Methylamine and dimethylamine are the analogs of methyl alcohol which, moreover, they resemble in many of their chemical and physical properties. Trimethylamine is formally, as well as in its general behavior, an ammono methyl ether. Methylenediamine like methylene glycol, and ortho-ammonoformic acid like ortho-aquoformic acid are known only in the form of their alkyl derivatives. The ammonia analog of orthocarbonic acid is not known either in the free state or in the form of its esters.

Methylene-imine is a representative of a class of substances unknown in the water system. Formally, it is a mixed alcohol aldehyde (or acid aldehyde) of the ammonia system. It is not known in the free state. Alkyl and especially aryl derivatives have been prepared in large numbers and are known as Schiff's bases which possess conspicuous aldehydic properties. Nor has monomolecular ammonoformaldehyde been prepared. When aquoformaldehyde is ammonolyzed to ammonoformaldehyde the latter immediately polymerizes to hexamethylenetetramine which is a dimeric modification of ammonoformaldehyde. Formamidine is an ammonoformic acid. Hydrocyanic acid shows the properties simultaneously of an acid anammonide, of an ammono aldehyde and of an ammonocarbonous acid. The compounds represented by the formulas given in the last column have already been discussed.

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THE ELECTRIC MOMENTS OF TYPICAL ORGANIC MOLECULES

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The electric moment of a molecule is a fundamental property dependent upon the arrangement of the electric charges within the molecule.[1] If we adopt the view that the average position of an electron in an orbit may be treated as the actual position of the electron in the molecule of which it is a part, it becomes possible to calculate the location of the centers of gravity of the electrons and of the positive charges in the molecule in much the same way that the center of gravity of a system of rigid bodies is located. When these two centers of gravity do not coincide, the molecule may be regarded as containing an electric doublet the moment of which is equal to the product of the distance between the two centers of gravity and the total electric charge of either sign in the molecule. The method of calculation has been explained in a recent paper.[2]

[1] Compare Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Company, **1923**, p. 56.

[2] Smyth, *Phil. Mag.*, **47**, 530 (1924).

A method has been described[3] in which the Gans theory[4] of dielectric media is applied to the calculation of the electric moment of the molecule of a substance by means of the following equations,

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{D} = C + \frac{4}{3}\sqrt{\frac{s^3\,\mathrm{N}_0}{M\,D} - \frac{3\,C^2}{2\pi}}\,\psi(\tau) \tag{1}$$

in which ϵ is the dielectric constant, D is the density, s is the molecular diameter, N_0 is Avogadro's number, 6.061×10^{23}, M is the molecular weight, and C is a constant characteristic of the substance, calculable from the dispersion curve for the visible region of the spectrum by means of the following equation,

$$C = \left(1 - \frac{\lambda_0^2}{\lambda^2}\right)\left(\frac{m^2 - 1}{m^2 + 2}\frac{1}{D}\right) \tag{2}$$

in which m is the index of refraction for light of wave length λ, and λ_0 is the wave length corresponding to a characteristic vibration frequency in the ultraviolet region. Knowledge of the quantities enumerated makes possible the calculation of the value of the function $\psi(\tau)$, from which the corresponding value of τ is obtained by a graphical representation of the relation between τ and $\psi(\tau)$ given by the theory of Gans. The moment μ is then obtained from the equation,

$$\mu = \sqrt{\frac{3\,R\,T}{4\,\mathrm{N}_0\,\tau}\sqrt{\frac{s^3\,M}{\pi\,\mathrm{N}_0\,D} - \frac{3\,M^2\,C^2}{2\,\pi^2\,\mathrm{N}_0^2}}} \tag{3}$$

in which R is the universal gas constant, 8.315×10^7, and T is the absolute temperature.

The values necessary for these calculations are obtainable by direct experiment, with the exception of s, which Gans defines as the smallest distance by which the centers of any two molecules can be separated. This may be calculated without serious error from the value of the constant b in van der Waals' equation. The values of s used in the present work have been obtained in this way, and when b had not been determined for a substance, it was calculated as an additive property with due regard for constitutive influences, the results being checked in relation to one another by comparison with the molecular volumes given by Le Bas.[5] The assignment of one value of s to a molecule of irregular shape is, at best, an approximation, but it has been shown that a large error in the value of s ordinarily introduces only a small error in the result obtained for μ, which justifies this method. In a few cases, it has been necessary to obtain the index of refraction from the molecular refraction calculated as an additive property. It has also been shown that molecular association in a liquid causes the value calculated for μ to be too low, but as the association de-

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[3] Smyth, *Phil. Mag.*, **45**, 849 (1923).

[4] Gans, *Ann. Physik*, **64**, 481 (1921).

[5] Le Bas, "The Molecular Volumes of Liquid Chemical Compounds," Longmans, Green and Co., **1915**.

creases with increasing temperature the calculated value of μ increases, being generally close to the true value in the neighborhood of the boiling point. Increasing temperature frequently causes a slight increase in the apparent value of μ for liquids supposed to be unassociated, the effect being small.

In the determination of the position of the center of gravity of the electrons in a molecule, it is assumed that the center of gravity of the inner electrons of each atom is located in the nucleus of the atom and is never displaced by external forces, and it has seemed best, for reasons which have been previously discussed by the writer,[2] to assume tetrahedral arrangements of the electron pairs in the outermost atomic shells.

