of harmonics of small amplitude can have little effect upon the results, as the dielectric constants measured were found not to change through the range of frequency studied.

Three coils, which were readily interchangeable, were used in position C; they were wound over frames of pyrex tube and had inductances of 55, 160 and 1875 microhenries. The switch S consisted of six copper mercury cups mounted on quartz rods 15 cm. high. The condenser system was surrounded by a screen 20 cm. high, not closer than 15 cm. to any of the wiring except where a rigid lead to the grid passed through a hole in it. It was open at the top and underneath the gas condenser G, which was suspended from a wooden arm.

The condenser K, upon which all the measurements were made, was of the usual semicircular rotary vane type, with five fixed plates of radius 45 mm. and four moving plates, the gap being just under 1 mm., and the total capacity 250 $\mu\mu$F. The fixed plates were soldered to brass strips and supported by three quartz rods platinised at the ends and soldered into sockets. Before assembly, these rods were heated to redness for some time and then dropped into paraffin wax. The spindle carrying the moving plates had carefully ground long conical bearings and carried two light wooden arms and two mirrors at right angles at its upper end. The vanes could be rotated through about 100° by two threads, one passing over a free pulley and supporting a weight, the other similarly arranged, but passing round a friction pulley controlled by the operator. By changing the threads to the other arm the condenser could be rotated through 180°. The position of the plates could be read by means of the telescope T and a semicircular scale A two metres in length. The whole condenser was silvered and covered with a brass cover, through a mica window in which the lead to the fixed plates passed.

The gas condenser G was somewhat similar to the one described by Zahn (*loc. cit.*) and is shown in fig. 2. *a*. The inner cylinder had tightly fitting ends and contained a durosil glass bulb to reduce the volume of gas. The outer cylinder had a cap over the end as a shield. Two quartz discs held the inner cylinder in position. These were platinised at three points at the edges and secured to the outer cylinder with small fragments of solder. The inner cylinder was soldered to the top plate, but was kept in position at the bottom with a nut and spring washer to avoid strains. The metal used was brass, well gilt before assembly. The clearance between the cylinders was 0·5 mm. and the capacity 133$\mu\mu$F. Gilt platinum leads were used, and the whole was sealed into a durosil tube.

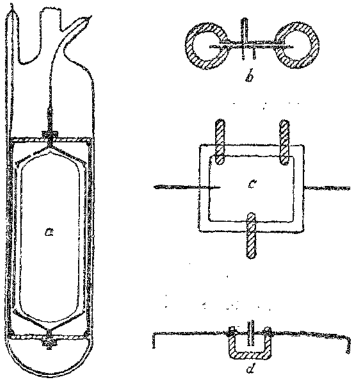

FIG. 2.

The circuit for the production of beats is also shown in fig. 1. This portion of the apparatus was situated about 2·5 metres from the oscillating circuit, and an aerial 1 metre long was used for the two lower frequencies. The portion A consists of an oscillating detector and note amplifier, B is an audio-oscillator which modulates the output at a frequency of about 600, the intensity being controlled by the variable shunt *r*. C is another note magnifier connected with a loud speaker. S.P. 18 red and green spot valves were used in this receiver, and the total plate current was only 2 milliamperes. The double system of low-tension batteries employed by several other observers was used, and by regulating the discharge from the battery D, the effects of changing filament and anode voltage in the whole system could be largely compensated. A screen was originally placed between the observer and the receiver, but it was found to be unnecessary, as the taking of readings through a telescope involved the observer's remaining in the same position. Small movements had no effect.

When making measurements, the beat note between the two high-frequency circuits was adjusted to the exact frequency of the audio note by observation of the beats between the two.

CALIBRATION.

As has been pointed out by Zahn (*loc. cit.*) the accurate determination of dielectric constants is largely a problem in calibration. Great attention has been paid by other observers, notably E. C. Fritts (*Physical Rev.*, 1924, **23**, 345), who used a photographic method for recording beats, to the constancy of the oscillation generators and the exact coincidence of the beats, but it is evident from their results that the main errors are constant ones arising probably from incorrect calibration.

In the present experiments the simple oscillation generators already described were found to be quite satisfactory, although possibly not altogether suitable for gases with a very low dielectric constant or for observations extending over considerable periods, but any errors arising from this source were certainly small when compared with those due to other causes.

The accuracy aimed at for the final results was 1 per cent., and to attain this it was considered desirable to attempt to make all calibrations with an accuracy of 1 part in 1000 and to measure pressures and temperatures to 0·5 mm. and 0·2° respectively.

All the condensers used were specially constructed or selected so as to have a very low power factor. Any defect could at once be detected by the grid current readings. The insulation throughout the oscillating system was very high, and, consequently, energy losses in the condensers were assumed to be zero.

