POLYMERIZATION

AND THE

DIELECTRIC CONSTANT

NATURE OF POLYMERIZATION AND ITS RELATION TO THE DIELECTRIC CONSTANT

and

THE ELECTRIC MOMENT IN RELATION TO THE STRUCTURE OF ORGANIC COMPOUNDS

by

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DISCUSSION OF RESULTS

INTRODUCTION.

The phenomenon of polymerization has attracted considerable scientific attention during recent years. This activity is due to the fact that many naturally-occurring materials, important from both the scientific and industrial standpoints, such as cellulose, starch and other complex polysaccharides, resins, rubber and proteins, have been shown to be products whose properties were similar, if not identical, with those of highly polymerized compounds produced in the laboratory.

Considerable confusion has occurred because of the indiscriminate use of terms concerning the phenomena whereby very large molecules are constructed from smaller ones and in which a definite structural unit is shown to recur. At present, the generally-accepted definition of the terms "association", "polymerization", "condensation", and "aggregation" will be given.

"Association" is considered to be a loose union of molecules involving physical changes only, due to electrical attraction of oppositely-charged parts of the molecules involved, with no transfer or sharing of valence electrons. It is difficult to separate the forces associated with unsaturated or secondary valences from those concerned with "association", but such forces may be pictured as coming into play when molecules form addition compounds with the sharing of electrons, or possibly of hydrogen nuclei, between their structures. In some cases, these two distinct types of forces may be virtually equivalent, though the former are usually much stronger. The above view is put forward in contradistinction to that of Meerwein,(1) who considered the phenomenon of association as proof of the presence of secondary valence forces. This flexibility of definition precludes the assumption of the formation of complex molecules to which chemical formulas are often assigned in a manner somewhat taxing to the imagination.

"Polymerization" is the union of two or more molecules of similar chemical individuals through primary valence forces,(2) with neither the addition nor removal of atoms or molecules, to form a molecule of higher molecular weight. No example is yet known in which a small molecule of known structure simulates a material of high molecular weight without undergoing any change in structure.(3) The transformation into polymers is thus a real chemical process, whose structure may be represented by the general formula $(-R-)_n$, where -R- is the recurring structural unit and "n" is any integer greater than unity. For polymers, the structural unit -R- has an independent existence, which is termed the "monomer". The transformation of polymers of the first type into their monomers is brought about simply by heating, and the reverse transformation occurs spontaneously or by catalysis. It will be pointed out later that the results obtained show a fundamental difference between the two phenomena of association and polymerization.

There is another type of polymerization which has not been specifically mentioned. It is the interaction of two or more compounds of similar structure, such as mixtures of aldehydes,(4) or vinyl acetate and acetaldehyde.(5) Such polymeric products are usually known as mixed polymers. Wagner-Jauregg(6) has proposed that this type of reaction should be called "additive heteropolymerization" and the term "homopolymerization" applied to the union of several identical molecules. Like the terms "multimolecular", "macromolecular" and "supermolecular",(7) they do not tend to clarify an already highly complicated nomenclature and might be conveniently discarded.

"Condensation" is usually reserved for that process which is similar to polymerization in that molecules of higher molecular weight are the resulting products, but differs in this respect, that (n - 1) simple molecules (such as water, ammonia, alcohols, halogen acids, salts, etc.) are eliminated when "n" molecules of the compound unite. This type of reaction would be called by Carothers(8) and others(6) condensation or "C" polymerization. The reason for the double term is not evident, except that it includes as two branches of a similar phenomenon a process whose resulting products differ but slightly in structure from one another. In the "C" polymers, degradation to the monomer, H - R - OH, occurs by hydrolysis, and the reverse process could only take place by "polyintermolecular condensation", i.e., the elimination of water from a large number of monomeric molecules.

Levene(9) has suggested that polymerization should be reserved for the process defined here as association, and that polymerization itself should be termed "condensation through primary valence forces". In the light of present-day knowledge concerning the fundamental nature of these processes, this position is hardly tenable.

It is immediately evident that there is considerable overlapping of the two fields covered by the two latter definitions, and thus a single polymer might be regarded as belonging to both classes, depending on the synthetic method employed. Thus, the polyethylene glycols of structure (I)

$$HOCH_2CH_2O-(CH_2CH_2O)_n-CH_2CH_2OH \qquad (I)$$

might be considered as linear polymers of ethylene oxide in which the terminal linkages of the chain had been saturated by the univalent groups -OH and -H. On the other hand, they are equally as much the products resulting from polyintermolecular condensation of ethylene glycol. In fact, both of these monomeric forms have been used as starting material in the formation of (I). It also appears that cellulose might be classified as either a true addition (A) or a C polymer. The former would be correct whether cellulose is the polymerization product of a glucosan or cellobiosan, while it would belong to the latter class if it were synthesized by the dehydration of glucose.

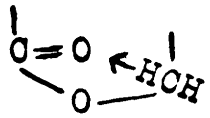
"Aggregation" is a very ill-defined term, often used in connection with physical or colloidal change. It has been described as both simple and spontaneous. It usually denotes a process whereby simple molecules are loosely or vaguely grouped together without indicating why or how. Thus Manley(10) found that intensively dried benzene showed a maximum index of refraction during drying, which he attributed to the formation of molecular assemblages of unusual density and complexity. In colloid chemistry "degree of dispersion" and "degree of aggregation" are identical, depending on the perspective, in that they both refer to particle size.

Many hypotheses have been put forward to explain what appeared to be an unusual type of reaction, and it was believed that forces of an unusual kind were involved in the formation of polymers. Thus Thiele (11) suggested the molecules were bound together with partial valences; Rohm (12) said that polymerization was an allotropic change; and Schroeter (13) concluded that the transformation was due to an excess of peripheral external force about the monomeric molecules, but later modified his viewpoint by suggesting the union was due to molecular valence forces without change in structure of the monomers. Hess (2) admitted that perhaps finer valence forces exist through which the supermolecular state can be expressed.

The only two theories at present under discussion which are concerned with the structure of natural and synthetic polymers fall into separate classes. The first of these, the Association Theory, has received its support from molecular weight determinations in a variety of solvents, but no agreement was observed in the values obtained. This was taken as evidence that the binding forces were not those of primary valence, but the variations have since been shown to be largely errors in technique. It was also believed that x-ray studies gave support to the association theory, but the correlation of investigations on natural and synthetic polymers proved these deductions to be incorrect. According to this theory, the cause of the association was supposed to be secondary valences associated with unsaturation of a molecule, or residual valences centered in the bridge oxygen of heterocyclic rings. Support of the theory was accorded mainly by Abderhalden, Hess, Bergmann, Pringsheim and Karrer. (14)

Of recent years, the claims of the proponents of the association theory have been disproved and superseded by the Normal Valence Structural Theory which has had two branches of opinion, one stating that polymers were of cyclic structure, and the other that the products were long open chains, with free end valences or with functional end groups saturating the molecule. Wagner-Jauregg(15) claims to have shown that all polymers of isoprene are cyclic, and adds that "the only aliphatic polymer of isoprene that is known is rubber, if that be an aliphatic compound." Staudinger(16) in his researches since 1927 on isoprene, rubber and related compounds, has conclusively shown that rubber molecules are long chains consisting of 100-200 isoprene building units. There are some polymers of low molecular weight, principally dimers, which have been shown to possess a cyclic structure. Among these are diprene,(17, 18) dicyclopentadiene,(19) glycollide, lactide, tetramethylene oxalate and sebacic anhydride,(3) ethylene succinate,(20) trimethylene carbonate,(21) and ω-hydroxy-decanoic lactone.(22) All of these compounds are dimeric. Another cyclic polymer of interest is the decamer of 2,3,4-trimethyl-l-arabono-lactone. Drew and Haworth(23) definitely state this is a ring compound, though Carothers(3, 24) says they ascribe a linear polyester structure to this polymer. He also doubts its absolute homogeneity, and suggests it as much more probably a polymeric mixture. Carothers(3) has shown on the basis of the Sachse-Mohr theory(25) of ring structure and the known mechanism of polymerization that the possibility of the formation of cyclic polymers of high molecular weight is exceedingly small. It is concluded that no high polymer is certainly known to have a cyclic structure, although cyclic formulas have been assigned to some of them due to failure to detect unsaturation or terminal groups in the molecule.

There has also been a rather marked tendency to show that polymerization is peculiar to unsaturated compounds, and that a very high degree of mobility in the relation between a monomer and its polymer precludes the intervention of real primary valence forces in the process. That this is decidedly not so is shown by the polymerization of adipic anhydride and the six-membered cyclic esters,(24) although all of these molecules contain oxygen atoms and carbonyl groups, which could conceivably possess properties in common with unsaturated linkages, which properties might be the cause of, at least, addition polymerization. This effect would not be found in cases of condensation polymerization of hydrocarbons by the Wurtz or Friedel-Craft reactions, but it is a pertinent question whether such reactions should, or should not, be classed among polymerization processes.

It has also been suggested by Hibbert(26) that polymerization of certain compounds is due partially to the presence of the specific grouping $-CO-O-CH_2-$, a factor which has not hitherto been recognized as calling for serious consideration. It has been observed that all six-membered cyclic esters and lactones which undergo polymerization are characterized by the presence of this group, which is also characteristic of esters. Whether this tendency to polymerize can be attributed to the electronic condition of the $-CO-O-CH_2-$ group, or to a strain resulting from a tendency of the hydrogen atom to shift thus, 

we do not know. It can be readily demonstrated, however, that this factor does not play a very deciding role in the process, as merely the substitution of one H atom of the $-CH_2-$ group by any alkyl radical retards the polymerization enormously. Also, γ-lactones, which contain this grouping, do not polymerize under any conditions.

The most widely accepted theory, then, is that polymerization is a process in which the molecules are linked together by primary valence forces, and that the resulting products are long open chains of high molecular weight, with the exception of the few examples of cyclic compounds mentioned above. These conclusions find their basis principally on the work of Staudinger, Haworth, Freudenberg, Meyer & Mark, Sponsler & Dore, and Carothers,(27) which has been confirmed by many others.

In the foregoing paragraphs, an attempt has been made to outline the most generally accepted ideas of polymerization and the conclusions which have been formed concerning the structure of these complicated products. No attempt has been made to give in any detail the arguments for or against any particular theory, and, since the short review is not intended to be complete, only the more important ideas have been touched. The terms which have been defined will be used throughout with the meanings which are here ascribed to them. Considerably more will be said in Part II concerning the Theory of Association.

Since polymerization has been investigated but little from the quantitative standpoint, this study was commenced with a view to linking one physical measurement, the dielectric constant, with the state of polymerization of some organic molecules. From the data obtained, the dipolar or electric moment could be calculated, which should give definite information concerning the structure of the polymerized molecules, thus showing a definite relationship between the electric moment and the degree of polymerization. While an increase in moment would be expected for compounds of high molecular weight, no predictions can be made concerning the simplest polymeric forms if the structure of these is unknown. The electric moment of such compounds ought to be governed by two factors:

I. The length of the chain, if such is found.

II. Whether the polymer is of circular configuration (spiral) or is a true closed ring.

In this connection, very different results should be expected from I and II, and it would be possible to determine whether a given polymer possesses one or the other type of structure.

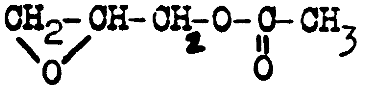
In the determination of the dielectric constants, conduction should be avoided, consequently compounds were chosen which could be polymerized readily by the action of either heat or light, or both. Certain compounds were selected as their polymerization had already been investigated in this laboratory.(71) The other compounds were analogues of these compounds and certain unsaturated compounds which polymerized without the aid of catalysts.

These compounds are--

1. Glycidol,

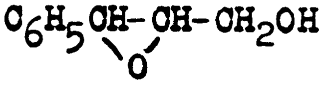
CH_2-CHCH_2OH (with O bridging the first two carbons)

2. Glycidol acetate,



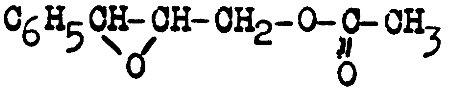
$CH_2-CH-CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

3. Phenyl glycidol,



$C_6H_5CH-CH-CH_2OH$

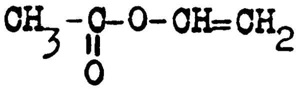
4. Phenyl glycidol acetate,



$C_6H_5CH-CH-CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

5. Di-vinyl ether, $CH_2=CH-O-CH=CH_2$

6. Vinyl acetate,



$CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-O-CH=CH_2$

The objects of this part of the work may be summarized:

1. To prepare the above compounds (except vinyl acetate),
2. To study their slow and controlled polymerization,
3. To measure the dielectric constants, densities, molecular weights, and refractive indices of the polymers, and the

dielectric constants and densities of their solutions in a non-polar solvent at low concentrations.

4. From the physical data to calculate the electric moment of the individual polymers, thus indicating their type of structure, and correlating the electric moment with the degree of polymerization.

SURVEY OF THE LITERATURE.

The preparation of vinyl acetate(28) from acetic acid and acetylene in the presence of mercuric salts according to the secondary reaction

$$CH_3COOH + C_2H_2 \rightarrow CH_3COOCH{=}CH_2$$

was first recorded in a German patent of 1912. It is a colorless liquid, of low viscosity, completely miscible with water, soluble in most organic solvents, boils at 72°, $d^{20}_{4} = 0.9317$, $n^{20}_{D} = 1.39558$, $\eta_{abs.} = 0.004213$(53). It saponifies or hydrolyzes more readily than ethyl acetate. The enolic ester is easily detected. In the presence of alkalies (borax) its rapid saponification is due to the acid character of the enol; in aqueous solution the rapid hydrolysis is to be referred to the double linkage.(61)

It was soon discovered(29) that vinyl esters, alone or in admixture with each other, would polymerize readily by the action of "chemical rays" or simply by heating. Natural or artificial light, both the visible and ultraviolet, have been used to initiate and accelerate polymerization. As a source of illumination, Taylor & Vernon(30) used a vertical mercury arc of the Cooper-Hewitt type, operating at 175 watts. The liquids were contained in Pyrex glass vessels, and the reaction carried out at 100° C. An examination of the quantum yield of these photo-reactions showed that a large number of molecules react per light quantum absorbed, and that the light absorbed, therefore, starts a chain of secondary oxidation processes. Mixtures of vinyl acetate and acetaldehyde have also been polymerized by exposure to light.(31) Mixtures of vinyl acetate and 10% acetic acid and acetaldehyde, paraldehyde and potassium acetate, have been polymerized by heating under reflux to initiate the reaction, with subsequent completion of polymerization in a separate vessel.(32)

It was also observed that the polymerization of vinyl esters was catalyzed by organic peroxides, ozonides, organic acid anhydrides in combination with oxygen or agents yielding oxygen, such as perborates, percarbonates, silver oxide, etc.(29) Other catalysts which have been used successfully are--

1. Water, or an aqueous solution of hydrogen peroxide and borax.(33)
2. Hydrochloric, lactic or acetic acids, $AlCl_3$, $ZnCl_2$, and formaldehyde.(34)
3. 2-4% tetraethyl lead.(35)

Inactive vinyl esters have been rendered active and polymerizable by treating with gaseous oxygen in the presence of natural or artificial light.(31) It is worthy of note that the most efficient and the greater proportion of the catalysts employed are substances which are capable of taking part in auto-oxidation reactions. It thus seems that in many cases a very definite relation exists between polymerization of unsaturated compounds and auto-oxidation. It had been previously shown that other polymerization reactions of various unsaturated organic substances were affected similarly. Some examples are the "drying" oils in the paint and varnish industry, and the slow resinification of terpene-like substances and other essential oils in the presence of air. Engler & Weissberg(36) have pointed out the influence of auto-oxidation in the polymerization of styrene and its derivatives, cyclopentadiene, indene, coumarine, etc.

The elucidation of the mechanism of these reactions had its origin in the work of Stobbe and Posnjak,(37) who arrived at the conclusion, from kinetic studies of the polymerization of styrene, that the acceleration of such a polymerization was due to the initial formation of an "Autokatalysator" or a "Polymerizationskern". Almost simultaneously, Heinemann(38) found that oxygen or ozone effected the polymerization of isoprene to rubber. Since the work of Heinemann an enormous number of patents taken in various countries describe the polymerization of numerous organic substances in the presence of oxygen, organic peroxides, ozone and ozonides. Several years later, Moureu (39,40) demonstrated the existence of a relationship between the autooxidation of acrolein and its polymerization. Light or oxygen alone readily effected the polymerization, but the absence of both entirely prevented the reaction. Excess oxygen inhibited polymerization, due to rapid oxidation of the acrolein. Recently several very interesting contributions in connection with this work have been made: the polymerization of styrene, (41) vinyl acetate, (47) and isoprene, under high pressures, (42) by benzoyl peroxide; that of styrene and cyclopentadiene by diphenylethylene peroxide, (43) and that of styrene, indene, etc., catalyzed by octylene ozonides. (44) Once again it must be pointed out that unsaturation is not a necessary prerequisite to polymerizations catalyzed in the above manner. Conant and Peterson (45) have made a thorough investigation of the polymerization of n-butyraldehyde under high pressure, and have shown that minute amounts of a "peroxide", to which they assign no formula, are sufficient, but necessary, for catalysis.

That polymerizations of the type here described have a chain mechanism was first suggested from various considerations by Milas, (46) and later confirmed by Starkweather & G.B. Taylor (47) and by H.S.Taylor and Vernon. (30) In the acceleration of polymerizations by organic peroxides, the latter act as "trigger" catalysts in starting reaction chains. Benzoyl peroxide, when used, is itself destroyed in the process, since chemical tests always showed its absence when the catalyzed reaction stopped. With oxygen, polymerization is undoubtedly effected by the energy liberated during formation of the dative peroxides, their subsequent rearrangement and decomposition of the rearranged product, then polymerization or reaction with the active unoxidized molecules of the monomer. The energy liberated as the result of polymerization of the unoxidized monomer should not be overlooked.

It will be necessary to explain what is meant by a "dative peroxide", a term used by Milas(45) in an electronic interpretation of auto-oxidation recently proposed by him. Briefly stated, this interpretation assumes that auto-oxidation proceeds by a preliminary addition of molecular oxygen to atoms or groups of atoms containing molecular valence electrons comparable to the molecular valence electrons of the various elements, with the subsequent formation of highly metastable or dative peroxides which are characterized by high instability and energy content. The term "dative" is used to denote a type of covalence in which one of the atoms in the dative bond contributes both electrons. In this case, the auto-oxidant contributes both electrons to the oxygen molecule.

If A: represents a molecule of an auto-oxidant containing molecular valence electrons, e_1 the energy of activation, and e_2 the energy due to pairing of spins of the electrons forming the dative bond, the changes which may occur during the first stages of the auto-oxidation of A: may be represented as follows:

$$A: + e_1 \rightarrow A \overset{e_1}{\rightarrow} : \qquad (1)$$

$$A \overset{e_1}{\rightarrow} : + \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: \rightarrow A:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: (e_1 + e_2) \qquad (2)$$

The electrons which are directly responsible for the formation of the dative peroxide shown in equation (2) have probably undergone an increase in their principal quantum numbers due to the absorption of energy e_2. Molecules containing these electrons would be characterized by a very low energy of dissociation and extremely high instability. Mere collisions with other molecules will suffice to effect rearrangement or even decomposition of the dative peroxide, with liberation of energy. This energy, according to Christiansen,(49) may be utilized to initiate reaction chains.

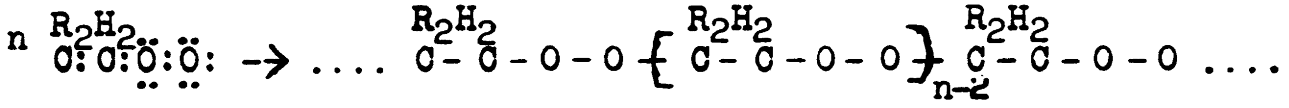
$$A:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: (e_1 + e_2) + A: \rightarrow A\!<\!\begin{matrix}O\\|\\O\end{matrix} + A \overset{e_3}{\rightarrow} : \qquad (3)$$

where $e_3 = e_1 + e_2$. This energy increases with each subsequent reaction chain and eventually, according to Semenoff,(50) may, and probably does, lead to explosive reactions, such as the polymerization of ethylene oxide.(51)

In cases in which polymerization and auto-oxidation occur simultaneously, three possible reactions should be considered:

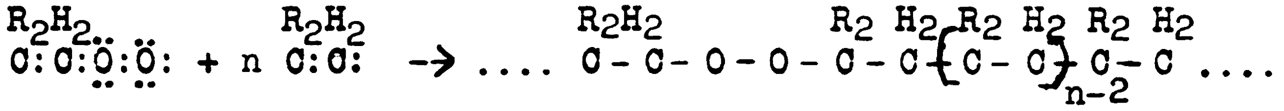
(a) Auto-oxidation of the unsaturated substance. Under ordinary conditions and in the dark, this reaction is indispensable to polymerization, and usually precedes the latter. This may not always be the case, as will be shown later.

(b) Polymerization of or through the dative peroxides. Staudinger's formulation,(52) such as that advanced for unsym-diphenylethylene, is not free from criticism, but it seems to be the simplest and most probable formulation at present.



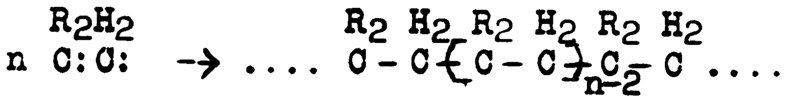
$$n\;\overset{R_2H_2}{C{:}C}{:}\underset{..}{\ddot{O}}{:}\underset{..}{\ddot{O}}{:}\;\rightarrow\;\ldots\;\overset{R_2H_2}{C-C}-O-O-\left\{\overset{R_2H_2}{C-C}-O-O\right\}_{n-2}\overset{R_2H_2}{C-C}-O-O\;\ldots$$

For the mixed peroxide auto-oxidant polymer the following scheme is possible:



$$\overset{R_2H_2}{C{:}C}{:}\underset{..}{\ddot{O}}{:}\underset{..}{\ddot{O}}{:}\;+\;n\;\overset{R_2H_2}{C{:}C}{:}\;\rightarrow\;\ldots\;\overset{R_2H_2}{C-C}-O-O-\overset{R_2}{C}-\overset{H_2}{C}\left\{\overset{R_2}{C}-\overset{H_2}{C}\right\}_{n-2}\overset{R_2}{C}-\overset{H_2}{C}\;\ldots$$

(c) Direct polymerization of the active auto-oxidant molecules. That polymerizations of this type are exothermic may be readily shown by a simple calculation of the heats of polymerization from the heats of combustion of the monomers and polymers. This reaction can be initiated and accelerated by light, as well as by catalysts. It may be briefly formulated as follows:



$$n\;\overset{R_2H_2}{C{:}C}{:}\;\rightarrow\;\ldots\;\overset{R_2}{C}-\overset{H_2}{C}\left\{\overset{R_2}{C}-\overset{H_2}{C}\right\}_{n-2}\overset{R_2}{C}-\overset{H_2}{C}\;\ldots$$

Besides the positive catalysts mentioned above, for vinyl acetate, there are a number of substances which have been found to act as negative or anti-catalysts or inhibitors. It is claimed that oxygen acts both as a positive and negative catalyst for the reaction, depending largely on the experimental conditions and accessory means of activation of the simple monomeric molecules. As already mentioned, the patent literature claims oxygen gas is a positive catalyst in the presence of natural or artificial light.(31) Taylor and Vernon(30) state that oxygen inhibits the photopolymerization of vinyl acetate. In their work, a 30% solution by volume of vinyl acetate in ethyl acetate was employed. In preparing these solutions for illumination, each constituent was distilled in hydrogen separately (no physical data are given). The two were mixed separately in an atmosphere of hydrogen and stored over hydrogen. The solution was separated into two parts, one part now being stored over oxygen. Samples were removed at various time intervals and allowed to undergo photopolymerization at 100° under identical conditions. No correction was made for thermal polymerization in these tests, although it is well known that polymerization of vinyl acetate is readily caused by heat. Yet it is stated that the evident conclusion is that light alone may cause polymerization and that the true rate of the photo process is obtained with the hydrogen-distilled samples. No tests are recorded for the detection of peroxide, although Conant and Peterson(4) found that isoprene "distilled in nitrogen" still contained enough oxygen to catalyze the reaction, and that on further removal of oxygen the rate of polymerization is reduced ten-fold. Taylor and Vernon's results are given in Table I.

Table I.

Effect of Oxygen Absorption on Photopolymerization of Vinyl Acetate.

Time of Storage Hours	Contact with H_2 % polymerized per hour.	Contact with O_2 % polymerized per hour.
0	29.0	29.0
18		20.0
24	29.0	
48		12.0
90	29.5	
114		2.0
138	32.0	

The effect of oxygen upon the polymerization of vinyl acetate is different from that of styrene. They state: That oxidation of styrene, whether thermal or photochemical, is also accompanied by polymerization is evident, and hence the result of the polymerization of solutions stored over oxygen indicate the sum total of both these effects. The increase due to complete oxygen saturation is about 50%, but the polymerization due to a very small percentage of oxygen in the hydrogen-prepared solution would be negligible compared to that due to the ultraviolet light.