The symmetry of many molecules is obvious without any calculation. The hydrogen and methane molecules might be expected to have no electric moments. From the temperature dependence of the dielectric constants of these gases Riegger[6] has calculated the moment of the hydrogen molecule to be less than 0.043×10^{-18} and that of the methane molecule to be less than 0.048×10^{-18}. Calculation shows that if the structure of the methyl group may be regarded as that of a regular tetrahedron it should be possible to substitute it for a hydrogen atom without altering the moment of the molecule, provided that the hydrogen nuclei in the methyl group are at the same distance from their bonding electron pairs as was the replaced hydrogen nucleus from its bonding pair. As no appreciable change of moment occurs in going from the hydrogen to the methane molecule, it will be interesting to see how the replacement of a hydrogen by a methyl group affects the moments of higher hydrocarbon molecules.

Table I

Electric Moments of the Hydrocarbons

		$\mu \times 10^{18}$			$\mu \times 10^{18}$
Methane[6]	CH_4	<0.048	Benzene[7,8]	C_6H_6	0.20
Hexane[7]	C_6H_{14}	.0	Toluene[7]	$C_6H_5CH_3$	.40
Octane[7]	C_8H_{18}	.0	Ethylbenzene[7]	$C_6H_5C_2H_5$	.46
Decane[7]	$C_{10}H_{22}$	.0	*n*-Propylbenzene[7]	$C_6H_5CH_2C_2H_5$	.43
Amylene[7]	C_5H_{10}	.49	*iso*Propylbenzene[7]	$C_6H_5CH(CH_3)_2$	.46
Hexylene[7]	C_6H_{12}	.28	*iso*Butylbenzene[7]	$C_6H_5CH_2CH(CH_3)_2$	.44
Octylene[7]	C_8H_{16}	.50	*o*-Xylene[7]	$C_6H_4(CH_3)_2(1:2)$	.58
Decylene[7]	$C_{10}H_{20}$	.55	*m*-Xylene[9]	$C_6H_4(CH_3)_2(1:3)$	.46
			p-Xylene[7]	$C_6H_4(CH_3)_2(1:4)$	.23
			Cymene[7]	$CH_3C_6H_4CH(CH_3)_2(1:4)$	.29
			Mesitylene[7]	$C_6H_3(CH_3)_3(1:3:5)$	.36
			Pseudocumene[7]	$C_6H_3(CH_3)_3(1:2:4)$	.45

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[6] Riegger, *Ann. Physik,* **59**, 753(1919).

[7] Landolt and Jahn, *Z. physik. Chem.,* **10**, 289 (1892).

[8] Graffunder, *Ann. Physik,* **70**, 225 (1923).

[9] Isnardi, *Z. Physik,* **9**, 153 (1922).

In Table I are given the values of the moment, μ, calculated for a number of hydrocarbons by means of Equations 1, 2 and 3. The number attached to the name of each substance refers to the paper from which the value of the dielectric constant was taken for the calculation of the moment.

Hexane, octane, and decane show values of $\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{D}$ so close to those of C that their electric moments may be regarded as practically zero. It appears that the double bond in amylene, hexylene, octylene and decylene causes a slight decrease in the symmetry of the electronic structure so that these molecules have small moments. The value for hexylene is the mean of the results calculated from measurements upon two different samples, which showed only fair agreement. The structure of the benzene molecule is so symmetrical that a moment close to zero might be expected. Some of the measurements of its dielectric constant indicate a value of zero for the moment, while others give a value slightly larger than that of 0.25×10^{-18} calculated from Graffunder's measurements; in any event, the moment of benzene is very small. It is evident that, when a hydrogen atom in benzene is replaced by a methyl group, the conditions for the equivalence of a methyl radical to a hydrogen are not precisely fulfilled, for a small moment appears in the toluene molecule. However, when a hydrogen of this attached methyl group is replaced by another methyl group to form ethylbenzene and further replacements are made to form propyl-, *iso*propyl-, and *iso*butylbenzene, little change is produced in the electric moment, the small differences observed being within the limit of experimental error. When two of the benzene hydrogens are replaced by methyl groups, two small electric doublets are formed in the molecule. When these doublets reinforce each other as in *o*-xylene, the resultant moment of the molecule is appreciably larger than that of the toluene molecule. In *m*-xylene the axes of the two doublets appear to make a greater angle with each other, so that the moment differs little from that of toluene; but in the symmetrical molecule of *p*-xylene, the two doublets oppose each other so that the resultant moment of the molecule is as small as that of benzene. The molecule of cymene which should contain the same doublets opposing each other as in *p*-xylene has a moment only a trifle higher, the difference arising possibly from experimental error or possibly from the effect of induction upon the carbon chain to be discussed later. Mesitylene has a slightly higher moment and the less symmetrical molecule of pseudocumene has a moment a little larger. Although the moments of the molecules which have been considered are small and the differences in their values arising from actual differences in structure are not much greater than those arising from experimental error, it is indicated that the molecular moment is not directly affected by the replacement of a hydrogen by a methyl group and that an unsaturated bond may cause a slight lack of symmetry in the electronic system in its neighborhood.