In setting up apparatus in which connections have to be made to condensers, if the leads are short and the condensers close together, stray capacities of uncertain magnitude may be introduced, while if the leads are long, it is necessary to correct for their inductance. In the present experiments the latter alternative has been adopted, as it was possible to determine the corrections with sufficient accuracy, while the location of the gas condenser a little distance (40 cm.) from the variable condenser was convenient for its immersion in the constant temperature baths.

If l, the inductance of the leads to a condenser of capacity C, is small enough to make $l\omega^2C$ a small quantity compared to unity, as it was in the present experiments, the apparent capacity may be written $C\ (1 + l\omega^2C)$. When two condensers C_1 C_2 are in parallel, the inductance of the leads to C_1 being l_1 and between C_1 and C_2, l_2, the correction becomes approximately $l_1\omega^2\ (C_1 + C_2)^2 + l_2\omega^2C_2^2$.

These formulæ were verified experimentally during the calibrations, and, on applying the corrections, the values found for the capacity of every condenser under different conditions were the same to less than 1 part in 1000, except in certain cases which are mentioned later.

The condenser, which was used as a standard of capacity, consisted of a quartz tube platinised and heavily silvered inside and out and fitted with terminals. This, together with its leads, was standardised at the National Physical Laboratory and found to be of constant capacity at frequencies from 300 to 1500 k.c., although increasing in apparent capacity at somewhat higher frequencies. The actual capacity was 156·0 $\mu\mu$F. The absolute value does not, however, affect the results.

By means of this condenser Q, the setting of the variable condenser K at which it had the same capacity as Q was determined, and also several pairs of settings between which the difference in capacity was equal to that of Q. A step-by-step calibration, using the small fixed condenser C shown in fig. 2, *b* and *c*, was then made, and a table of values drawn up giving the capacity at all settings. In making this calibration the frequency varied, but the coil inductance L was constant. The inductance of the leads to C was negligible, and thus, if l is the inductance of the leads to K, the lead correction is $l\omega^2K^2 = Kl/L$ with sufficient accuracy. The actual value of l/L with the three coils used was 0·0065, 0·0022 and 0·0002, and was thus not negligible in the first two cases. The inductance l was determined by measuring the apparent value of the standard Q at different frequencies. It is evident from these figures that considerable errors may arise when the coil inductances are very small unless allowance is made for lead inductance.

The behaviour of the variable condenser K was remarkably satisfactory. The absolute value over certain ranges was checked against Q at frequent intervals, and no change greater than 1 scale division in 2500 was ever observed. The portion which was used for the majority of the readings was uniform within the limit of experimental error, and two careful step-by-step calibrations at the beginning and end of the experiments, using different inductances, gave, when corrected for lead inductance, identical calibration values to 0·1 $\mu\mu$F.

The next stage was to determine the capacity of a condenser of approximately 1500 $\mu\mu$F. capacity for use in parallel with K. It was desirable that this should be as small in dimensions as possible to avoid stray capacities. One or two commercial mica condensers were tried and found to stop oscillations in the circuit owing to their bad power factor. A series of condensers was then constructed by platinising and silvering thin sheets of mica. These had a satisfactory power factor, but were rather fragile. Subsequently Dubilier type 610 mica condensers were found to be almost as good, and these were employed throughout the experiments. A series with nominal capacities 200, 300, 500, 1000, 1500 and 2000 $\mu\mu$F. were used for the calibration in conjunction with K, the useful capacity of which was about 200 $\mu\mu$F. Permanent leads were attached, which fitted into the mercury cups and suspended the condensers clear of surrounding objects. Each condenser was calibrated in three different positions, and this afforded a means of calculating the inductance of the leads and allowing for stray capacities, which, however, were very small. When the smallest inductance was used, corrections for these factors did not yield quite concordant results, owing, no doubt, to the somewhat complex nature of the circuits. For example, in order to determine the value of D_{1000}, as the 1000 $\mu\mu$F. condenser was designated, it was placed in parallel with K and then replaced by D_{500} and D_{300} in different pairs of mercury cups, and the change in K necessary to bring the frequency to its previous value determined. The circuit contained several loops, and the simple lead correction appears to be insufficient for the smaller values of L. If no corrections at all are applied, the difference is quite marked; for example, D_{1500} was found to have the values 1528·5 and 1533·6 when using the medium and small inductances respectively. On the other hand, two distinct calibrations, with an interval of two months between them, using the large and medium inductances, after applying corrections, both gave the figure 1526·0 at 17·6°. It was found that this condenser had an appreciable temperature coefficient (— 0·00033 per 1°), which was allowed for. Owing to the slight uncertainty of the calibration with the small inductance, it was assumed that the true value of the capacity of this condenser at the higher frequencies was the same as the one determined with the other inductances.

