The slightly larger value of P for the *trans*-isomer than for the *cis*-isomer is to be expected in view of the less compact structure of the former compound. At 20° this difference is close to 0.45. This is small but greater than the limits of error in the measurement of the dielectric constant. The polarizabilities (α) have been calculated in the usual manner and compared with those of benzene in Table II.

TABLE II

COMPARISON OF THE MOLAR POLARIZATIONS AND POLARIZABILITIES FROM RESULTS AT 20°

	P	α_{20}
Benzene	26.71	1.05×10^{-25}
cis-Decalin	44.4	1.75×10^{-25}
trans-Decalin	44.9	1.77×10^{-25}

Again it appears that the polarizability of the *trans*- is slightly greater than that of *cis*-isomer.

A comparison of the dielectric constants and the squares of the refractive index for the D line of sodium is made in Table III for benzene, cyclohexane and the two bicyclic hydrocarbons.

TABLE III

COMPARISON OF THE DIELECTRIC CONSTANT WITH THE SQUARE OF THE REFRACTIVE INDEX

	n_{20}	$(n_{20})^2$	ϵ_{20}	$\epsilon_{20} - n_{20}^2$
Benzene	1.50142	2.254	2.289	0.035
Cyclohexane	1.42635	2.033	2.052	.019
cis-Decalin	1.48113	2.194	2.219	.025
trans-Decalin	1.46968	2.160	2.184	.024

It is seen that even for the simple theory which is not directly applicable to liquids the agreement is quite satisfactory. All results indicate a zero or a very small dipole moment for both isomers.

Summary

1. The dielectric constant of *cis*-decalin has been measured at 3.5 megacycles and 20° and has been found to be 2.219 ± 0.003. The temperature coefficient between the freezing point and 100° is 0.0010 per °C. No anomalous behavior in any of the samples tested was observed between −40 and 100°.

2. Under the same conditions, *trans*-decalin has been found to have the values 2.184 ± 0.003. The temperature coefficient between the freezing point and 100° is also 0.0010 per °C. As in the *cis*-isomer no anomalous behavior was observed.

3. The dielectric constant has been measured through the freezing point and to the solid phase. A marked difference in the behavior of the two isomers was observed. Furthermore, the curves for heating and cooling for both the decahydronaphthalene isomers and cyclohexane are quite different. Both *trans*-decalin and cyclohexane show a pronounced and unexplained maximum at the freezing point.

4. The molar polarizations of *cis*- and *trans*-decalin have been calculated at a number of temperatures and the variation with temperature has been found to be the same as the variation of the polarization of liquid benzene with temperature. Furthermore, the squares of the refractive indices are in close agreement with the dielectric constants.

5. The molar polarization of the *trans*-isomer is slightly larger than that of the *cis*-isomer. This indicates a looser or less compact molecular structure for the *trans*-isomer.

VANCOUVER, B. C., CANADA RECEIVED JULY 11, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Electric Moments of Hydrogen Fluoride, Hydrogen Chloride and Hydrogen Bromide in Several Non-polar Solvents[1]

BY A. J. WEITH, JR.,[1a] MARCUS E. HOBBS AND PAUL M. GROSS

Introduction

The electric moments of hydrogen fluoride, hydrogen chloride and hydrogen bromide in dilute solutions of non-polar solvents are of particular interest since measurements[2] by Fairbrother on some of the hydrogen halides in a limited number of solvents indicated that hydrogen chloride, hydrogen bromide and hydrogen iodide all exhibit a positive solvent effect. Hydrogen fluoride was not measured by Fairbrother; in fact, only recently has a value for the electric moment for this molecule been reported[3] and this was for the gas state. The present measurements were undertaken to establish the magnitude of the solvent effect for these solutes in a more extended series of solvents, to determine the value of the electric moment of hydrogen fluoride in solution and finally to establish the effect of bonding of these acid molecules to acceptor solvent molecules by measuring the electric polarization of the solutes in solutions of dioxane. It was hoped that, because of the relative simplicity of the halides, the data obtained would be useful in future attempts toward elucidation of the origin and mode of action of the solvent effect in electric moment measurements and that some insight might be gained into

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[1] Part of a Thesis of A. J. Weith, Jr., submitted in partial fulfillment of the requirements of the Ph.D. degree in Chemistry at Duke University, June, 1947.

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[2] F. Fairbrother, *Trans. Faraday Soc.*, **30**, 862 (1934).

[3] Hannay and Smyth, THIS JOURNAL, **68**, 171 (1946).

the process occurring when solutes combine with solvents to which proton transfer might occur.

Materials, Apparatus and Procedure

Solvents.—Benzene (Jones and Laughlin reagent grade) which was found to be thiophene free was stored over calcium chloride and then refluxed and finally distilled over sodium through a 2-meter Dufton column. The middle fraction, of essentially one-half the total volume, was collected directly in a transfer flask so the solvent could be transferred directly to the dielectric measuring system. The middle fraction boiling range never exceeded 0.02°. Recovered benzene from previous measurements occasionally was used. It was treated with solid sodium hydroxide to neutralize the acid, totally distilled and finally distilled as above over sodium. No differences in the constants of this benzene and that of a fresh sample were noted.

