6. *The Dielectric Polarisation of Hydrogen Chloride in Solution. Part I. Benzene,* cyclo*Hexane, and Carbon Tetrachloride.*

By Fred Fairbrother.

The dielectric polarisation of gaseous hydrogen chloride has been measured by several observers and the permanent electric moment calculated from the temperature coefficient according to the method of Debye. The results thus obtained are $\mu = 1{\cdot}034 \times 10^{-18}$ e.s.u. (Zahn, *Physical Rev.*, 1924, **24**, 400), $\mu = 1{\cdot}180 \times 10^{-18}$ e.s.u. (Braunmühl, *Physikal. Z.*, 1927, **28**, 141). Falkenhagen (*ibid.*, 1922, **23**, 87) has published a value of the electric moment $\mu = 2{\cdot}15 \times 10^{-18}$ e.s.u., obtained from dielectric-constant measurements, but no values of the latter are given and only a brief description of the method. Frivold and Hassel (*ibid.*, 1923, **24**, 82), by means of electrostriction measurements, estimated the dipole length of the hydrogen chloride molecule to be $0{\cdot}31 \times 10^{-8}$ cm., which corresponds to a value of $\mu = 1{\cdot}48 \times 10^{-18}$ e.s.u.

When hydrogen chloride is dissolved, it exhibits properties which depend to a very great extent on the chemical properties of the solvent. In water and other hydroxylic solvents it behaves as a strong electrolyte, whilst in solvents which possess little or no affinity for the hydrogen ion it behaves as a weak or even as a non-electrolyte, although the solvent may be a good ionising solvent for other strong electrolytes such as salts. For instance, Wright, Murray-Rust, and Hartley (J., 1931, 199) state that dissolution of hydrogen chloride in nitromethane (D.C. = 37 at 25°) scarcely alters the resistance of the solvent, and Murray-Rust, Hadow, and Hartley (J., 1931, 215) state that in nitrobenzene (D.C. = 35) it behaves as a very weak electrolyte.

These facts are in accord with Brønsted's definition of an acid (*Rec. trav. chim.*, 1923, **42**, 718; *J. Physical Chem.*, 1926, **30**, 777), according to which the ionisation of the acid is dependent upon the basic properties of the solvent, *i.e.*, upon the affinity of the solvent molecules for the hydrogen ion; thus in water we have $HCl + H_2O \rightleftharpoons H_2OH^{\bullet} + Cl'$, the equilibrium, except perhaps in very concentrated solution, lying almost completely to the right.

It is well known that in gaseous hydrogen chloride there is strong evidence from spectroscopic data of a considerable degree of penetration of the proton into the electron system of the chlorine atom, and that an oscillation of the proton relative to the chlorine nucleus takes place along the line joining them. Moreover, the effective dipole length, as calculated from measurements of electric moment, is about one-sixth of the value of the nuclear separation as calculated from infra-red measurements. This indicates a deformation of the electronic atmosphere of the chlorine by the electric field of the hydrogen ion (Debye, "Polar Molecules," 1929); that is, the gaseous hydrogen chloride, although undoubtedly polar in character, cannot be regarded as made up of a positive hydrogen ion combined with a negative chloride ion, with the centres of the respective positive and negative charges located in the mass centres. In fact, it is usual now to regard the binding in gaseous hydrogen chloride as homopolar, the chlorine and the hydrogen being intimately bound together and requiring a considerable amount of energy to separate them (compare Garner and Lennard-Jones, *Trans. Faraday Soc.*, 1929, **25**, 623).

On the other hand, the proximity of a molecule with which the proton can readily form a covalent link causes the hydrogen and the chlorine to part entirely.

It is of interest to know therefore what is the state of the molecule in solution in a solvent in which it is un-ionised, for it is not unreasonable to expect that, when dissolved in a solvent which has no affinity for the proton, the electric fields of the solvent molecules should nevertheless affect the configuration of the hydrogen chloride molecules, especially if the former possess an appreciable electric moment. For example, a change in the relative vibrations of the hydrogen and chlorine nuclei or of the distortion of the electronic atmosphere of the chloride ion by the proton, would be manifested by a change in the effective electric moment of the hydrogen chloride. Hassel and Uhl (*Z. physikal. Chem.*, 1930, *B*, **8**, 187) have measured the electric moments of a number of substances in various solvents, some being of a polar character. They find that the dipole moment is but little dependent on the solvent used, so long as a high accuracy is not in question. The solutes which they used, however, were not such as readily undergo complete ionisation in the presence of a suitable solvent, as does hydrogen chloride.