As already mentioned, when measurements of dielectric constant were made, the gas condenser was placed in series with the large mica condenser, and this introduced complications in the form of stray capacities. Two systems of connections were used, which are shown diagrammatically in fig. 3, *a* and *b*, the numbers 1–6 denoting the mercury cups in the switch. Each lead may be regarded as having two capacities, one to earth and one to adjacent leads. If C is the self-capacity of the inductance coil and K and G are the capacities of the variable and gas condenser respectively, the stray capacities c, k and g may be represented as being in parallel with them, as indicated in the diagrams. D is the large mica condenser and M a very small condenser, which will be referred to later.

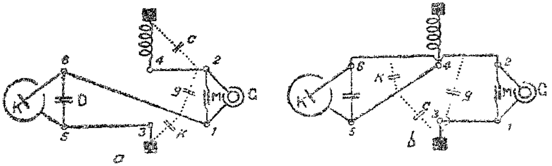

FIG. 3.

If, now, G increases by an amount dG and K is decreased by dK in such a way as to keep the capacity of the whole system constant, it is easy to show that

$$dG = \frac{(G+g+M)^2}{(D+K+k)^2/dK - (D+K+k+G+g+M)} \text{ or } \frac{G'^2}{(D+K')^2/dK - (K'+G'+D)}, \qquad (1)$$

where G', K' indicate the sum of all the apparent capacities in parallel at the points 1, 2 and 5, 6 respectively. The quantities C, c do not enter into the equation, although in case (*b*), where c has a considerable value, the resonant frequency of the whole system is appreciably lower than in case (*a*). The inductance of the leads connecting the points 1–6 or 2–6 does not affect the calculation. It will be observed that the quantities G' and D occur in the equation as squares, so that any calibration errors are doubled in the result.

In order to determine g and k, two small platinised mica condensers, M_{137}, M_1 were constructed as similar in physical dimensions as possible, except that in M_1 two pieces of mica were platinised and separated by spacers, so that the capacity was only 1·45 $\mu\mu$F., that of M_{137} being

137·45 μμF., approximately equal to that of G. M_1 was placed in the position 1–2 and a reading of K taken. M_{137} was substituted for M_1 and the frequency restored to its original value by adjusting K. It might reasonably be assumed that this substitution did not alter the stray capacities, and that the change in capacity was equal to the difference in the capacities of the two condensers. Consequently, two readings for different settings of K were sufficient to determine g and k. Actually several were taken, one with the condenser D_{1500} in parallel with K. This was repeated with G immersed in the various baths used when measuring dielectric constants, the value of G being determined immediately afterwards by placing it in parallel with K. With connections (*a*), g was small and varied very slightly, while k changed appreciably (6·6 to 13·4 μμF.) according to the bath used, but this had no great effect, as it was always in parallel with a capacity of about 1600 μμF. With connections (*b*), k was almost negligible but g, though constant, was of considerable magnitude, the values for G' under the same conditions being 136·6 for (*a*) and 140·6 for (*b*). Other observers do not appear to have allowed for these stray capacities. In the present case the effect is perhaps exaggerated owing to the length of the leads, but with shorter leads more closely screened the error might well amount to several parts per 100.

Measurements similar to the above were made for each inductance, but as they were somewhat tedious and the frequency corrections not altogether certain when using the small coil, an alternative method was adopted. Two small brass condensers (fig. 2, *d*), very similar to each other but with different spacing between the plates, were constructed. Bent quartz rods, to which the leads were soldered, served both as spacers and insulators. The difference in capacity was approximately 0·8 μμF., of the same order as the change in capacity of G when filled with gas. One of these condensers was placed in position 1–2 and the connections arranged as if for a determination of dielectric constant by admitting gas to G. Instead of this, the other condenser was substituted and the change in K necessary for restoration of the original frequency observed. It was found that, with care, the condensers could be removed and replaced without producing any measurable alteration in frequency. The mean of a number of observations with each coil was taken, with the following results, the figures being scale divisions change measured from a fixed point :—

Coil.		Small.	Medium.	Large.
Connections (*a*)	. .	2036	2027	2023
,, (*b*)	. .	1884	1883	1884

The observed changes obtained when measuring the gas can consequently be corrected for frequency, for, making the reasonable assumption that the difference in capacity of the small condensers does not change with frequency, since they have air as dielectric and very high insulation, it is evident that a change in capacity corresponding with 2036 scale divisions when the small coil is used will give rise to a change of 2027 with the medium one.