The values of the moment calculated for water and the lower alcohols at ordinary temperatures are low because of association but, since many of these substances have been investigated at higher temperatures as well, and a few even in the vapor state, it is possible to obtain their moments with some degree of accuracy. Water, for example, gives an apparent value for the moment of only 0.99×10^{-18} at 4° and of 1.04×10^{-18} at 30°,[10] while its vapor, between 117.4° and 178.4°, shows a relatively constant value of 1.98×10^{-18}, which is presumably the true value of the moment. This is slightly higher than the value 1.87×10^{-18} calculated by Jona[11] by a different method. For methyl alcohol the apparent value of μ increases steadily from 1.62×10^{-18} at 0° to 1.85×10^{-18} at the boiling point and, as this value agrees well with the relatively constant results obtained for the vapor, it is regarded as the true value of the moment. *n*-Butyl and amyl alcohols show little change in the value of μ with temperature, indicating a practically negligible effect due to associa-

Table II

Electric Moments of the Alcohols, Ethers and Analogous Sulfur Compounds

		$\mu \times 10^{18}$			$\mu \times 10^{18}$
Water[11]	HOH	1.98			
ALCOHOLS			ETHERS		
Methyl[11,12]	CH_3OH	1.78	Methyl[15]	$(CH_3)_2O$	1.37
Ethyl[12,13,14,15]	C_2H_5OH	1.85	Ethyl[14,9]	$(C_2H_5)_2O$	1.37
Propyl[14]	C_3H_7OH	1.98	Amyl[17]	$(C_5H_{11})_2O$	1.22+
Butyl[14,16]	C_4H_9OH	2.06	Anisole[13]	$C_6H_5OCH_3$	1.14
*iso*Butyl[12,7]	$(CH_3)_2CHCH_2OH$	2.07	Cresol methyl[13]	$CH_3C_6H_4OCH_3$	1.00
*sec.*Butyl[16]	$CH_3CHOHC_2H_5$	1.95			
*tert.*Butyl[16]	$(CH_3)_3COH$	1.84	SULFUR COMPOUNDS		
Amyl[12,10]	$C_5H_{11}OH$	2.15	Hydrogen sulfide[19]	H_2S	1.02
*iso*Amyl[14]	$(CH_3)_2CH(CH_2)_2OH$	2.10	Ethyl mercaptan[20]	C_2H_5SH	1.42
Allyl[17,18]	$CH_2{:}CHCH_2OH$	1.71+	Dimethyl sulfide[13]	$(CH_3)_2S$	1.27
Benzyl[13,16]	$C_6H_5CH_2OH$	1.74	Diethyl sulfide[20]	$(C_2H_5)_2S$	1.58
Glycol[13]	$CH_2OH.CH_2OH$	1.67+			
Glycerol[8]	$CH_2OH.CHOH.CH_2OH$	2.20+			

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[10] Ratz, *Z. physik. Chem.*, **19**, 94 (1896).

[11] Jona, *Physik. Z.*, **20**, 14 (1919).

[12] Abegg and Seitz, *Z. physik. Chem.*, **29**, 242 (1899).

[13] Walden, *ibid.*, **70**, 569 (1910).

[14] Grimm and Patrick, THIS JOURNAL, **45**, 2794 (1923).

[15] Bädeker, *Z. physik. Chem.*, **36**, 304 (1901).

[16] Löwe, *Wied. Ann.*, **66**, 390 (1898).

[17] Drude, *Z. physik. Chem.*, **23**, 267 (1897).

[18] Thwing, *ibid.*, **14**, 286 (1894).

[19] Eversheim, *Ann. Physik*, **13**, 507 (1904).

[20] Augustin, *Dissertation*, Leipzig, **1898**.

tion. The results given are those which may be regarded as nearest to the true values, and those which are almost certainly too low are marked with a plus sign. The values for methyl, amyl and cresol methyl ethers and for ethyl mercaptan, dimethyl sulfide and diethyl sulfide are based upon more limited data than are those calculated for the other substances which, with the exception of those marked with a plus sign, are known with an accuracy of approximately ± 0.1×10^{-18}, although their accuracy relative to one another is somewhat greater.

A water molecule may be represented by the structure shown in Fig. 1, in which the oxygen nucleus is located at N, the two inner electrons not being shown, the average positions of the four electron pairs in the outer shell are represented by small circles at the corners of a regular tetrahedron, the edges of which are not shown, and the hydrogen nuclei are shown at A and C. MN is the projection of AN or CN upon the line bisecting the angle ANC. If there were no distortion of the symmetrical structure, the center of gravity of the electrons would lie at N, where all but two of their charges would be neutralized by the charge of the nucleus, and the center of gravity of the two remaining positive charges would lie at M, so that the moment of the molecule would be $2e \times$ MN, or $1.155ep$, where e is the electronic charge, and p equals AN = CN. If $p = 1.0 \times 10^{-18}$ cm., as calculated by Eucken[21] from the ultra-red absorption spectrum, the value of the moment should be 5.51×10^{-18}, while the value calculated from the dielectric constant is 1.98×10^{-18}. As has been shown by the writer in a previous paper, the difference is due largely to the attraction of the electrons by the hydrogen nuclei, which displaces the center of gravity of the electrons from N toward M. Another factor, however, may contribute to the discrepancy. Mutual repulsion of the positive charges will tend to force the hydrogen nuclei farther apart, not merely along the line AC but, because of the forces binding the nuclei, from Positions A and C to, let us say, A′ and C′, thus displacing the center of gravity of the positive