The dielectric polarisation of hydrogen chloride has now been measured in solution in benzene, *cyclo*hexane, and carbon tetrachloride, and work is in progress with other solvents. One would not expect much distortion of the molecule in these non-polar solvents, but the results show that even here, the dielectric polarisation is greater than in the gaseous state.

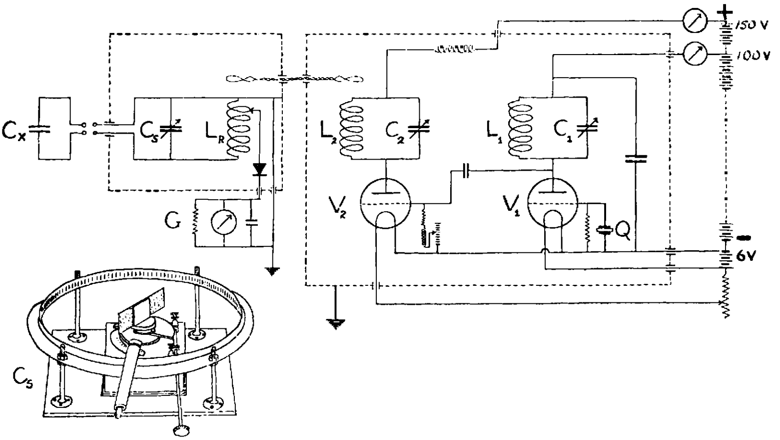
Solutions in these three solvents were of immediate interest on account of the difference in their electro-endosmotic behaviour (Fairbrother and Balkin, J., 1931, 1564): in the same work it was shown that these solutions possess no appreciable conductivity.

EXPERIMENTAL.

The magnitudes actually measured included the dielectric constants, the refractive indices, the densities, and the composition of the solutions.

Dielectric Constant.—This was measured at 1000 kc. (300 metres) by a resonance method. The electrical circuits and the arrangement of the standard condenser are shown in Fig. 1. In any method for the measurement of dielectric constant which depends on the frequency of the current used, as does any resonance method, the final accuracy depends on the accuracy with which the frequency is known or is kept constant. In the present work the frequency of the main oscillating valve V_1 was kept constant by a piezo-electrically oscillating plate of crystalline quartz, Q. The plate used had a very small temperature coefficient, and was allowed to oscillate for some time before a measurement was made. It was sometimes found, when using a single valve, that the quartz ceased to oscillate when the measuring system was brought into resonance. A second valve V_2 was therefore coupled to the first and served to minimise the effect of the load of the resonance circuit on the latter. Various combinations of valves were found to work satisfactorily : those actually used were, V_1, Mullard PM5X; V_2, Ediswan R (bright emitter).

FIG. 1.



V_1 and V_2 were supplied with high-tension current from a battery of large wireless accumulators, the voltage of the mains not being sufficiently constant. The accumulators were frequently recharged, and the oscillator was allowed to run until the voltage was practically constant. The drift of the galvanometer was timed frequently and found to be negligible over the time taken for the measurements. Coupling between the coil L_2 and the resonance coil L_{R} was effected by a single turn of 40's d.s.c. wire on each coil former, connected by twisted wire. The turn on L_{R} was 5 cm. from the end of the resonance coil : with a much closer coupling it was found that the setting of C_{S} was affected to a slight extent by changes in C_2.

The variable condenser C_{S} was a Sullivan's laboratory air condenser of 1200 μμf capacity, fitted with a worm-gear slow motion. It was arranged as shown, with the axis of its spindle coincident with the axis of a circular scale about 1800 mm. long, mounted on the inside of a turned ring of L-section. A mirror silvered on the surface (a photographic reflex camera mirror) was mounted on the condenser spindle so that the axis of the latter was in the plane of the mirror. Readings were taken through a telescope rigidly mounted on the scale ring, and could be made easily to ± 0·01°, the field of the telescope covering about 1°. The scale ring and condenser were fixed to a heavy teak base which was clamped at the ends with heavy iron clamps to prevent distortion. An improvement in the reading at the ends of the scale and the avoidance of double images was effected by fixing wings of thick black paper at the sides of the mirror. The condenser was calibrated in position, by the step-by-step method with the aid of another variable air condenser and a small air condenser of fixed capacity equivalent to about 10° on the scale of C_S.