This method is of no value for checking the values of G' obtained in the way previously described, because with these very small condensers the capacity of the leads is of the same order as that of the condenser itself. Mere reversal of the apparently symmetrical condenser required a change in K of 50 scale divisions for compensation. It was evident, therefore, that to make a measurement of this nature it was essential not to move any metallic conductors. To fulfil this condition, the capacity of the larger condenser was changed by the insertion of a small piece of mica. Removal and replacement of the mica in such a way as to obtain quite consistent readings was a matter of considerable difficulty, but it was eventually accomplished with the help of small paraffin wax guides on the mica. The capacity change on inserting the mica was then calculated, using two corresponding values for G' for connections (*a*) and (*b*) previously determined, viz., 136·6 and 140·6. The results were identical, 0·960 $\mu\mu$F.

There is one further correction. The above figures suffice to show that a small change in the capacity of a condenser directly between the mercury cups 1–2 can be measured with some accuracy, but the gas condenser is not in this position, being connected by leads some 15 cm. in length. The inductance of these leads was measured by constructing two similar dummy leads and determining the apparent change in capacity of a 1,000 $\mu\mu$F. condenser on moving it from the end of these leads to the position 1–2. The value was 0·28 μH.

If G_a is the apparent capacity of G at the points 1–2, by a slight modification of formula (1), $dK = K^2 . \; dG/G_a^2$ very approximately, and, therefore, if the value of G_a were reduced to G, the change dK would become $dK . \; G_a^2/G^2$ for a given value of dG. That is to say, if the gas condenser could be made coincident with the small testing condensers, the changes in K would be increased to the expression just given, which may be written $dK\,(1 + 2l\omega^2 G)$. It may thus be calculated that, if the two condensers were coincident and the change in K corresponding with a given change in G were 2027 scale divisions with the medium inductance, it would not be 2036 for the small one, as found experimentally, but $2036\,(1 + 2lG\,(\omega_1^2 - \omega_2^2))$ or 2049 for the frequencies actually employed. By using this correction, the necessity of a separate calibration for each inductance was avoided.

EFFECTIVE VALUE OF THE GAS CONDENSER.

The gross value of G was frequently determined by inserting the condenser in parallel with K. It changed slowly during the experiments from 2252 scale divisions, measured from a fixed point on K, to 2264. The theoretical temperature co-efficient was zero, and this was found in practice, although heating the condenser rapidly occasionally produced a small permanent change due to a shift in the position of the cylinders.

The capacity due to the leads was found by constructing two dummy leads mounted on a quartz ring. The total capacity introduced by these leads was measured, and then the capacity between them by removing the earthed one. This was repeated with the leads shortened to the length which was not in the gas. In this way it was found that the stray capacity due to the leads (excluding the capacity between the portions of the leads in the gas) was 1·45 $\mu\mu$F. To this had to be added the capacity of the link 2–4, which was 1·25 $\mu\mu$F. The capacity due to the quartz discs was determined by constructing a dummy condenser with a wire of correct size instead of an inner cylinder, and observing the change in capacity when a glass disc of measured dielectric constant and the same size as the quartz discs was slipped over the wire inside the cylinder. The value found for two discs together was 0·20 $\mu\mu$F. Thus, when the measured value of G was 136·2, the effective value or capacity which was altered by admission of gas was only 133·3 $\mu\mu$F.

PREPARATION OF GASES.

Ammonia was prepared from specially purified ammonium chloride solution and potassium hydroxide. Most of the moisture was removed with solid potassium hydroxide and the gas was then liquefied and the middle fraction used for the experiments.

Phosphine and *arsine* were kindly lent by Sir Robert Robertson. The former was prepared from phosphonium iodide and the latter from zinc arsenide. Both were liquefied and carefully fractionated from a considerable quantity of the gas, and were thus in a high state of purity.

The whole apparatus used for manipulating the gases was made of durosil glass, and a drying tube containing calcium oxide was attached to the pump to absorb initial traces of moisture.

TEMPERATURE.

For simplicity, measurements were made at three temperatures only, these being approximately—47°, 16° and 99°. The presence of stray conductors anywhere near the gas condenser was early recognised as undesirable, and this was the main reason why Zahn's method of measuring temperature by means of a platinum wire wrapped round the condenser was not adopted, another reason being the fear that the platinum might accelerate the decomposition of arsine. Steadiness of temperature was of more importance than its absolute value, since a slight difference in temperature between the walls of the condenser produced a relatively large error. Thus, in the case of arsine, a difference in temperature between the walls of 0·1° had the same effect on the dielectric constant as an error of 7° in the absolute temperature.