Staudinger (53) found that, in quartz vessels under the influence of light, polymerization of vinyl acetate takes place more rapidly in nitrogen or carbon dioxide than in oxygen or air. Polymerization began after 3 hours in nitrogen, but only after 44 hours in oxygen; further polymerization also occurs more rapidly in nitrogen than in air, but in the latter case polymerization can be completed by continued illumination. On the contrary, thermal polymerization of vinyl acetate freed completely of oxygen will not occur below 180°, but will take place after 60 hours' heating at 200°. A possible explanation for this apparently contradictory behavior of vinyl acetate towards oxygen may be found in the results (Table II) of Starkweather and G. B. Taylor, though they state that results obtained with "air-distilled" vinyl acetate varied appreciably.

Table II.

% by vol.	Temp. °C.	Time in minutes to reach indicated % polymerization. 10	20	30	40	50	60	70	$k \times 10^4$	
		Vacuum Distillation								
100	82	100	230	375	530	725	1000	1320	11	(1)
100	101	20	45	75	112	157	205	261	53	(2)
100	111	7.5	16	25	36	49	68	102	140	(3)
60	82	200	500	930	1470	2200	---	---	5	(4)
60	101	40	88	162	272	400	675	1580	26	(5)
60	111	17	40	75	120	200	380	760	62	(6)
		Air Distillation								
100	101	5.5	12	19.5	28	40	56.5	88	191	(7)
80	101	13	34	65	115	185	320	580	81	(8)
60	101	32	105	175	320	600	1340	---	33	(9)
20	101	800	3000	a	---	---	---	---	----	(10)

If we compare (2) and (7) it seems evident that oxygen, as much as remains in air distillation, has accelerated the polymerization. Comparing two <u>solutions</u> of the same concentra-

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a = 25% in 90 hours.

tion (60%) of vinyl acetate in toluene, (5) and (9), we see that the initial rate of polymerization of the air-distilled sample is greater than that of the vacuum distilled ester, up to 10%. Above this percentage of polyvinyl acetate the reverse is true. It would therefore appear that the conclusion arrived at would depend on how far polymerization was allowed to proceed. Above 10% polymerized product, the results of H.S.Taylor and Vernon, and Starkweather & G.B.Taylor seem to agree. At the lower concentration (20%, No. 10), polymerization was greatly retarded, and the inhibition of the reaction by toluene may be explained on the basis that activated molecules give up their energy to the toluene molecules before they can combine to form polymers. In other words, toluehe has the same effect in breaking reaction chains that walls exhibit in some homogeneous gas reactions.

It was found that in no case did the reaction in toluene solutions go to completion, although in some experiments the heating was continued for nine days. It is perhaps significant that in the uncatalyzed reactions the polymerization of 40, 60 and 80 per cent solutions apparently stopped when they contained approximately 2.0 moles of monomer per litre, while the polymerization of the 20% solution appeared to stop when it contained 1.5 moles of monomer per litre. These statements are for thermal polarization at 101°.

H. S. Taylor & Vernon arrived at an entirely different conclusion for photopolymerization of vinyl acetate solutions in ethyl acetate at 100°. They state that the change in reaction rate with concentration is due entirely to the change in absorption of light with concentration (that is, that the percentage of activated molecules is less at lower concentrations of the solute, and that the rate of combination is the same). A calculation of the percent polymerized at the various concentrations shows a practically constant value, which lends further proof to the explanation.

Sulphur (55) has also been found to inhibit the thermal polymerization of vinyl acetate, presumably through interrupting the reaction chains. (54) Other anticatalysts mentioned in patents are iron and copper. (56) Vinyl acetate may be stabilized against polymerization by keeping over copper compounds, or by subjecting the polymerized product to distillation over copper or its compounds to prevent further thermal polymerization. (57)

The mechanism of inhibition of polymerization is unknown. Luther (58) first proposed the theory that negative catalysts destroyed the positive catalysts originally present in the compound, a theory which would have but limited application. A theory put forward by Milas (59) plausibly accounts for the mechanism of inhibition of polymerization, where this reaction may be assumed as initiated through auto-oxidation.

In a number of processes sensitive to light, the chain reaction theory has been shown to account satisfactorily for the phenomenon of inhibition of oxidation in such systems. It would appear that the light absorbed starts a chain of secondary reaction processes. It has been known now for some time that many polymerization processes are light sensitive and also show the phenomenon of inhibition by added agents. It has been shown by Alyea & Bäckström,(60) in certain reactions, that the inhibitor in oxidation processes is oxidized in the process of breaking the reaction chains. However, as Taylor(30) suggests, such a fate for the inhibitor molecule is impossible in polymerization processes carried out in the absence of oxygen. In photo-reactions, as pointed out by Anderson & Taylor,(61) an inhibitor may act by absorbing light which would otherwise produce the reaction, or by some special inhibitor mechanism. In the polymerization of vinyl acetate, using hydroquinone as inhibitor, Taylor & Vernon found that inhibition of polymerization varied as the concentration of hydroquinone. The only factors present in their case being screening by absorption of the active light and deactivation by collision, it seemed clear that the effect was due to both causes. Deactivation by collision was further substantiated when it was shown that hydroquinone in small concentrations also inhibited thermal polymerization.

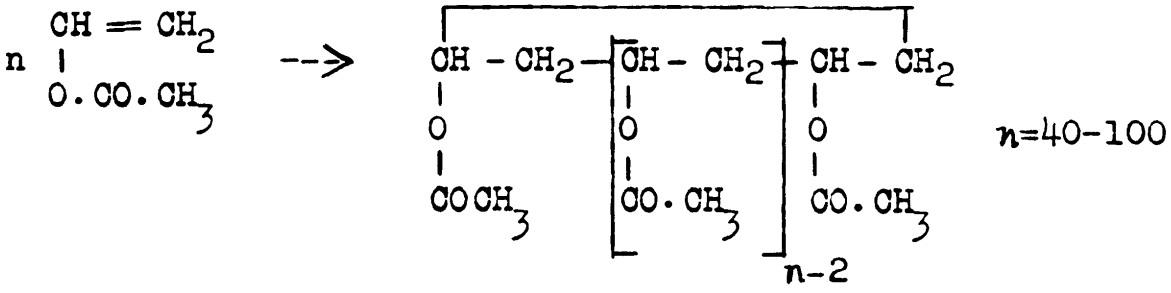
Staudinger (53) found that polyvinyl acetate prepared in oxygen always had a lower viscosity and molecular weight than that prepared in nitrogen, and suggested that the impossibility of preparing the longest chains in oxygen is probably due to attachment to the terminal valences of the element, whereby further growth of the molecule is inhibited.

Polyvinyl acetate was first mentioned in scientific work by Staudinger, (62) who showed that the acetate was readily hydrolyzed to give polyvinyl alcohol, a process which could be reversed by the action of acetic acid. Hermann & Haehnel (63) confirmed this work and pointed out the striking properties of polyvinyl alcohol which, from its carbohydrate nature, may be placed between sugar and starch. Staudinger later (64) showed that the hydrolysis was not entirely reversible. The benzoate and nitrate were also prepared.

The polymer is readily soluble in alcohol, acetone, benzene, etc., to form more or less viscous, colloid solutions. It is insoluble in water, a fact which can be used to separate the unchanged ester from the polymer.

The lower the temperature at which the polymerization takes place, the more viscous is the resulting resin and the higher the molecular weight. He explains the fact that higher polymers are obtained at lower temperatures by assuming that cracking takes place at the higher temperature. The longer the chain the more unstable it is, so that at a definite temperature only a chain of such length will be produced which will remain stable at that temperature. This behavior is analogous to that of other polymerizable substances, such as isoprene,(65) styrene,(63) indene(66) and dimethyl butadiene.(67)

Whitby(68) also showed that polyvinyl acetate was highly heterogeneous, being composed of a mixture of an unbroken series of polymers of different molecular sizes. He separated the complex polymers into molecular weights ranging from 400 to 5000 by fractional precipitation of their benzene solutions with ligroin. When heated alone to a high temperature, polyvinyl acetate decomposes, with formation of various complex products, but no monomer is obtained, such as is the case with polystyrene. On oxidation with nitric acid, polyvinyl acetate gives oxalic acid. Staudinger suggested that the polymer had a ring structure, although the nature of the free end valences is uncertain.



$$n\begin{array}{l}CH=CH_2\\ \mid\\ O.CO.CH_3\end{array} \longrightarrow \begin{array}{l}CH-CH_2-\\ \mid\\ O\\ \mid\\ COCH_3\end{array}\left[\begin{array}{l}CH-CH_2\\ \mid\\ O\\ \mid\\ CO.CH_3\end{array}\right]_{n-2}\begin{array}{l}-CH-CH_2\\ \mid\\ O\\ \mid\\ CO.CH_3\end{array}\qquad n=40-100$$

For pure vinyl acetate, Starkweather and G.B.Taylor(54) found the temperature coefficient of thermal polymerization was 2.7 per 10° rise, and the heat of activation 25,000 calories.

Vernon & H. S. Taylor (30) found that the temperature coefficient of photopolymerization of solutions of vinyl acetate in ethyl acetate was 1.3 per 10° rise, from 40° to 70°. No change in light absorption was observed with temperature. The quantum yield was a maximum for light from λ3000-4000 Å., the yield being 935 molecules/$h\nu$ The results presented indicate that the polymerization process has many of the characteristics of a chain mechanism.

The effect of pressure on the rate of polymerization of vinyl acetate is much greater than on most reactions. Tamman and Pape (69) found that these reactions behave in a unimolecular fashion. This is explained by the supposition that some preliminary change must take place in the individual molecules prior to their combination the velocity of which is less than their rate of actual combination. There is a decrease in volume on polymerization, and therefore the decrease in pressure at constant volume is taken as a measure of the reaction velocity. A temperature range from 0° to 400° and pressures up to 3000 kg./sq.cm. were studied. With increasing pressure, the temperature at which the polymerization begins decreases.

Great industrial importance is attached to polyvinyl acetate because of its unusual physical properties. It forms colorless or pale yellow resins which are tough, transparent, fireproof and odorless. It dissolves in many organic solvents, giving solutions which vary in viscosity and which may be used in varnishes, lacquers, etc. Solutions may also be prepared by polymerizing the monomer in the dissolved state. The lower polymers are also solvents for cellulose esters and ethers. Solid, brittle polymers when heated become plastic and possess elastic properties above 40°.(68) Foreign substances may be admixed with the softened mass. The solid may be sawed, cut, filed, cemented by solvents, etc. It has been used for gears with paper and wood; in adhesives; for making small articles, films, records, telephone parts, etc.; for impregnating and waterproofing fabrics; and as a substitute for celluloid and glass. The pure polymer has been vulcanized with sulphur chloride, and mixtures of polyvinyl acetate and glycocol, naphthalene, colophony, albumen, casein and other proteins improve the elasticity and give vulcanizable products.

When the work on polymerization of vinyl acetate was modified*, due to certain impracticabilities, a review of the work on polymerization showed that the problem had been attacked, scientifically, chiefly from the organic standpoint, namely that of preparation of the polymers of well-known compounds and determination of their structure. From the physical side, work has been limited to molecular weights, boiling points, rates of polymerization, and in a few instances attempts have been made to correlate viscosity and the degree

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* January, 1931.

of polymerization.(68) Industrially, polymerization has been merely a means to an end, the degree of polymerization being followed by change in refractive index. But this has been done only with a view to the properties of the final state, and no quantitative basis has been considered. Since that time two different values of the temperature coefficient of the polymerization of vinyl acetate have been measured, and the quantum yield for light of wave-length 3000 to 4000 A. calculated as mentioned above. Starkweather and Taylor(54) also established a linear relation between percentage contraction on the original volume of the monomer and the degree of polymerization, by density measurements and by evaporating mixtures of the monomer and polymers to constant weight, the polymers being non-volatile. The average value is 3.65% polymerization for 1% volume contraction of vinyl acetate at 101°. The densities of vinyl acetate and its completely polymerized products are given in Table III.

Table III.

Temperature °C.	Density	
	Vinyl Acetate	Polymer
"Room temperature"(?)	-----	1.190 ±0.002
20°	0.9317(53)	-----
82°	0.850	1.142
101°	0.823	1.125
111°	0.812	1.116

On the basis suggested by the work done in the experimental part, the electric moments(70) of various mixtures of polyindene and polystyrene were calculated from measurements of the refractive index, density, molecular weight and dielectric constant at 25°.

Table IV.

Polyindene		Polystyrene	
Molecular weight	$\mu \times 10^{18}$ e.s.u.	Molecular weight	$\mu \times 10^{18}$ e.s.u.
116 (monomer)	0.40	104 (monomer)	0.56
603	1.33	2,820	6.32
855	1.68	7,750	7.98
1,039	1.70	23,000	8.61
1,135	1.74		
1,140	2.11		

Since the electric moment is a property of the individual molecule, these results have no practical or theoretical significance, and it could have been reliably predicted from previous knowledge that the apparent electric moment of a mixture of high molecular weight polymers would show an increase. These facts justify the temporary postponement of the original research.

DISCUSSION OF EXPERIMENTAL RESULTS.

I. Preparation of Glycidol.

In the preparation of glycidol, the presence of water or alcohol in the reaction mixture reduces the yield greatly, though it has been shown recently that it is fairly stable, when pure, toward distilled water or absolute alcohol.(72) The yield also depends on the length of time of contact of metallic sodium with glycidol, which is readily polymerized by it. Thus the best method offered at the time, which was employed in the first preparation, used metallic sodium in small pieces and glycerol α-monochlorohydrin in anhydrous ether solution. The essential change in method was reducing the time of contact of sodium and glycidol. Rider and Hill(72) have since published further precautions in method.

II. Preparation of Phenyl Glycidol Acetate.

This was the same method as used by Jahn.(71) 10% excess above the theoretical weight of acetic anhydride increased the yield from 86% to 93%. A difference in boiling point was observed. Jahn found 135°-138° at 9 mm. Observations here recorded gave 129°-130.5° at 9 mm.; 131°-132° at 9.5 mm.

III. Preparation of Divinyl Ether.

The apparatus must be absolutely air-tight except the receiver, due to the high volatility of the product. In place of a litharge-glycerol seal, a ground glass joint, well lubricated, may be inserted in the fitted neck of a copper flask. If the temperature of the KOH is too high (above 200°), copious white fumes are evolved and the yield is cut down. The first vertical condenser must be kept cold. A better yield is obtained when the accumulated product is distilled every few hours rather than continuously. The boiling point of 30-31° is lower than that previously published of 34.5-35°,(73) while Beilstein gives 39°. A boiling point of 28.3° has since been reported.(74)

IV. Vinyl Acetate.

Since so little was known concerning the degree of polymerization obtained by the usual methods employed to bring about the reaction, it was desirable to commence work on some compound obtainable in large quantities. Since vinyl acetate met these requirements and is important commercially, the investigation was confined to this compound.

Only the purest chemicals may be employed in the measurement of dielectric constants. The vinyl acetate used had a constant boiling point of 72°. The benzene was obtained from Schering-Kahlbaum, "For Molecular Weight Determinations". No further purification was attempted. The dielectric constant apparatus used was the same as that employed in the measurements on glycol monochloroacetate and glycol dichloroacetate. No variation in dielectric constant of the polymers was detectable from the slight evaporation of unchanged vinyl acetate from the dielectric cell during measurement.

The densities of the polyvinyl acetates are slightly less accurate than the value for the pure monomer. When the specific gravity bottle was standing in the thermostat, some unchanged vinyl acetate always evaporated. Since the polymers are non-volatile, the evaporated liquid was replaced with pure vinyl acetate, and the bottle cooled to 20° immediately on removal from the thermostat.

V. Polymerization of Vinyl Acetate.

A. Preliminary.

It was shown that refluxing vinyl acetate would polymerize it very slowly, while the action of visible light at room temperature caused no change. Test-tube experiments showed polymerization could be brought about slowly by the union of these two agencies, and that both light and heat energy were absorbed. It was found that the dielectric constants of these polymers increased with the degree of polymerization. An equal quantity of vinyl acetate was added to this mixture of polymers and the dielectric constant determined. This value, which agreed within 0.1% of the calculated value, showed that no abnormalities resulted from variation of the relative concentration of monomer and polymer, such as might be caused by change in the degree of association.

B. Positive and Negative Catalysis.

Benzoyl peroxide catalyzed the reaction but the rate of polymerization was too great. It was observed for the first time that finely divided metallic mercury catalyzed the reaction. While this catalysis must be due to some increase in energy absorption with consequent activation of the mercury atoms, it is not to be expected that they possess electrons in the 2^3P_1 state. This type of activation has been shown to be requisite for the photopolymerization of acetylene and ethylene catalyzed by activated mercury.(75)

It was also shown for the first time that metallic copper entirely prevented the polymerization, although patents on the same subject appeared shortly afterward.(56) The vinyl acetate was decomposed with formation of acetic acid and subsequent formation of copper acetate, probably through an intermediate oxide. The same behavior was noted with copper and vinyl acetate in the dark. Acetic acid did not inhibit the reaction, as it has been shown to catalyze it.(34) Copper acetate prevented polymerization, a fact which had been observed in industrial plants. Even a trace of copper acetate retarded the change. The original light blue-green solution turned light brown, showing decomposition of the copper acetate.

A sample of vinyl acetate containing copper acetate did not polymerize on refluxing with benzoyl peroxide, so that the copper acetate even inhibited the accelerating effect of a positive catalyst, possibly absorbing the energy of activation.

Some evidence was obtained for autocatalysis in polymerization of two brown bottles of vinyl acetate, containing about 2 kg. each, apparently identical products except that the first had been recovered from a polymeric mixture; the first polymerized to a solid, while the latter is unchanged after 18 months in the dark. Milas (59) states that, in the dark, auto-oxidation of the polymerized substance is indispensable to polymerization and usually precedes the latter. If this is so, it is difficult to account for the variation in behavior of the two samples.

C. Final Method of Polymerization.

It was known that the purest sample of vinyl acetate would polymerize most rapidly. In this method, the thermometer was omitted, as it was shown that the temperature never rose above 76°, even in the case of very viscous polymers. As a result, it is evident that the polymers obtained were complex mixtures dissolved in unchanged monomer.

The important details are the stirrer and the means of illumination. Since, in polymerization, a mixture of polymers which may have definite limits of molecular size is to be expected, it was thought that stirring might narrow these limits. Although this makes no appreciable difference, the liquid must be stirred to prevent localization of the polymer and consequent inhomogeneity. The stirrer must be of such a shape that the total liquid is very thoroughly stirred, or local heating will occur with amazing ease. The effect is visible as small "spots" of polymer which form on the side of the flask nearest the light, which grow rapidly and solidify. For a light source, three 200-watt tungsten bulbs were placed symmetrically under the flask, at about the same distance from it, and inclined 20-30° to the horizontal. The nearest bulb formed the first "spot".

VI. Dielectric Constant of Benzene.

In Table VII of the experimental work, A and B were made 40 days apart, before and after ~~the work on~~ the dielectric constants of the polyvinyl acetates were measured. The difference of less than 0.2% is comparable with experimental error, and affords a good check on the reproducibility of the method employed. In these and the following readings, the second place of decimals could be read accurately to ±0.05 cm. on the scale. Actual scale readings are given. The standardization of the apparatus is given in Part II.

VII. Dielectric Constants and Densities of Polymers of Vinyl Acetate.

The most important result obtained is that the dielectric constant of polyvinyl acetate varies directly as the time of exposure and as the degree of polymerization, but that this increase corresponds in no way to the high dielectric constants of certain well-known liquids, which values are usually explained on the basis of some theory of molecular association. Water, for example, of dielectric constant, $\epsilon = 79.2$ at 25°,(76) has its value explained by the accepted theory of complex molecules of di- and tri-hydrol chiefly, which are in no way to be confused with the dimeric and trimeric forms of a true polymer. Those molecules which are highly associated have high dielectric constants, such as hydrocyanic acid, $\epsilon = 95$ ca., but the reverse is not true, as shown by acetone, $\epsilon = 21$ ca., and nitrobenzene, $\epsilon = 34.9$(76). A very rough approximation of the dielectric constant of completely polymerized vinyl acetate from the data obtained gives $\epsilon = 8\text{-}9$ (see Table V). The experimental results show great differences from those obtained for liquids which are known to be associated, which leads to the conclusion that there must be some fundamental difference between the two phenomena. Strong support is lent to the most widely accepted theory of polymerization, that the molecules are linked together by normal valence bonds. The dielectric constant for liquids is usually defined as a measure of the force required for orientation of the molecule under an electrostatic field against the energy of thermal agitation. It depends also on the electron shift within the molecule, which would be approximately the same in molecules of similar constitution. Thus the increased "length" of the polymerized molecule would result in increasingly difficult orientation, hence an increase is both the found and expected result.

The density of polyvinyl acetate also varies directly as the degree of polymerization. The density of fully polymerized vinyl acetate has been given as 1.190 ± 0.002, "at room temperature".(54) Assuming this value as correct, we see from Table V that the percentage polymerization obtained by the method outlined here varied from 2.6 to 20.5%. Thus one might detect with accuracy the polymerization of vinyl acetate, and probably other liquids capable of polymerization, by means of dielectric constant measurements, when the reaction had proceeded less than one-half of one per cent. This is a fact of great potential importance. With polymers of higher dielectric constant, a much smaller degree of polymerization could be measured with accuracy.

Conant and Peterson,(4) in a footnote, state "The degree of polymerization of the aldehydes is estimated by the viscosity of the product if still liquid, or roughly judged by the consistency of the paste if sufficient polymerization has occurred; quantitative results cannot be obtained." The polymers they obtained could be kept in vacuo over calcium chloride at 5° for considerable periods of time. The results of our investigation show that the above statement is hardly correct, and that this new method can be used to measure quantitatively the degree of polymerization of any organic liquid. Since these measurements were carried out, reconstructions of the apparatus used here and the addition of certain refinements, have decreased the error of measurement to 0.1%.

The Clausius-Mosotti law(77, 78) states that, if we consider the molecular polarizability as an invariable molecular constant, then the quotient $\epsilon - 1/\epsilon + 2$ will be proportional to the density; that is $\frac{\epsilon - 1}{\epsilon + 2} = Kd$ or $\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d} = K$.

Table V.

Compound	d^{25}_{4}	% Polymerized	Hours exposure	ϵ	K
Vinyl acetate	0.9258	0.0	0	5.825	0.666
Polyvinyl "	0.933	2.6	10	5.862	0.663
" "	0.946	7.6	20	6.021	0.662
" "	0.957	11.7	30	6.123	0.659
" "	0.966	15.1	40	6.201	0.656
" "	0.982	20.5	50	6.457	0.657
" "	1.190	100.0		8.5 8.7 } calc.	0.605 (extrapolated)

The values of K in the fifth column show this is not constant, which indicates that the molecule is polar. For non-polar molecules,

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = MR_D$$

where P = the molar polarization, ϵ = dielectric constant, M = molecular weight, d = density, n = index of refraction, and MR_D = molar refraction. If we substitute the values for vinyl acetate, we find $P = 57.33$ c.c. and $MR_D = 22.26$ c.c., which also shows that the vinyl acetate molecule is polar.

The value $\epsilon = 8.5$ for completely polymerized vinyl acetate is calculated by finding the change in dielectric constant for 1% polymerization. $\epsilon = 8.7$ is calculated from the extrapolated value, $K = 0.605$ by the Clausius-Mossotti equation.

VIII. Attempted Fractionation.

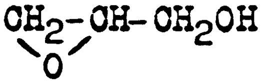
Attempted vacuum distillation showed that even the polymers of lowest molecular weight were non-volatile, so that a separation into fractions could not be obtained. The polymerization is thus irreversible, quite unlike styrene or indene, which give the monomer on heating, or the aldehydes, which revert to the monomer spontaneously. Fractional precipitation gave only products of no value for the problem.

Polyvinyl acetate has been utilized as a superior substitute to collodion for making air-tight seals in vacuum distillation. In a great many organic distillations, rubber stoppers and tinfoil-coated cork stoppers are unsatisfactory. In such cases, cork stoppers coated with the polymer can be used to advantage. It is dissolved in vinyl or ethyl acetate, or benzene, and used as a mobile solution. This elastic coat does not harden with time like collodion, and so it may be readily removed when necessary.

EXPERIMENTAL WORK.

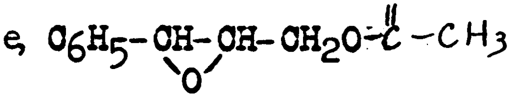
The following compounds were prepared:

1. Glycidol,



$\underbrace{CH_2-CH}_{O}-CH_2OH$

2. Phenyl glycidol acetate,



$C_6H_5-\underbrace{CH-CH}_{O}-CH_2O-\overset{O}{\overset{\|}{C}}-CH_3$

3. Divinyl ether, $CH_2=CH-O-CH=CH_2$

I. Preparation of Glycidol.

This method was originally used by Bigot(79) and modified by Nivière.(80)

300 g. of dried monochlorhydrin was dissolved in one litre of absolute ether and 65 g. of metallic sodium in shavings was added during three hours. The mixture was kept at 30°. Hydrogen was evolved freely for eight hours, when the reaction was complete. The solution was decanted, the residue washed with anhydrous ether, dried and the solvent removed. The fraction 60-100° at 15 mm. was retained. From the residue 55 g. of polymerized glycidol was extracted with anhydrous alcohol-ether solution.