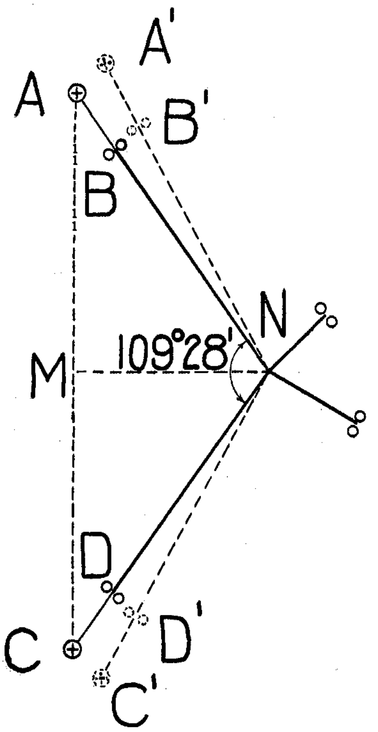

Fig. 1.—The structure of the water molecule.

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[21] Eucken, *Jahrb. Radioakt. Electronik*, **16**, 408 (1919–20).

charges along MN toward N. If the two pairs of electrons which bind these nuclei remain at B and D, the center of gravity of the electrons remains at N, toward which the positive center of gravity has shifted, thus decreasing the moment of the molecule. If, however, the two pairs of binding electrons follow the nuclei and shift from B and D to B′ and D′, the shift of four electrons displaces the negative center of gravity from N toward the right by a distance considerably greater than the shift of the positive center unless A′B′ and C′D′ were to approach B′N and D′N in length, which is improbable, so that the electric moment increases. If the binding electrons are held by strong forces in the molecule and thus lack mobility, they will shift little from the positions B and D but, if they are easily displaceable, they will tend to follow the nuclei in their displacements and occupy the positions B′ and D′. Thus, the effect of this repulsion upon the moment of the molecule will depend upon the amount of the repulsion and the mobility of the binding electrons.

The effect of repulsion in the water molecule is probably small but if the hydrogen nuclei are replaced by bulky groups, the repulsion is greater. Methyl alcohol has a moment smaller than that of water and methyl ether has one smaller than that of the alcohol, because of the mutual repulsion of the methyl groups. Increase in the bulk of these groups near their points of attachment to the oxygen increases the amount of the repulsion, but the effect upon the repulsion of mere lengthening of the chain is subordinate to other factors. It appears that the displacement of the electron pairs binding these groups to the oxygen must be small, since the repulsion decreases the moment. The writer[22] has calculated the forces necessary to displace an electron through unit distance in the following molecules.

Substance	Water	Ammonia	Methane	Hydrogen sulfide
Dynes × 10^{-6}	1.24	0.84	0.71	0.51

These figures indicate the order of magnitude of the mobilities of the electrons in the molecules. The electrons binding the attached groups to the nitrogen in ammonia and the amines are much more easily displaced than those binding the attached groups to the oxygen in the water, alcohol and ether molecules, and this is evidenced by the smallness of the decrease in moment produced by the repulsion of the attached groups in the amines. The electrons binding groups to the carbon atom are somewhat more mobile as indicated by the figure for methane, which agrees well with the data for the higher hydrocarbons. Consequently, in the aldehydes and ketones, where the mutually repelling groups are attached to the carbonyl carbon by electron pairs under restraints not very different from those in the methane molecule, the electrons shift sufficiently to nearly balance the shift of the positive charges, so that repulsion has little effect

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[22] Ref. 2, p. 534.

upon the moments of these molecules. The ease of displacement of the electrons binding groups to the sulfur atom prevents decrease in the moment because of the mutual repulsion of these groups, and may even cause increase in the moment of the molecule.

In considering the dielectric constants of methyl, ethyl and propyl alcohols, J. J. Thomson[23] has pointed out that the intense electric field due to the principal moment of the molecule might be expected to give rise by induction on the rest of the molecule to moments of the same sign as the original moment, thus increasing the moment of the molecule as a whole. The increase in the moment of the molecule due to the production of these small moments would be greater, the greater the length of the carbon chain, as indicated by the experimental results shown in Table II. It would be interesting to study this effect through a long series of carbon chains but, unfortunately, the few data upon the dielectric constants of alcohols higher than amyl have been determined at frequencies so high as to render them useless for these calculations. The decrease in moment on passing from *n*-butyl and *iso*butyl alcohol to the secondary and then to the tertiary alcohol is the result to be expected from the increase in the bulk of the carbon chain in the neighborhood of the hydroxyl hydrogen, which should be repelled more and more as this bulk increases. It is probable that the moment of allyl alcohol differs little from that of propyl, but, as the value obtained is low on account of association, speculation is unwise. It appears that in benzyl alcohol the bulky phenyl group is sufficiently near the hydroxyl hydrogen to cause an appreciable widening of the angle between the attached groups, which causes a decrease analogous to that occurring in the case of secondary and tertiary butyl alcohols.