The oscillator and resonance circuits were enclosed in earthed metal and metal-lined boxes, respectively. In the case of C_S the telescope eyepiece and a long ebonite extension of the slow-motion screw projected through the box, the scale, when required, being momentarily illuminated by an electric lamp.

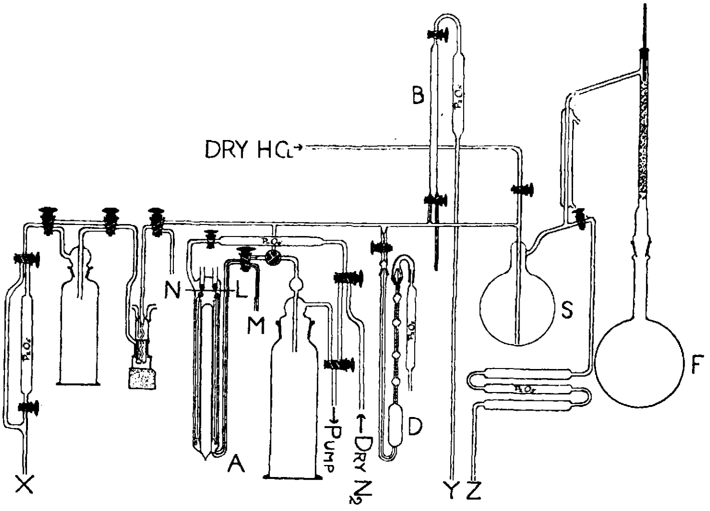
One end of the resonance circuit was earthed, which avoided much difficulty with stray capacities to earth. All the leads were well insulated, twisted together, and fixed rigidly in position. It was considered preferable to minimise the inductance of the leads at the cost of a slight increase in their mutual capacity, the latter being easier to allow for.

Connexion between the resonance circuit and the experimental condenser was made by a mercury-cup switch, so arranged that the positions of the contacts could be reproduced closely: for such a switch possesses an unavoidable capacity which it is necessary to keep constant.

The resonance was indicated with the aid of a carborundum–steel permanent detector and a sensitive galvanometer. This method was adopted after attempts with different types of valve-voltmeter. For the present purpose, the convenience and constancy of the carborundum–steel detector outweigh the theoretical superiority of the valve-voltmeter. The main objection to a crystal rectifier is that it takes current from, and therefore imposes a load upon, the resonating circuit, this in turn causing, as is well known, a " flattening " of the capacity–current curve, rendering the maximum less well defined. The load may be reduced, however, and the tuning sharpened by including only a portion of the resonance inductance in the rectifier–galvanometer circuit. In the present instance, 3 turns out of a total of 15 were thus included.

Readings of the condenser C_S were taken when the (pointer) galvanometer deflexion was 40°, 60°, 80°, and 100°, on both sides of the resonance curve : the average of the mean positions was then taken as the resonance capacity, which was usually reproducible to 0·01°. This corresponds to about one part in 3000 parts of the air capacity of the dielectric container, which was the smallest capacity measured. The dielectric constants are therefore given to 4 significant figures. As a further check against possible error due to change in voltage of the high-tension accumulators, and consequently of the resonance current, readings of C_S were quickly made with the galvanometer pointer at 60° on both sides of the resonance curve : this took only a few seconds.

Fig. 2.



A change in capacity of C_S corresponding to 0·1° on the circular scale produced a change of about 10 divisions on the galvanometer scale. Any damping caused by the rectifier, therefore, did not impose any further restrictions on the accuracy of the measurement. There is a limitation to the sensitivity of the galvanometer that can be used, owing to the minimum current that can be efficiently rectified by a carborundum–steel rectifier. The galvanometer with its shunt resistance used in the present work had a sensitivity of about 1 div. per microamp. The sensitivity of the method was greatly improved by placing a small mica condenser (0·004 μf) across the terminals of the galvanometer to shunt the A.C. component present in the current owing to incomplete rectification.