A second preparation used the method of Rider and Hill,(72) at the time, unpublished. They used less than the theoretical requirement of metallic sodium in the form of wire wound around the stirrer, the optimum temperature being 10-15°. 231 g. (2 moles) of monochlorohydrin were dissolved in 1300 cc. anhydrous ether in a 3-necked flask equipped with a thermometer and a mechanical stirrer. 30 g. (not more than 0.7 mole) of metallic sodium in the form of fine wire was wound around the stirrer in solution. The mixture was stirred vigorously at 10° for 8 hours, when the evolution of hydrogen ceased. The solution was treated as before, the fraction from 60-100° at 15 mm. was united with the same fraction from the first preparation and kept for further purification, as a large quantity of the pure monomer was required.

II. Preparation of Phenyl Glycidol Acetate.

50 g. of cinnamyl alcohol, 76 g. of acetic anhydride and 10 g. solid sodium acetate were placed in a flask fitted with a reflux condenser. Considerable evolution of heat occurred, so contents were first cooled, heated on a water bath at 50° for 1-1/2 hours, and finally heated to boiling for 30 minutes. The mixture was cooled, but not till solid, poured into 500 cc. ice water, when an oily layer separated. This was separated from the water, washed with 100 cc. distilled water, and dried with fused sodium sulphate. Distillation gave 57 g. of pale yellow liquid, $b_{9.5 \text{ mm.}}$ = 131-2°. Yield 78%. A second preparation using 10% excess acetic anhydride gave 65 g., $b_{9.0 \text{ mm.}}$ = 129-130.5°. Yield 93%. The cinnamyl

acetate formed was placed in a chloroform solution of benzoyl hydroperoxide containing 5.30 g. active oxygen, stirred 2 hours at -10°, then kept at 0° for 115 hours. Test showed reaction had gone 85%. The mixture was washed with 300 cc. 10% sodium hydroxide, 300 cc. water, and dried with fused Na_2SO_4. The chloroform was removed and distillation gave 31.5 g. phenyl glycidol acetate, $b_{5 \text{ mm.}}$ = 135-8°. A second preparation gave a yield of 32.4 g. (50%).

III. Preparation of Benzoyl Hydroperoxide (Prileschajew's Reagent.(81)

The procedure followed in this preparation was that outlined by Hibbert & Burt,(82) which has been published in detail. Two preparations gave yields of 66% and 75%.

IV. Preparation of Divinyl Ether.

Divinyl ether is prepared by dropping 350 g. dichlorethyl ether on 1 kg. potassium hydroxide at about 200° C. in a copper flask. A condenser with Pyrex core is sealed to a Pyrex tube which just fits inside the neck of the copper flask, and is sealed to it by a cement made of litharge and glycerol. The condenser must be quite long, about 3 feet, and kept as cold as possible. This is connected in turn to a second condenser, and the product is condensed in a coil surrounded by an ice-salt mixture. The liquid in the flask was refluxed at a moderate heat 3-6 hours, the water in the first condenser was shut off and the ether distilled over, 5-10 g. each time. The fraction from 28-35° was retained, the larger portion boiling at 30-31°, bath temperature = 65°. Yield 80 g., 53%. Recovery dichloroethyl ether and chloroethylvinyl ether, 27%.

V. Vinyl Acetate.

A. Dielectric Constant.

Pure vinyl acetate* was redistilled and kept in brown bottles in the dark. b, 72°, $N_D^{25} = 1.3948$, $MR_D = 22.263$. The dielectric constant, ϵ, of the pure liquid was determined, at 25° ± 0.05°, using the apparatus and method described in Part II. Assuming the value of the dielectric constant of benzene to be 2.276,(83) the average of three accurate determinations of the dielectric constant of vinyl acetate was $\epsilon = 5.825$.

B. Density.

The densities of pure vinyl acetate were measured at 20° and 25° ±0.05°, with a specific gravity bottle. This was standardized with distilled water and pure benzene. The method and calculations followed are given in Findlay.(84) The values obtained were $d_4^{20} = 0.9320 \pm 0.0002$; $d_4^{25} = 0.9258 \pm 0.0002$. Staudinger's value is $d_4^{20} = 0.9317$.

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* We are indebted to Shawinigan Chemicals Limited, Shawinigan Falls, P.Q., for this generous donation of vinyl acetate, and for favors received.

VI. Preliminary Experiments on Polymerization of Vinyl Acetate.

No information was given in the literature about the degree of polymerization obtainable by the ordinary methods of polymerization employed, or how the process might be controlled. Thus it was necessary to perform a large number of preliminary experiments. Since it was impracticable for the purpose to use chemical catalysts, the only means was to utilize the action of light or heat or some combination of them.

A. Thermal Polymerization. Benzoyl Peroxide.

Vinyl acetate was refluxed for 3 periods of 5 hours each, and then for 18 hours. After each period, the dielectric constant was measured but no measurable change occurred. 0.5% of benzoyl peroxide was added and reflux continued. After 40 minutes the product was very viscous. The dielectric constant had increased 5.6% to 5.983.

B. Photopolymerization.

125 g. vinyl acetate was placed in a Pyrex flask fitted with a stirrer. It was exposed to visible light from a 200-watt bulb for 28 hours at room temperature. The dielectric constant was unchanged, as it was after 33 days exposure.

Nine test tubes were then placed in such positions about light bulbs that they were heated at temperatures from 25-72°. All polymerized, with the exception of those at 25°, which polymerized when exposed at a higher temperature, but which required a longer time though a few drops of polymer were added to each test-tube.

VII. Dielectric Constant of Pure Polymers.

The most viscous products were placed in the dielectric cell container, the plates immersed in the liquid, and the cell allowed to stand overnight to ensure the absence of air-bubbles from between the plates. Great care is necessary to prevent their inclusion in the polymers, which would be a source of considerable error. The dielectric constant was 5.969, an increase of 5.3%. Since a mixture of polymers in unchanged vinyl acetate was used in this determination, an equal volume of vinyl acetate was added to the mixture and allowed to become homogeneous. The dielectric constant was 5.824, the theoretical mean being 5.818. The difference is 0.1%, comparable with experimental error.

VIII. Polymerization of Vinyl Acetate by the Simultaneous Action of Visible Light and Heat.

Having found that polymers of vinyl acetate had a higher dielectric constant than the original compound, polymerization was undertaken on a practical laboratory scale. A 50-C.P. 6-8 volt automobile headlight bulb, using 5 amperes at 5.5 to 6.1 volts, was connected through a bank of lamps with a 110-volt D.C. circuit and immersed in 500 grams of vinyl acetate in a 3-neck 1-litre flask. The temperature rose to 56-57°, and the exposure lasted 5, 10, 5, 10, and 6-1/2 hours consecutively, with vigorous stirring. No change was found in the dielectric constant after each of these periods. Redistillation of the slightly colored liquid gave a distillate B.P. 72-73.5°. Considerable ground glass present may have helped to prevent polymerization, though the action of silica is unknown.

The distillate was replaced in the flask, fitted with a reflux condenser, and a 200-watt bulb placed underneath. The boiling liquid was exposed 59 hours, with no change. The liquid was light brown. The metal end of the immersed bulb and the copper wires had turned black. The product gave a distinct test for acetic acid with silver nitrate, and titration showed it was 0.12 N.

A. Action of Metallic Copper on Vinyl Acetate.

A test-tube containing vinyl acetate and copper wire was placed in the dark. A green solution formed which tested for acid as above. This sample was exposed to light and heat 67 days without change. Copper acetate was precipitated.

B. Action of Copper Acetate on Polymerization.

The vinyl acetate from the last 59-hour exposure was redistilled, and four samples were exposed to light at 48°. The results are as follows:

Table VI.

No.	Treatment	Time of Exposure	Product
1	Add $CuAc_2 \cdot 2H_2O$	67 days	No change; soln.of salt.
2	Trace $CuAc_2 \cdot 2H_2O$	29 "	Light brown. Very viscous.
3	None	21 "	Clear. Very viscous.
4	Add Cu wire	67 "	No change. $CuAc_2$ precipitated.

A fifth sample was refluxed 5 hours with benzoyl peroxide, but was unchanged.

C. Action of Traces of Copper on Polymerization.

A new sample of vinyl acetate was found to contain particles of tin and copper on filtration. No test was obtained for acetic acid in the vinyl acetate, but it gave a faint test for copper. The ester was not purified. It was photopolymerized at reflux temperature for 45 hours, dielectric constants being measured after 20, 25, 35 and 45 hours exposure. Some polymer was lost on manipulation. The increase in dielectric constant was 8.66%, compared with 10.85% increase for a purer sample exposed 50 hours.

These preliminary experiments indicated --

(a) That the simultaneous action of heat and light on vinyl acetate gave a slow, controllable means of polymerization at reflux temperature;

(b) That the reaction was catalyzed by benzoyl peroxide, and inhibited by the action of copper and copper acetate;

(c) That the rate of polymerization increased with increase in purity of the sample; and

(d) That the dielectric constants of the complex mixture of polymers increased with the degree of polymerization.

IX. Final Method of Polymerization.

In its final form the polymerization apparatus was quite simple, and the thermometer was omitted. A bolt-necked 250-cc. Jena round-bottom flask was fitted with a mechanical stirrer with mercury seal and a reflux condenser with a calcium chloride tube. Three 200-watt bulbs were placed symmetrically under the flask as before. 1500 cc. of vinyl acetate were redistilled, b.p. 72-72.5°. 150 cc. was placed in the flask for each experiment. Exposures lasted 10, 20, 30, 40 and 50 hours. A 60-hour exposure was not successful. In the last three cases the rate of stirring had to be increased after 25 hours because of the increase in viscosity. The final products were placed in the dark and are being retained. The dielectric constants and densities of each have been measured. Viscosities were not measured. Visual observation alone showed an increase with increased time of exposure, the difference in adjacent samples being very marked.

X. Dielectric Constant of Benzene ("Kahlbaum, for Molecular Weights").

Table VII.

T = 25° ± 0.05°

C_3	A. C_2 (aver.)	B. C_2 (aver.)
81	141.10	144.20
71	138.50	141.65
61	135.70	138.90
51	133.20	136.25
41	130.60	133.70
31	128.10	131.20
21	125.45	128.60
11	122.90	126.00

$$\frac{dy}{dx} = \frac{28.75}{15.00} \qquad \frac{dy}{dx} = \frac{28.80}{15.00}$$

$\epsilon = 2.276$, the most accurate value for benzene at 25°.

C_3 and C_2 are the readings on the dielectric cell condenser and tuning condenser, respectively. $\frac{dy}{dx}$, is the slope of C_3/C_2. ϵ is the dielectric constant.

XI. Dielectric Constants of Vinyl Acetate and Its Polymers.

Table VIII.

T = 25° ± 0.05°

C_3	Original C_2 (aver.)	Exposure I 10 hours C_2 (aver.)	Exposure II 20 hours C_2 (aver.)
81	182.60	184.00	186.80
71	176.15	177.30	180.10
61	169.05	170.15	172.60
51	162.50	163.70	165.90
41	155.85	157.10	159.20
31	149.35	150.45	152.50
21	142.55	143.75	145.50
11	135.90	137.00	138.90
	$\frac{dy}{dx} = \frac{33.70}{45.00}$	$\frac{dy}{dx} = \frac{33.55}{45.00}$	$\frac{dy}{dx} = \frac{32.60}{45.00}$
	$\epsilon = 5.825$	$\epsilon = 5.862$	$\epsilon = 6.021$

C_3	Exposure III 30 hours C_2 (aver.)	Exposure IV 40 hours C_2 (aver.)	Exposure V 50 hours C_2 (aver.)
81	188.50	189.50	191.15
71	181.50	182.30	183.75
61	174.10	174.65	175.85
51	167.25	167.65	168.55
41	160.50	160.70	161.40
31	153.70	153.85	154.15
21	146.50	146.75	146.60
11	139.55	139.65	139.40
	$\frac{dy}{dx} = \frac{32.10}{45.00}$	$\frac{dy}{dx} = \frac{31.70}{45.00}$ or $\frac{35.25}{50.00}$	$\frac{dy}{dx} = \frac{30.40}{45.00}$ or $\frac{33.80}{50.00}$
	$\epsilon = 6.123$	$\epsilon = 6.201$	$\epsilon = 6.457$

XII. Densities of Vinyl Acetate and Its Polymers Given in Section XI.

The method for the polyvinyl acetates was the same as for the monomeric ester, but due to difficulty in filling the specific gravity bottle and some loss by evaporation, the results are only given to the third place.

Table IX.

Compound.	d_4^{25}	Time of exposure hours 72 - 75°	ϵ
Vinyl Acetate,	0.9258	0	5.825
Polyvinyl Acetate, Exp.I,	0.933	10	5.862
" " " II,	0.946	20	6.021
" " " III,	0.957	30	6.123
" " " IV,	0.966	40	6.201
" " " V,	0.982	50	6.457

d_4^{25} = density, ϵ = dielectric constant at $25^\circ \pm 0.05^\circ$

XIII. Catalytic Effect of Mercury on the Polymerization.

When the first trial was made for a 30-hour exposure, some mercury leaked through the stirring apparatus and was found in the final product. This caused a marked increase in the dielectric constant compared with the values where mercury was absent. The value $\epsilon = 6.530$ represents an increase in dielectric constant of 12%, compared with a normal increase of 5% for the same time of exposure.

XIV. Further Note on Polymerization.

The first samples of vinyl acetate were redistilled at 72.0-72.5° and kept in clear glass bottles in the dark. After six months standing, the vinyl acetate had polymerized and was more viscous than glycerol. The unchanged vinyl acetate was removed by fractionation from a Claisen flask, the distillate collected boiling at 72.5-73° and placed in a brown bottle in the dark. The density of the product was identical with the value previously obtained. The second sample of vinyl acetate was redistilled and stored in a brown bottle the same as the first. After 18 months, the vinyl acetate recovered from the polymer had become almost solid. The other sample, never in contact with polyvinyl acetate, shows no traces of polymerization.

XV. Attempted Fractionation of Polyvinyl Acetate.

A. Fractional Distillation.

The large samples which had spontaneously polymerized gave quantities of polymer with which to work, so fractional distillation was attempted. This proved quite unsuccessful. The mixture was placed in a Claisen flask, and despite careful heating and a good vacuum only unchanged vinyl acetate distilled over, after which the polymer hardened continuously until it became quite solid.

B. Fractional Precipitation.

A small volume of the complex polymers was dissolved and then precipitated with ligroin. The precipitate was the usual pasty mass, which formed a unit on shaking. After removal of the liquid, it was kept in a vacuum desiccator for days, but in no case was any product except a solid obtained. These, of course, would be dissolved in benzene and the moments obtained by the method of binary mixtures. This would not be very far ahead of the original mixture, and the average molecular weight would be higher. Again, with these highly polymerized compounds of unsettled constitution, methods of molecular weight determination are of somewhat doubtful value, so it was decided to work upon compounds of better known constitution and low molecular weight.

CONCLUSIONS.

1. Glycidol, phenyl glycidol acetate, and divinyl ether have been prepared. A slight modification increased the yield of phenyl glycidol acetate somewhat. The preparation of divinyl ether fully confirmed the method originally used, although some difference in boiling point was noted.

2. The boiling point, density, and refractive index of vinyl acetate are given, and confirmed by later results published in the literature. The dielectric constant has also been measured.

3. The polymerization of vinyl acetate has been investigated. In common with other workers, the author found that benzoyl peroxide catalyzed the reaction, while copper acetate acted as an inhibitor. Metallic mercury is shown for the first time to accelerate the reaction, and metallic copper is added to the list of anticatalysts. A slow, reproducible laboratory method of polymerization has been worked out, by the simultaneous use of visible light and heat from the light source, at reflux temperature. All previous photochemical methods used ultraviolet light. Minute impurities retarded the reaction.

4. The correlation of the change in dielectric constant with the degree of polymerization of vinyl acetate shows that another physical measurement is applicable to one of the most complex and scientifically and industrially important branches of organic chemistry. The dielectric constants and densities of five samples of polyvinyl acetate exposed for varying periods of time are given. Both these values are shown to vary directly as the time of exposure and as the degree of polymerization. The method of measuring dielectric constants given here is shown to be applicable to mixtures of polyvinyl acetate and unchanged monomer in any proportion. The dielectric constant values indicate a fundamental difference between the phenomena of association and polymerization. Support is lent to the "normal valence" theory of polymerization. The observed increase in dielectric constant in polymerization is accounted for on theoretical grounds.

The approximate percentage polymerization of the polyvinyl acetates have been calculated from density measurements, and a density reported in the literature for completely polymerized vinyl acetate. It is shown that, by the method outlined, polymerization of organic liquids can be detected when the reaction has proceeded a fraction of a percent, with greater accuracy obtainable. The application of this method to other problems of the same nature is pointed out.

The constant of the Clausius-Mosotti law has been calculated, showing the molecular polarizability is not constant for vinyl acetate and its polymers. Rough values of the dielectric constant of 100% polymerized vinyl acetate calculated by two methods show substantial agreement.

5. Attempted fractional distillation and fractional precipitation showed that liquid polymers of vinyl acetate of low molecular weight could not be obtained by these methods. The non-distillability of polyvinyl acetate also proves that this polymerization is thermally irreversible.

6. A practical use for the polymers in organic preparations is suggested.

INTRODUCTION.

I. General.

During the past twenty years, there has been a rapidly growing tendency among chemists to regard the electrical properties of molecules and their resultant effects as of paramount importance, and an attempt is being made, with varied success, to apply the ideas and implications of the newer quantum mechanics to classical and modern chemical theory. No less do we find physicists taking a lively interest in the fundamental process of chemistry, the chemical union of atoms to form molecules, and applying physical data to the elucidation of the mechanism of this problem. Many physical methods are being increasingly used in the determination of molecular structure, such as ultraviolet and infrared absorption spectra, x-ray analysis and Raman spectra. One of the chief reasons for this new attitude on the part of chemists was the origination by P. Debye(85) in 1912 of the theory of dipoles, as an explanation of the variation with temperature of the dielectric constant of certain substances which have since been classed as "polar molecules". An immediate result of this has been the formulation of older theories in terms of the new concept,(86) and an attempted correlation of the physical magnitude of the dipole, the electric moment, with the properties of the molecule.

One branch of this work which, in general, has enjoyed conspicuous success, is the relation established between electric moment and molecular structure. The usual method is to measure the electric moment of compounds of known constitution, and correlate the results with known chemical data. The process has often been the deciding factor leading to the preferential acceptance of one specific type of structure. The one outstanding case on record where electric moment values have been used in analysis is in the case of cis-trans isomerism. In the investigation to be reported here, both paths of approach have been followed, in an attempt to show that an otherwise unaccountable difference in the electric moments of certain molecules can be explained by the theory of isomerism, and to examine some assumptions made by classical stereochemistry in the light of recent theory and experimental data.

Considerable progress has been made in explaining the rules of substitution in the benzene nucleus by reference to the moments of the substituent groups. No exceptions have been found to date.(87, 88)

Electric moment and dielectric constant investigations on the solid state(89) have shown a relation between solids and highly viscous liquids.

The conclusions of other workers(90, 91, 92) on the phenomena of free and restricted rotation in organic compounds have been confirmed and extended by electric moment studies of Zahn,(93) Smyth,(94) and Ebert.(95) A review of the evidence has been recently published by Bergmann and Engel.(96)

The causes of molecular association in the vapor and liquid states and the consequent effects of this phenomenon are almost entirely explained, both qualitatively and quantitatively, on the basis of the dipole theory.(94, 97)

An interesting, if somewhat abortive, attempt has been made to correlate the electric moment and the velocity of reaction.(100) Smyth concludes that one cannot expect a close connection to be established between reaction velocity and electric moment. Hückel's treatment shows(98) that there are so many cases in which correlation is unjustified that it leaves but a small field in which to work. Waters(99) made predictions concerning the velocity of benzene substitution and the moment of the entering substituent. A possible explanation has also been offered for the Markownikow and Ipatiev addition rules.(101)

Other phenomena related to electric moment and dielectric constant data may be listed, such as anomalous dispersion for radio frequencies in liquids and solids, the Kerr effect and the scattering of light in gases and liquids, electrostriction, and the dipole rotation effect.

The dipole theory has also received considerable attention industrially as an explanation of the breakdown of dielectrics under stress. The methods have also been employed to investigate dielectric and power losses, and the insulating efficiency of dielectrics under conditions of varying temperature and frequency.(102)

It is evident, then, how great is the importance of the dipole in modern scientific theory from the brief outline given, and an explanation is obvious why the literature on this subject is growing with such great rapidity. In this regard, acknowledgement is made of the especially helpful contributions of the books by Smyth(94) and Debye,(103) and the collected papers of Smyth(104) and Williams(86, 105) and their coworkers, which have been used extensively in the preparation of this work.

II. Definitions.

1. Polar and Non-Polar Molecules, Electric (or Dipolar) Moment.

What is a non-polar or polar molecule, and what is the electric (or dipolar) moment? Most of the molecules that we now know as having a symmetrical spatial configuration are non-polar in character, that is, the centers of gravity of the positive and negative charges as distributed among the atoms coincide. The converse of this statement is often employed, viz. when the measured value of the moment is zero, this molecule is proved to be symmetrical. Some molecules previously considered to be symmetrical have proved to be otherwise.

If the center of gravity of the positive charges does not coincide with that of the negative, the molecule may be regarded as containing an electric doublet, two equal charges, $\underline{e}$, of opposite sign close together, the imaginary line joining them being termed the axis of the doublet, $\underline{a}$, and its magnitude being measured by the electric moment, μ, which is the product of the length of the axis by the magnitude of one of the charges, i.e., $\mu = ea$. In an electric field, a polar molecule tends to arrange itself with its negative end towards the positive pole. Every isolated atom is non-polar. When two atoms share electrons, if they share them equally, the molecule produced will also be non-polar, but if unequally, it will be polar, the atom which has the greater share being at the negative end of the dipole. Covalent links between unlike atoms are, in general, polar.

Non-polar, electrically symmetrical molecules may be isotropic, giving negative results in an applied field, or anisotropic with a polar orientation along the line of maximum dielectric constant. Common non-polar organic molecules are carbon tetrachloride, carbon disulphide, dioxane, saturated hydrocarbons, unsaturated hydrocarbons with a symmetrically situated multiple bond, and benzene, but not its homologs.

Polar molecules may be "dipole" molecules, which orientate in a field along the dipole axis, or "ionogenic", giving rise to ions. For the present purpose, dipole molecules are most important. Organic polar molecules include all unsaturated compounds with unsymmetrically located double or triple bonds, and those compounds containing oxygen, nitrogen, sulphur, halogen atoms, etc.

2. Bond and Group Moments.

The electric moment of a molecule may be made up of a number of individual moments pertaining to each of the bonds or linkages. Thus each "bond" moment would be a directed quantity, and the vectorial sum of all these bond moments is the moment of the whole molecule. The moment of such a molecule as ethylene chlorohydrin is made up of the $H \leftarrow C$, $C \leftarrow O$, $C \leftarrow Cl$, and $H \leftarrow O$ bond moments. The partial moment of the group $--CH_2Cl$ would be referred to as its group moment.

3. Polarity and Electronegativity.

Polarity has often been used in different ways to express molecular properties more or less connected with the actual arrangement of, or the mobility of the charges of which molecules are supposed to consist. It has, however, been frequently misused as referring to the electropositive or electronegative character of certain groups or atoms in the molecule, the sign of which need have no necessary connection with the polarity of the molecule as a whole. This incorrect usage only leads to confusion, and so it would be preferable to reserve the terms polar and polarity to these molecules possessing a finite electric moment.

4. Natural (or Rigid) Electric Moment.

The term "rigid" electric moment has also crept into the literature, although rigid molecules really exist only as the ideal limiting case. Ebert (95) says the choice of word seems an unhappy one, and suggests we should call this moment the "natural" electric moment for a simple molecule in a normal equilibrium state. By a "simple" molecule, one is meant which closely resembles a system of material particles possessing a well-defined position of equilibrium for which the energy of the system is a minimum.

5. The Dielectric Constant.

The dielectric constant, ϵ , is not subject to complete and exact definition for a liquid. In solids it is a measure of the ease of electron displacement, and is defined as the diminution of electric field through the shift of electrons. The electric field, f, set up by two charges, e and e', separated by a distance d, in a medium of dielectric constant ϵ, is given as $f = \frac{e\,e'}{\epsilon\, d^2}$. (1)

The greater the electron displacement the greater the dielectric constant, so that for metals ϵ is very large. From Equation (1), <u>f</u> is very small, that is, the electric field set up in a metal is minute.