For the lower temperature a bath of chlorobenzene partially frozen in a vacuum vessel by the addition of solid carbon dioxide was used and proved satisfactory although as the material was not quite pure the temperature was somewhat below the normal freezing point, − 45·5°. The temperature was measured by two copper-eureka thermojunctions standardised at the freezing point of mercury and the boiling point of carbon dioxide. A check was afforded by measuring the vapour pressure of ammonia in the condenser. The thermocouples were removed during an experiment. The temperatures found are probably correct to 0·5°.

For the higher temperature a similar vacuum vessel containing oil was used. A glass spiral through which steam could be passed at a constant rate enclosed the condenser at the sides and bottom. Temperatures were measured with a standardised thermometer and were probably accurate to at least 0·2°. Both baths were stirred occasionally, but not during or for some time preceding an actual measurement. At room temperature either bath was used.

METHOD OF MEASUREMENT.

The oscillators were started and the condenser brought to the required temperature at least an hour before making any measurements. When conditions were steady, as determined by the constancy of the beat note, the setting of K for zero beats was observed, and a small side tube connected with the apparatus was then immersed in liquid air. This reduced the pressure to a negligible amount and the new reading of K for zero beats was taken. The side tube was then warmed and another reading taken with the condenser full. The condenser could be filled or evacuated and a reading taken in 1·5 minutes, thus reducing any effect of creep. A number of such double readings were taken in each experiment.

The rate of reduction of pressure on cooling was a very effective method of checking the purity of the gas, for any impurities not condensible in liquid air accumulated in the side tube and diffusion through them was very slow. For example, when measuring arsine at 99°, the pressure sank only to 19 mm. in 1·5 minutes, and then remained fairly steady, indicating decomposition, but when the residual gas was pumped off and again admitted, most of it was condensed, and, on repeating the process several times, very little hydrogen was obtained. In this way it was found that the percentage decomposition in the time mentioned was of the order of 0·08 instead of the far larger figure suggested by the pressure measurements.

Certain small irregularities were observed in the individual readings, particularly at the highest temperature. The first reading of a series after a long wait was frequently somewhat high, and the apparent rate of change of capacity of the condenser (due to creep) was different according as the condenser was full or empty, pointing to some temperature effect. The phenomenon was most marked in the case of phosphine, but as the variations were of the same order as the experimental error it was difficult to assign a cause to them. Numerous observations with ammonia were made, and the effect appeared to be caused to some extent by admitting cold gas into the condenser, as it became less marked on passing the gas through a U-tube containing quartz granules immersed in the bath. No evidence of a change due to adsorption, as recorded by Bädeker, (*loc. cit.*) was obtained, the slow changes after admitting or removing gas being in the opposite sense to those which would occur owing to the formation or removal of an adsorbed layer. Bädeker's gas was only dried over soda-lime and was probably not as dry as the samples used in the present experiments. In the present case also most of the adsorbed water was removed from the condenser by heating to 150° in a high vacuum before admitting gas.

In addition to readings for the full range of pressure, several series were made by the reduction of the pressure in stages by letting the gas into the pump. Readings were taken immediately before and immediately after reducing the pressure, the time required being 0·5 minute.

At the end of each series of experiments the readings of K were tested by comparison with Q and the value of G was measured. On several occasions G^1 was also determined by inserting the condenser M_{137} in the manner already described. M_1 was retained in position throughout the experiments.

RESULTS.

The following figures give details of one experiment chosen at random and show how the results were calculated. Actually condenser readings were taken every minute but these have not all been included.

Date 21—2—27. *Experiment.* NH_3. 28. Hot.
Medium coil, frequency (a) 1070.

Time	K. Sc. divs.	Diff.	Diff. for $dp = 751$ and $K = 1846$	p. Corr.
2·59	541			752·7
3· 1¼	1811	1270	1271	2·2
3· 9	1841			0·0
3·10½	575	1266	1265	751·7
3·15	575			752·4
3·16½	1847	1272	1270	0·0
3·19½	582	1265	1265	750·8
3·22	580			751·6
3·23½	1843	1263	1262	0·0
4·22	647			750·5
4·24	1916	1269	1264	0·2
4·27½	650	1266	1265	748·3
			Mean 1266 or K_{1846}-K_{580}	

The room temperature rose from 18·6 to 19·3° and the bath temperature was steady at 98·0°.

In taking the differences no correction has been applied for 'creep' as it was small and the errors tend to cancel in taking the mean.

To save trouble in calculation the fourth column has been calculated for a constant pressure difference of 751 mm. and a small correction applied to allow for the fact that a constant capacity change in the gas condenser requires a greater change in K the larger the absolute valve of K. The mean value then refers to the setting of K at 1846 when the gas condenser is evacuated.