1,4-Dioxane (Carbide and Carbon Chemical Corp., C. P. Grade) was refluxed over solid sodium hydroxide for several hours, then totally distilled. This product was then refluxed and finally distilled over sodium, the middle fraction being collected directly in the transfer flask. The distillation was carried out only when the sodium showed and retained a bright metallic surface and, in addition, when there was no visible evidence of reaction of the sodium and dioxane. The b. p. range for the middle fraction used was generally 0.06° or less. Recovered solvent from previous measurements was used after being subjected to the same treatment as a fresh sample of dioxane.

n-Heptane (California Chemical Co.) in two-liter portions was shaken repeatedly with about 500 ml. of concentrated sulfuric acid until no further darkening of the sulfuric acid layer was observed. In general four portions of acid were required. The heptane was washed with dilute sodium hydroxide solution and distilled water and finally dried with fused calcium chloride. It was then refluxed and distilled over sodium wire and the middle fraction collected directly in the transfer flask. The middle fraction had a maximum b. p. range of 0.04°. Recovered samples of heptane were used in some runs.

Carbon tetrachloride (Eastman Kodak Co. best quality sulfur free) was purified according to the method suggested by Williams and Krchma.[4] The middle fraction distilled over fused calcium chloride was collected in the transfer flask. The fractions used had a b. p. range not exceeding 0.03°.

The actual boiling points of all samples of solvents were not recorded but samples of the same solvents have, on repeated tests in this laboratory, shown b. p. (cor.) falling within the range indicated: benzene, 80.06 to 80.08°; 1,4-dioxane, 101.25 to 101.45°; *n*-heptane, 98.47 to 98.52°; and carbon tetrachloride, 76.73 to 76.76°.

The average values of the dielectric constant for the solvents at 30.0° based[5] on benzene, $E = 2.263$, are 1,4-dioxane, 2.218; *n*-heptane, 1.906, and carbon tetrachloride, 2.216.

Solutes

Hydrogen flouride (anhydrous) obtained from E. I. du Pont de Nemours and Co., in steel tanks was represented as better than 99% pure. No attempt was made to effect further purification except that slow distillation at room temperatures through a monel metal trap was effected to reduce possible carry-over of liquid from the cylinder. Two cylinders were used during the course of the investigation and the results show no measurable differences. The hydrogen fluoride was distilled directly into the mixing chamber containing the solvent, all operations being carried out so as to exclude moisture.

Hydrogen chloride (anhydrous) was obtained from the Dow Chemical Co. in a steel tank. A typical analysis by them showed 98.2% hydrogen chloride, the chief impurity being nitrogen. This material was allowed to pass at atmospheric pressure through three conventional tube-packed traps maintained a few degrees above the liquefying temperature of the gas with Dry Ice–alcohol mixture. A fourth trap in the same cooling mixture consisted of ten feet of closely coiled 7-mm. o.d. tubing. At no time during the measurements was a visible deposit found in any of the traps.

Hydrogen bromide (anhydrous) obtained from the Dow Chemical Co. in a steel tank was stated to contain no known impurities other than bromine and water. The same trap system and cooling arrangement as for the hydrogen chloride was used on the hydrogen bromide since it was expected that both known impurities would be effectively removed by this method. Repeated measurements with both hydrogen chloride and hydrogen bromide showed no variations other than those that could be accounted for by the normal experimental error in the method used.

Water was used for one measurement in dioxane. It was purified by treatment with potassium permanganate and distilled from a silica still with the middle fraction being collected in a silica receiver.

Apparatus.—The heterodyne beat method of measuring capacity change has been used in this investigation. The oscillator circuits of a modified Hartley type were obtained commercially in the form of a beat frequency Clough–Brengle Audio Oscillator (No. 79-E). The variable oscillator circuit of the Clough–Brengle generator was altered by placing the measuring condenser and the compensating standard precision condenser in parallel with the capacitance in the variable oscillator circuit. With the two condensers at proper capacity, the original capacitance in the variable circuit was then reduced so that the over-all effect was that of the original capacitance. Variations in the capacity of the measuring condenser could then be compensated for and measured by the standard precision condenser, the reference point in all cases being that setting of the standard precision condenser that would give a zero beat frequency between the variable oscillator and the fixed oscillator. The "zero" beat was determined by the electron tube "eye" mounted in the front of the Clough–Brengle Oscillator. The two oscillating circuits in this equipment are very well decoupled so that there was no significant tendency for the two circuits to synchronize as they were tuned to the same frequency. High quality coaxial cable that was relatively insensitive to mechanical movement was used for all connections between the Clough–Brengle and the measuring and precision condensers, single contact microphone connectors being used for the actual connections. The standard precision condenser used was a 500 m.m.f. General Radio Company Precision Condenser, Type 222-B, with 2500 scale divisions. This capacitance was calibrated in arbitrary units which served as the unit for dielectric constant measurements.

It was obviously necessary to carry out all mixing and handling operations as well as the actual measurement in the absence of moisture. This was done by the construction of a completely enclosed measuring system which included a mixing chamber and a measuring condenser (see Figs. 1 and 2). The system was so constructed as to allow concentration and density samples to be withdrawn without contamination of the system. Movement of the solution from one vessel to another was effected by application of gas pressure at the proper point from a well dried (two liquid air traps) nitrogen source. All of the system that came in contact with the solution before or during a measurement was constructed either of monel, silver or nickel. Pure silver was used throughout for all welding. Connections between metal and glass portions were accomplished by means of ground glass–ground metal joints lubricated with graphite and sealed on the outside with De Khotinsky cement.