Suppose a field is set up in a liquid between the plates of a condenser, we may then measure the dielectric constant of the medium. As it is not infinity, the field will have a finite value, and this field will cause a slight shift of electrons in the molecules of the liquid as in the solid. But another factor is also present, viz., the orientation of molecules against their energy of thermal agitation, and this portion of the dielectric constant is proportional to the absolute temperature, if it be assumed that there exist, as Debye suggested, permanent electric dipoles in the molecules. With a highly polar compound, this value becomes very large because of association, since the associated molecules must first be de-associated by the external field. If alternating current of very high frequency is used, the molecules would not have sufficient time to orientate and the dielectric constant measured would be the first factor only, the electron shift among the constituent atoms. Another factor which contributes to the dielectric constant is the shift of atoms or radicals in the molecule on application of the external field. Very little is known of this effect quantitatively, but (comparatively) it is very small.

III. Determination of Polarity.

To determine whether a molecule is polar or non-polar, it is necessary to measure the dielectric constant and density at different temperatures. Then the molar polarization, P, is calculated according to the equation

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} \qquad (2)$$

and it is plotted as a function of $\frac{1}{T}$ (see Fig. I).

We have two possibilities:

1. P is independent of T, and we get a straight line, Class I, parallel to the T-axis, which indicates a non-polar molecule of electric moment = 0.

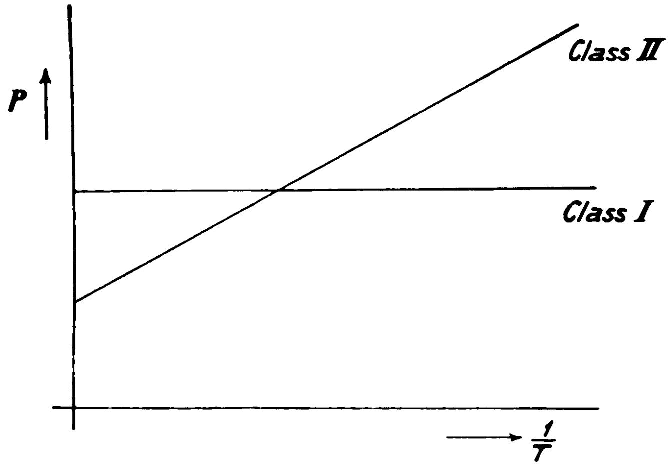
2. P depends on T. Class II. We again expect a straight line from the equation

$$P = \frac{4}{3} \pi N \left(\alpha_0 + \frac{\mu^2}{3KT} \right) \qquad (3)$$

In this case the molecule is polar, and the electric moment will have a finite value. The explanation of these equations will be given later.

IV. Polarity of Certain Molecules.

A rapid review of the polarity of a few common substances will be sufficient to indicate the importance of the relations between electric moment and the structure of molecules. All elementary molecules in the normal state will be non-polar, although there was some question about the polarity of Br_2 and I_2.



sation-temperature curves for polar (II) and nonpolar (I
stances.

Fig. I.

Polarization-Temperature Curves for Polar (II) and Non-Polar (I) Substances.

The hydrogen atom, however, with one electron, would be polar. The hydrogen halides are all polar, the moment decreasing with increase in the size of the electronegative atom. Carbon monoxide has a slight polarity, suggesting slight electrical dissymmetry of the molecule and a highly condensed structure. Triatomic compound molecules AB_2 will be non-polar if all the links are identical and if the molecules are rectilinear, as CO_2, CS_2, and N_2O. The molecules of H_2O, H_2S, and SO_2 are polar, hence the structure must be triangular. For a triatomic molecule ABC, such as COS, a linear structure still possesses polarity, due to a difference in the polarizability and size of the two electronegative atoms. A tetratomic molecule AB_3 will be non-polar only if all atoms lie in a plane. Therefore NH_3, a polar molecule, must be pyramidal. AB_2X would be polar, the degree of polarity depending on B and X. AB_4 could only be non-polar for a tetrahedral or plane structure; but the latter is ruled out, because AB_2C_2 would then be non-polar and no non-polar molecules of this type are known. However, tetrahedral AB_4 is not necessarily non-polar, as is seen in the case of penta-erythritol ($\mu = 2$)* and its tetra-acetate, although the tetra-halides are non-polar. This first suggested to Ebert(109) and to Weissenberg(110) that the

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* Values of electric moments given without references are taken from tables by Smyth.(94) All values of moments given are multiplied by 10^{18} e.s.u.

carbon atom in these compounds possessed a pyramidal structure. The correct explanation was later given by Højendahl(111) and Williams(112) who pointed out that in each case where these molecules possessed a finite electric moment, there is an oxygen atom in the substituent group. This gave a strong indication of the important part to be played in electric moment data by the stereochemistry of the oxygen atom. That the significance of this role and the resultant complexity which it causes in interpretation of experimental results has not been sufficiently realized will be later evident. It has also been shown that such atoms as nitrogen and sulphur produce similar effects. Thus it is evident that *simple* groups of one bond moment, e.g. C←Cl, obey a simple rule, but that *complex* groups, especially those containing oxygen (and nitrogen) belong to a different class of substituent. This is because -OH, etc., consist of two or more bond moments, ←O and H←O.

Benzene and its derivatives have been the subject of years of intensive research, and the chemistry and structure of these compounds has offered a wide field for diverse theory and speculation. Benzene was immediately established as a non-polar molecule with a plane structure,(113, 106) and all its monosubstitution products are polar, including toluene. For disubstituted benzene where the simple substituents are identical, we obtain a maximum for the ortho, an intermediate for the meta, and a minimum (zero) value for the para compound. The rule is reversed if the substituents are of unlike sign. See Table I(a). In the case of ortho- and meta-dichlorobenzene, it was believed that the chlorine atoms were mutually repelled, and the angle between their doublets was calculated from the difference of the observed moment and that calculated for an angle of 60° and 120° between the doublets for the ortho and meta compounds.(114) It was later shown that this difference was due principally to the inductive effects of the two doublets.(115) It is also evident that if an electrical character is assigned to any one substituent, the signs of all other substituents are definitely fixed.

Table I.

Moments (x 10^{18}) of Disubstituted Benzene

(a) With Simple Substituents

Compound	o.		m.		p.	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$C_6H_4Cl_2$	2.63	2.25	1.52	1.48	0	0
$C_6H_4Br_2$	2.60	1.8	1.50	1.4	0	0
$C_6H_4I_2$	2.16	1.63	1.25	1.01	0	0
$C_6H_4(NO_2)_2$	6.76	6.03	3.9	3.76	0	0
C_6H_4ClBr					0	0
C_6H_4BrI	2.38	1.73	1.39	1.14	0.25	0.49
$C_6H_4ClNO_2$	4.89	4.0	3.40	3.3	2.38	2.45
$C_6H_4BrNO_2$					2.40	2.53
$C_6H_4ClCH_3$	1.36	1.39	1.75	1.60	1.92	1.74
$C_6H_4NO_2CH_3$	3.72	3.75	4.12	4.20	4.3	4.50

(b) With Complex Substituents

	o.	m.	p.
$C_6H_4(OH)_2$	2.16		
$CH_3C_6H_4OH$	1.44	1.60	1.64
$CH_3C_6H_4OCH_3$	1.0	1.17	1.20
$CH_3OC_6H_4OCH_3$	1.31	1.58	1.81
$C_2H_5OC_6H_4OC_2H_5$	1.37	1.70	1.76
ClC_6H_4OH	1.43	2.17	2.68
BrC_6H_4OH	1.36		2.86
$NO_2C_6H_4OH$	3.10	3.90	5.05
$C_6H_4(NH_2)_2$	1.45	1.80 *	1.50
$NO_2C_6H_4NH_2$	4.45	4.72	7.1
$CH_3COOC_6H_4OOCCH_3$	2.5		2.2

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* m-Phenylene diamine is the only known case, even for complex substituents, where the moment of the meta- is greater than either the ortho- or para- derivatives.

In the case of complex substituents, Table I(b), the moment usually increases from the ortho to the para compound. If the two substituents are of like sign the increase is especially marked. The table also shows that the introduction of an oxygen atom into the system complicates the situation just as in the case of aliphatic compounds.

Similar methods have been employed to investigate the electric moments of substituted naphthalenes and diphenyls, and the conclusions drawn concerning the relationship of structure and electric moment are comparable to the case of benzene.

V. Utility of Electric Moment Measurements.

Electric moment measurements have not contributed greatly in the initiation of new molecular structures or scientific theory, and have been used largely as confirmatory evidence, of a very valuable nature, for conclusions based on existing chemical and physical data. The notable exceptions are--

1. It has been possible to determine absolutely which of two isomers is cis and which trans,(116) the former giving a maximum value and the latter a minimum. The only doubtful cases have occurred where oxygen atoms were present in the molecule.

2. A decision between the theories of Hantzch and Meisenheimer has been promoted by electric moment determinations on syn- and anti-oximes.(117) The syn- compounds of Meisenheimer had moments much greater than the anti- compounds, thus offering unqualified support of the latter's theory.

3. Carbon monoxide and the isocyanides are shown to have the carbon triply linked to the oxygen and nitrogen atoms, the third link being a co-ordinate bond.

4. The values of the moments of aromatic and aliphatic azides and diazo compounds (118, 119) definitely favors the ring structures of these compounds, opposing the evidence of x-ray and chemical examination. The ring structure gives a small value, whereas other structures would give a comparatively large moment.

5. In the methyl α- and δ-aminovalerates, Estermann (120) found the former had a moment of 1.6 and the latter of 2.7, from which he concluded the molecule was a straight chain. The complexity of the groups involved renders interpretation inconclusive, although Smyth and Kamerling (121) decided the zig-zag rod-like structure above explained the moments of the polymethylene bromides.

6. The magnitude of the carbon valence angle has been determined as 114-119° by Smyth and Walls (122) from a consideration of the moments of compound C_6H_5X and $pXC_6H_4CH_2Y$, the variation from the tetrahedral value being no more than the probable error.

A similar treatment (122) of the diphenyl ethers gives the angle between the oxygen valence bonds as 121° ±5°.[*]

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[*] This paper on the oxygen and sulphur valence angles appeared after the investigation outlined here had been concluded.

The results for the anisoles and phenetoles do not give dependable values of the oxygen angle, although they may be explained in terms of an oxygen angle not far from 130°.

The oxygen angles in various heterocyclic compounds calculated from the interatomic distances vary from 65° to about 140°, and the moments are in excellent qualitative agreement with predictions based on the size of the angles.

Limited data for the sulphur angle in the diphenyl sulphides give a value of about 146°, which may be too high. The behavior of thiophene is strictly analagous to that of the corresponding oxygen compound.

VI. Objects of This Investigation.

(a) Ring-Chain Isomerism.

In Part I, it was mentioned that the measurement of electric moments of polymers should offer valuable data concerning the chain or ring structures of these molecules. When the aim of this investigation was altered, it was still believed that some indication would be given by the magnitude of the moments of certain isomeric compounds whether a particular molecule possessed a chain structure or if it were the corresponding ring isomer.

(b) Oxygen Valence Angles.

A problem of equal, if not greater, importance was to attempt a determination of the magnitude of the angle between the two valence bonds of the oxygen atom in organic compounds (hereafter called the oxygen valence angle) to explain the stability of a ring isomer, which on the basis of classical stereochemical theory should be quite unstable. The work was also extended to include other compounds which could possibly confirm or deny a hypothesis which was suggested to explain the values of the moments of the ring isomer.

Existing physical data gave no indication at the time of the magnitude of the oxygen valence angle, although calculations of the moments of certain compounds revealed the possible non-validity of the assumption of a tetrahedral oxygen atom. Chemical data had also suggested that a difference existed between the stereochemistry of homocyclic and heterocyclic rings containing oxygen atoms.

The oxygen valence angle in the water molecule was calculated to be about 64°,(103) but the validity of this value is seriously questioned.(123, 94)

To obtain agreement between the experimental and calculated moments of the p-oxybenzenes, Wolf(124) found it necessary to assign a positive sign to the H-O- and CH_3-O- groups, on the assumption of a tetrahedral oxygen atom. Similarly Eucken and Meyer(123) are unable to calculate satisfactorily the values of the moments of the dialkyl ethers of hydroquinone. Werner(124) found an increase in the moment of hydroquinone diethyl ether with rising temperature, contrary to expectations. The only possible explanation (95) seems to be in contradiction with the angles given by classical stereochemistry.

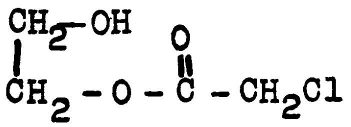
Quantum mechanics gave the oxygen valence angle as 90°, in accordance with the values of the valence angles of other atoms obtained from crystal structure data, which should be of the same magnitude as the oxygen valence angle. Williams and Fogelberg (125) in a study of the electric moments of substituted phenols, state "The angle between the directions of the two valencies of the oxygen atom is as yet uncertain and unobtainable. It is usually assumed to be 110°; however, all that can be said with certainty is that it is less than 180°."

The fact has long been known in carbohydrate chemistry that many derivatives containing a five-membered furanose (gamma, active) ring have a very strong tendency to pass over to an apparently more stable six-membered pyranose ring under the influence of a trace of acid, on heating, and even on standing in solution. This is in remarkable contrast to the well-known fact that five-membered homocyclic carbon rings are more stable than the six-membered variety. It has also been established that the five-membered γ-lactones are more stable than the six membered δ-lactones, (130) which is shown by the relative ease of hydrolysis of the latter.

In an attempt to explain at least some of these discrepancies, it was deemed highly desirable that this investigation should be carried out.

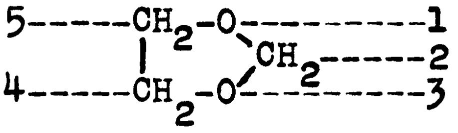
(c) Selection of Compounds.

The two compounds selected whose moments were to be measured first were glycol monochloroacetate (I) and glycol dichloroacetate (II) or the corresponding ring isomer, 2-hydroxy-2'-dichloromethyl-1·3-dioxolane. The nomenclature is that suggested in "Chemical Abstracts" of the American Chemical Society, in which compounds of this latter type are considered derivatives of the parent ring, 1·3-dioxolane (III).

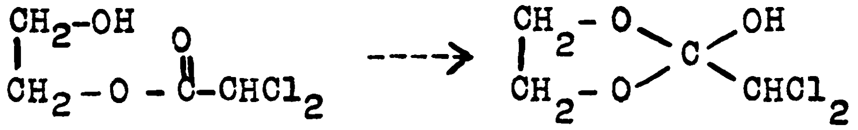


$HOCH_2-CH_2-O-C(=O)-CH_2Cl$

(I)



(III)

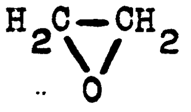


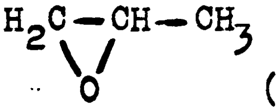
(II)

This work was undertaken in collaboration with others in this laboratory in a study of a series of glycol monoesters of remarkable interest -- glycol monoacetate, glycol monochloroacetate, glycol dichloroacetate, and glycol trichloroacetate or 2-hydroxy-2'-trichloromethyl-1·3-dioxolane. The two compounds selected out of four possible in the present case have been chosen because other data and properties showed that each belonged to a different class of compounds.(126) The second compound of the series is a normal half-ester, while the third is a dioxolane ring. It was hoped that the determination of the electric moment of these compounds might throw some light on their relative structure, and the results obtained show definite indications that such has been the case.

The experimental value of the moment of the dioxolane compound seemed best explained by assuming an oxygen valence angle less than 109° 28', and theoretical considerations showed that this decrease in the oxygen valence angle might be the greatest factor determining the relative stability of the furanose and pyranose rings in carbohydrates and polysaccharides. Obviously, when difficulties are encountered in the interpretation of the moments of simple compounds, it would be futile to measure the moment of any carbohydrate such as a glucopyranose or furanose compound. The simplest compounds were chosen, tetrahydrofuran (VII) (tetramethylene oxide, 1·4-oxide-butane) and tetrahydropyran (VIII) (pentamethylene oxide, 1·5-oxido-pentane). It was later found that Smyth had determined the electric moment of tetrahydrofuran, although it was unpublished till recently.(122)

It has been found that the substitution of hydrogen by a methyl group in any hydrocarbon, or member of an homologous series(128, 157) such as the alcohols, ketones, and esters,(94) did not alter the electric moment of the resulting compound. Thus, all 22 saturated paraffins so far examined are non-polar, but Wolf and Gross(129) have claimed that for the homologous series mentioned, at least for the primary members, the value of the moment alternately rises and falls, the molecules with an even number of carbon atoms giving a maximum value. Since the moment of ethylene oxide (IV) had been measured,(127) propene oxide (V) (propylene oxide) was selected to see what difference would be observed in the moments of these two compounds. The electric moment of trimethylene oxide (VI) was measured to complete this heterocyclic series.


(IV)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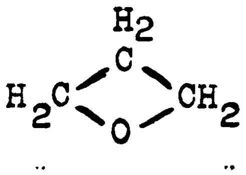
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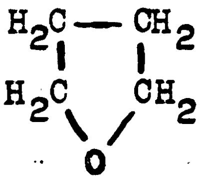
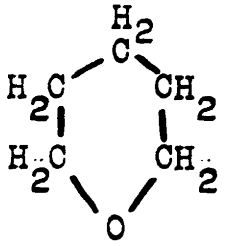

(VII)


(VIII)

VII. Summary.

A summary of the objects of Part II may be outlined.

1. The preparation and measurement of the electric moments of two glycol half-esters, one of which is an open-chain compound while the other is a closed ring, to determine if a ring isomer could be detected by electric moment measurements.

2. To determine the magnitude of the oxygen valence angle in the ring compound in an attempt to explain the stability of its structure.

3. To test the validity of the assumption of a tetrahedral oxygen atom in heterocyclic compounds, with a view to possible explanation, by analogy, of the relative instability of the furanose contrasted with the pyranose-ring systems in carbohydrates and polysaccharides. To this end, tetrahydropyran was prepared and its electric moment measured.

4. To measure the electric moment of propylene oxide to compare the experimental value with that of ethylene oxide.

5. To prepare and measure the moment of trimethylene oxide as an additional test of the hypothesis put forward, and to complete the heterocyclic series.

6. To correlate the values obtained with existing physical and chemical data, in an attempt to clear up certain discrepancies, apparent or otherwise, which have appeared in the literature.

7. To calculate the values of the electric moments mathematically on the basis of No. 2, to observe if even rough agreement could be obtained between predicted values and experimental results. Small success has attended previous efforts.(131) along this line.

SURVEY OF THE LITERATURE.

I. Mathematical Theory.

The treatment employed in this short summary will be similar to that followed in the texts mentioned. (103, 104, 132)

(a) Interpretation of the Dielectric Constant.

The dielectric constant, , has already been given in the equation

$$f = \frac{e\ e'}{\epsilon\ d^2} \qquad (1)$$

It is also the proportionality factor of the two capacities of a condenser, when the first capacity, C_0, is measured with a vacuum between the plates, and the second capacity, C_1, is measured with a different medium between the plates. ϵ is the dielectric constant of the medium. The dielectric constant is intimately related to n, the refractive index of a substance, in fact, under ideal conditions,

$$\epsilon = n^2 \qquad (4)$$

Lorenz and Lorentz developed an equation for the molecular refraction of a substance, on a sound theoretical basis, which was independent of the state of aggregation. They assumed that molecules are spherical conductors and that, when placed in an electric field, they have opposite charges induced on opposite sides of the sphere with a consequent shift in the distribution of electrons in the molecule. The molecules act as induced dipoles, diminishing the forces causing the electric field, and thus the dielectric constant is accounted for.

Clausius showed in 1869 that if u is the fraction of the volume actually occupied by the molecules, then

$$\epsilon = \frac{1 + 2u}{1 - u} \qquad (5)$$

or

$$u = \frac{\epsilon - 1}{\epsilon + 2} \qquad (6)$$

The gram-molecular volume is $\frac{M}{d}$. Then if P_o is the fraction of volume occupied by the molecules in a gram molecule, we have

$$P_o = \frac{u\,M}{d} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} \qquad (2)$$

P_o is the Molar Polarization and is independent of the density. Since it is connected with the volume of the molecules, the term P_o is given in cc.

Since $\epsilon = n^2$, from Maxwell's wave theory of light, the molar refraction may be written

$$M\frac{u}{d} = P_E = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \qquad (7)$$

Where P_E is also the electric polarization given in cc., which is the contribution of the shift of electrons in the molecule to the total polarization, P, which will be given later in the Debye equation.

The expression P_E was deduced from the expression P_o, and they should thus possess the same validity. The laws of additivity. however, which hold for the molar refraction, are not valid for the molar polarization except in a few cases. P_o varied as well with the temperature, the state of aggregation, and was also inapplicable to mixtures.

Now u̲ is the actual volume occupied by the molecules of a substance. From Van der Waal's equation, the quantity b̲ is four times the volume of the molecules, or

$$b = 4 P_o \tag{8}$$

From critical data,

$$b = \frac{V_c}{3} ; \qquad \therefore \; P_o = \frac{V_c}{12}$$

Also,

$$V_e = \frac{3 R T_c}{8 P_c}, \text{ so that } P_o = \frac{1}{32} \frac{R T_c}{p_c} \tag{9}$$

Thus two expressions are obtained for P_o, (3) and (9), but the molecular volumes calculated from these two equations agree only in a limited number of cases.

If the variation of P_o with temperature is examined, it is found that only in gases and very dilute solutions is P_o invariant with temperature as the theory demands.

On the basis of these facts, and by the analagous explanation by Langevin of the magnetic behavior of paramagnetic gases, Debye assumed the existence of permanent electrical dipoles, which explained the temperature variation of the dielectric constants of certain substances, and the non-additivity of the molar polarization.

It will be noted that the molar refraction is a highly additive property, even for polar molecules. This is because the frequency of visible light used in the determination of <u>n</u> is so high that the molecules with their high inertias and low frequencies of rotation cannot respond by orientation; hence the electronic polarization P_E is not affected by the magnitude of the electric moment. It is evident that this is a correct interpretation, as in certain cases where the frequency of the light waves, in the far infra-red, approaches the frequency of rotation of the dipole, the additivity law begins to break down.

(b) <u>The Clausius-Mosotti Law</u>.

In an electric field, E, every element of an insulator dS acts on the field as if it possessed an electric moment IdS, where I is the electric moment per unit volume or the polarization (<u>not</u> the Molar Polarization, P_o). Under specified conditions, a unit charge in a small cavity of this field will be acted on by a force called the electric displacement D which is greater than the field E, because of the induced charge on two plane surfaces cut in the polarized insulator, the difference being $4\pi I$, so that

$$D = E + 4\pi I \qquad (10)$$

From Maxwell's classical theory we have

$$D = \epsilon E \qquad (11)$$

where ϵ is the dielectric constant as before.

Suppose now any dielectric molecule is placed in a homogeneous field where the conductivity plates are large in comparison with the distance between them. If the actual electric intensity is F, the molecule will have induced upon it a moment, $\underline{m}$, which averaged over a period of time can be written

$$m = \alpha_0 F \qquad (12)$$

where α_0 is the "polarizability", a characteristic molecular constant.

The new intensity, F, may be considered by supposing a unit positive charge in the medium is located in a small sphere, the dimensions of which are large compared with a molecule but small compared with ordinary magnitudes. The force may then be considered as consisting of three components, and

$$F = F_1 + F_2 + F_3 \qquad (13)$$

F_1 is due to the uniform charge on the plates of density σ, so that

$$F_1 = 4\pi\sigma \qquad (14)$$

F_2, the additional force due to polarization of the medium external to the sphere, is given by

$$F_2 = -4\pi I + \frac{4\pi I}{3} \qquad (15)$$

F_3 is difficult to evaluate, and is usually assumed to be zero. This is true for gases, and liquids in which there is no molecular interaction. Then

$$F = 4\pi\sigma - 4\pi I + \frac{4\pi I}{3} \qquad (16)$$

From electrostatics, we have

$$D = 4\pi\sigma = E + 4\pi I \quad \text{(Equation 10)}$$

$$\therefore \quad F = E + \frac{4\pi I}{3} \qquad (17)$$

Let n = number of molecules per cc. Since I is the electric moment per cc., and m = $\alpha_0 F$

$$I = nm = n\alpha_0 F = n\alpha_0 \left(E + \frac{4\pi I}{3}\right) \qquad (18)$$

A previous relation gave

$$D = E + 4\pi I \qquad (10)$$

and

$$D = \epsilon E \qquad (11)$$

By elimination of I from (10) and (18) and substitution of the value ϵ, we obtain the equation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n \alpha_0 \qquad (19)$$

In other words, if α_0 is constant, $\frac{\epsilon - 1}{\epsilon + 2}$ should be proportional to the density, which is the Clausius-Mosotti law. If both sides of the equation are multiplied by the molecular volume $\frac{M}{d}$, since $M_n = N$, where N is Avogadro's number (6.06×10^{23})

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \alpha_0 \qquad (20)$$

which is the term P_0 obtained previously for the molar polarization. Since P_0 is expressed in cc., α_0, the polarizability, will have the dimensions of a volume.

(c) Derivation of the Debye Equation.