The condenser C_X, which is shown in section in Fig. 2, was made from three seamless, pure silver tubes about 1 mm. thick and of outside diameters approximately 29 mm., 37 mm., and 43 mm. and approximately 30 cm. long. The first and third, which constituted one plate of the condenser and were earthed, were silver-soldered to an annular ring turned out of thick (2 mm.) pure silver sheet. In this ring were 6 equidistant holes through which projected stout platinum wires attached at 60° intervals to the second tube. Corresponding wires were attached to the outermost tube. When the tubes had been assembled, the wires were cut off as close to the silver as convenient and fastened together in pairs by beads of glass fused on to the wires : the high conductivity of the silver permitted the platinum wires to be heated to bright redness without affecting the silver solder a few mm. away. The condenser was enclosed in a containing vessel, as shown, resting on a projection round the inner glass tube. The latter was partially evacuated and sealed. The capillary tube *A* was so arranged that almost the last drop of liquid could be withdrawn from the condenser. The advantages of this condenser, which in some respects resembles that used by Smyth (*J. Amer. Chem. Soc.*, 1928, **50**, 1547), are (1) good shielding of the non-earthed plate of the condenser, (2) no series resistance due to the resistance of the plates, a common fault with silver-coated glass condensers, (3) good temperature regulation due to the thickness and high thermal conductivity of the silver, (4) a minimum amount of solid dielectric, and (5) a large replaceable capacity. The measured capacity of the cell containing air, the leads and mercury-cup switch, was about 200 μμf, of which 95% was replaceable. The non-replaceable capacity, consisting of stray, fixed, and lead capacities, was estimated by calibration with pure dry benzene (Kahlbaum's "for analysis and molecular-weight estimations"), of which the dielectric constant was assumed to be 2·273 at 25·0° (Oliver and Hartshorn, *Proc. Roy. Soc.*, *A*, 1929, **123**, 664). The benzene was distilled from pure phosphoric oxide, and transferred to the condenser out of contact with the atmosphere, with the complete apparatus assembled.

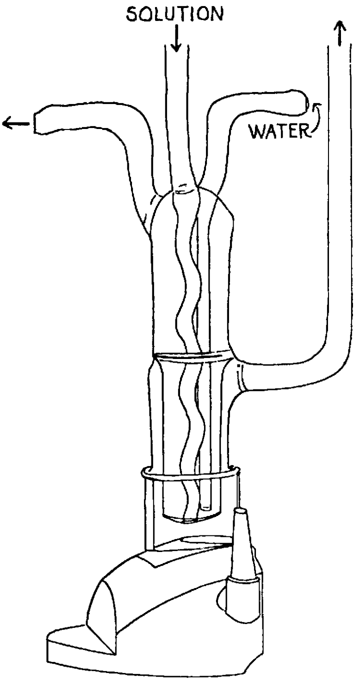
The condenser was fixed in a thermostat filled with a second-quality medicinal paraffin. The liquids were introduced, removed, and the cell was rinsed with pure solvent and dried (with dry nitrogen), without moving it, thus eliminating changes of non-replaceable capacity due to small changes in the disposition of the apparatus. The condenser vessel was filled each time just to the level *L*, where the leads entered the glass tubes.

Refractive Indices.—These were measured with a Pulfrich refractometer at 25·0° for the wave-lengths 6708 Å. (Li), 5893 Å. (Na), 5461 Å. (Hg), and 4359 Å. (Hg). The refractometer was first calibrated at the different wave-lengths by means of a quartz block cut to give the ordinary and extraordinary rays, as described by

Lowry (*Proc. Opt. Convention*, 1912, **2**, 291). This was necessary since the tables provided with the instrument were unsuitable for use with the lithium and mercury lines.