After much difficulty with the insulation problem a sample of polytetrafluoroethylene from the E. I. du Pont Company proved very satisfactory. No apparent deterioration occurred over a period of one and one half years of service.

The measuring condenser cell was constructed (see Fig. 2) of three concentric monel metal cylinders. The two inner cylinders were mounted integral with the top and

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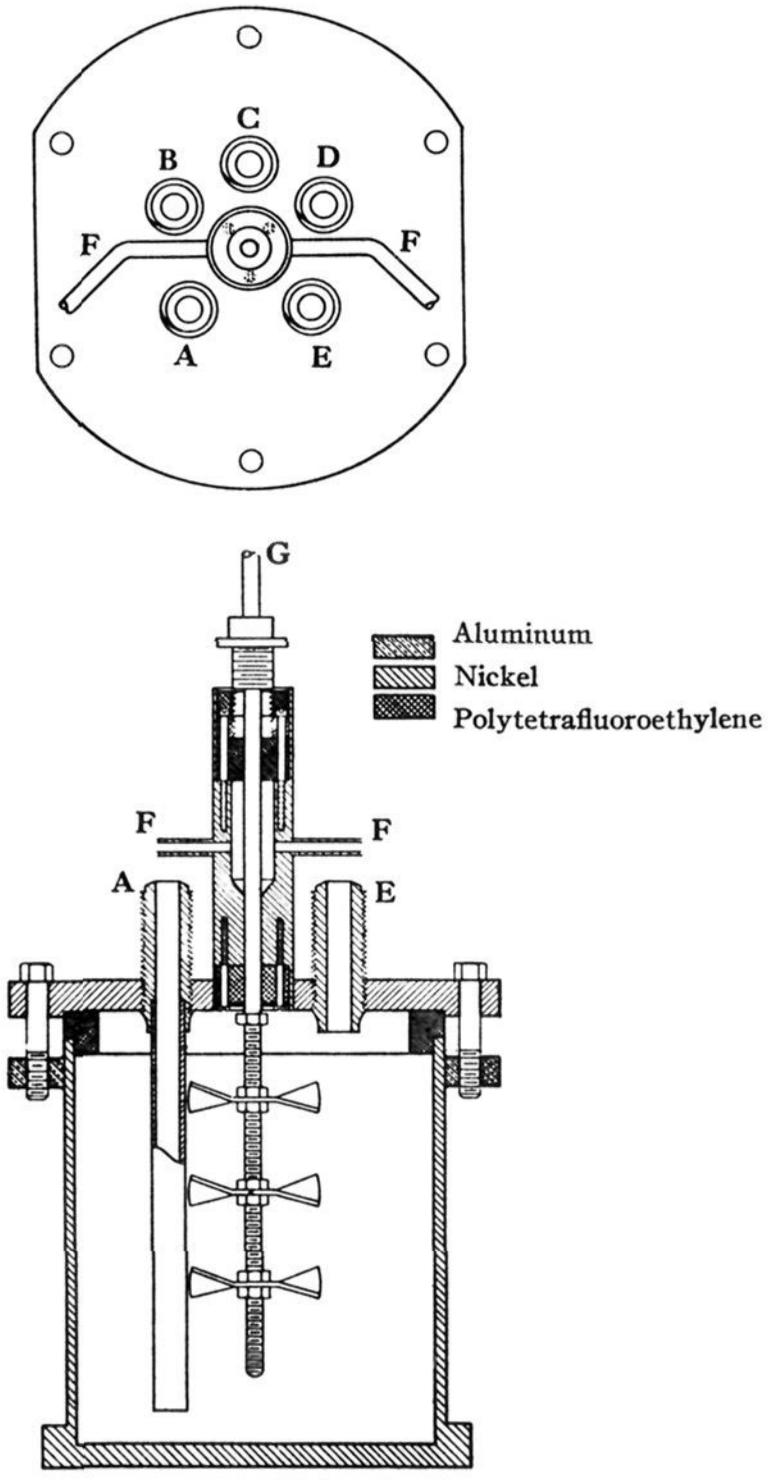
[4] Williams and Krchma, THIS JOURNAL, **48**, 1888 (1926).

[5] Hartshorn and Oliver, *Proc. Roy. Soc.* (*London*), **A123**, 684 (1929).



Mixing chamber.

Fig. 1.—Solution mixing chamber: A is the connection to the measuring condenser, B is the inlet tube for nitrogen, C is the inlet tube for the solute gases, D is the exit tube for the mixing chamber vapors, E is the inlet connection for the solvent, F is the inlet and exit tubes for nitrogen which flowed around the stirrer and G is the variable speed stirrer.