This derivation involves the Langmuir function L(x), which will not be derived here. $L(x) = \frac{\bar{m}}{\mu}$ and $x = \frac{\mu F}{k T}$, where $\bar{m}$ is the mean moment produced by orientation of the dipoles, μ is the electric moment, k is Boltzmann's constant (1.372×10^{-16}), and T is the absolute temperature. L(x) can be expanded as a series, but for the weak fields usually used, i.e. small values of x,

$$L(x) = \frac{x}{3}$$

and

$$\bar{m} = \frac{\mu x}{3} = \frac{\mu^2}{3kT} F \qquad (21)$$

This mean moment will be added to the induced moment given by (12). Consequently the total moment is

$$m = \alpha_0 F + \frac{\mu^2}{3kT} F = \left(\alpha_0 + \frac{\mu^2}{3kT}\right) F \tag{22}$$

where α_0 is the polarizability by distortion, and $\frac{\mu^2}{3kT}$ is the polarizability by orientation.

Then the total polarizability, α, must be

$$\alpha = \alpha_0 + \frac{\mu^2}{3kT} \tag{23}$$

When the molecule contains a permanent electric dipole, $_0$ of equation (18) must be replaced by α. From (20) we get

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = P = \frac{4\pi N}{3} \alpha = \frac{4\pi N}{3} \left(\alpha_0 + \frac{\mu^2}{3kT}\right). \tag{3}$$

(d) Identification of the Distortion Polarization with the Molar Refraction; an Approximation.

The classical theory shows that the polarization due to distortion is equal to the molar refraction, i.e. from equation (20)

$$\frac{4\pi N}{3} \alpha_0 = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \tag{24}$$

This equation, however, is only true when the polarization and refraction are determined under identical conditions. The refractive index, as ordinarily measured with visible light, is due primarily to a shift of electrons, hence may be called the electronic polarization P_E (Equation 7). The dielectric constant is measured at a comparatively less frequency and, in this slowly alternating field, atoms or radicals may undergo a slight shift and so make a small contribution to the polarization. This is called the atomic polarization, P_A. As the refraction varies with frequency, P_E may be extrapolated to infinite wave-length, which is equivalent to the frequency used in dielectric constant measurements, by the use of the simple dispersion formulas of Coudry or Sellmeier. However, this is only possible when the wave-length corresponding to a characteristic vibration frequency in the ultra-violet is known, which is not commonly the case. This part of the total polarization may be approximated in several ways;

1. By adding the atomic refractivities, making allowance for the types of linkage present.
2. By determining the refractive index and density at some second temperature.
3. By measuring $P_o = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$ for the solid state, as suggested by Errera.(89)

(e) <u>The Atomic Polarization, P_A.</u>

The atomic polarization can not be measured directly, but only as a difference of terms. It is, moreover, not an additive property of the molecule. Since there is this shift among the constituent atoms of the molecule, the induced polarization is the sum of the atomic and the electronic polarizations. Thus the total polarization, $P = P_E + P_A + P_M$. If P_M is known, and it can be calculated from the temperature variation of the polarization of a gas or dilute solution, P_A may be calculated, if P_E is known, as it may be by No. 3 above. Smyth (94) has fully discussed the problem and has tabulated some probable values of P_A. It is concluded that P_A tends to be greater the greater the number of atomic nuclei or groups in the molecule; probably also, the smaller the forces binding these nuclei or groups, the greater the number of electric doublets in the molecule and the more unsymmetrical the arrangement of the doublets and, it may also be added, the greater the size of the atoms constituting the molecule. In general, P_A may be disregarded only when the moment is large and the molecule is small. Thus it will not enter appreciably in the calculation of the moments of the cyclic oxides. For the glycol monoesters, it is probably of the same order of magnitude as the experimental error.

II. Molecular Association -- Liquid State.

In Part I, molecular association was defined, and a qualitative connection was established between the degree of association and the dielectric constant. Studies of electric moments and the theory of dipoles have established some of the causes of association as well as a means of further quantitative examination of the phenomenon. Since association of polar molecules produces a definite effect upon the total polarization, the discussion is pertinent. Elementary physical evidence of association is too well known to be discussed. Pure liquids, on the basis of physical chemistry, are thus classed as (1) normal or unassociated and (2) abnormal or associated. Electric moment data class the same liquids as (1) non-polar and (2) polar. Williams(86) says that there appears to be absolutely no relation between the conclusions concerning association which have been drawn from cryoscopic measurements and those which result from a consideration of the polarization data of the same system.

(a) Causes of Association.

Debye(133) has suggested that in the neighborhood of polar molecules there exist strong fields of force which tend to associate the molecules of a liquid.

Sidgwick(134) has proposed that association involves the sharing of electrons of the molecules with the operation of co-ordinate covalences. Smyth has shown that much smaller forces are more than sufficient to cause types of association such as are evident by their effects on the polarization of the solute in some binary mixtures and, moreover, that the shape of only a small portion of the polarization-mole fraction curves are explained by Sidgwick's assumptions.

Staudinger(135) considered forces causing association as related to those involved in crystal structure. They are also analagous to the forces operative in soap solutions, in which the ions, because of their electric charges, are able to form complex aggregates of simple soap molecules. Ionic forces, however, vary inversely as the square of the distance.

In binary mixtures of a non-polar solvent (1) containing a polar solute (2), the properties of such mixtures depend on forces 1--1, 1--2, and 2--2. This may be caused by--

(1) Dipolar association, due to the permanent dipoles in the molecule. The forces are determined by the size and location of the dipole and the shape of the molecule, and vary inversely as the third power of the distance between the dipoles.

(2) Non-polar association, due to forces of the Van der Waal's type, which vary as higher powers of the distance.

The two types of association may exist simultaneously, and variations from one type to the other are possible. The forces causing dipolar association are not usually considered to be of the same origin as the forces associated with "unsaturated" or secondary valence forces, which are involved in the formation of molecular complexes.

(b) Types of Association.

It was shown that $P = P_E + P_A + P_M$. Since $P_E + P_A$ is unaffected by molecular association, polarization data can afford information only about the dipolar association. The course of the polarization-mole fraction curve, according to Williams,(86) indicates clearly the effect of several postulated types of association.* If two molecules associate in the manner (a) or three in the manner (b), the polarization will increase with increasing concentration of the solute. If two molecules

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* See Fig. II, p. 93a.

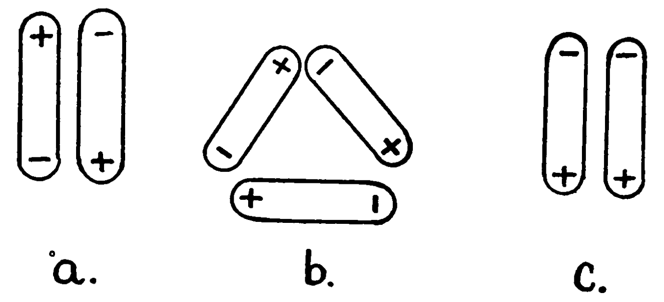

Fig. II (Reference 86)

Types of Association Postulated by Williams.

associate in the manner (c), the molar polarization of the solute will increase with increasing solute concentration. Type (a) would account for the behavior of nitrobenzene in benzene solution. For a complex curve such as an ethyl alcohol-benzene solution, the two types of association (b) and (c) would account for the observed variations, where a small decrease in polarization is followed by a correspondingly large increase.

Smyth(94) considers two possible simple orientations which two doublets in adjacent molecules might adopt relative to one another.* Variations from one extreme to the other may exist to account for changes in polarization with changing solute concentration. Formation of complexes of Type I would double the value of P_M, while a double molecule such as II would not contribute to the orientation polarization, and the total polarization observed would be the electronic and atomic polarizations.

(c) Quantitative Aspect of Association.

Højendahl(111) assumed the formation of double complexes of Type II in the case of nitrobenzene in benzene solution. These double molecules would make no contribution to the orientation polarization, P_M, so that the number of single molecules contributing to P_M would be given by

$$y = \frac{P_M}{P_{M\infty}} \qquad (25)$$

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* See Fig. III, p. 94a.

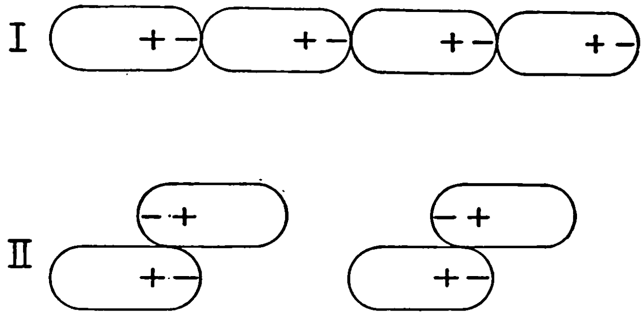

FIG. 23.—Types of orientation of dipole molecules.

Fig. III.

Fig. 23 from C. P. Smyth, page 171.

Where $P_{M\infty}$ is the orientation polarization at infinite dilution. As P_M shows variations with concentration, y gives the degree of association at any solute concentration. This equation does not hold for Type I orientation, as is evident from the data tabulated by Errara,(97) who found y less than 1 for the highly associated heptands.

Rolinski(136) has developed a modified Debye equation which recognizes an association factor. Because of incorrect assumptions in the derivation of this equation, it is not suitable for accurate quantitative treatment of the problem.

Debye(133) has developed an equation which can only account for an increase in polarization due to association, and Smyth, using the Ganz equation, obtained an equation which represented association as bringing about only a decrease in polarization. It would seem that the best way to detect dipolar association without regard to type, would be to consider the observed solution polarization ($P_{1,2}$)-- mole fraction of solute (f_2) curve. If the slope of this curve is identical with the tangent to the observed curve at $f_2 = 0$, i.e., if the $P_{1,2}$-f_2 curve is a straight line, the degree of association is 1.

(d) Qualitative Aspect of Association.

As this work is concerned chiefly with typical oxide molecules, it will be interesting to observe the qualitative relation of molecular structure and the degree of association. In the water molecule, the hydrogen atoms, which lie very close to the surface of the oxygen atoms, occupy very little of the space surrounding the oxygen atoms. In the presence of two large doublets, the very strong field of force set up about the molecule will affect neighboring molecules greatly, with the result that considerable association should be expected in the pure liquid. This is just what happens, and water is a highly abnormal liquid. When one hydrogen atom of the water molecule is replaced by a methyl group and methyl alcohol is formed, we should expect a definite amount of screening of one of the doublets to occur. Coupled with this screening, the polarity of the molecule has suffered a decrease, and the oxygen valence angle has undoubtedly increased in magnitude. These three factors would decrease the effect of a methyl alcohol molecule on neighboring molecules, thereby rendering methyl alcohol less abnormal than water. In the higher alcohols, the increase in length of the hydrocarbon chain not being contiguous to the oxygen atom, the only effect is the diminishing frequency of approach of neighboring doublets, so that even octyl alcohol shows a degree of association almost equal to methyl alcohol. When the hydrogen atom of the alcoholic hydroxyl is replaced to form an ether, the strong field of force is still further diminished by screening, and possibly some increase in the oxygen valence angle. The resultant liquid, the ether, although still possessing a moment of considerable magnitude, is practically normal and shows no association.

III. Methods of Measurement of the Electric Moment.

The first electric moment was determined in 1901 by Baedecker.(137) From that date until the beginning of 1927, only eighteen papers on the subject had appeared, which accentuates the rapidity of modern development of this field. It is also worthy of note that Baedecker's value for the sulphur dioxide molecule, $\mu = 1.60$, compares very favorably with the recent value of 1.61 by Zahn, which is considered as correct.

(a) Temperature Variation of the Dielectric Constant. -- For Gases.

The earlier investigators used the very accurate method of determination of the electric moment from the temperature variation of the dielectric constant of a gas. If we consider the Debye equation

$$P = \frac{4\pi N}{3}\left(\alpha_0 + \frac{\mu^2}{3kT}\right) \qquad (3)$$

we may write

$$P = a + \frac{b}{T} \qquad (26)$$

where $a = \frac{4\pi N}{3}\alpha_0$ and $b = \frac{4\pi N}{3} \cdot \frac{\mu^2}{3k}$

Then $PT = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} . T$ plotted against T (See Fig. I)

gives a straight line. Extrapolation of the curve to absolute zero gives the value of "b". The value of "a" is given by the slope of the line. The method holds unqualifiedly for gases, the only inherent difficulty being the fact that many molecules cannot be vaporized sufficiently, and,of those which can, many are unstable in the vapor state.

Smyth and co-workers first applied the above method to dilute solutions of a polar solvent in a non-polar solvent, and found that the method was suitable for calculation of the electric moment of the solvent molecule. It was found that for certain substances the polarization of the solute was constant over a range of concentration, such as for benzene-ether solution. For other solutions the method only applied to the limiting case, at infinite dilution, where the effect of a single solute molecule between the condenser plates is obtained and all effects of molecular interaction are avoided.

(b) The Method of Binary Mixtures

The first method,while exact, is not of universal application and consequently has been supplemented by a much simpler method which is more generally applicable. It is, however, restricted to the use of a "suitable" binary mixture which is defined as one in which one of the components, the solvent, is non-polar. Benzene and hexane have been used most frequently as solvents, also carbon tetrachloride and carbon bisulphide. Dioxan is a non-polar solvent, although it gives slightly higher values of the electric moment than solutions of the same solute in benzene, possibly due to the two ether bridges in the molecule. While dioxan has this drawback, it is of value where the compound is insoluble in other non-polar solvents. Linton and Maass (138) have recently used ether as a solvent (although it is a polar molecule) and have found that values of the electric moment measured in ether solution are slightly less than the values obtained in dioxan solution.

The original Debye equation is not applicable, as it stands, to liquids, as it assumed random orientation of the molecules. For dilute solutions, the molecules will be relatively far apart, and interaction between solute molecules will be negligible. Thus it may be assumed that the total polarization $P_{1,2}$ of a suitable binary mixture will be the sum of the polarizations of the mole fractions of the non-polar solvent (1) and the polar solute (2).

For a binary mixture, we have

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} n_1\alpha_1 + \frac{4\pi}{3} n_2\alpha_2 \qquad (27)$$

where α_1, n_1, and α_2, n_2 are the polarizabilities and the number of molecules per c.c. of components (1) and (2) respectively. Then the mole fractions are

$$f_1 = \frac{n_1}{n_1 + n_2} \quad \text{and} \quad f_2 = \frac{n_2}{n_1 + n_2}$$

The molar polarizations are

$$P_1 = \frac{4\pi N}{3} \alpha_1 \quad \text{and} \quad P_2 = \frac{4\pi N}{3} \alpha_2$$

The density of the mixture is

$$d = \frac{n_1M_1 + n_2M_2}{N} \qquad (28)$$

where M_1, M_2 are the molecular weights. Substitution and rearrangement give

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{f_1M_1 + f_2M_2}{d} = \frac{4\pi N}{3} f_1n_1 + \frac{4\pi N}{3} f_2\alpha_2$$

or

$$P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{f_1M_1 + f_2M_2}{d} = f_1P_1 + f_2P_2 \qquad (29)$$

Now $f_1 = 1 - f_2$,

$$P_2 = \frac{P_{1,2} - f_1P_1}{f_2} \qquad (30)$$

Since P_1 is the polarization of the non-polar solvent, it is given by

$$P_1 = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d},$$

which is known, so P_2 may be calculated. P_2 is then plotted against f_2, the curve extrapolated to infinite dilution ($f_2 = 0$) which gives the value of P_∞.

$$P_\infty = MR_D + \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} \qquad (31)$$

$$= (P_E + P_A) + P_M$$

Since P_A is very small and is usually neglected and P_E, the electronic polarization, is evaluated as shown previously, P_M is known. From equation (31) substituting the numerical values, we have the electric moment

$$\mu = 0.0127 \times 10^{-18} \sqrt{P_M T} \text{ e.s.u.} \qquad (32)$$

This method of calculation of the electric moment, while perhaps not so sound theoretically as the first one is much easier from the experimental viewpoint and gives results in good, if not exact, agreement with the first method outlined. The method is limited only by the solubility relations of the solute and solvent.

IV. Apparatus for Experimental Measurement of the Dielectric Constant.

The method used in this investigation for measuring the dielectric constants is known as the heterodyne heat method, consequently this type of apparatus as at present employed will be described fully and other previous and less exact methods will receive brief attention. Complete surveys are found in various texts(139).

1. Measurement of Electrical Force

The first methods were based on a law discovered by Faraday and first verified by Coulomb that f , the attraction and repulsion between two electric charges, e and e' separated by a distance r , varies with the nature of the intervening medium or dielectric.

Thus

$$f = \frac{e\,e'}{\epsilon\, d^2} \qquad (1)$$

where ϵ is a specific property of the medium known as the dielectric constant. Faraday himself used two identical condensers with media of air ($\epsilon = 1$) and the substance to be measured. The force, f, was obtained by observing the deflections of a quadrant electrometer needle. The ratio of the deflections gave the ratio of the forces, and from this the dielectric constant could be calculated.

Silow(140) in 1875 used the above method, observing the difference in capacities of two condensers in air and in the medium for the same change of angle. Perot (141) later improved this method which was further improved and modernized by Carman(142).

Cohn and Arons(143) used alternating instead of direct current to charge the electrometer and by their method were able to investigate liquids of appreciable conductivity.

Other methods are those of Quincke(144), Michaud and Balloul (145) and Furth(146).

2. Measurement of Velocity of Propagation of Electromagnetic Waves.

From the theory of electrical oscillations it follows that the velocity of propagation of an electric wave in a wire is inversely proportional to the square root of the dielectric constant of a medium. This arrangement enables the dielectric of good conductors to be measured for short electric waves. It necessitates some arrangement for producing stationary waves and for measuring their wave-length. A type of apparatus first used by P. Drude(147) is fully described by Smyth(94). A specially designed vacuum tube oscillator used by Holborn(148) improved the method considerably. Mesny(149) and Wachsmuth(150) made further alterations which gave increased accuracy. The latest type of apparatus used by Devoto and Stevenson(151) based on a method of Grechowa(152) has improved this method considerably.

3. Measurement of Capacity

(a) Bridge Methods

The principle of the Wheatstone bridge was first used by Nernst(153), employing four condensers for the four arms of the bridge. One of these condensers contained the liquid under observation. C_1, C_2 and C_3 are known. Since $C_1/C_2 = C_3/C_4$, C_4 may be calculated, and from this the dielectric constant of the liquid. Due to conductivity in C_4, it may be necessary to shunt a resistance across it, or use some other convenient arrangement, depending on the magnitude of the conductance. Hertwig(154) and Joachim (155) later used this method adapting it to higher frequencies than had been previously used.

In his first investigations in the field of dielectric constants, Smyth(156) used a highly sensitive bridge apparatus which is described in detail. Some modifications were added later(157). In 1931, the apparatus used was of the newer and more accurate heterodyne heat type(158). Ball(159) has described with great theoretical and experimental detail the construction and operation of a Nernst bridge method, which gave accurate results. A newer modification is given by Chrétien(160) who used an electron tube oscillator to excite the bridge by induction, eliminating errors caused by changes in frequency. Other improvements are added.

The introduction of the vacuum or triode tube and its subsequent successful adaptation to many scientific problems has rendered possible several new and accurate methods for the determination of the dielectric constant.

(b) Resonance Methods

The second most important method is known as the resonance method. In a circuit consisting of inductance L, capacity C, and resistance R in series, the effective current flowing in the circuit is

$$I = \frac{E}{\sqrt{R^2 + (\omega L - \frac{1}{\omega C})^2}}$$

E is the potential, and $\omega = 2\pi f$, where f is the frequency of the current. I is a maximum when $L = 1/\omega C$, a condition called resonance. In the usual apparatus, R and I are fixed, C is a condenser of variable capacity, and the condition of resonance is brought about by variation of C. The frequency, f, for which resonance is obtained is known as the characteristic frequency of the circuit. The condition of resonance may also be written

$$\omega = \frac{1}{\sqrt{LC}} \quad \text{or} \quad f = \frac{1}{2\pi\sqrt{LC}}$$

The equation is valid only for small values of R. Of the many investigators using this method, only Lattey(161), Walden, Ulich, and Werner (162), and Williams (163) will be mentioned. Walden employed three circuits, one an electron tube generator, like Holborn (148), as primary circuit, which is loosely coupled inductively to a secondary or resonance circuit containing capacity and inductance. Resonance is attained by adjusting the condenser in the second circuit, the condenser immersed in the liquid (dielectric cell condenser) is connected in parallel and the system adjusted for resonance, the difference in reading of the first condenser giving the capacity of the cell. The secondary resonance circuit is coupled in the same way to a detector circuit consisting of a vacuum thermo-element and a galvanometer to measure the current.

The apparatus used by Williams (163) is worthy of more detailed description, since it contains several novel features. A diagram of the apparatus is given. It consists of a simple wave-meter circuit containing inductance and capacitance, with a two-stage amplifier, inductively coupled connected in series. The circuit is caused to oscillate by means of the "Feed-Back Regeneration Principle". This oscillation is maintained constant, great care being taken to prevent variations in batteries,

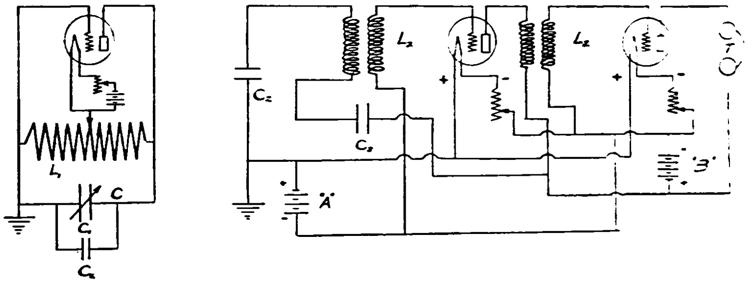

Fig. 1.

Fig. IV.

Apparatus Used in the Electrical Resonance Method by

Williams and Krchma, 1926.

inductance and capacitance in the circuit. The telephone receivers are connected in series in the plate circuit of the second vacuum tube. This circuit acts both as an oscillatory and receiving circuit, thereby eliminating a third circuit which is generally employed for the reception of beats in the usual heterodyne method for the measurement of capacities.

The dielectric container C_x, which is used for the determination of the liquid is connected in parallel with condenser C_1, of Circuit I, which consists of two standard variable air condensers connected in parallel.

In a determination, the filaments of the tubes in both circuits are lighted from isolated sets of storage batteries, the current being carefuuly maintained constant by means of suitable rheostats. Circuit 2 is caused to oscillate by increasing the plate current until regeneration begins, when the circuit is maintained perfectly constant so that the waves generated have a constant frequency. Circuit 1 is now adjusted to this frequency by means of the condensers, C_1. The dielectric cell C_x is connected in the circuit at all times. The position of resonance just mentioned is determined with the plates in air and set at a definite and perfectly reproducible position, which may be called "A". The plates are now adjusted to a new position "B" and the circuit is again brought to resonance with the constant Circuit 2. The difference in capacity of the dielectric cell in air with the plates in these two positions is determined by means of the calibrations of the standard condensers in C_1. The difference in capacity between the positions A and B of the dielectric cell with the plates immersed in the liquid whose dielectric constant is to be measured is now determined. The dielectric constant of the liquid is then calculated by dividing the difference in capacity between positions A and B when the plates are immersed in the liquid by the difference in capacity in air between these positions. This method entirely eliminates any correction for the capacity of the leads, etc. a distinct advantage, since these capacities, though small, are uncertain, and should be avoided for accurate determinations.

The accuracy and consistency of the measurements are illustrated by fifteen consecutive observations in benzene at 25° which gave a mean value of 2.282 ± 0.0025, and a maximum deviation from the mean of 0.004.

Golubkov (164) used a modified resonance method in his determinations of the dielectric constant. Instead of tuning the circuits to resonance and reading the maximum amplitude of the galvanometer, he observed the relative throw of the galvanometer with air, a reference liquid, and with the liquid under observation.

Kniepcamp (165) modified the resonance method by introducing in inductionless shunt across the capacity in an oscillating circuit so that the apparatus could be employed for measuring the dielectric constant of weakly conducting liquids.

Astin (166) still further improved this method to give absolute values directly.

The resonance method has been used by Wyman (167) who made determinations on the changes of frequency of a resonator immersed in a reference liquid and then in the medium, rather than by measuring changes in inductance or capacitance. The method is suitable for conducting media.

Most recently, Smith (168) has described a simple reliable form of resonator useful for determining the dielectric constant of dilute solutions for electric moment determinations. A fairly powerful oscillator is used of a quartz-crystal-controlled type similar to that of Williams as described below in the heterodyne beat method. Resonance in the pick-up circuit is detected by a low resistance thermo-junction, similar to that employed by Walden, Ulich and Werner (162). The description is detailed.