In the ethers, the two carbon groups which have replaced the hydrogens of water repel each other more than do the one carbon group and the hydrogen in the alcohols, so that the moments are distinctly lower. The bulky phenyl group in anisole causes a greater widening of the angle between the attached groups than that occurring in methyl or ethyl ether so that the moment is lower, and a similar effect is evident in the case of cresol methyl ether, the orientation of which is not given in the original data used.

The moment of the hydrogen sulfide molecule is much lower than that of the water molecule because of the greater ease of displacement of its electrons but, although the moment of ethyl alcohol is lower than that of water because of the mutual repulsion of the groups attached to the oxygen, that of ethyl mercaptan is considerably larger than that of hydrogen sulfide because of the shift of the mobile binding electrons, which tends to displace the center of gravity of the negative charges farther from that of the positive charges. This electron shift prevents any decrease in moment

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[23] Thomson, *Phil. Mag.*, **46**, 497 (1923).

because of the repulsion of the attached groups and may actually increase the moment, while the presence of a carbon chain instead of a hydrogen atom gives opportunity for the induction of secondary moments so that the moment of the molecule as a whole is considerably increased. In diethyl sulfide the opportunity for the induction of secondary moments, as well as the mutual repulsion, is greater, so that the moment of the molecule is greater, while in dimethyl sulfide the smaller opportunity for the induction of secondary moments causes the moment of the molecule to be smaller. On the basis of the hypotheses which have been advanced, one would expect the moment of dimethyl sulfide to be higher than that of ethyl mercaptan, but the fact that it is lower may easily arise from errors in the very limited data from which these values were calculated.

The dielectric constants of a considerable number of aldehydes and ketones have been determined at a single temperature only, so that the moments cannot be calculated exactly because of molecular association, but the apparent values of the moments given in Table III should be roughly comparable with one another. The temperatures for which these apparent values are calculated are shown in the table but where determinations of the dielectric constant at the boiling point have made possible the calculation of values which should be close to the true moments of the molecules, these values are shown in the column next to the apparent values.

TABLE III

ELECTRIC MOMENTS OF THE ALDEHYDES AND KETONES

		t °C.	$\mu \times 10^{18}$ Apparent value	True value
Acetaldehyde[13,17]	CH_3CHO	10	1.69	..
Propionaldehyde[17]	C_2H_5CHO	17	1.81	..
Butyraldehyde[14]	C_3H_7CHO	26	1.86	..
*iso*Valeraldehyde[17]	$(CH_3)_2CHCH_2CHO$	17	1.86	..
Benzaldehyde[13]	C_6H_5CHO	19.5	1.88	..
Acetone[14,8]	CH_3COCH_3	17	1.93	2.08
Methylethyl ketone[17]	$CH_3COC_2H_5$	17	1.93	2.29
Diethyl ketone[17]	$C_2H_5COC_2H_5$	17	2.08	..
Methylpropyl ketone[17,20]	$CH_3COC_3H_7$	17	1.98	..
Dipropyl ketone[17]	$C_3H_7COC_3H_7$	17	2.18	..
Pinacolin[17,24]	$CH_3COC(CH_3)_3$	17	2.08	..
Methylhexyl ketone[17]	$CH_3COC_6H_{13}$	17	2.21	..
Acetophenone[13,14]	$CH_3COC_6H_5$	14	2.00	2.56
Benzophenone[13]	$C_6H_5COC_6H_5$	63	2.20	..

In considering the aldehydes and ketones, the simplest procedure is to treat them as derivatives of formaldehyde by the successive replacement of hydrogens by methyl groups. If we neglect all distortion of the molecule and assume that the outer electrons are at the same distance from the nucleus in the carbon and oxygen atoms, we may calculate the moment

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[24] Eggers, *J. Phys. Chem.*, 8, 14 (1904).

of the formaldehyde molecule as 1.155ep, where p is the distance of the hydrogen nuclei from the carbon nucleus. As this distance, on the basis of the assumptions which have been made, would be practically the same as that of the hydrogen nuclei from the oxygen nucleus in the water molecule, the moment of formaldehyde might be expected to be very close to that of water. Data for the calculation of the moment of formaldehyde are not available, and the value for acetaldehyde is low because of association, but the moment of acetone is slightly higher than that of water, probably because of the effect of induction. Comparison of the true values of the moments of acetone and methylethyl ketone with those of methyl and ethyl ether and of that of acetophenone with that of anisole shows the first named to be higher in each case, presumably because of the difference in the effect of the mutual repulsion of the attached groups, which arises from difference in the mobilities of the binding electrons.