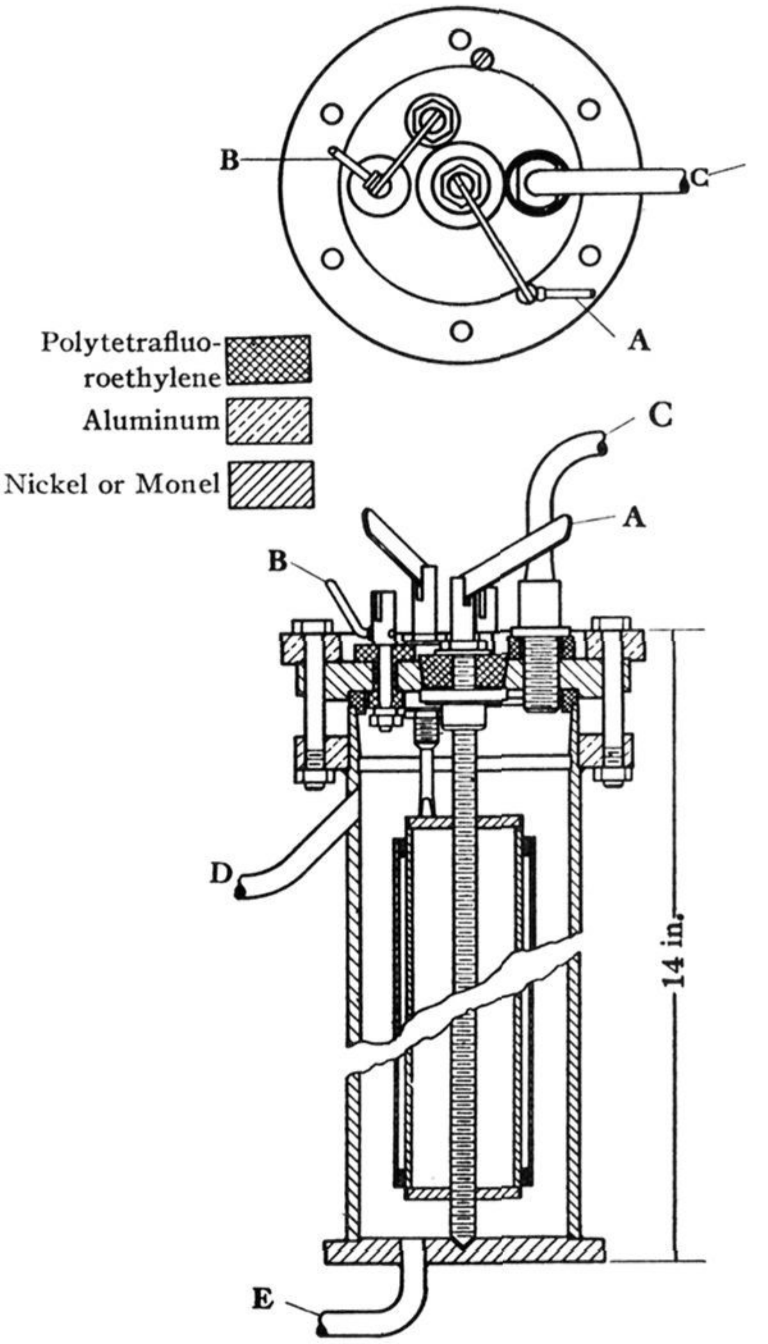


Fig. 2.—Dielectric measuring condenser: A is the ground potential lead, B is the high potential lead, C is the inlet tube for nitrogen, D is the liquid overflow constant level tube, and E is the connection tube to the mixing chamber.

the outer one served as a container for the liquid and as support for the top. The top and bottom were formed from nickel plate. The bottom was "sweated" into proper place as determined by an undercut on the inside of the outside pipe. A gas-tight joint was made between the top and the outside pipe by means of compression of a polytetrafluoroethylene gasket. The middle cylinder was connected so that it could be placed either at high or ground potential by means of a switch on the top. This connection was insulated from the top by means of polytetrafluoroethylene. The middle cylinder was rigidly spaced and insulated from the innermost cylinder (which was always at ground potential) by four small pieces of polytetrafluoroethylene, two pieces being placed at each end of the cylinder assembly. The plastic pieces were put into place between the cylinders while the middle cylinder was sprung out of shape. On relieving the pressure on the middle cylinder, the plastic pieces were clamped quite securely between the two cylinders. Where necessary leads through the top were insulated by means of the polytetrafluoroethylene.

The capacitance change in air when the middle cylinder was switched from ground to high potential was approximately 150 mmf. The condenser was calibrated by the use of air and benzene using Hartshorn and Oliver's value[5] for the dielectric constant of benzene. The liquid capacity of the cell was approximately 800 ml.

The density of the hydrogen fluoride solutions was determined by means of a monel metal pycnometer consisting of a tube equipped with a ground tapered plug at each end. A small hole in one of the ground plugs allowed the liquid to escape and was finally closed off after temperature equilibrium was established with a small tapered monel plug. This method of density determinations would, in general, be far from satisfactory if high precision were required, but in the hydrogen fluoride series the density term contributes less than 1% to the molar polarization so that the accuracy obtained was satisfactory.

The density determinations in the hydrogen chloride and hydrogen bromide series were determined in a conventional[6] glass pycnometer of 100-ml. capacity.

The density of all concentrations for several measurements was determined to test the consistency of the $\Delta d/f_2$ ratio, where f_2 is the solute mole fraction and Δd is the difference in density between the solution and solvent. The results showed that $\Delta d/f_2$ for these systems could be considered constant.[7] Thus, in most cases, only the density of the solvent and one or two of the solutions was determined, the other densities being calculated in turn from these. Several checks of the value of $\Delta d/f$ were made between runs of the same components. All measurements were carried out at 30.0°.