(c) Heterodyne Beat Methods

1. For Insulating Liquids

The best method for measurement, which leads to the most accurate results, and which is now used very generally, is known as the heterodyne beat method. In design, the apparatus is not exceedingly complex, and the theory of operation is relatively simple. The method takes advantage of the dependence of the frequency of a simple triode tube oscillator on the capacitance, inductance and resistance of its circuits. It has been used successfully by Herweg (169), Whittington (179), Isnardi (171), Grützmacher (172), Højendahl (111), Stranathan (173), Williams (163, 174, 175), and Smyth and Walls (83). As the apparatus employed is the one used in this investigation, no detailed description of it will be given here.[*] Differences only will be mentioned at present between the apparatus used by the two latter investigators on which the one here employed is based. Williams employs a quartz crystal controlled oscillator and a P T - 8 electron tube to avoid changes in frequency on the part of this oscillator of fixed frequency which would be a source of error.[**] Smyth uses two coupled inductances instead of the crystal control. In Circuit II, Williams used two variable tuning condensers, and a variable condenser dielectric cell as shown.[†] Smyth has used a 1500 $\mu\mu F$ precision condenser (General Radio Company Type 222) with an accuracy in capacity reading about 0.06 $\mu\mu F$. The dielectric cell is the fixed condenser concentric cylinder variety. In earlier work, Fig. V, (163, 174), a transformer-coupled amplifier was used by Williams. This was later replaced by a resistance coupled arrangement,[‡] also used by Smyth. These methods mentioned have all been used for non-conducting liquids.

2. For conducting media

For conducting liquids, the method has been modified by setting a variable resistance across the measuring capacity

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[*] See Fig. V, page 109a.
[**] " " VI, " "
[†] " " VII, " 109b.
[‡] " " VIII, " 109c.

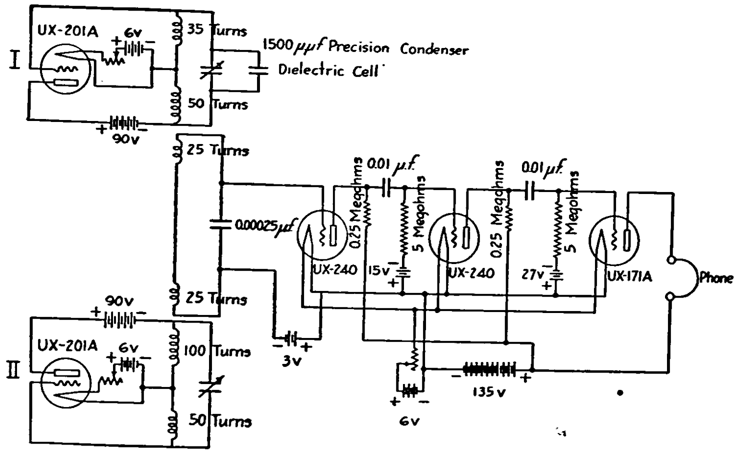

Fig. 11.—Heterodyne beat apparatus for liquids.

Fig. V.

Apparatus Used by Dr. C. P. Smyth (For detailed description see Reference 94, p. 55).

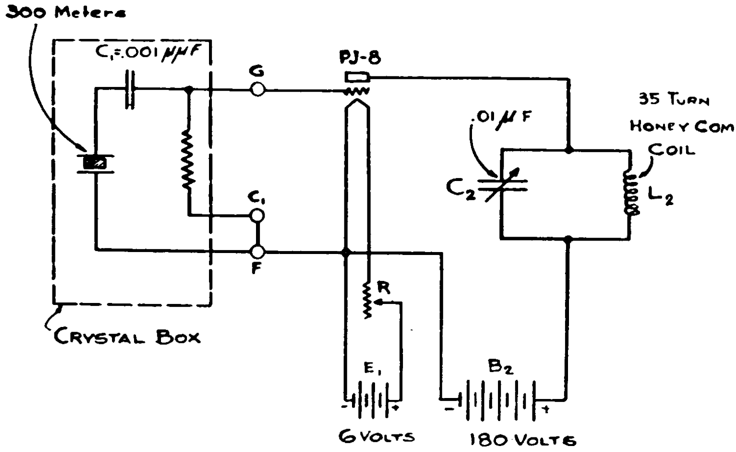

Fig. 1.—Crystal oscillator.

Fig. VI.

Circuit I: Crystal Oscillator Used by Dr. J. W. Williams(175) for Accurate Frequency Control of Fixed Frequency Oscillator.

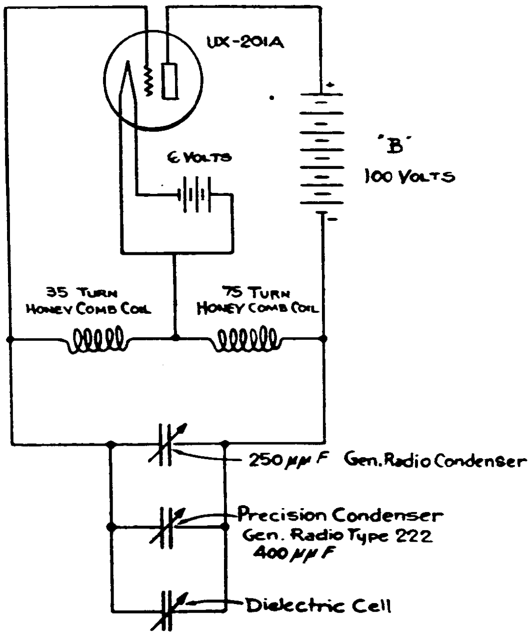

Fig. 2.—Variable oscillator.

Fig. VII.

Circuit II: Variable Oscillator Used by Dr. J. W. Williams.(175)

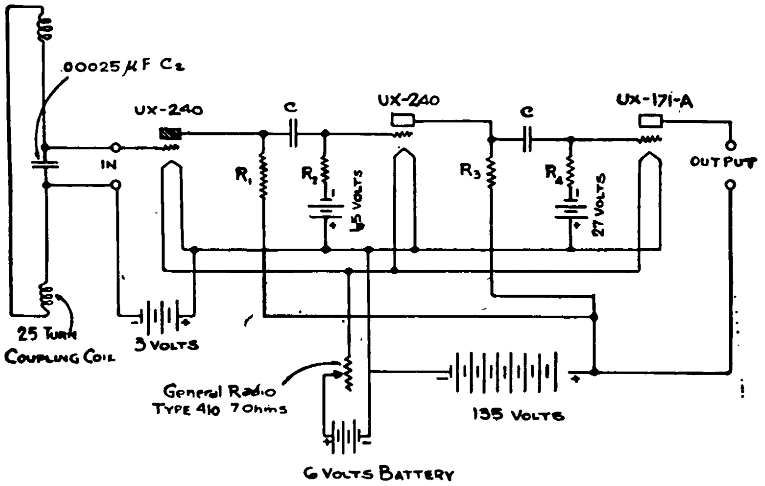

Fig. 3.—Detector-amplifier. CF 0.01$\mu\mu$F.; R_2F 5 megohms; R_1 = R_3F 0.25 megohms; R_4F 5 megohms.

Fig. VIII.

Resistance-coupled Detector-amplifier Used in Heterodyne Beat Apparatus by Dr. J. W. Williams.(175)

and this resistance is adjusted so that the damping is the same if the capacity containing the conducting liquid is connected to the circuit or the measuring capacity plus resistance. Graffunder and Weber (176) used a valve voltmeter to control the damping and a variable resistance of constant capacity is constructed from two vacuum tubes, the resistance being altered by variation of the filament current.

3. For gases

Extremely accurate measurements have been made of the dielectric constants of gases first by Jona (177) and later Stuart (178), Sänger and Steiger (179), Zahn (180), Ghosh and Mahanti (181) and Andrews (182). The apparatus used by Zahn is similar to the heterodyne circuits described and details of construction and use have been carefully given (94). In this apparatus a third source of frequency is used, such as a tuning fork of suitable audible frequency. The frequency difference of the oscillators is tuned to the same frequency as that of the tuning fork, instead of tuning to zero frequency difference (or zero beat). As a difference of less than one beat per second can be detected readily, the method gives a frequency adjustment accuracy of one part in a million.

Williams and Schwingel (183) used a modified method adaptable to measurement of dielectric constants over a range of several hundred degrees.

Andrews has described a new method in which he has eliminated the difficult condenser calibration of earlier heterodyne methods. The dielectric constant is obtained in terms of a single frequency standard, the absolute frequency of which is determined by auxiliary apparatus. The method gives absolute values to 0.5%. Complete details of apparatus and method are given, and its use at pressures up to seven atmospheres. The method is considered an improvement over that of Zahn.

V. The Dielectric Cell Condenser

A great variety of dielectric cell condensers have been in general use depending upon the requirements which must be fulfilled. These condensers have varied from the merest terminals where a low capacity is required, for measurements using ultra short waves, to those of very high capacity where the detection of small capacity differences is essential. By far the greater proportion of the cells employ a variable unit, although fixed condensers are used in many cases. As few investigators use the same type of condenser, some of the important types will be mentioned here.

In the measurement of dielectric constants, the largest single source of error is in the dielectric cell so that elimination of any factors contributing to this error constitute an important improvement. Different investigators have suggested different requirements that should be satisfied in the design of the condenser (159, 184).

1. It should possess a capacity of at least $100 \mu\mu F$, or at least, the capacity should be a maximum. The obvious objection is that many organic liquids which might be investigated are difficult to prepare pure in quantity. The first requirement would necessitate a value of about 200 c.c., an impossibly large quantity in many cases.

2. It should be mechanically rigid, since handling must in no way affect the relative position of the plates, and so that the geometrical configuration of the condenser must be the same for the measurement of capacity in air or liquid.

3. It must be possible to disconnect the plate systems from the leads with the smallest possible alteration in the position of the leads. This effect, which is troublesome like the estimate of the stray and lead capacities, has been entirely eliminated in certain types of cells.

4. The condenser should be enclosed in a conducting screen, from which the plate systems should be insulated.

5. Any tendency to form air bubbles inside the condenser when filling with the liquid must be avoided.

6. It must permit of accurate temperature control, and (of somewhat less importance) should be of such shape that it acquires the temperature of the thermostat fairly rapidly.

7. One other condition, not always required, is that the condenser should be an absolute one, so that it can afford direct proportionality between the dielectric constant and the measured capacity.

Sayce and Briscoe (185) used two concentric tubes, the opposite faces of the tubes being heavily silvered. The connection was made with platinum foil and platinum wires subsequently connected to mercury cups. When heavily silvered and carefully dried, the equivalent parallel resistance is very low.

Williams (163) used a very ingenious device for the elimination of errors caused by lead capacities. The condenser is essentially of the ordinary variable type with two sets of interlocking plates, one fixed set, the stator plates, and the other set, the rotor plates, movable. The cell was specially designed for the purpose and constructed in the University of Wisconsin shops. It is contained in a Pyrex vessel and is fitted with a hard rubber cover. External to the dielectric cell is a perforated copper container which is bolted to a thermostat, thus allowing the water to circulate about the cell. The copper container protects the cell from stray capacity effects. The depth of the cell is such that the plates of the condenser are remote from any ungrounded metallic portions of the cover. The method of comparison of capacity readings of the dielectric cell, when the medium is first air and then liquid, and calculation of the dielectric constant by this method are outlined above. The values obtained are absolute.

Smyth suggests that the disadvantages of this cell are that bakelite used in insulation comes in contact with the liquid to be measured, and the cell has not been developed for use at high and low temperatures. However, for measurements near room temperature on liquids which do not attack the insulating material, this cell is admirable.

Smyth and Morgan (157) used a fixed capacity condenser made of three concentric platinum cylinders*. To estimate the lead capacity, they constructed a set of leads identical with those of the cell and inserted this arrangement in place of the cell and its leads. Thus any inducance was included in this estimated lead capacity. The theory, construction of the cell, and its use are fully described. This cell was adaptable

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* See Fig. IX, page 114a.

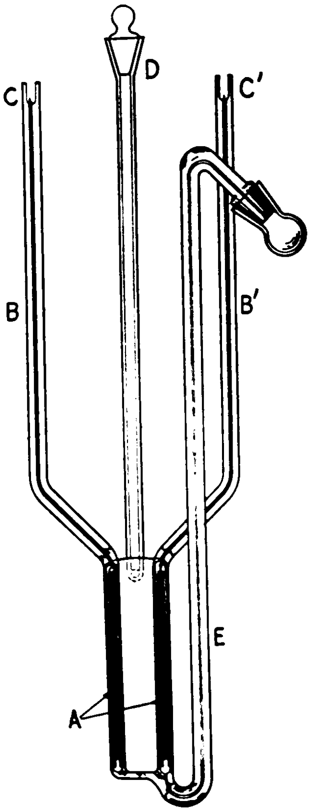


FIG. 13.—Measuring cell.

Fig. IX.

Fixed Capacity Condenser Used by Dr. C. P. Smyth for Dielectric Measuring Cell. (See Fig. 13, page 60, Reference 94, for Construction and Method.)

for use over a large temperature range, had a small temperature lag, small volume and a large capacity. The objections are that it did not give absolute values, but had to be calibrated with a standard liquid. In use, it was found that the mica blocks used to insulate the platinum cylinders were continually becoming loosened.

Hartshorn and Oliver (184) used a fixed condenser type suitable for measurements over a range of values. The design satisfied the conditions they outlined, except number 3, which they ignored. The volume was a practical minimum.

Ball (159) has designed three types of condensers which met the requirements proposed. One was similar to the Sayer and Briscoe type, and it had the advantage of extremely rapid and efficient temperature control. Two later condensers were constructed which eliminated undesirable end effects found in the first condenser. It was also claimed that errors from series resistance and polarization capacities were eliminated.

Morgan and Lowry (131) modified Smyth's condenser so that conductances could be reproducibly measured. They also designed five other condensers, some of them similar to condensers already given in the literature. They observed the experimental conditions under which these various types could be employed for measurements on liquids and solids, and pointed out their limitations.

Another fixed condenser cell was constructed by Sutton (87) which had the advantage that it could be used for a series of solutions without dismantling or disconnecting it.

The newest and probably the best type of dielectric cell has been designed by Linton and Maass (76). It is the variable condenser type, and possesses the distinct advantage that mechanical errors in setting are completely eliminated. It can be cleaned without dismounting or removal. It is admirable adapted for measurement of temperature coefficients of the dielectric constant over a wide range of temperature. Although used with large volumes of liquid, it could be modified for smaller quantities. The only drawback is that it must be calibrated, so that relative values obtained depend on the absolute value of the standard liquid.

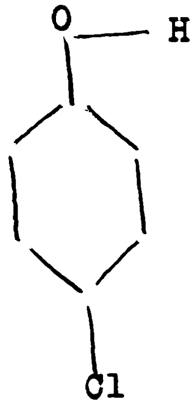
VI. Electric Moments and the Stereochemistry of Oxygen Atoms

It was soon evident that some stereochemical effect of the oxygen atom had to be taken into consideration in the interpretation of the electric moments data of water, alcohols, ethers, etc. Classical stereochemistry, based on extensive chemical data, assumes three fundamental principles to explain molecular structure, particularly for aliphatic substances: (a) the constancy of the distances between the atoms; (b) the constancy of the angles between the valences; and (c) the possibility of free rotation. Assumption (a) will be discussed later. The general conclusion is that in covalent links the effective radii are surprisingly constant, and are but little affected by conditions of state, or by other atoms which the molecule contains. The angles between the valences are much more subject to change. In the older stereochemistry, great stress was laid on the valency angles, but relatively little attention was paid to the interatomic distances. It is now clear that the constancy of the two factors is in the reverse order.

The possibility of free rotation is too involved to be discussed here. Free rotation is a theory put forward to meet a demand of organic chemistry for explanation of the non-isomerism of such compounds as the $XCH_2.CH_2X$ type. A perusal of reviews on intramolecular motions and free rotation (95, 180, 189) will convince the reader that this idea is nothing more than a convenient hypothesis, and that two halves of a molecule whose rotation about a single bond is supposed to be "free", in no way implies that the rotation is continuous. Mutual forces of attraction between groups and the fulfillment of requirements of minimum mutual potential energy in a system of doublets requisite for stability cause the rotation to be restricted even in simple compounds. On the assumption of free rotation in glycols and similar compounds, Williams (186) calculated the angles through which the carbon tetrahedra were distorted as a result of repulsion of the polar groups. As this distortion was unjustifiably large, it can only be concluded that all positions of projection in a plane of the doublets relative to one another are not equally probable and that any equation derived on such an assumption cannot represent the facts. In such a system, therefore, free rotation is denied.

Stuart (187) has concluded as a result of his investigation in this field that butane has a very restricted rotation, from which it follows that the saturated aliphatic hydrocarbons in the gaseous state tend to form ziz-zag chains. This observation is quite in accordance with the results of other investigations on the electric moment of long-chain molecules with "ideally decoupled" (mutually independent) dipole groups, and the relative orientation of dipole molecules in thin films on aqueous and mercury surfaces. In the saturated aliphatic alcohols,in particular,negative values of the Kern constant suggest that in liquids long extended zigzag chains are very frequent. Stuart found such restricted rotation for the ether molecule as well.

The existence of definite valence angles in molecules containing oxygen and nitrogen atoms has been established beyond all doubt. Thus p-chlorophenol which, of the three isomers, was expected to have but a small electric moment, actually gave a maximum. The explanation offered is that the resultant doublet of the hydroxyl group is not linear makes an angle with the plane of the benzene ring and the following structure is postulated (IX).



(IX)

Similarly, in CH_2X_2, Smyth and Rogers (188) have calculated that the angles between the two C-X doublets are 124°, 120°, 135° for X = Cl, Br and I, assuming constancy of the C-X separation. In agreement, Debye (189) and Wierl (190) by X-ray measurements and electron scattering determined the Cl-Cl distance in CCl_4 and other chlorinated methanes. The results gave C-Cl = 1.85 ± 0.06 and valence angles between adjacent C-Cl linkages as 123.8°, 116.4° and 109.5° for CH_2Cl_2, $CHCl_3$ and CCl_4 respectively. Both types of calculation assumed ~~that~~ the internuclear C-Cl distance to be constant. The carbon valence angle would therefore appear to be increased about 6-7% on each replacement of H by Cl. Such as assumption has been made in the Thorpe-Ingold theory.

Further evidence of the existence of valence angles for oxygen atoms is given by Kerr constants by Wolf (190). If the Kerr constant is negative, the moment in every case is (at least approximately) at right angles to the axis of maximum polarizability. On the other hand, the constant is not necessarily negative if the moment is at right angles to such an axis. From tables given, it is evident that negative or small positive Kerr constants occur only in molecules with a large moment if the substituted group (in benzene) is an OH or NH_2 group. But since in benzene the axis of maximum polarizability lies in the plane of the ring, this means that in these two groups, the moment must be inclined at a large angle to the plane of the ring. It is also shown that the same effect is found in aliphatic compounds.

VII. Structure of the Water Molecule

A very interesting study has been made on the oxygen valence angle in the water molecule. The electric moment of the water molecule in both the vapor and liquid states is 1.85×10^{-18} e.s.u. There, its molecule is unsymmetrical. A linear and symmetrical model, as suggested by Kossel (191) or Langmuir (192), is thus impossible, as this structure would lead to zero moment. Attempts made to explain the moment of the water molecule with rather unsatisfactory calculations based on an ionic structure with strong polarization of the oxygen anion in the field of the protons have proved inconclusive. A detailed analysis of the structure of the water molecule has been carried out by Heisenberg (193) and by Hund (194), and the probability of a triangular model for the molecule has been established. As a matter fact Hund has shown from energy considerations that the water molecule cannot be represented except by an angular model and that the triangular model has a lower energy value than the linear molecule. Debye (103) gives an exhaustive mathematical treatment of the subject, using the principal moments of inertia calculated by Eucken (195) from the infra-red absorption spectrum and, after eliminating all other possibilities, concludes that the molecule which best fits the experimental results is one in which the bonds are at an angle of 64° with one another. He also suggests that this is the most probable structure for the ethers, alcohols, phenols, etc. In this derivation, two solutions for the water molecules were obtained one with a vertical angle θ of 64°, and the other with $\theta = 110°$. Both solutions give approximately the same value for the H - O internuclear distance (1.07 and 1.02 x 10^{-8} cm.) If the polarizability of the O ion is introduced and the moments corresponding to the two models calculated, two values are obtained $\mu = 1.34$ and 4.32. At first glance this would appear to favor the acute-angled model but Hund has emphasized the fact that either theoretical value may be consistent with the experimental value.

Pauling (196) has calculated the valence angles for 2-, 3-, and 4-covalent atoms, and has shown that the latter has the tetrahedral value of 109° 28'. For covalencies of 2 and 3, he states that the bonds formed in an atom tend to be oriented at right angles to one another. Thus, a water molecule will result in which the angle formed by the three atoms is 90°, or somewhat larger because of interaction of the two hydrogen atoms.

In drawing these conclusions, it has been assumed that the type of quantization of the two p electrons of the oxygen atom involved in the formation of a water molecule is not changed. It is shown to be quite improbable that it should be. From the same type of reasoning, an upper limit for the oxygen (and nitrogen) bond angles is fixed, theoretically, at the tetrahedral angle, 109° 28'. Crystal structure data (197) give values for the bond angles of arsenic = 97°, antimony = 96°, bismuth = 94°, molybdenum sulphide (S--Mo) = 82°, $Co_4(As_4)_3$ (As--As) = 90°, all of which function with covalencies of 2 or 3, similar to oxygen and nitrogen.

Plyler (198) has very recently calculated the fundamental frequencies of water vapour by examining the band at 1.87 μ under high resolution, and has calculated that the angle between the lines connecting the atoms is 115°. This value is claimed to be of the order of magnitude predicted by Slater's theory of directed valence (199), but is in no way to be considered as a contradiction of the value suggested by Pauling, which is supported by Slater's investigation of the problem of molecular energy levels and valence bonds.

VIII. The Tetrahedral Oxygen Atom

All previous calculations of the electric moments of oxygen compounds from the equations of vector addition have been based on the assumption, without proof, of the tetrahedral nature of the oxygen atom. Thus Wolf (124) was forced to assume an electrical character inconsistent with the facts for the $CH_3 - O$ and $H - O$ groups in order to obtain agreement between experimental and calculated values. Eucken and Meyer (123) have calculated the group moments of many substituents assuming a value of 110° for the oxygen angle. They assign the value 1.1 (see Table III) to the group moment of the $CH_3 - O$ linkage, a value which is believed to be too small for various reasons. The value which will be used throughout for the group moment of $CH_3 - O$ is 1.2×10^{-18} e.s.u. designated as $m(C - O) = 1.2$ If the moment μ is the resultant of two vectors, each of moment m_1 and m_2, which make an angle θ with one another (200), then

$$\mu = \sqrt{m_1^2 + m_2^2 + 2m_1m_2\cos\theta} \qquad (33)$$

Since $m_1 = m_2 = m(H\text{--}O)$ for water,

$$\mu = m_1\sqrt{2(1 + \cos\theta)} \qquad (34)$$

The value of μ, thus depends on that assigned to the angle θ between the two valence bonds, as indicated below.

TABLE II

	m(H--O)
109° 28'	1.60 (201)
90°	1.31 (201)
64°	1.09

Eucken and Meyer use the value m(H--O) = 1.6, but there is no reason to believe that this group moment could not be either 1.09, or any intermediate value which could be justified. The last value assumes an oxygen valence angle of 64°.

TABLE III

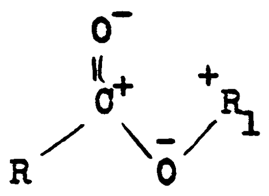
Bond Moments (x 10^{18}) calculated by Eucken and Meyer

Bond	Calculated from		Moment
C - C	C_2H_6	0	0
H - O	H_2O	1.8	1.6
C = O	$(CH_3)_2CO$	2.7	2.3
H_3C - C	$C_6H_5CH_3$	0.4	0.4
H - C	CH_3	0.4	0.4
C - O	$(C_2H_5)_2O$	1.2	0.7
		1.12	.57*
	$(CH_3)_2O$	1.29	.72*
C - Cl	C_6H_5Cl	1.5	1.5

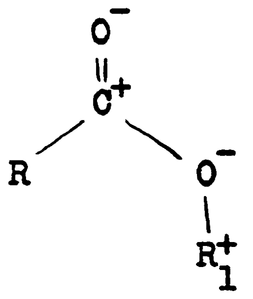
* The value of C - O is obtained as the difference of CH_3 - O and H- C. Eucken and Meyer's values give 1.1 for CH_3- O. However they use 1.2 for ethyl ether instead of 1.12. The corrected value gives CH_3 - O = 0.97. On the same assumption m(CH_3 - O) = 1.12 from the value for methyl ether.

Williams and Fogelberg (125) and Hojendahl (111) had considered the effect of an oxygen valence angle on the resultant moments of different compounds previous to the quantitative work of Wolf, and Eucken and Meyer. Although their suggestions gave a qualitative explanation of abnormal observed values of the moments, no qualitative results were obtained and Williams arrived at the conclusion that the oxygen valence angle was as yet uncertain and unobtainable.

Smyth and Walls (83) in their work on carboxylic acids and their esters, suggest two possible structures, (a) and (b)



(a)



(b)

the former of which is considered more probable under ordinary circumstances. They do not assign any definite value to the oxygen valence angle. It is possible, however, that the oxygen valence angle will be smaller in the esters than the ethers, due to the mutual attraction of the positive ester radical R_1 and the negative carboxyl group.

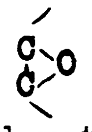
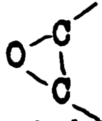
Sidgwick and Bowen (201) in 1931 concluded by saying, "The tetrahedral atom has received the fullest support, not only for atoms forming four, but also for those forming two and three covalent links, tho in the last two cases Pauling's theoretical conclusions give this angle as 90° rather than 109.5°, a view which it is not yet possible to test experimentally. The valency angles can change to some extent with the nature of the groups in the molecule, but apparently not much more than 15%... The form which the molecule assumes, through the liberty of free rotation of singly linked atoms, without change of valency angles or the length of the links, is largely determined by the intramolecular attractions of its dipoles, especially when these are close together."