The ordinary form of Pulfrich refractometer is unsuitable for use with solutions which have a considerable vapour pressure at the temperature of measurement, owing to evaporation and consequent change in composition of the liquid. This was particularly so with the solutions of hydrogen chloride used, which fumed strongly in the air. The apparatus shown in Fig. 3 was therefore designed to get over this difficulty. The apparatus is made entirely of glass and takes the place of the refractometer heater, the ground flange being cemented to the top of the refractometer cell. In the present experiments, seccotine was used as the cement, control estimations having shown that the refractive indices were not affected by it. Moreover, as can be seen, the refractometer becomes a closed system, and successive quantities of a solution may easily be transferred to the surface of the prism. The solutions were washed completely from the cell by the passage of considerable quantities of purified solvent, and the cell and prism face were dried by filtered and dried air. The glass water-jacket was placed in series with the usual refractometer heater, the temperature of the circulating water being read by the thermometer in the latter. A powerful rotary piston pump maintained a rapid stream of water from the thermostat through the system. The temperature control was further assisted by lagging the glass apparatus, above the usual wooden block, with black cotton wool, and by enclosing the refractometer within a wooden box, the air in which could be warmed by small electric lamps to approximately 25°, and through the front and sides of which the telescope and adjustments projected. The scale was read through a hole in the front of the box. With these precautions it was possible to maintain the temperature of the liquid under observation constant to within ± 0·05°.

Fig. 3.



The apparatus in Fig. 2 was designed for the measurement also of the dielectric constants and refractive indices of other solutions, which were introduced at *M* and *N* respectively, as were also pure solvents for rinsing out the apparatus.

Densities.—These were measured with the aid of the dilatometer *D* (Fig. 2). The left limb was ground to fit both the joint on the main apparatus and its own cap. The dilatometer, which held about 30 c.c., was graduated as shown, with bulbs on the stem, for use over a wide temperature range. In the present work only a single estimation of the density of a solution at a temperature other than 25·0° was carried out, owing to the loss of hydrogen chloride at higher temperatures.

Temperatures in each case were referred to a standard thermometer graduated in 0·01° and calibrated at the N.P.L. to 0·005°.

The benzene was of the quality previously specified (p. 49); the *cyclo*hexane was purified as described by Fairbrother and Balkin (*loc. cit.*). The carbon tetrachloride was a Kahlbaum product which still contained a trace of carbon disulphide. This was removed by repeated treatment with alcoholic potash as suggested by Schmitz-Dumont (*Chem.-Ztg.*, 1897, **21**, 510). The product after drying and fractionation was free from sulphur compounds. The solvents were all subjected to a preliminary drying with phosphoric oxide and redistilled in dry apparatus.

The general arrangement of the apparatus used in the preparation and manipulation of the solutions is shown in Fig. 2. The apparatus was cleaned and dried, and sufficient of the previously dried solvent placed, together with phosphoric oxide, in the flask *F*, where it was kept for several days with the taps on the apparatus closed. It was then distilled, an electrical heater being used, through an efficient fractionating column into the absorption vessel *S*. The column served to minimise the risk of phosphoric oxide being carried over mechanically in the spray.

Dry hydrogen chloride, from pure sulphuric acid and A.R. ammonium chloride, after passage through phosphoric oxide, was passed into the solvent in *S* for a greater or less time, and the solution forced into the different portions of the apparatus by application of pressure at *Z*. By an arrangement of taps (not shown), *X*, *Y*, and *Z* could, as desired, be placed in connexion with the atmosphere, pressure, or suction; *Z*, in addition, could be placed in connexion with an arrangement for the absorption of excess hydrogen chloride. No lubricants were used on taps or ground joints where there was a risk of its coming into contact with the liquids.

The solutions used for the density and refractive index measurements were discarded after use, that from the measuring condenser being sucked back into S and additional solvent distilled into it, if necessary, from F. So long as the pressure over the solutions was not reduced during manipulation, the loss of hydrogen chloride was small, and was chiefly confined to the surface layers of the solutions. These were not used, except in the density measurements, where the consequent error would be small, and have the least effect on the final result.

The estimation of the composition of the solutions was carried out (in duplicate in each case), by running about 20 c.c. from the burette B into small, tared, stoppered flasks containing an excess of caustic soda solution. The flasks were then re-weighed, gently shaken, the solvent carefully evaporated, and the chloride content estimated by Volhard's method. The tip of the burette was kept close to the surface of the solution in the flask, below which the hydrogen chloride solution was projected in a very fine stream.