Actual measurements were carried out in the usual manner for solutions except that unusual precautions were taken to see that no air entered the measuring system during the course of a determination. The concentrations of the acids were determined from aliquots delivered directly from the measuring system into excess 0.1 N alkali. It was found that in the process of filling and emptying the measuring condenser some small striations of concentration occurred in the case of solvents where the solubility of the solute was low. Therefore, four samples were withdrawn for analysis from various levels of the measuring condenser and the average of these concentrations used as the concentration value in such cases. The average deviation of a series of measurements for such cases was generally less than 2% of the mean value. These uncertainties and other random ones caused the measurements for hydrogen fluoride in carbon tetrachloride and n-heptane to spread so much that the values of the electric moment are reported only to the tenths of an electric moment unit for these solvents.

Calculations and Data

The results recorded are the following: P_2 is the molar polarization of the solute calculated from an expanded form[8] of the usual Debye expression; R is the molar refraction; μ_D is the electric moment in debyes calculated from the average (or extrapolated) value of P_2; and μ^* is the external electric moment as calculated for infinite dilution from the Onsager[9] expression for this case, namely

$$(\mu^*)^2 = \frac{E_{12} - E_1}{N_2}\frac{3kT}{4\pi} \tag{1}$$

where N_2 is the number of solute molecules/cc., E_1 is the dielectric constant of the solvent, and E_{12} is the dielectric constant of the solution. N_2 is given more explicitly by

$$N_2 = \frac{f_2 d_{12} N_A}{(1 - f_2)M_1 + f_2 M_2} \tag{2}$$

The subscript 12 refers to the solution, 1 to the solvent, and 2 to the solute. M is the molecular weight, and N_A is Avogadro's number. The other terms of this expression have their usual meaning. In writing the above expression for $(\mu^*)^2$ the assumption has been made that there is no difference between the square of the refractive index of the solvent, n_1^2, and the dielectric constant of the solvent, E_1.

In the usual case of "so-called" non-polar solvents this assumption would be well taken, but it happens that for dioxane there is a rather large difference (*i. e.*, 0.23 at 30.0°) between the square of the refractive index n_1^2, for sodium light and the dielectric constant. It is recognized that the n_1 of Onsager's expression has reference to the value for the electron and atomic polarizability in a static field but this value is not available and rather than use a dubious extrapolation for n, it was felt that E_1 should be used.[10] μ_0 is the permanent electric moment as calculated from μ^* using the expression

$$\mu_0 = \frac{(2E_1 + n_2^2)}{E_1(n_2^2 + 2)}\mu^* \tag{3}$$

There was some question as to the value of n_2^2 proper to the calculation. It is of course possible to calculate a value of n_2^2 from the molar refraction expression using a value of the density obtained from the density equation for the liquid state. For present purposes this expedient has been followed but it is recognized that the values obtained are truly approximate since the density functions used[11] have been extrapolated considerably beyond their indicated limits of validity.

Results

The results of the measurements at 30.0° are summarized in Table I, and detailed data for the halides are shown graphically in Figs. 3, 4 and 5.

TABLE I

Solute	R_D (cc.)	n_D^2	P_2 (cc.)	μ_D	Solvent	μ^*	μ_0
HF	2.1	1.329	(84)	2.0	CCl_4	2.8	2.2
			(99)	2.2	n-C_7H_{14}	2.8	2.3
			76.7	1.91	C_4H_4	2.63	2.04
			114.1	2.34	1–4$C_4H_8O_2$	3.32	2.60
HCl	7.1	1.577	29.8	1.06	CCl_4	1.48	1.12
			36.1	1.19	n-C_7H_{16}	1.55	1.23
			38.7	1.25	C_6H_6	1.62	1.22
			98.9	2.12	1–4$C_4H_8O_2$	2.92	2.21
HBr	10.0	1.566	27.8	0.93	CCl_4	1.23	0.93
			31.2	1.02	n-C_7H_{16}	1.27	1.00
			33.6	1.08	C_6H_6	1.43	1.08
			176	2.85	1–4$C_4H_8O_2$	4.05	3.07
H_2O	3.7	1.775	78.5	1.89	1–4$C_4H_8O_2$	2.64	1.96

Discussion

The results as summarized in Table I are recapitulated in Table II in terms of the difference between μ_D and the gas values as available in the literature[12]; *viz.* HF = 1.91D, HCl = 1.03D, HBr = 0.78D and H_2O = 1.84D.

TABLE II

	CCl_4	n-C_7H_{16}	C_6H_6	1,4-$C_4H_8O_2$
HF	0.1	0.3	0.00	0.43
HCl	.03	.16	.22	1.09
HBr	.15	.24	.30	2.07
H_2O				0.05

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(6) Connell, Vosburgh and Butler, *J. Chem. Soc.*, 933 (1933).

(7) If one takes $V_{12} = f_1V_1 + f_2V_2$ where V is the molar volume and 1 refers to solvent, 2 to solute and 12 to the solution, it can be readily shown that $\Delta d/f_2$ is given by $M_2(d_2 - d_1)d_1/(M_2d_1 + M_1d_2(1 - f_2))$ where M is the molecular weight. Since generally $f_2 \ll 1$ it is consistent with the assumption of additive molar volumes that $\Delta d/f_2$ should be independent of f_2 as long as the solutions are sufficiently dilute.

(8) Brooks and Hobbs, THIS JOURNAL, **62**, 2851 (1940).

(9) L. Onsager, *ibid.*, **58**, 1486 (1936).