$G' = 136{\cdot}6$ $D_{1500} = 1525{\cdot}3$ at 19°, $k = 10{\cdot}5$ $K_{1864} = 120{\cdot}85$, $dK = 76{\cdot}05$
hence by (1) $dG' = 0{\cdot}544$ for 751 mm. $= 0{\cdot}551$ for 760 mm.
Correction to 100° $-0{\cdot}006$, correction for condenser leads $-0{\cdot}001$
Final value $0{\cdot}544$. $G = 133{\cdot}7$ $\therefore$ $\epsilon = 1{\cdot}00407$.

The same mica condenser D_{1500} was used in all the experiments except those with carbon dioxide. For these a larger one with a capacity of 2006 $\mu\mu$ F was employed to increase the range of movement of K which was about 500 scale divisions. With the smaller condenser it would have been only 300.

The final results are shown in Table I. Each value recorded is the mean of at least four concordant determinations. The actual temperature and pressure at which the measurements were made is given in each case, but the final results are calculated for 760 mm. and $-47°$, 16° or 100°. The pressure calculations at constant temperature have been made by means of formula (3) on p. 57 and the temperature corrections have been deduced from the final results. In both cases the corrections are small, as most of the measurements were made at a pressure near to 1 atm., while the temperatures varied very slightly from those given. The only exception is ammonia, which had to be measured at reduced pressure at the lowest temperature to avoid condensation. The letters, *a*, *b* in the first column indicate the connections used.

TABLE I.

Dielectric Constants of Ammonia, Phosphine and Arsine.

Experiment No.	Pressure, mm.	Temperature, °C.	Frequency, *kc.*	$(\epsilon - 1) \times 10^5$.
		Ammonia.		
1	563	15·2	1065	658
2	771	15·0	1070	656
5	670	14·0	1070	656
11*a*	735	97·1	1070	406
12*a*	780	97·5	1070	405
13*b*	779·5	97 6	1020	406
14*b*	779·5	97·8	290	406·5
15*a*	779 5	97·7	303	406
16*a*	777·5	97·2	1820	406
17*b*	776·5	97·2	1745	406·5
18*a*	782	13·9	1070	659
19*b*	776	14·6	1013	658
20*a*	775·5	16·2	1810	662
20*b*	776	16·2	1735	661
21*a*	776	15·7	303	659·5
21*b*	776	15·7	209	656·5
22*a*	775·5	16·2	1070	661
23*a*	341	−46·5	1070	1098
24*b*	341·5	−46·0	1015	1100
26*a*	775	98·0	1070	405
27*b*	775·5	98·0	1015	406
28*a*	751	98·0	1070	407
28*b*	751	98·0	1015	406·5

Experiment No.	Pressure, mm.	Temperature, °C.	Frequency, *kc*.	$(\epsilon - 1) \times 10^5$.
Phosphine.				
1*a*	755	16·0	1070	239·1
1*b*	756	16·0	1015	238·0
2*a*	791	16·3	303	237·6
2*b*	790·5	16·3	290	237·8
3*a*	790·5	16·3	1820	238·0
3*b*	790·5	16·3	1735	238·2
5*a*	769	99·6	1070	169·0
5*b*	768	99·6	1015	168·3
6*a*	789·5	99·4	1070	169·3
7*b*	750	—46·7	1015	337·4
7*a*	745	—47·0	1070	337·2
Arsine.				
1*a*	723	16·0	1070	190·2
1*b*	723	16·0	1015	188·7
2*b*	723	16·0	1735	192·3
2*a*	723	16·0	1810	192·0
3*b*	764	16·2	1015	193·0
3*a*	762	16·3	1070	192·3
4*a*	764	16·3	303	191·8
4′*a*	763·5	16·3	1810	192·0
6*a*	671·5	—46·8	1070	251·0
6*b*	670	—47·5	1015	251·0
8*a*	770	99·2	1070	145·5

The first three experiments with ammonia were of a preliminary nature under conditions somewhat differing from those already described. They have not been included in calculating the mean. The experiments up to No. 17 were made before the measurements with phosphine and arsine, and the rest afterwards. The last value for arsine is the mean of five readings, agreeing within 2 per cent., but it is not very reliable, as the gas was decomposing slightly. Further experiments were not performed at this temperature owing to the risk of spoiling the condenser insulation.

For the sake of comparison with the results of other observers, a few determinations were made of the dielectric constants of dry CO_2-free air and carbon dioxide, but the results are not intended to be at all comprehensive. The value for a sample of benzene was also measured with the idea of checking the corrected capacity of the gas condenser, but the result differed so widely from the most recent determinations that it was useless for this purpose. This matter is under investigation and will form the subject of a separate communication.