The calculation of polarisation and of the dipole moment of molecules dissolved in a non-polar solvent, according to the classical theory of Debye, has been frequently described at length in recent years (*e.g.*, Debye, *loc. cit.*; Hunter and Partington, J., 1931, 2062). The results of the dielectric-constant and density measurements, and the calculated polarisations are given in Table I, in which P_{12} is the molar polarisation of the solution calculated from the equation

$$P_{12} = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{(m_1 f_1 + m_2 f_2)}{\rho}$$

ε being the dielectric constant and ρ the density of the solution, and m_1, m_2, f_1, f_2, being respectively the molecular weights and mol.-fractions of the solvent and solute : the expression in parentheses is therefore the fictitious molecular weight of the solution.

TABLE I.

Benzene.

f_2.	ϵ.	ρ.	P_{12} (c.c.).	P_2 (c.c.).
0·000	2·273	0·8728	26·64	—
0·0069	2·288	0·8733	26·75	41·9
0·0139	2·303	0·8737	26·86	41·8
0·0203	2·317	0·8742	26·93	41·5
0·0222	2·321	0·8743	26·98	41·4
0·0302	2·339	0·8746	27·11	41·8

cycloHexane.

f_2.	ϵ.	ρ.	P_{12} (c.c.).	P_2 (c.c.).
0·000	2·011	0·7733	27·41	—
0·0039	2·018	0·7737	27·48	44·7
0·0101	2·028	0·7740	27·58	43·3

Carbon tetrachloride.

f_2.	ϵ.	ρ.	P_{12} (c.c.).	P_2 (c.c.).
0·000	2·225	1·5836	28·17	—
0·0026	2·232	1·5835	28·23	—
0·0107	2·247	1·5811	28·33	43·5

The total polarisation of the solute P_2 has frequently been computed by plotting P_{12} against f_2 and drawing the tangent to the curve at $f_2 = 0$, to cut the P-axis at $f_2 = 1$. The present values of P_{12} for benzene–hydrogen chloride, when plotted against f_2, yield practically a straight line, the equation of which, calculated according to the method of least squares, is $P_{12} = 26{\cdot}65 + 14{\cdot}84 f_2$. This when extrapolated to $f_2 = 1$ gives $P_2 = 41{\cdot}5$ c.c.

The range of concentrations, however, is small, especially in *cyclo*hexane and carbon tetrachloride, and the alternative procedure has also been followed by making the assumption that the molar polarisation of the solvent P_1 is constant over the range of solutions and equal to that of the pure solvent—this is probably a very safe assumption for the dilute solutions used in the present case; P_2 is then calculated in each case from $P_{12} = f_1P_1 + f_2P_2$.

The total polarisation P_2 is made up of the three quantities, P_e the electron polarisation, P_a the atomic or vibrational polarisation, and P_0 the orientation polarisation of the electrical doublets. For the purpose of calculating P_e, the refractive indices at the different wave-lengths were measured, and the corresponding molar refractivities (MR_λ) calculated from the Lorentz–Lorenz relation

$$MR_\lambda = P_e = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{m_1 f_1 + m_2 f_2}{\rho}$$

where n is the refractive index at the particular wave-length. The results for benzene are given in Table II.

TABLE II.

Refractivity of hydrogen chloride in benzene solution.

f_2.	λ (cm. × 10^8).							
	6708.	5893.	5461.	4359.	6708.	5893.	5461.	4359.
	M_λ (solutions).				MR_λ(HCl) = P_e.			
0·000	1·4924	1·4977	1·5018	1·5195	—	—	—	—
0·0069	1·4915	1·4966	1·5007	1·5184	—	—	—	—
0·0139	1·4912	1·4963	1·5003	1·5181	—	—	—	—
0·0210	1·4905	1·4957	1·4997	1·5173	5·9	5·9	5·9	5·9
0·0222	1·4899	1·4953	1·4993	1·5168	5·4	5·4	5·4	5·4
0·0302	1·4893	1·4946	1·4984	1·5159	5·9	5·9	5·6	5·6

The accuracy of measurement, coupled with the low concentrations available is, even in benzene, only sufficient to measure approximately the molecular refraction of the dissolved hydrogen chloride, and is insufficient to indicate the dispersion. The refractive indices of gaseous hydrogen chloride (Cuthbertson, *Phil. Trans.*, *A*, 1914, **213**, 1) give $MR_{6708\text{Å}} = 6{\cdot}57$ and $MR_{5461\text{Å}} = 6{\cdot}64$. The refractive indices of the solutions in *cyclo*hexane did not differ from those of the pure solvent by more than one unit in the fourth decimal place, which is the same as the uncertainty of the measurements. The refractive indices for the most concentrated solution in carbon tetrachloride were more significant, showing a difference of 5—7 units in the fourth decimal place, which is still too small to permit of the calculation of the molar refractivity of the solute. No figures are therefore given for these refractive indices.