(10) It may be remarked that dioxane in the gas state [see Schwingel and Greene, *ibid.*, **56**, 653 (1934)] has no permanent moment.

(11) For HF, Simons and Bouknight, *ibid.*, **54**, 129 (1932); for HCl and HBr, "Int. Crit. Tables," Vol. III, p. 22.

(12) C. T. Zahn, *Phys. Rev.*, **24**, 400 (1924), for HCl and HBr; ref. (3) for HF; R. Sanger, *Physik. Z.*, **31**, 306 (1930), for H_2O.

The results in Table II show quite clearly the very significant positive solvent effect for the halides and in the case of dioxane the effect is so large that it may indicate "incipient" ionization.

We may infer that since the acid strength of H_2O is so much lower than the halides its bond moment is only slightly affected by the presumed coördination of the dioxane oxygen and hydrogen of the water. It may be remarked that in general the effects observed appear to be free from serious association effects since the graph of polarization against mole fraction as shown in Figs. 3, 4 and 5 shows trends only in a few cases, and in these the trend is not particularly large.

It should be noted in Table I that the lack of agreement between the μ_D values and corresponding μ_0 is not serious. This is rather important in that the same direction of solvent effect is shown by calculation using either the Debye of Onsager formulation. Furthermore, our data as are shown in Figs. 4 and 5 agree rather well with those of Fairbrother's, and the moment for hydrogen chloride in benzene of 1.25 debyes is to be compared with the value 1.21 debyes found in the same solvent by Mizushima,[13] *et al.*

In considering the results in more detail it appears that, if one excludes the dioxane solutions the observed solvent effects may be explained on the basis of the interaction of a polarizable dipolar molecule with a polarizable solvent. The generalized effect of solvents on the values of electric moments as determined in solution has been considered in some detail by Weigle,[14] Higasi[15] and Frank.[16] For the particular case of some diatomic molecules Fairbrother[17] has given what seems to be a rather specialized treatment which depends on the interaction of the solute in its totally ionic state with the surrounding solvent. From a rather general consideration of the solvent effect as originating from a polarizable solvent and the electric moments induced in it by the dipolar solute molecule the order of the maximum solvent effect to be expected can be shown to be about ±15 to 20% of the electric moment of the polar molecule. The sign of the effect is determined mainly by the geometry of the solute molecule and the location and direction of the electric moment within it.

Review of the data of Table II in the light of this anticipated maximum solvent effect of the order of ±15 to 20% of μ_1 indicates that outside of the dioxane solutions the solvent effects observed can for the most part be accounted for by solute–solvent interactions of the type considered above. Hydrogen bromide in benzene appears to be somewhat high as is hydrogen fluoride in *n*-heptane. Hydrogen fluoride in benzene is anomalously low. As is well known hydrogen fluoride is very prone to associate, and in the case of hydrogen fluoride in *n*-heptane this may explain the apparently high though admittedly uncertain solvent

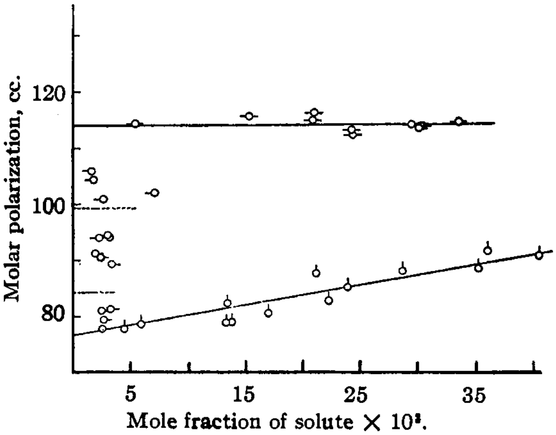

Fig. 3.—Hydrogen fluoride at 30° in: —O—, 1,4-dioxane; ȯ, benzene; -O, *n*-heptane; O-, carbon tetrachloride.

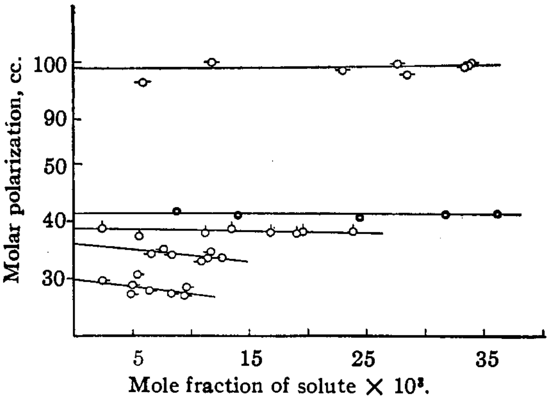

Fig. 4.—Hydrogen chloride in: -O-, 1,4-dioxane at 30°; -O, *n*-heptane at 30°; ȯ, benzene at 30°; O-, carbon tetrachloride at 30°; ◎, benzene (Fairbrother) at 20°.