Although a decrease in molecular association with increase in the size of the molecule would make the apparent values of the moment increase with increase in the length of the carbon chain, it appears that the increase noted is not entirely due to this effect, but results, in part, from the moments induced upon the chains as in the case of the alcohols. It is interesting to compare the moments of isomers. The apparent moment of a ketone is found to be higher than that of the aldehyde of equal carbon content. This might arise from three causes: greater molecular association of the aldehydes, difference between the mutual repulsion of the hydrogen and the carbon chain in the aldehydes and the two carbon chains in the ketones, and difference in the induced moments due to difference in the lengths of the attached groups. This last effect is fairly evident. The charges in the end carbon atom of propionaldehyde are farther away from the principal moment of the molecule than they would be if this carbon were attached directly to the carbonyl carbon to form acetone. Consequently, the induced moment arising from displacement of these charges is less in propionaldehyde than in acetone. The same argument applies to the cases of the other isomeric aldehydes and ketones, but the effect is brought out more strikingly in the case of methylpropyl ketone and diethyl ketone, which should not differ appreciably in molecular association. The end carbon of the propyl group in methylpropyl ketone is farther from the principal moment of the molecule than would be the case if it were attached to the one carbon of the other chain, as in diethyl ketone. Consequently, the moment induced upon this end carbon is less than it would be if separated by only one carbon atom from the principal moment, and the moment of the molecule as a whole is less. From an apparently similar cause, the moment of dipropyl ketone is practically as large as that of methylhexyl ketone, which contains one more carbon atom.

The approximate values for the moments of a considerable number of amines are given in Table IV, the number attached to each value referring to the paper from which the value of the dielectric constant was taken for the calculation of the moment. Most of these values are probably a little low on account of molecular association, this being indicated by the fact that the value calculated for the moment of liquid ammonia at —34° is 0.97×10^{-18} and that at 15° is 1.10×10^{-18}, while the value calculated for the gas is 1.55×10^{-18}. In the heavier amines, the effect of association is presumably small, as indicated by the fact that the apparent moment of aniline at 18° is 1.27×10^{-18}, while at 75° it has increased only to 1.35×10^{-18}. The value for methyl amine is enclosed in parentheses as the value of the dielectric constant used in its calculation is very uncertain.

TABLE IV

ELECTRIC MOMENTS OF THE AMINES

	t°C.	$\mu \times 10^{18}$
Ammonia (liquid)[25]	15	1.10+
Ammonia (gas)[15,11]	..	1.55
Methylamine[26]	21	(1.22)
Trimethylamine[26]	4	0.86
Ethylamine[26]	21	1.26
Diethylamine[26]	21	1.10
Triethylamine[26]	21	1.11
*iso*Propylamine[26]	20	1.32
Dipropylamine[26]	22	1.00
Butylamine[26]	21	1.36
*iso*Butylamine[26]	21	1.25
Di-*iso*butylamine[26]	22	0.98
Amylamine[26]	22	1.32
Aniline[27]	18	1.27
Aniline[10]	75	1.35
Methylaniline[13]	20.8	1.31
Dimethylaniline[13]	20	1.19
Ethylaniline[13]	19.8	1.43
Benzylamine[13]	20.6	1.14
Dibenzylamine[26]	20	1.15
o-Toluidine[26]	20	1.30
m-Toluidine[26]	20	1.30
1:3:4-Xylidine[26]	20	1.26

If all distortion of the molecule is neglected, it may be calculated that the moment of the ammonia molecule should be ep, where p is the distance of the hydrogen nuclei from the nitrogen nucleus. If this distance is the same as that of the hydrogen nuclei from the oxygen nucleus in the water molecule, the moment of the water molecule should be 1.155 times that of the ammonia molecule. Actually, the ratio is somewhat greater than this because the greater ease of displacement of the electrons in the ammonia molecule causes a greater decrease in moment by distortion of the symmetrical structure.

In Table IV, it is evident that the differences between individual substances due to differences in structure are frequently less than the experimental errors in the results. However, consideration of the general trend of the results shows that there is a decrease in moment on going from

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[25] Schaefer and Schlundt, *J. Phys. Chem.*, **16**, 253 (1912).

[26] Schlundt, *ibid.*, **5**, 503 (1901).

[27] Turner, *Z. physik. Chem.*, **35**, 385 (1900).

ammonia to the primary, to the secondary, and, finally, to the tertiary amines, this decrease being relatively less than in the case of the alcohols and ethers, presumably because of the greater displacement of the bonding electron pairs in the nitrogen atom. It is also apparent that the moment increases with increase in the length of the attached chains, this increase being less marked than in the case of the alcohols and ketones because the principal moment is less. These results, although less accurate than might be desired, appear to be consistent with the hypotheses previously advanced.

The moments of a larger number of halides have been calculated and assembled in Table V, in which the first column gives the formula of the halide, X representing a halogen atom, and the second, third, and fourth columns give the corresponding values of the moments when X is chlorine, bromine or iodine, respectively. The small numbers following each value refer to the papers which give the dielectric constants used in the calculation of these values. In a number of cases, the dielectric constants have been measured over a considerable range of temperature and, frequently, at temperatures at which molecular association has ceased to occur but, in any event, it appears that molecular association does not seriously lower any of the values given.

In a previous paper,[2] the writer used the value 2.15×10^{-18} reported by Falkenhagen[28] for the moment of hydrogen chloride, but this figure must now be superseded by the accurate value 1.03×10^{-18} just determined by Dr. C. T. Zahn in the Palmer Physical Laboratory of Princeton University from measurements of the dielectric constant of the gas over a wide range of temperature. This value is close to those calculated from the limited data given by Bädeker for the gas and by Schaefer and Schlundt for liquid hydrogen chloride, values which had already led the writer to the conclusion that Falkenhagen's result was incorrect. A single value calculated for each of the liquid hydrogen halides at a low temperature, but not included in Table V, was a little lower than the value obtained by Zahn for the corresponding substance, probably because of association. The value for ethyl chloride is calculated from data so uncertain as to render it without significance, that for butyl chloride is based upon data of doubtful accuracy, and that for methylene chloride is calculated from limited data upon the substance in the gaseous state. The majority of the other values should not differ by more than 0.1×10^{-18} from the true values.