In the case of air, the condenser was filled with the gas and then evacuated rapidly to 16 mm. The result is the mean of five readings with an extreme variation of less than 1 per cent. The carbon dioxide was condensed in liquid air in the same way as the other gases. The two results are each the mean of nine agreeing among themselves to 0·6 per cent. Table II shows the values for 16° and 760 mm., the actual measurements being made within 1° of this temperature at a pressure of 770 mm. for air and 789 mm. for carbon dioxide. A few of the results obtained by other observers calculated to the same temperature and pressure are also given.

TABLE II.

Dielectric Constants of Air, Carbon Dioxide and Benzene. 16°.

	Frequency, *kc.*	ϵ.	Other observers.	
Air	1070	1·000568	1·000557[1] 516[3] 540[5]	1·000554[2] 510[4] 561[6]
Carbon dioxide, 1	1028	1·000950	1·000894[1] 1045[3]	1·000930[2] 896[4]
,, 2	1070	1·000944	937[7]	
Benzene	656	2·290	2·2897[8] 2·2654[10]	2·2583[9]
,, ...	1150	2·283		

In order to determine the densities of the gases at the temperatures employed and the magnitude of the pressure corrections, use has been made of the formula

$$pv = \mathrm{RT}\left(1 - \frac{\mathrm{B}}{v}\right), \tag{2}$$

which is simplified from the general expression given by G. Holst (*Leiden Comm.*, 1913, No. 144). From this, assuming that $\epsilon - 1$ is proportional to the density or inversely proportional to v, the expression

$$\frac{(\epsilon - 1)_{p_1}}{(\epsilon - 1)_{p_2}} = \frac{p_1}{p_2}\left(1 + (p_1 - p_2)\frac{\mathrm{B}}{\mathrm{RT}}\right) \tag{3}$$

may be deduced, connecting the dielectric constants at pressure p_1, p_2 but at the same temperature, where B is a small quantity. In this formula R = 1/273 and p is measured in atmospheres.

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[1] L Boltzmann, *Sitz. Akad. Wiss. Wien*, 1874, 69, 795.

[2] J. Klemencic, *Sitz. Akad. Wiss. Wein*, 1885, 91, 712.

[3] M. Jona, *loc. cit.*

[4] E. C. Fritts, *Physical Rev.*, 1924, 23, 345.

[5] C. T. Zahn, *loc. cit.*

[6] A. P. Carman and K. H. Hubbard, *Physical Rev.*, 1927, 29, 299.

[7] H. Rohmann, *Diss. Strassbourg* (1910).

[8] M. Grützmacher, *Z. Physik*, 1924, 28, 342.

[9] L. A. Sayce and H. V. A. Briscoe. *J. Chem. Soc.*, 1927, 127, 315.

[10] H. Harris, *ibid.*, vol. 1927, 127, 1049.

The values assumed for B were as follows:—

	$-47°$	$16°$	$100°$
NH_3	0·029	0·0085	0·0048
PH_3	0·016	0·0065	0·002
AsH_3	0·021	0·008	0·004

The figures for ammonia are taken from the determinations of Holst (*loc. cit.*). Those for phosphine were calculated from the critical constants and the values for ammonia by means of the theory of corresponding states, but the results were reduced by 20 per cent. in order to make the value at 16° agree with the one deduced from Ter Gazarian's density determination (*Compt. rend.*, 1909, **148**, 1397). In the case of arsine there are no data, and so the value at the lowest temperature was calculated from the rate of change of dielectric constant with pressure over two different pressure ranges. A similar calculation at room temperature led to the value 0·012, but the experimental error was very large, and it seemed more satisfactory to adopt the figure given, which is obtained merely by analogy with the other two gases, as is also the value for 100°.

Table III gives the results of three experiments upon the variation of dielectric constant with pressure at $-47°$; $\epsilon - 1$ was actually measured by determining the change in capacity as the pressure was reduced from one pressure given to the next. The value in the table is the sum of all these changes from 0 to the given pressure. The units are arbitrary, being scale divisions with a small correction to make the figures proportional to the change in capacity. The calculated values are obtained by means of formula (3), taking the figures in brackets as the basis.

TABLE III.