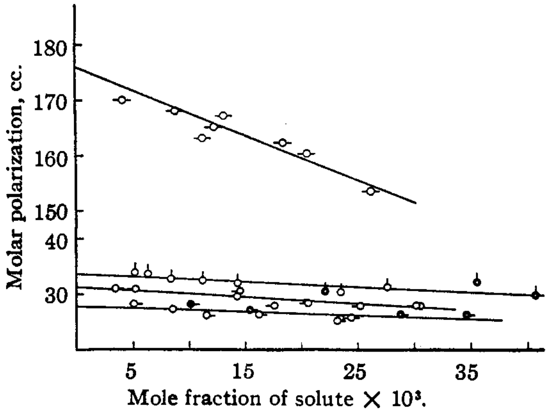

Fig. 5.—Hydrogen bromide in: -O-, 1,4-dioxane at 30°; ȯ, benzene at 30°; -O, *n*-heptane at 30°; O-, carbon tetrachloride at 30°; ◎, benzene (Fairbrother) at 20°; ◎-, carbon tetrachloride (Fairbrother) at 20°.

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[13] Mizushima, Suenaga and Kozima, *Bull. Chem. Soc. Jap.*, **10**, 167 (1935).

[14] J. Weigle, *Helv. Phys. Acta*, **6**, 681 (1933).

[15] K. Higasi, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **14**, 146 (1935).

[16] F. C. Frank, *Proc. Roy. Soc. (London)*, **A152**, 171 (1935).

[17] F. Fairbrother, *Trans. Faraday Soc.*, **33**, 1507 (1937).

effect shown in Table II. In benzene the calculated molar polarization of hydrogen fluoride rises with increasing concentration. This suggests an increasing tendency toward an end to end type association of the hydrogen fluoride as the concentration increases. Buswell,[18] *et al.*, have by means of infrared absorption measurements concluded that dilute solutions (<0.002 mole fraction) of hydrogen fluoride in carbon tetrachloride show very little association of the hydrogen fluoride. Although our data on hydrogen fluoride in carbon tetrachloride are somewhat uncertain it does appear that end to end association in this solvent at the concentration used was not unduly serious. However, in the case of benzene considerably higher concentrations of hydrogen fluoride were reached than was the case with carbon tetrachloride, and if such end to end association did occur at the high concentrations the extrapolation of the polarization curve to the zero concentration axis might well give a value of $P_2{}^\infty$ which was lower than the actual value of the molar polarization of the single molecule of hydrogen fluoride in benzene. With the apparatus and technique used in the measurements values of molar polarization obtained for f_2 values less than 0.005 were for the solutes used too uncertain to warrant detailed investigation of the hydrogen fluoride–benzene system below this value of concentration.

As previously noted the solutions of the halides in dioxane exhibit, as may have been expected, a somewhat different order of solvent effect than was encountered with the other solvents. The oxygen of the ether linkage can presumably bind the hydrogen of the halides by means of a hydrogen bond and because all of these solutes are relatively strong acids in even mildly basic solvents one might expect a sensible change in the apparent ionic character of the solute molecules. Considerable infrared[19] and raman[20] spectroscopic work on these types of solutions has given evidence of a significant change in the hydrogen halide vibration characteristics when the halides form hydrogen bonds with oxygenated or other acceptor type solvents. For the case of the hydroxyl group, rather than the halides, Badger[21] has attempted to show a rather simple relation between the heat of formation of the hydrogen bond and the shift in frequency that occurs in the second harmonic of the OH stretching vibration. Gordy and Martin[22] have shown that for oxygenated solvents the maximum shift of the hydrogen chloride bond occurs in ether type solvents and that, in particular, dioxane causes the hydrogen chloride band that appears at 3.49 μ in benzene solution to shift to 4.05 μ in a 1.1 molar dioxane solution. The presumption is that both hydrogen fluoride and hydrogen bromide would, in dioxane solutions, show similar shifts of major magnitude in their characteristic frequency. To the knowledge of the authors no spectroscopic data is available for these two solutes in dioxane.

Gordy and Stanford[23] have observed a most interesting relation between the magnitude of band shifts for a particular solute in several solvents and the logarithm of the basicity constant[24] of the solvents. It is found that these two quantities are almost linearly related for about twenty observed cases, when the solutes used were D_2O and CH_3OD and the frequency shift observed was for the OD bond in these substances. One might infer that for a given basic solvent and several acids the relative shift for the acids might be in order of the increasing acid strength. In the case of water, hydrogen fluoride, hydrogen chloride and hydrogen bromide the dielectric evidence as will be noted later seems to show some parallelism of apparent shift in electric moment and the acid strength. Spectroscopic data on this series in dioxane is not at present available; therefore, the inference above regarding the frequency shifts cannot be checked.

The fact[22] that hydrogen chloride in dioxane shows absorption bands in a region that can be ascribed to the perturbed hydrogen chloride molecule is good evidence that the solute has not gone over into an ion-pair system in the dioxane. Gemant[25] has recently investigated by potentiometric methods hydrogen chloride in dioxane that was slightly diluted with water (solution of lowest dielectric constant, $E = 2.85$). In this investigation he calculated a dissociation constant, K, of 10^{-14} when $E = 2.85$. There is little reason to suppose that the conductivity or hydrogen ion concentration in these solutions was due to dioxane and hydrogen chloride since it would appear reasonably certain that water would be the ionizing agent as well as dissociating agent in a solution that consisted of a mixture of dioxane and water. The solvation by water of the negative chloride might aid materially in effecting actual dissociation of the hydrogen chloride; in anhydrous dioxane hydrogen chloride solution there would seem to be no reasonable method of achieving solvation effects of sufficient magnitude to energetically favor the existence of dissociated chloride ions in the solution.