IX. Ethylene Oxide

(a) Electric Moment

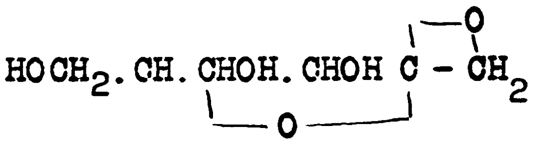
Ethylene oxide has received considerable attention because of its simple structure and analogy with the homocyclic carbon ring, cyclopropane. The electric moment of ethylene oxide is 1.88, the value of which is explained by Smyth (94) as follows: "In ethylene oxide, the same doublets should exist as in methyl ether and methyl alcohol, but the positive ends of the doublets are drawn toward one another because of the bond between the carbons and the angle between the doublet axes is thus made less than in alcohol, so the resultant moment is larger." It is to be understood that this statement is permissible only in a very qualitative manner. Smyth and Walls (122) have calculated the oxygen valence angle in ethylene oxide as 65°, and the carbon angles in the ring as 57.5°, which necessitates a higher moment than that of tetrahydrofurane (1.71) although the difference is less than would be expected. It is assumed that the interatomic distances are unchanged in the triangular molecule. They used the values of the internuclear distances as C - C = 1.54A, and C - O = 1.43A (206). A previous calculation made in this laboratory (207), assuming C - O = 1.18A showed the same oxygen valence angle to be about 80°.

(b). 1,2-Anhydro-sugars

In carbohydrate chemistry, the ethylene oxide ring has been examined from the standpoint of the stability of the resulting structure. Pictet and Castan (202) claim to have prepared a crystalline alpha-glucosan, soluble in cold water without decomposition, which gave 3.4.6-trimethyl glucose on methylation, and which was hydrolysed to glucose on boiling with water. The ethylene oxide ring thus appeared to be fairly stable, more so than in the 3.4.6-triacetyl-α-glucosan of Brigl and Schinle (203) who stated that the  ring possessed great reactivity, since solution in cold water gave 3.4.6-triacetyl glucose. While Pictet's results could not be duplicated by Brigl and Schinle, the work of the latter has been repeated and confirmed by Hickinbottom (204). Hickinbottom observed that the ethylene oxide ring is surprisingly stable in α-glucosan to reagents in comparison with that in triacetyl glucosan. He considered that the latter compound was possibly rendered more reactive by the presence of the acetyl groups. Bergmann and Schotte (205) apparently obtained a mannosan on oxidizing glucal with extreme care. The product was amorphous and could not be purified, but on addition of water gave mannose. They considered the mannosan had the ethylene oxide ring  on the opposite side to that found in alpha-glucosan, which might account for its greater reactivity. Compounds of corresponding structure containing a trimethylene ring are unknown.

Two 1.2 anhydrides of pentosans, a rhamnosan and a β-ℓ-arabinosan, have been prepared by Vogel (208). Both of these compounds give characteristic ethylene oxide reactions, the latter undergoing polymerization to a dimer on heating with $ZnCl_2$.

Schlubach and Elsner (209) have synthesized an anhydrofructose (fructosan) which shows a striking stability toward the hydrolytic action of acids. It is considered to be the elementary building unit of inulin, by changing first to difructose and then difructosan, which by secondary molecular forces form inulin. It is shown to have the formula

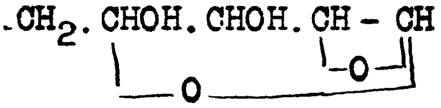


$$HOCH_2.CH.CHOH.CHOH\ C - CH_2$$

It will be noted that this anhydride contains both a furanose and an ethylene oxide ring. Schlubach and Elsner consider this compound is either identical or isomeric with levan, but there is considerable difference in their optical rotations.

Hibbert, Tipson and Brauns (210) supported the view that levan is a polymerized anhydro-fructofuranose through the medium of carbon atoms 2 and 6.

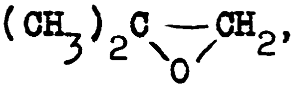
Hurd and Isenhour (211) found that when α-d-xylose is heated alone the major product is xylosan. It is assigned the ethylene oxide structure



$$.CH_2.CHOH.CHOH.CH-CH$$

It is easily oxidizable, polymerized to a trimer in aqueous solution, but not in acetic acid. Diacetyl xylosan shows the same tendency to polymerize, except in acetic acid. Diacetyllyxosan or a mixture of it with diacetyl xylosan is formed by the action of per-benzoic acid on diacetyl xylal. They also prepared glucosan in the same manner as xylosan, and found it had properties comparable with the latter anhydride. The properties differed somewhat from the properties of the glucosan recorded by Pictet and Castan (202). It could not be crystallized from methyl alcohol.

(c) <u>Stability and Reactivity of Ethylene Oxide</u>

It was first believed that the ethylene oxide molecule was less stable than the cyclopropane ring and its derivatives, and that this was so because the oxide ring was more strained than the cyclopropane ring. Thus Brookes (212) says, "The greater instability of the ethylene oxide ring as compared with the trimethylene is shown in the case of isobutylene oxide  $(CH_3)_2C\overset{}{—}CH_2$, which reacts to form glycol merely on shaking with water at room temperature." (Meerwein (222) however, obtained some isobutylene oxide in small yield when $CH_3CH(OH)CN$ was treated with diazomethane, and Pogorzelski (242) obtained the oxide on passing isobutylene into iodine-potassium iodide solution.) "The group $(CH_3)_2C$ in cyclopropane usually results in greater stability. As with carbocyclic rings, a great increase in stability is noted, compared with ethylene oxide when the oxide has five or six atoms. Thus dioxan is the principal product when glycol is distilled with 4% sulphuric acid... Dioxan, in contrast to ethylene oxide gives addition products with H_2SO_4, Br_2, etc... Derick and Bissell (213) have called attention to the fact that trimethylene oxide is markedly more stable than ethylene oxide, due to the presence of the four atom ring."

It now appears that the ethylene oxide ring is not so unstable because of ring "strain" as the cyclopropane ring, and that its apparent instability is due to the high reactivity of the bridge oxygen atom, which first forms an addition product with one of the reactants. The resulting unstable addition product then rearranges with scission of the ethylene oxide ring. The fact is emphasized here that scission of the ethylene oxide ring takes place by change of the C - O and not of the C - C linkage. The mechanism by which this addition takes place might be similar to that proposed for the formation of oxonium compounds. This involves the coordinate link, or the idea of addition by means of molecular valence electrons such as are considered in the suggestion by Milas (59) mentioned in Part I concerning the theory of auto-oxidation. Smith, Wode and Widhe (214) studied the kinetics of water addition to ethylene and trimethylene oxides in the presence of acids which did not appreciably form additive compounds. Ethylene oxide was also studied in the presence of perchloric and nitric acids, and trimethylene oxide in the presence of sulphuric acid. These reactions showed hydrogen ion catalysis. They concluded that the resistance to hydrogen ion catalysis in the hydrolysis of lactones is caused by the presence of the carbonyl group.

It is worthy of note that many, if not all, molecules which form addition compounds with a "bridge" oxygen atom, such as is found in ethylene oxide, are heteropolar compounds. Rider and Hill (72) showed that glycidol, when pure, was fairly stable toward distilled water and absolute alcohol. Horne and Shriner (220) found that pure dry diethyl amine did not react with ethylene oxide, but in the presence of water or alcohol the reaction takes place. It seems probable that an addition compound is first formed similar to that between Grignard reagents and ethylene oxide, which must be subsequently rearranged. Meerwein (215) has shown, as Kossel's ideas (191) suggested, that in the case of reactions depending primarily on the formation of ions, the formation of complexes will lead to a considerable rise in the velocity of the reaction. While it is not suggested that addition reactions with the ethylene oxide ring are ionic, it would be expected that the addition of a highly polar molecule to the ring would change the electric moment of the molecule owing to induction or association of two dipolar molecules. If there is any definite correlation between the electric moment and the velocity of reaction, it may be established in such a case as this. In the addition of diazomethane to ketones, Meerwein (221) found the reaction velocity was very small in the absence of catalysts, but that electrolytes and compounds of pronounced dipolar character, such as water, the alcohols, and formamide catalysed the reaction. This accelerating action of the polar compounds supports the view that it is the polar character of these substances which is the decisive factor in determining their catalytic influence, i.e. that their action depends on the formation of complexes of greater dipolar moment, and which, because of the greater electrostatic forces radiating from them, have a greater additive power toward diazomethane. Very recently Meerwein and Maier-Hüser (223) have developed thesis that the decomposition of ethyl ether by acid chlorides and anhydrides is due to the formation of molecular compounds of these with the catalysts. New molecular compounds of ethyl ether, dioxan and other molecules are described.

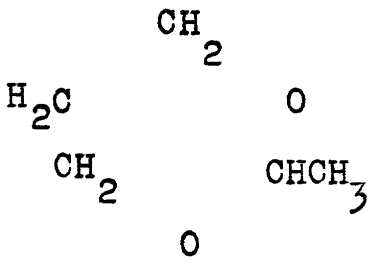
(d) Effect of Substituents on Ring Stability.

The usual effect of substituents in a ring is to increase the stability of that ring, as was shown for 1.1' dimethyl cyclopropane. However, when glycerol is acted on by hydriodic acid, allyl iodide is formed, and Sattler (216) has postulated the formation of cyclopropanol as an intermediate in the reaction. The instability of cyclopropanol is pointed out, and it is suggested that the compound decomposes spontaneously to form allyl alcohol, and then the iodide by reaction with hydriodic acid. Thus when glycerol α-α'- dichloro-or-dibromohydrin is treated with metallic zinc or sodium, allyl alcohol is formed and not cyclopropanol as expected. (217, 218, 219) It would appear that the action of the hydroxyl group on the cyclopropane ring is to cause a decrease in stability, although ease of formation of a compound is not a necessary criterion of stability.

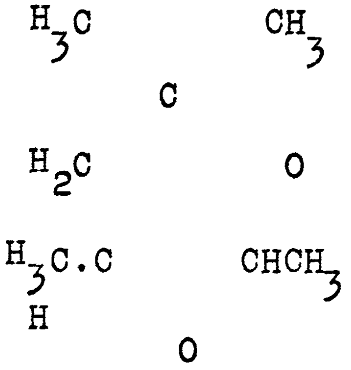
It is a well-known fact that unsaturated hydroxy-acids do not form lactones easily, but that the lactone may be formed by starting with other compounds. $\alpha\beta$ - and $\beta\gamma$- unsaturated acids, which exist in equilibrium, will give γ lactones on heating (224) which are in equilibrium with the corresponding hydroxy-acids. Aldehyde succinic acid (which is an unsaturated lactone) does not form an anhydride, while on the other hand, the anhydride, once formed, is hydrolyzed only with difficulty. (225). The fact that other unsaturated lactones are formed by indirect methods shows that the ease of formation of a compound might indicate that space relations were suitable for its formation rather than that the product of reaction was unstable.

That other factors influence the formation of ring molecules is evident from the fact that the action of metallic sodium on trimethylene bromide yields cyclopropane and not cyclohexane although the latter compound is a strainless ring of lower energy content per unit. The action of a concentrated solution of NaOH on ethylene Chlorhydrin also yields 90% ethylene oxide (240) instead of dioxan, as in the dehydration of ethylene glycol. Tiffeneau (241) treated 1.-Hydroxy-2-iodo-cyclopropane with silver nitrate and instead of the expected isolation of an isomeric aldehyde, 1.2 cyclopentene oxide was formed by the elimination of hydriodic acid.

Hill and Hibbert (228) studied the relative ease of formation of the five-and-six-membered cyclic acetals and found by partition experiments that these rings were formed in the ratio 1:2. Experiments, in which the formation of similar rings was studied, showed that the presence of methyl groups attached to the glycol carbon atoms favors cyclization. Thus II is formed in preference to I in the ratio 2:1



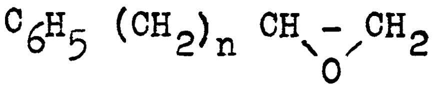
I



II

It is not known whether the presence of the methyl groups caused an increase in stability of the product or whether cyclization was favored through restriction of rotation of the two halves of the glycol about the C - C axis.

Tiffeneau and co-workers (226) attempted to eliminate the primary hydroxyl group of $(C_6H_5CH_2)_2\,C(OH)CH_2OH$ to form a ketone. Dehydration with 20% sulphuric acid or anhydrous oxalic acid resulted in the surprising formation of the ethylene oxide derivative $(C_6H_5CH_2)_2-C\underset{O}{\diagdown-\diagup}CH_2.$ It is stated that the dibenzyl ethylene oxide was remarkably stable, and attempts to isomerize it with slightly acidulated water and the usual isomerizing agents were fruitless. In the series of oxides $C_6H_5CH\underset{O}{\diagdown-\diagup}CHR$, where R = Me, Et, Pr, iso Pr, and $CH_2\,C_6\,H_5$, all these oxides, except the last which isomerizes on distillation, are very stable and needed distillation in vacuo over 50% sulphuric acid or zinc chloride for their isomerization.

Levy and Sfiras (227) studied the action of ammonia and dimethyl amine or ethylene oxide derivatives. Oxides of the general formula  $C_6H_5\ (CH_2)_n\ \underset{\diagdown O \diagup}{CH - CH_2}$ react in the cold, but the oxides of phenyl cyclohexene and 1- phenyl-4-methyl-cyclohexene do not react under 100°. They concluded that the activity of the ethylene oxides towards NH_3 and $(CH_3)_2$ NH is an inverse function of their thermal stability. Tiffeneau found that those oxides which isomerize with difficulty and only in the presence of anhydrous $ZnCl_2$, react at room temperatures with NH_3 and $(CH_3)_2$ NH to give amino-alcohols.

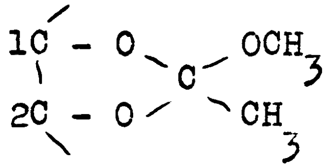
The chemistry of ethylene oxide has been reviewed in some detail, because the hypothesis to be advanced concerning the magnitude of the oxygen valence angle is closely allied with the stereochemical structure and the stability of the ethylene oxide molecule, especially the latter as compared with the cyclopropane ring.

X. Dioxolane Rings.

In the mechanism first proposed by Emil Fischer (228) to explain the migration of β-acyl radicals in the case of the glycerides of fatty acids, the formation of an intermediate dioxolane ring was postulated. Hibbert and Greig have shown (126) that the isomer of glycol trichloroacetate is the dioxolane ring compound, and Meerwein and Sonke (229) have confirmed this fact. Further evidence has shown likewise that the isomer of glycol dichloroacetate is the analogous dioxalane ring. (230,231, and although the method of preparation from ethylene oxide and dichloroacetic acid would lead one to expect the open chain product, apparently the ring isomer alone was formed. The product was a colorless, sweet-smelling liquid, practically insoluble in water. It decomposed on ordinary distillation.

Though the formulation of dioxolane rings is a rather recent development, yet it appears that under certain definite conditions, this ring is always formed as one step in the acyl radical migration, which intermediate may be isolable. It has also been postulated that the migration of hydrogen from the aldehyde to the carbonyl group of the adjacent acetyl radical in various hexose acetates also involves the dioxolane ring. Hibbert and Carter also adopted this view (232) and Hibbert and Greig (126) draw the conclusion that "all organic monoesters of polyvalent alcohols, carbohydrates, polysaccharides, o-amino phenols, etc., containing a free hydroxyl group, the hydrogen atom of which is spatially in close proximity to the carbonyl group of the acid radical tend to pass over into a ring isomer." The existence is postulated of a definite equilibrium between the open chain ester and the corresponding ring isomer in all monoesters of this type. They also state -"From theoretical considerations it seemed highly probable that with any glycol monoester containing a carbonyl group of very pronounced negative polarity, the tendency to undergo cyclisation would be so pronounced as to permit of the isolation of the corresponding dioxolane ring."

Haworth and Freudenberg have explained the special properties of certain beta isomerides of the methyl acetylrhamnosides (233,234) and -mannosides (235) by showing that the 2-acetyl group is also intimately linked with carbon atom 1 in a dioxolane ring,



This ring is exceedingly stable as the acetyl group is retained even in the presence of hot alkali.

Levo- or beta-glucosan (236) has been shown to be stable towards hydrolysing agents, and has no tendency to polymerize at ordinary temperatures. Karrer's synthesis of beta-glucosan also shows it to be stable (237). This compound may be considered as bi-cyclic, containing one dioxolane and one pyranose ring, both of which are stable structures. Similarly Hibbert and Anderson (238) have determined the constitution of sedosan (anhydrosedoheptose) and have shown it to be a bicyclic structure of the same type as beta-glucosan. It also shows no tendency to polymerize.

Crieger (239) has studied the production of formaldehyde by oxidation of sugars with lead tetraacetyl. The non production of formaldehyde from isoprophylidene - mannonolactone (234) indicates that compound formation occurs unexpectedly with the 5.6 - hydroxyl groups. The resulting structure contains the dioxolane ring. Hibbert, Platt and Carter (257) showed that if the six-membered cyclicacetal h-nitro-benzylidene glycerol, is treated with dry HCl gas or in 1.1N HCl, at 100°, isomerization forms the five membered acetal, the ratio of the six-to the five-atom ring being 112 and 1.3 respectively. The results indicate the ease of transformation of oxygen rings in cyclic acetals. This interconversion with preferential formation of the dioxolane compound would suggest that the five- possesses greater stability than the six-membered ring.

XI. Stability of Homocyclic and Heterocyclic Rings.

(a) Homocyclic Rings.

For a five-membered homocyclic carbon ring, Stereochemical theory and x-ray data indicate a uniplanor strainless ring, and chemical evidence shows that this ring possesses remarkable stability.

That the cyclohexane (hexamethylene) ring is "puckered" or multiplanar is shown by x-ray data (243) and is to be expected from the theory of Sachse and Mohr (25). It is assumed that two forms of this molecule co-exist, the "step" form in which two opposite carbon atoms are on opposite sides of a plane in which the four remaining atoms lie, and a "trough" form the reverse of the above. Cyclohexane derivatives appeared to be less stable than those of cyclopentane as examples of ring shrinkage are known in which a six-contracts to form a five-membered ring. (241). In the same way Stoermer and Keller (244) showed that in the degradation of α- truxillaminic acid, the four-membered cyclobutane ring contracted to form a three-membered cyclopropane. Ring contraction apparently has but little connection with ring stability. Recently, Vogel (245) has stated that "the work of Thorpe and Ingold (246) and Thorpe and others on ring-chain tautomerism (247) and numerous other observations make it extremely probable that cyclohexane is relatively strained" (compared with cyclopropane (?)) "and has a uniplanar structure." The multiplanar structure of cycloheptane, however, is admitted.

(b) Heterocyclic Rings.

1. Cyclic Oxides.

Previously it has been assumed that heterocyclic rings containing one oxygen atom in the ring have the same structure as the homocyclic carbon rings, though a marked difference in properties had been observed on numerous occasions. Linnell and Melhuish (253) explained the properties of aceto-propyl and - butyl alcohol on the assumption that they existed as cyclic structures, viz: 2-methyl-2-hydroxytetrahydrofuran and - tetrahydropyran. Their methoxy-derivatives were mobile liquids, b. 115-7° and 116-7° respectively. The much greater ease with which the first named compound lost water to form an anhydride indicates that in this respect the six atom ring is less stable than the five. No other difference in stability was detected in the two alcohols or their methoxy-derivatives, hence the great differences observed in normal and γ -sugars are not reflected in these compounds which possess cyclic structures analagous to those attributed to the (keto-) sugars in question. Here, again, ease of formation cannot be taken as evidence of stability. Also, the boiling points are identical, a fact which would cast doubt on the identity of the two compounds, since tetrahydrofuran boils at 64° (755 m.m.) and tetrahydropyran boils at 88°.

Some evidences of preferential formation of a six-membered ring is given. Franke showed that 1.10-decanediol with 50% H_2SO_4 or 89% H_3PO_4 gave 1.5- oxido-decane, $b._{14}$ 84^{o} Saponification gives 75% 1.5-decanediol, $b._9$ 157^{o}, and this new glycol gives the same oxide as before (254). Similarly, 1.12 - dodecanediol gives 1.5-oxidododecane (255) and 1.14 tetradecanediol gives (256) the same oxide. These remarkable facts would clearly indicate that some very deciding factor must control the formation of the six-membered oxide ring in absolute preference to all other possible structures. From x-ray work on the sugars, it is concluded that the five-membered ring is uniplanar. Cox (248, 249) has suggested structures for some carbohydrates including arabinose, β-methyl xyloside, and the two α-methyl mannosides. (α-methyl mannofuranoside and α-methyl mannopyranoside). Arabinose has five coplanar carbon atoms and the oxygen atom is not in the same plane as the remainder of the ring. The carbon atoms are co-planar or nearly so in β-methyl xyloside, and the oxygen atom is not in the same plane. The principal results of x-ray examination of the compound which Haworth (250) called the mannopyranoside showed it to be a diplanar ring, with all the carbon atoms in the same plane. The furanoside formula assigned by Haworth (251, 252) is also confirmed, and a planar structure for the furanose ring is indicated.

Haworth (258) has conclusively shown that the pyranose ring structure is the stable form of all normal sugars, and that the members of furanose series are all labile compounds.

2. Lactones.

Two types of lactones are commonly known, namely, 5-membered γ-lactones, and six-membered δ-lactones. As above, Haworth has definitely established the differences between the two types of ring, and has shown that the γ-lactones are more stable than δ-lactones. This fact would appear to contradict the conclusions arrived at for the simple sugars. An explanation of the difference will be suggested later.

Carothers (3) studied the six-membered cyclic esters and found that only these ring esters would undergo polymerization. He suggests that the presence of some strain in such esters is indicated by the great instability of δ-lactones compared with γ-lactones. The Sachse-Mohr theory permits the existence of six atom rings in two isomeric strainless forms; but in simple rings these two isomers have never been realized, and one is forced to conclude either that such rings are uniplanar and hence highly strained, or that the two isomeric forms are in dynamic equilibrium. Practically, this amounts to the same thing, since at each conversion, the molecule must pass through the uniplanar position of strain. These strains can be relieved by an ester interchange resulting in the formation of the polyester. Cyclic esters of five atoms or of more than six atoms are not polymerized because then cyclic systems are free from strain.

Irvine and McGlynn (259) have pointed out that the oxidation of one and the same substance may give rise under varying conditions to either γ or δ-lactones, thus rendering the structural evidence ambiguous. Crystalline 2.3.6.-tri-methyl-glucose if oxidized with bromine water, under conditions which permit of the accumulation of hydrogen bromide, yields directly the δ-lactone. In sharp distinction when the sugar is oxidized by the same reagent but in the presence of halogen acid, the δ-lactone is produced, in preponderating amount. (Quantitative results are not given.) They conclude that there is probably no reaction of a reducing sugar in which similar changes of the internal oxygen ring do not take place, provided the necessary hydroxyl groups are unsubstituted, and this possibility cannot with safety be overlooked. It would appear that this evidence is not conclusive.

EXPERIMENTAL

I. Preparation of Glycol Monochloroacetate

11.5 gm. of metallic sodium was dissolved in 65 c.c. absolute methyl alcohol in a 3-necked flask fitted with a reflux condenser. The colorless product was suspended in ether in a Claisen flask and 47 gm. of pure ethylene glycol (50% excess) added. Dry nitrogen was passed through the system to prevent discoloration of the sodium derivative. 60 cc. of methyl alcohol was recovered. 65 gm. of chloroacetyl chloride dissolved in 125 cc. of ether was added slowly to the sodium glycolate, the mixture being kept at 10°C. At 20°, evolution of heat occurred, and some ether distilled. The liquid was decanted from the salt residue and the ether removed at as low a temperature as possible. The residual liquid was yellow. The solution was dried with anhydrous sodium sulphate but on heating in vacuo some water distilled over, so activated alumina was employed later as a drying agent. The mixture was poured into water and the upper layer retained. Glycol bis-monochloroacetate is insoluble. The monochloroacetate was precipitated with common salt, extracted with ether, dried, and the ether removed. Three fractions were obtained by vacuum distillation. Crude yield, 79%. Repeated distillation gave two main fractions. The first fraction was hygroscopic like ethylene glycol, while the second was much less so. Yield 18 gm. (25%) 87-90°/0.60 mm. Final distillation gave 8.1 gm. at 85°/0.15 mm. Bath temperature = 110°. This product was kept in a desiccator until used for determination of its electric moment.

Glycol monochloroacetate was prepared more easily from ethylene oxide and chloroacetic acid in smaller yield though no by-products were formed in this reaction. Redistilled chloroacetic acid in ether was placed in a pressure bottle, the ethylene oxide (50% excess) added in the cold, and allowed to stand four days. The solvent was removed, the residue poured into water and the glycol monochloroacetate salted out with NaCl. It was extracted with ether, shaken with sodium or potassium bicarbonate, dried and the ether removed. Repeated vacuum distillation gave a pure product, b. 83°/0.08 mm. 240°/760 mm. (with decomposition) $n_D^{25} = 1.4585$.