The value of P_a is taken as 1·2 c.c., as calculated by Errera ("Polarisation Diélectrique," 1928) from the temperature coefficient of the dielectric constant of the gas as determined by Zahn (*loc. cit.*) and the refractive indices of the gas as given in Landolt–Börnstein's tables and extrapolated to zero frequency. P_a is probably quite small, but there is some doubt as to its actual value. As Smyth (*J. Amer. Chem. Soc.*, 1929, **51**, 2051) has pointed out, P_a is generally determined as a small difference between relatively large quantities, and consequently all the errors of experiment and method are accumulated in its value. Van Vleck (*Physical Rev.*, 1927, **30**, 31) has calculated, from a consideration of the infra-red absorption spectrum, that the vibrational polarisation (*i.e.*, P_a) is negligibly small for gaseous hydrogen chloride, and attributes to experimental error the difference found between the total induced polarisation and the extrapolated refraction.

If, then, for benzene we take $P_2 = 41{\cdot}5$ c.c., $P_e = 5{\cdot}9$ c.c. (from the refractive power in benzene), and $P_a = 1{\cdot}2$ c.c., then the orientation polarisation $P_o = P_2 - (P_e + P_a) = 34{\cdot}4$ c.c. and, making the substitutions in Debye's equation, $P_o = 4\pi N\mu^2/9kT$ where μ is the electric moment of the molecules, N Avogadro's constant, k the Boltzmann gas constant $= 1{\cdot}37 \times 10^{-16}$ ergs, and T the absolute temperature, we have $\mu = 1{\cdot}28_6 \times 10^{-18}$ e.s.u. By taking $P_e = 6{\cdot}6$ c.c. from the refractivity of the gas, a value of $\mu = 1{\cdot}27_3 \times 10^{-18}$ e.s.u. is obtained. The difference is less than the error of the experiment. Similarly, if for solutions in *cyclo*hexane and carbon tetrachloride, we take $P_2 = 44$ c.c., $P_e = 6{\cdot}6$ c.c. (from the refractivity of the gas, in the absence of data in solution), and $P_a = 1{\cdot}2$ c.c. as before, we obtain $\mu = 1{\cdot}32 \times 10^{-18}$ e.s.u.

In the solutions in *cyclo*hexane and carbon tetrachloride there is an uncertainty in the value of P_2 of the order of 5%, due chiefly to the low solubility of the gas in these solvents and to loss during manipulation; the values of P_2 given are probably somewhat high. In the benzene solutions the uncertainty is less. It was found that the stronger solutions in benzene and the solutions in the other solvents tended to lose hydrogen chloride during the dielectric-constant measurements; estimations of the concentration were therefore also made in these cases after the measurement.

Taking these sources of error into consideration, we can say that the electric moment of hydrogen chloride in solution in *cyclo*hexane and in carbon tetrachloride is not significantly different from its value in benzene.

Zahn (*loc. cit.*) found a value of $1{\cdot}034 \times 10^{-18}$ for the electric moment of gaseous hydrogen chloride, which corresponds to an orientation polarisation of 22·24 c.c. according to the present method. The difference between this and the figure actually found, which is more than 50% greater, is considered to be much too great to be attributed to experimental error.

We must conclude, therefore, that the polarisation of hydrogen chloride even in these non-polar solvents is greater than that in the gaseous state. This is supported by the fact that a calculation of the dielectric constants of such solutions, as carried out by Bell (J., 1931, 1371) for saturated solutions, presumably on the assumption of a polarisation similar to that in the gaseous state, leads to values which are below those actually found. In the case of carbon tetrachloride, Bell calculates the dielectric constant of the saturated solution to be less than that of the pure solvent, whereas the measurements show that it is greater.

In conclusion, I wish to thank Mr. J. Rigg for assistance with the purification of the solvents, and Messrs. Imperial Chemical Industries Ltd., by means of whose grant to this Department part of the apparatus was purchased.

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