The spectroscopic and potentiometric evidence may be taken to at least indicate the absence of serious amounts of ionization or dissociation in the hydrogen–dioxane solutions. This being the case one may tentatively conclude that the large solvent effect calculated for this solution has its origins in an incipient hydronium formation between the HCl and dioxane and that possibly this complex is

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(18) Buswell, Maycock and Rodebush, *J. Chem. Phys.*, **8**, 362 (1940).

(19) D. Williams, *Phys. Rev.*, **50**, 719 (1936); West and Edwards, *J. Chem. Phys.*, **5**, 15 (1937); Buswell, Rodebush and Roy, THIS JOURNAL, **60**, 2528 (1938); W. Gordy, *J. Chem. Phys.*, **9**, 215 (1941).

(20) West and Arthur, *ibid.*, **5**, 10 (1937).

(21) R. M. Badger, *ibid.*, **8**, 288 (1940).

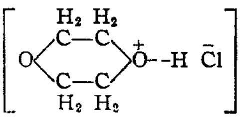
(22) Gordy and Martin, *ibid.*, **7**, 999 (1939).

(23) Gordy and Stanford, *ibid.*, **9**, 204 (1941).

(24) L. P. Hammett, "Physical Organic Chemistry," 1st ed., McGraw-Hill Book Co.,New York, N. Y., 1940, p. 222.

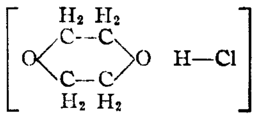
(25) A. Gemant, *J. Chem. Phys.*, **12**, 79 (1944).

stabilized by both ionic and exchange forces. One may imagine exchange forces playing a significant part by considering that such structures as



I

make significant contributions to the ground state of the complex. It is presumed that in this case the most stable contributing structure would be



II

where this bond between the H and Cl is the HCl bond with its usual partial ionic character but in a slightly perturbed state because of the nearness[26] of the ether oxygen with its slightly negative charge. It does not seem unreasonable to suggest that in the case of hydrogen fluoride and dioxane one might expect, because of the great ionic character and bond energy of the HF bond and of the lower acid strength of this molecule, that this complex might partake more of the structure shown as II than that shown by I. Hydrogen bromide in dioxane might be expected to favor structure I even more than does hydrogen chloride. Water on which data was also obtained in dioxane might be expected to favor structure II practically altogether since the acid strength of this substance is very small compared to any of the hydrogen halides. It may be remarked that substances similar to water such as alcohols, weak hydroxy acids, etc., might also favor structure II, and as such one might anticipate only small effects on the apparent electric moment of such substances because of the complex formation. The latter statement is somewhat borne out by measurements made in dioxane on a number of weak organic acids[8,27] and by our data and those of Linton and Maass[28] on water.

In an effort to depict more clearly the relative effects of the complex formation in dioxane solution on the electric moment, data are presented in Table III in the form of calculated ionic character of the respective bonds, it being assumed[29] that the ionic character of the single bonds is given by μ/er where μ is the observed dipole moment in debyes, e is the electronic charge × 10^{10} *e. s. u.* and r is the internuclear separation in Å. The column under $\Delta\mu/er$ is carried only to the tenths place as the entire procedure of calculation is predicated on the approximation that r stays constant and that the ionicity of the bond is calculable from the measured value of the moment in dioxane solution. This method neglects normal solvent effects and many other recognizable but rather indeterminable compromising effects so that the values under the $\Delta\mu/er$ column should be regarded as indicative of rather than a quantitative measure of the effects involved. In spite of the necessarily approximate methods used, the data of Table III appear to bear out in some detail the arguments advanced in the previous paragraphs. In view of this it seems reasonable to suggest that the electric moment evidence points toward intermediate structures in hydronium formation and that such structures are probably not representable simply by dipole or charge interactions such as is usually considered to be the case for hydrogen bonds. More probably these structures are hybrids which have contributing structures which lie intermediate between true ion pairs and totally separated molecules.

TABLE III

		Gas			Dioxane	
	r	μ	μ/er	μ	μ/er	$\Delta\mu/er$
HF	0.92	1.91	0.43	2.34	0.53	0.1
HCl	1.28	1.03	.17	2.12	.35	.2
HBr	1.42	0.79	.12	2.85	.42	.3
HO(H_2O)	0.96	1.51	.33	1.55	.34	.0

Summary

The electric moments of hydrogen fluoride, hydrogen chloride and hydrogen bromide have been determined in several non-polar solvents. The moment values of the halides each show definite positive solvent effects in agreement with some previous work along these lines. The moment of hydrogen fluoride in solution has been determined for the first time and it may be concluded from the present measurements that the probable value of the electric moment of hydrogen fluoride is between 1.9 and 2.0 debyes. With these data values of the partial ionic character of the hydrogen fluoride bond can be closely approximated. The agreement of the benzene solution value of hydrogen fluoride with the gas value is regarded as coincidence.

The values of the electric moments of hydrogen halides in dioxane solution seem to point toward an incipient ionization of these solutes in this solvent. This concept is considered briefly.

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[26] We would suggest a distance less than the sum of the van der Waals radius of the oxygen and chlorine atom.

[27] Wilson and Wenzke, *J. Chem. Phys.*, **2**, 546 (1934).

[28] Linton and Maass, *Can. J. Research*, **7**, 81 (1932).

[29] L. Pauling, "The Nature of the Chemical Bond," 1st ed., Cornell University Press, Ithaca, N. Y., 1939, p. 69.