Variation of Dielectric Constant with Pressure

Ammonia.			Phosphine.			Arsine.		
p	$(\epsilon-1)$calc.	$(\epsilon-1)$obs.	p	$(\epsilon-1)$calc.	$(\epsilon-1)$obs.	p	$(\epsilon-1)$calc.	$(\epsilon-1)$obs.
342·5	(1378)	1378	745	(1050)	1050	669·5	(701)	701
[illegible]	801	804	601·5	844	844	606	633	633
108·5	432	434	402·5	562	562	405	420	420
90·0	358	362	201	278	279	205·5	212	212
61·6	245	249	102	141	141	103·5	106	106
43·0	167	169	53·5	74	73	81	84	82
[illegible]	85	89				62	64	61
						42	43	40
						23	24	21

In the case of ammonia the correction for departure from the perfect gas law appears to be too large, as there is an appreciable difference between the observed and calculated values. The former are actually closer to the figures obtained on the assumption that $\epsilon - 1$ is proportional to the pressure. With arsine at low pressures there is some discrepancy between the two sets of values. This may be analogous to the effect observed by K. Wolf (*loc. cit.*) in the case of ammonia. On the whole, the differences are very small and only just beyond the limit of experimental error, so that the assumption that $\epsilon - 1$ is proportional to the density may be said to be justified at least to a first approximation.

Reverting to Table I, an examination of the results indicates that, although there is perhaps a slight tendency for the values at the higher frequencies to be greater than the others, the variation is probably within the limit of experimental error, so that all the figures for one temperature may be taken together in calculating the mean. The agreement between individual values is considerably closer than was anticipated when the experiments were started, but this does not reduce the possibility of constant error, one of the main sources of which was in the determination of G', the apparent capacity of the gas condenser. The experimental values varied by as much as 0·3 $\mu\mu$F., corresponding with an error of 0·2 per cent. from the mean. The internal temperature of the condenser when in the cold bath could not be relied upon to less than 0·5, while the small fluctuations at the higher temperature mentioned above form another source of error.

The final mean values are given in Table IV. The fourth column is derived by multiplying these values by $(1 - B/RT)$, and shows what the figures would be if the gases were perfect. The next column gives the values for a density equal to that of the perfect gas at 0° and 1 atm., that is to say, for equal numbers of molecules. From these, the value of BN in Debye's equation, $\epsilon - 1 = N\ (A + B/T)$, may be calculated for any two temperatures, the figures in the table being derived from the two lower and the two higher temperatures. Since B (not the B of the gas equation) is equal to $4\pi\mu^2/9k$, k being Boltzmann's constant, $1{\cdot}35 \times 10^{-16}$, and N the number of molecules $= 2{\cdot}705 \times 10^{19}$ in the present case, μ the electric moment may be calculated.

From these figures it appears that ammonia and phosphine conform approximately with the Debye formula, while in the case of arsine the value of B is substantially zero, so that this gas is similar to the permanent gases as far as its dielectric constant is concerned. The two values of B for ammonia are by no means coincident, although the difference corresponds with an error of only 1·5 per cent. on the lower value. This is, however, probably beyond the limit of experimental error as far as relative values are concerned.

TABLE IV.

Mean Values of Dielectric Constants at 1 Atm. Pressures.

Gas	t.	$(\epsilon - 1) . 10^5$ obs.	$(\epsilon - 1) . 10^5$ perfect.	$(\epsilon - 1) . 10^5$ eq. dens.	BN.	$\mu \times 10^{18}$.
NH_3 ...	—47	1099	1061	879	1·92	1·51
	16	659	654	692	1·79	1·46
	100	406	404·5	552·5		
PH_3 ...	—47	337·3	330·8	273·8	0·24	0·54
	16	238·1	236·6	250·4	0·26	0·56
	100	168·7	168·5	230·2		
AsH_3 ...	—47	251·0	245·0	202·8	0·01	0·13
	16	191·6	190·2	201·4	0·03	0·18
	100	146	146	199		

The absolute values for ammonia at 16° and 100° differ considerably from the figures 737 and 451 for the same temperatures calculated from Jona's results. This author, however, states that he does not consider his absolute values accurate. The ratio between corresponding results is the same within 1 per cent., so that in this respect the agreement is satisfactory. It follows that Jona's value for $\mu \times 10^{18}$, viz., 1·53, is approximately the same as those found in the present experiments.

Owing to the uncertainty as to the compressibilities of phosphine and arsine, the values of B for these gases are subject to revision.

In conclusion, I wish to tender my best thanks to Prof. F. G. Donnan for all the facilities he has placed at my disposal for undertaking this research, and to Sir Robert Robertson for the loan of the phosphine and arsine.

SUMMARY.

1. The dielectric constants of ammonia, phosphine, and arsine have each been measured at three temperatures and three frequencies particular attention having been paid to determining the absolute values. The variation of dielectric constant with pressure has also been examined.

2. The absolute values found for ammonia are considerably higher than those determined by Jona, but the value of the electric moment calculated by Debye's equation is approximately the same in both cases.

3. Ammonia and phosphine approximately satisfy Debye's equation for the change in dielectric constant with temperature, but there appears to be a slight deviation in the case of the former gas at the lowest temperature examined.

4. The value of the electric moment is much smaller for phosphine than for ammonia, while for arsine it is still smaller.

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