One might expect the symmetrical X_2 molecule to have practically no moment, but Lewis[29] has pointed out that "even a symmetrical molecule like that of hydrogen or iodine may from time to time become polarized

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[28] Falkenhagen, *Physik. Z.*, **23**, 87 (1922).

[29] Ref. 1, p. 83.

TABLE V

ELECTRIC MOMENTS OF THE HALIDES

	$\mu \times 10^{18}$		
General formula	X = Cl	Br	I
X_2	0.13[30]	0.58[13,31]	..
HX(liquid)	1.07[31]	0.92[31]	0.64[31]
HX(gas)	1.03[32]	0.79[32]	0.36[32]
CH_3X	..	..	1.15[27,14]
C_2H_5X	(2.3)[33,30]	1.56[13,14]	1.31[17]
$CH_2{:}CH.CH_2X$	1.49[13]	1.36[13]	..
C_4H_9X	(2.3)[34]	..	1.62[14]
$C_5H_{11}X$	1.63[35]	1.56[35]	..
$(CH_3)_2CH(CH_2)_2X$	..	1.80[14]	..
$C_2H_5CX(CH_3)_2$	..	1.84[35]	..
C_6H_3X	1.42[36,14]	1.39[36]	..
$C_6H_5CH_2X$	1.46[13]	..	..
$CH_3C_6H_4X$	1.32[35]	..	..
α-$C_{10}H_7X$	..	1.26[27]	..
CH_2X_2	1.73[37]	..	0.94[27]
CH_3CHX_2	1.65[7]	..	..
CHX_3	1.25[9,15]	0.97[27]	..
CX_4	0.48[9,15]	..	..
$X_2C{:}CX_2$	0.45[26]	..	..
$CHX_2.CHX_2$	..	1.37[13]	..
$CH_2X.CH_2X$	1.55[13]	1.07[27]	..
$C_5H_{10}X_2$	..	1.48[35]	..

in one direction or the other, as a consequence of the disturbance due to thermal motion." In liquid iodine, this polarization actually extends to the ionization of a few molecules. Lewis further points out that bromine, chlorine, fluorine and hydrogen, in the order named, show a diminishing tendency toward this ionization. This then is the order of decreasing polarity, and it is interesting to note that the decreasing order of the electric moments which have been determined is bromine, chlorine, hydrogen. It is possible that the small increases in the calculated values of the moments of symmetrical molecules, such as those of benzene, chlorine and carbon tetrachloride, which accompany rise in temperature, result from polarization caused by the increased disturbance due to the greater thermal agitation.

If distortion of the molecule is neglected, the moment of hydrogen chlor-

[30] Eversheim, *Ann. Physik,* [4] **13,** 492 (1904).

[31] Schaefer and Schlundt, *J. Phys. Chem.,* **13,** 669 (1909).

[32] Value of moment communicated to the writer by Dr. C. T. Zahn.

[33] Klemenčič, *Wien. Ber.,* [2] **91,** 712 (1885); *Exner Rep.,* **21,** 571 (1885).

[34] Löwe, *Wied. Ann.,* **66,** 390 (1898).

[35] Jahn and Möller, *Z. physik. Chem.,* **13,** 385 (1894).

[36] Lertes, *Z. Physik,* **6,** 257 (1921).

[37] Quoted in Landolt-Börnstein-Roth, "Tabellen," (5th edition), p. 1041, from private communication of K. Bädeker.

ide should be equal to the product of one electronic charge by the internuclear distance. The same would be true of hydrogen bromide and hydrogen iodide and, as their internuclear distances are greater, their moments should be greater. However, it has been shown by the writer[2] that the moment of the hydrogen chloride molecule is greatly decreased by the shift of its outer electrons under the attraction of the positive charge of the hydrogen nucleus and that these electrons are more rigidly bound than those in the bromine atom which, in turn, are more rigidly bound than those in the iodine atom. Greater ease of displacement of the electrons makes possible greater decrease in moment as the result of attraction by the hydrogen nuclei, so that the moment decreases from hydrogen chloride through hydrogen bromide to hydrogen iodide. It is apparent that this is the order of the moments in all the corresponding halogen compounds listed, and it is also apparent that the moments increase with increasing length of the carbon chain because of the small moments induced by the principal moment. In tertiary amyl bromide the mutual repulsion of the branches of the carbon chain should have little effect upon the moment, but the proximity of these branches to the principal doublet in the molecule makes possible greater induction of secondary moments than in the normal compound, so that the moment of the molecule is large.

It was calculated by the writer in the paper referred to that, if distortion were neglected, the moment of methylene chloride should be 1.155 times those of methyl chloride and chloroform, which should be equal. No data are available for the calculation of the moment of methyl chloride, but the values of the higher chlorides indicate that methyl chloride would be lower than methylene chloride, which is higher than chloroform, the value for which is one of the most accurate of the results given. The mutual repulsion of the two halogens attached to the carbon should decrease the moment, the decrease being greater, the greater the displacement of the binding electrons. The greater mutual repulsion caused by the greater bulk of the iodine atoms should explain the fact that methylene iodide has a smaller moment than methyl iodide.

The symmetrical molecule of carbon tetrachloride might be expected to have very little moment, and the small moment found for it may arise from disturbances due to thermal agitation, as suggested in the case of the halogen molecules. The fact that the apparently symmetrical molecule of tetrachloro-ethylene has practically the same moment as carbon tetrachloride indicates that the double bond gives rise to no great electronic shift. The molecules of the symmetrical di- and tetrahalogen substitution products of ethane may be regarded as consisting of two halves joined by the electron pair between the two carbons, each half containing a doublet like those which have been under consideration. One half may rotate about the bond until the field of its doublet opposes and balances that of the other half. The moment of the molecule as a whole will then be practically zero. On the other hand, one half may rotate until its doublet acts in the same direction and adds its field to that of the other half so that the moment of the molecule as a whole is practically double that of the doublet in either half. Intermediate positions of the two halves of the molecule would give intermediate values for the moment of the molecule. It is probable that these substances consist of molecules, the two halves of which occupy every possible stage between the positions for minimum and for maximum moment, although it does not follow that all positions are equally probable. It thus appears that the moment calculated from experimental data represents an average of values running from zero to a certain maximum value. Similar conditions probably exist in glycol, the molecule of which may be regarded as consisting of two mutually adjustable parts, each containing a doublet, and in glycerol, the molecule of which should contain three mutually adjustable parts, each containing a doublet.

In view of the influence of induced polarity upon chemical combination, an idea of the approximate extent of the electronic shift accompanying this phenomenon should be of interest. In the alcohol series the replacement of a hydrogen by a methyl group is accompanied by an increase in moment of about 0.1×10^{-18}. If we disregard the shift of the positive charges and all secondary effects in the rest of the molecule and arbitrarily assume the increase in moment to be due entirely to the shift of the six displaceable electrons which the methyl group has added to the molecule, the amount of this shift, d, may be calculated from the equation: $6 \times 4.774 \times 10^{-10} \times d = 0.1 \times 10^{-18}$, or $d = 3.5 \times 10^{-11}$ cm. This indicates that the length of the induced electronic shift is of the order of magnitude of about one one-thousandth the diameter of the outer atomic shell.

Summary

A method is outlined for the calculation of the electric moment of the molecule of a substance from the indices of refraction at two different wave lengths, the density of the substance under the conditions under which these indices are measured, the dielectric constant at one temperature, the density at this temperature, the value of this temperature itself, the molecular diameter and certain universal constants. The value of the moment thus calculated is much smaller than that obtained from consideration of the hypothetical molecular structure. This difference is due to shifting of charges under the forces of attraction and repulsion within the molecule and its magnitude is dependent upon the ease of displacement of the electrons.

The moments of the saturated hydrocarbons are very small, and those of the hydrocarbons containing double bonds are small, although of suffi-

cient magnitude to indicate a possible tendency toward an electronic shift in the neighborhood of the bond.

The alcohols, ethers, aldehydes and ketones have moments of the same order of magnitude as that of water, as required by the hypotheses as to their molecular structures, while ammonia and the amines have smaller moments than water, the difference being somewhat greater than that predicted on the basis of molecular structure alone, because of the fact that the electrons around the nitrogen nucleus are more easily displaced than those around the oxygen nucleus.

The mutual repulsion of the groups attached to the oxygen in the alcohols and ethers, the carbonyl carbon in the aldehydes and ketones, and the nitrogen in the amines, tends to decrease the moment of the molecule, the effect depending upon the resistance of the binding electron pairs to displacement from approximately symmetrical positions.

Among the hydrogen and the organic halides, the moments of the iodine compounds are lower than those of the analogous bromine compounds which, in turn, are lower than those of the analogous chlorine compounds, the inverse of the relative ease of electronic displacement in the halogens. In these compounds, the mutual repulsion of two halogen atoms decreases the moment of the molecule, the accompanying shift of the pairs of binding electrons adding to the decrease.

In the substances discussed the principal doublet in a molecule induces secondary doublets, which act in the same direction as the principal doublet, so that the moment of the whole tends to increase with increasing size of the molecule.

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THE AMMONIA, CARBON, HYDROGEN CYANIDE, HYDROGEN EQUILIBRIUM AND THE FREE ENERGY OF HYDROGEN CYANIDE

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Introduction

Probably the first synthesis of hydrogencyanide was effected by Clouet[1] by passing ammonia over wood charcoal at red heat. The reaction involved in this experiment is: $NH_3 + C(s) = HCN + H_2$. This reaction has subsequently been quantitatively studied, and its use has frequently been proposed for the commercial synthesis of hydrogen cyanide. Thus Bergmann[2] found that even at 1100° the reaction was measurably slow,

[1] Clouet, *Ann. chim.*, **11**, 30 (1791).

[2] Bergmann, *J. Gasbel.*, **39**, 117 (1896); see *Chem. Zentr.*, **49**, 943 (1896).