II. Preparation of Glycol Monodichloroacetate (2-Hydroxy-2'-dichloromethyl-1,3-dioxolane)

50 gm. redistilled dichloroacetic acid in anhydrous ether was placed with 30 gm. (50% excess) pure ethylene oxide in a pressure bottle and allowed to stand 56 hours, at 0°C. The mixture was washed with 50 cc. water, the layers separated, washed with saturated sodium bicarbonate solution till neutral, extracted with ether, dried, and ether removed, heating only

to 40°C. Repeated vacuum fractionation gave a colorless liquid, insoluble in water. B.p. 106°C/0.08 mm. (bath temperature 125°) $n_D^{25} = 1.4730$. Yield = 10 gm. This compound was also kept in a desiccator until the electric moment was determined.

III. Preparation of Trimethylene Oxide

Trimethylene oxide was prepared from γ-bromopropyl acetate and solid KOH. The method is by Noller,(271) who used γ-chloropropyl acetate.

γ-Bromopropyl acetate was prepared by a modification of a method used by Bogert and Slocum (272) 85 gm. trimethylene glycol was redistilled twice in vacuo until a faint color remained. 250 gm. acetyl bromide was distilled, very slowly, into the glycol at 0°. The mixture was allowed to stand 24 hours, then heated on a water bath for 2 hours, until evolution of HBr ceased. 300 cc. of CCl_4 was added and the mixture distilled slowly at a temperature of 72-85°. The distillate consisted of water and CCl_4. It was neutralized with Na_2CO_3 when 100 cc. had collected, and CCl_4 returned through a dropping funnel at the same rate at which the distillate condenses. The process was continued until no water appeared in the distillate, at which time about 500 cc. CCl_4 has been distilled. The mixture was heated to 120°, cooled, and washed twice with water to remove trimethylene bromohydrin. The lower layer, after separation, was neutralized with Na_2CO_3, and dried with alumina. Final fractionation in a Claisen flask gave 154 gm. (78% yield) b. 81-86°/20 mm. Bath temperature, 100°.

When this preparation was well-advanced, an unpublished, simpler method of Clarke and Rahrs became available, which suggested some of the modifications of the above method.

The apparatus used to prepare trimethylene oxide was similar to that used in the preparation of divinyl ether (Part I). The copper flask was connected to an air condenser four feet high by a well-fitting ground glass joint. The air condenser was fitted with a Claisen type fractionation head. 240 gm. KOH and 10 cc. water were placed in the copper flask. This mixture fused at 150°, and was kept at that temperature with an oil-bath at 170°. 148 gm. γ-bromopropyl acetate were added slowly drop by drop. White fumes were formed and reflux commenced with distillation of trimethylene oxide at the rate of a drop per second. As addition of the acetate continued the bath temperature was raised 10° every half hour to 200°. The crude distillate was dried with anhydrous K_2CO_3 and redistilled. Slow fractionation in a Claisen flask gave 11 gm. b.45-50°. Yield, 21%. This fraction was treated with liquid bromine at -10°. The reaction was violent. The treatment was continued until the color of bromine remained. The product was dried with anhydrous K_2CO_3 and redistilled. The distillate still showed unsaturation so the bromine treatment was repeated, using a considerable excess of bromine. It was dried 2 days with KOH scales. Two redistillations gave 2 gm. pure trimethylene oxide, b.47.5-47.9°; $n_D^{25} = 1.3895 \pm 0.0002$. $d_4^{25} = 0.8930$ (213). Bath temperature = 65°.

IV. Purification of Propene Oxide (Propylene Oxide)

Propylene oxides from the Carbide and Carbon Chemicals Corporation was dried with alumina. It was twice fractionally distilled. b. 34.75-34.90°; $d_4^{25} = 0.8249 \pm 0.0002$.

V. Preparation of Tetrahydropyran (Pentamethylene Oxide)

Pentamethylene dibromide was very carefully fractionated through a column of glass beads contained in the side arm of a Claisen flask. After three distillations, a fraction b. 93.5°/9 mm. was obtained. An attempted preparation of the tetrahydropyran using Dem'yonov's (273) method gave mostly unchanged dibromide.

25 gm. pure dibromide were mixed with 25 gm. distilled water and 8 gm. of pure zinc oxide. The mixture was sealed in a strong hard-glass tube, shaken to an emulsion and then heated in a bomb furnace for 40 hours at 150°C. The mixture was extracted three times with ether, the extract dried over

Na_2SO_4, and distilled. Fractionation gave a fraction b. 85-90°. The united yields of three preparations gave a pure product, b. 87.5-88.5°; $d_d^{25} = 0.8772$; $n_D^{21} = 1.4211$, $n_D^{25} = 1.4195$. Yield, 90%.

VI. Experimental Apparatus for Measuring the Dielectric Constant

The apparatus first employed was similar to that used by Cuthbertson and Maass (274) which was based in turn on the ingenious set-up, already described, by Williams and Krchma (163). The frequency of an oscillator is given by

$$\nu = \frac{1}{2\pi\sqrt{LC}} \qquad (35)$$

where L is the inductance and C is the capacity of the circuit. Suppose there is a vacuum tube circuit consisting of inductance, capacitance, and resistance. If the resistance is small, and the inductance is fixed, we may have an oscillator of constant frequency given by equation (35) by fixing any convenient value for the capacitance. Suppose that this fixed oscillator has a frequency of 1,000,000 cycles per second and that a second oscillator has a somewhat greater frequency than the first, say of 1,001,000 cycles. On loose coupling of the two circuits, an audible musical note of frequency 1000 cycles will be heard in the telephones. If the capacitance of the second oscillator is increased, the inductance being constant, the frequency difference of the two oscillators will be decreased, until the two frequencies are identical. Concomitantly, the pitch of the note will be lowered (with some alteration in intensity) until the note ceases, theoretically, when the frequency of the two oscillators is the same. In practice, the audible note ceases in the phones before the null point is reached and on further increase of the capacity the note is not heard until the frequency difference is a few cycles per second. This short range of inaudibility, theoretically a point, is called the "dead space". If we plot the condenser setting against the frequency difference, this space is represented by B C.* If the note ceases at D for one setting, and at C for another, although CD may be very small, there is a possibility of error. It is obvious that the "dead space" should be reduced to a minimum.

The two oscillators employed were of the Hartley type, on account of simple construction, purity of the wave-form obtained, and steadiness of operation. The sets are shown diagrammatically.** The inductances, L_1, L_2, L_3, L_4, of No.14 insulated copper wire straight-wound on a bakelite cylinder, consisted of 64 turns and 70 turns for Set I and Set II respectively. Those coils were covered with collodion to hold them rigid. A tap was taken off each coil at 42 turns from one end of the coil and connected to the positive filament lead. A variable air condenser C_1 was connected across the inductance of Set II and this capacity was kept fixed. Since

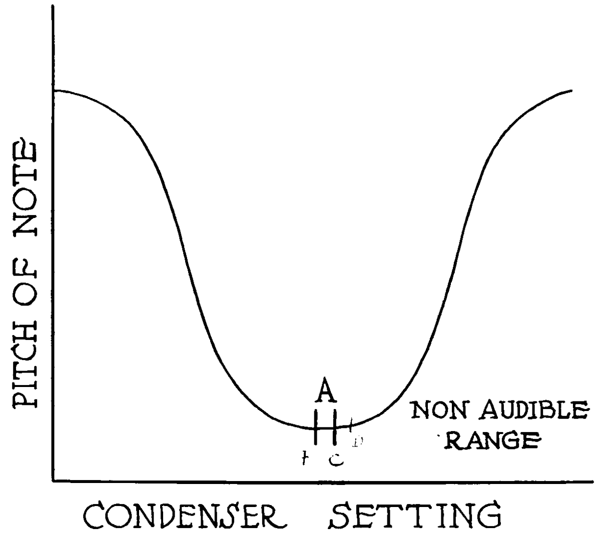


Fig. X.

Frequency-difference Curve Showing Dead Space at Zero Beat for Dielectric Constant Apparatus.

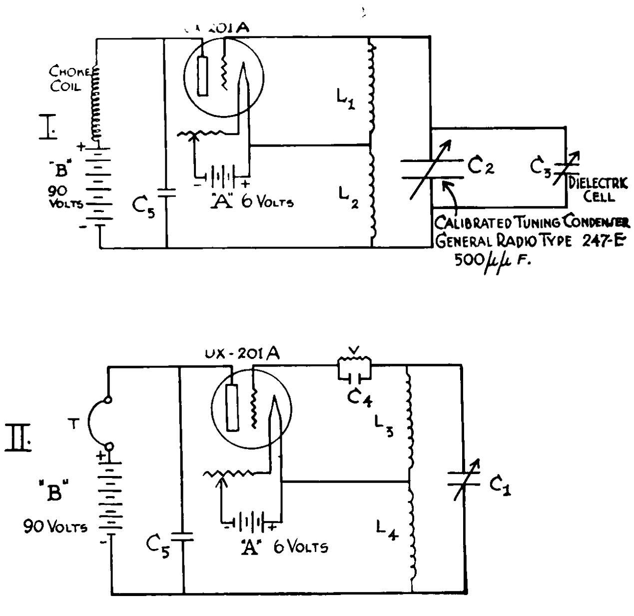


Fig. XI.

Hartley Oscillators Used Originally for Measurement of Dielectric Constants of Liquids.

L is fixed, it is evident from equation (35) that this set is now an oscillator of fixed frequency. Set I was a variable oscillator, and shunted with the inductance was a tuning condenser, General Radio Type 247E, capacity 500 $\mu\mu F$, which was calibrated against a precision condenser. A small by-pass condenser, C_6, was shunted across the telephones, to prevent distortion from the introduction of harmonics. The telephones of Set II occupying the same position as the choke coil of Set I, had an impedance of about 8000 ohms. The choke coil impedance was of the same order. Its purpose was to prevent the passage of radio frequency currents through the plate circuit.

Two UX -201 A vacuum tubes were employed as a source of electromagnetic waves. Since there was no absorption in the dielectric (benzene or benzene solution) sufficient energy was supplied by this arrangement, and it was not found necessary to use the 217 A power tube used by Cuthbertson and Maass. Satisfactory performance was obtained with a potential of 90 volts on the plate and 5 volts on the filament. The filament current was regulated by a rheostat placed in the negative lead of the "A" battery. The rheostat was kept at a fixed setting, connection being made through a switch. The operating current was only slightly above the minimum required to produce the oscillation.

The telephones were placed ten feet from the sets, and the connecting wires, like all other long connections were enclosed in copper tubing which was grounded. The sets were shielded with copper sheets which were also grounded. The "dead space" for this apparatus was about 1 cm. wide.

In making capacity measurements, it is customary to read capacities directly from a precision condenser. In this method the accuracy was increased somewhat. A small mirror was mounted on the central axis of the rotor plates of the tuning condenser, C_2, which was placed at the centre of a wooden disc five feet in diameter. The angle irons used to keep the disc rigid, were grounded. About the circumference of the disc, a millimeter scale was placed. For this purpose, graph paper was pasted to heavy cardboard. Experience shows it would be better glued to galvanized iron.

A lens is used to focus a beam of light on the far side of the scale, and, on placing the mirror in the path of light, an image of the slit is obtained on the side of the scale adjacent to the mirror. By careful manipulation, a sharp line may be obtained. The vernier knob of the tuning condenser is replaced by a small brass pulley. A stout cord connected it to a set of large wooden pulleys, so that the observer was sufficiently removed to avoid the effects of body capacity on the oscillators. This arrangement gave an accuracy in capacity readings of $0.02\mu\mu F$. The dielectric cell will be described later.

The accuracy of the set was calibrated by determining the dielectric constants of benzene, chlorbenzene, chloroform, ethylene bromide, and ethyl iodide, which agreed well with the values reported in the literature. An attempt was made to determine the dielectric constants of methyl alcohol and acetone, but there was sufficient energy absorbed by these liquids to make this measurement impossible.

This apparatus was employed for measuring the dielectric constants of the benzene solutions of the two glycol half-esters, but working in the summer showed the apparatus was not entirely suitable for accurate determinations without repeated standardization, due to rapid atmospheric temperature and humidity variations. Another great objection to the type of apparatus is the effect of body capacity on the telephones and unshielded portions of their connecting wires, which made it necessary for the observer to stand always in the same position to make a reading. The "dead space" also varied in width, which introduced small errors. It was also believed that the sets were imperfectly shielded, as readings made during the day could not be duplicated, although at night a perfect check on the readings could be obtained although the temperature was the same as during the day.

As a result of these difficulties, the complete apparatus was redesigned, although the oscillators still employed the Hartley principle. A complete diagram of the apparatus is given.* The new apparatus is used in the heterodyne beat method and is similar to the sets used most recently by Smyth and Williams, the diagrams of which are included here.

The first disturbing factor to eliminate was the body capacity effect on the telephones. This was possible through the use of a three-stage detector amplifier as shown, which is different in four details from the set described by Smyth (94):

1. The coupling coils are of four turns only, which gave a minimum "dead space" of the same magnitude as the error in capacity measurement, both of which are much smaller than the error of measurement of the dielectric cell capacity. The width of the dead space, less than 0.02 cm., could be detected only with a reading-glass.

2. The 5 megohm grid leak of the second UX - 240 amplifying tube is used with 1.5 volts negative grid bias and not 15 volts as given by Smyth. This error is probably typographical.

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* See Fig XII, p. 156a.

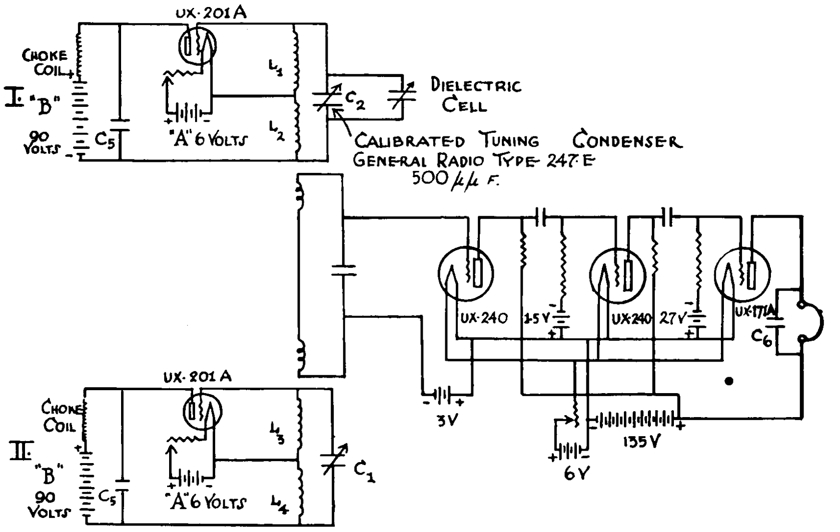


Fig. XII.

Improved and Redesigned Heterodyne Beat Apparatus for Liquids.

3. The filament current is supplied separately to the two UX- 240 tubes and the UX171A tube in order to obtain maximum output, if necessary, without increasing the UX-240 filament current.

4. The telephone is shunted with a .001μμF fixed condenser as before.

A loud speaker was not used for reception as it was believed that the extra impedance caused in the circuit would be too large. It was suggested that a hot wire ammeter would be a more sensitive detector of the position of resonance than ear-phones. Chrétien (160) has replaced a telephone by a sensitive galvanometer. The ammeter was placed in parallel with the telephone and a minimum current was registered on the ammeter at identically the same time as the note in the telephone ceased. Installation of a crystal control oscillator for Set II was not attempted, as the error introduced from frequency variation on the part of this oscillator is much less than the error introduced by imperfections of the dielectric cell. Such an arrangement does not permit of alteration of the frequency of oscillator II, should this ever be necessary.

All other heterodyne methods for liquids have used honeycomb coils for inductances, which are mounted on a bakelite frame. Variations in frequency may be made simply by substituting a coil of a different number of turns. However, the straight-wound type of coil is used by Smyth on an apparatus constructed for measuring the dielectric constants of gases where extreme accuracy is required. In place of two separate coils, the winding on the type of inductance used here is continuous and the filament lead taken from a given point on the inductance coil.

In Set I the small choke coil previously used was replaced by another of large inductance. The secondary (grid-filament) coil of a 4 to 1 ratio transformer was used for this purpose, to prevent the passage of high frequency currents in the plate circuit. Any good transformer coil, of inductance greater than 100 millihenries may be used. This detail is not given in any of the other diagrams (Figs. V, VI, VII).

In Set II, the variable grid leak V, and the condenser, C_4, were removed. The telephone was transferred to the amplifier and a choke coil similar to that of Set I was substituted. In both sets, the fixed condenser C_5 was left in although this condenser is omitted from the book diagrams. It is a blocking condenser, acting in this case somewhat as a safety valve. If condenser terminals are soldered, great care must be taken that the actual condenser is not heated, as this will ruin the condenser very easily. One terminal of a telephone is connected to a "B" battery and the condenser connected to the other battery terminal. When the circuit is completed, the charging of the condenser is registered as a slight click in the phones. Continued making and breaking the circuit produces no sound if the condenser is good.

The grid to condenser (C_1 or C_2) connection should be made as short as possible. Radio frequency currents in this circuit are easily dissipated and this must be prevented. It is advisable to use a solid plated copper lead rather than stranded wire for this connection.

The new sets and amplifier were shielded in separate galvanized iron boxes which were grounded, and the connecting wires used in coupling passed through small holes, since it is known that the decrease in shielding efficiency is less due to a small hole than to a slit of the same area (275). In the construction of the boxes, all metal joints must overlap at least one inch, and such connectionsshould be entirely soldered. The coupling coils of the amplifier were placed on rigid supports inside the shields of Sets I and II. All "B" and "C" batteries were placed insider the boxes as very accurate measurements necessitate their shielding from body capacity effects. The shielding employed was sufficient except for station CFCF (operating frequency 1,030,000 cycles) which was often heard faintly on tuning the two oscillators to zero beat frequency difference.

VII. The Dielectric Cell

A considerable number of dielectric cell condensers have been reviewed, but unfortunately the construction of most of them requires the services of a skilled technician. It was decided that the cell used by Williams was the simplest in construction and at the same time eliminated corrections due to capacity lead effects. The third requirement outlined previously is thus met. A cell was constructed which met all the other requirements except the fifth, which was met indirectly by grounding the two gallon enamelled iron container which was used as a thermostat. The actual cell (Fig. XIII) was a small calibrated variable condenser mounted on seven-inch brass extensions to allow it to be immersed in the dielectric medium contained in a Pyrex tube two inches in diameter. The condenser consisted of nine brass plates, five of which were fixed or "stator" plates, and four were movable "rotor" plates. The brass plates and the lower portion of the extensions were later gold-plated to prevent their reaction with compounds containing chlorine. The brass extensions to which the stator plates were attached were bolted to a bakelite frame, on which was rigidly mounted a small vernier dial. The rotor plates, attached to a brass axle, were adjusted to mesh symmetrically between adjacent stator plates, all of which were spaced with gold-plated washers. The brass axle passed through two supports,

Fig. XIII.

Stator-rotor Type Dielectric Cell Condenser.

one of brass, soldered to the stator plate extensions, one or two inches above the plates. The axle was insulated from the support by a piece of snugly fitting glass tubing. The tube was held rigidly in place by a small wedge of copper. The use of bakelite insulation, objected to by Smyth, was thus avoided. The other bearing was bolted to the insulating frame, and the upper end of the axle was connected to the centre of the vernier dial. The finished cell was absolutely rigid except for the circular motion of the rotor plates. The capacity was about 50 $\mu\mu$F and the volume 40 cc. The error is about 0.1% in the evaluation of the dielectric constant. The cell setting is designated as C_2.

The cell was immersed in a water thermostat kept at 25°, the temperature being controlled by a DeKhotinsky regulator. The accuracy of the regulator was increased by tapping the bimetallic coil with one vane of the stirrer.

For calibration the values at $C_2 = 21$ and 61 were taken as correct. The capacity difference measured by C_3 on the scale was divided by four, and the values of C_2 at condenser settings other than 21 and 61 were adjusted accordingly.

VIII. Operation of the Apparatus

In the operation of these sets many difficulties were encountered besides those already outlined. Some trouble by vibration was eliminated by increasing the rigidity of the apparatus.

Only one case of bad insulation was encountered, of a rather serious nature, and difficult to locate. In a certain type of 4-1/2 volt "C" battery on the market, small wire brads are used to hold the outer paper covering in place at the bottom of the cells. This wire had come in contact with the zinc container and a short circuit was caused with the iron shielding. This not only ruined the "C" batteries but an otherwise harmless contact of the positive "B" terminal burned out a set of tubes.

Two sources of noise, in the detector tube socket and the coupling resistances proved to be very annoying. The first was due to poor contact. The noise in the resistors was due to faulty construction, with replacement of tested resistances the only remedy. This difficulty was entirely unsuspected. The resistor may be tested by connecting it in series with a telephone and a set of "B" batteries, when any noises may be detected although the intensity is very small. For a five megohm resistor, 250 volts is required. Contact of several minutes may be necessary due to heating effects, to detect some noises.

It should be noted that the two sets of coupling resistors should be matched, that is, that the ratio of the two resistors of each set, in this case 1:20, should be maintained.

Commercially, 45 volt "B" batteries are often used until the voltage is quite low. In this work, as soon as a "B" battery tested not more than five volts below its normal rating, not only did considerable noise develop, but the oscillation would be stopped, due to the large impedance increase in the plate circuit. Finally, a throbbing, the source of which has not yet been located, is noticed irregularly when the oscillators are set at zero beat. This is often caused by a high "B" battery impedance, in which case the trouble may be eliminated by reducing the capacity of the $0.01 \mu F$ blocking condensers. This possibility is eliminated as the throbbing was present when the "B" batteries were new and of minimum impedance. The trouble may be of external origin.

IX. Experimental Procedure

The sets were kept in continuous oscillation during a series of measurements and were used only when complete temperature equilibrium was attained - usually after operation during half an hour. Due to certain room temperature effects, it was necessary to adjust a source of cold air so that variations were not more than 0.1° during a measurement. Why this is so is not entirely clear. As a result, it was necessary to standardize the capacity reading with benzene as dielectric for varying temperatures with change of season, and in every measurement the room temperature was kept at very nearly one of these temperatures of standardization. The dielectric cell condenser, C_3, was set at certain values with the plates in air as the dielectric, and the tuning condenser C_2 adjusted to zero beats. The procedure was repeated with the medium under examination. Thus we have

Air		Medium X	
C_3	C_2	C_3	C_2
61	140	61	145
21	132	21	125

Relative Capacity $C = 8$ Relative Capacity $C_x = 20$

$$\epsilon = \frac{C_x}{C} = 2.5$$

The determination of the dielectric constant of benzene will illustrate this procedure. The slope of the line $\frac{C_3}{C_2}$ was measured with air as the dielectric and the dielectric constant of air taken as unity. The same slope was determined with pure benzene in the cell and the dielectric constant calculated. The values which are given in Table IV, are the average of three reliable sets of readings.

TABLE IV

$T = 25° \pm 0.05°$

Air

C_3	C_2			Average
81	121.43	121.42	121.40	121.42
71	120.22	120.20	120.20	120.21
61	119.01	118.98	119.00	119.00
51	117.80	117.80	117.80	117.80
41	116.60	116.60	116.60	116.60
31	115.40	115.41	115.40	115.40
21	114.20	114.21	114.3	114.21
11	113.00	113.00	113.01	113.00

Slope $\frac{dy}{dx} = \frac{33.22}{8}$ $\epsilon = 1.000$

Benzene

C_3	C_2			Average
81	136.00	136.98	136.01	136.00
71	133.24	133.27	133.25	133.25
61	130.58	130.58	130.58	130.58
51	127.82	127.82	127.83	127.82
41	125.07	125.07	125.07	125.07
31	122.33	122.31	122.32	122.32
21	119.57	119.58	119.57	119.57
11	116.82	116.82	116.82	116.82

Slope $\frac{dy}{dx} = \frac{36.45}{20}$

$$\epsilon = \frac{33.22}{8} \times \frac{20}{36.45} = 2.278$$

A previous determination gave $\epsilon = 2.275$, both values in good agreement with those found in the literature (83,105,159,184). In the calculations the value $\epsilon = 2.276$ was used throughout. Further capacity readings will not be given in order to avoid repetition. It is merely necessary to say that for each standardization and dielectric constant measurement, three sets of readings were taken as shown above, the slopes plotted for each solution and dielectric constants calculated.

All measurements were made at 25° ± 0.05° at a frequency of about 10^6 cycles per second.

Refractive indices of the pure liquids were measured at 25° with an Abbe refractometer. The calculated values of the molar refraction were obtained using the following values of the atomic refraction: -

Carbon singly bound	2.501	
Hydrogen	1.065	
Oxygen (hydroxyl) O'	1.521	
Oxygen (ethereal) -O-	1.683	
Oxygen (ketonic) O=	2.287	
Chlorine	5.967	
3-ring	+0.71	(276)
4-ring	0.48	(276)

X. Density Measurements

A new density bottle was made (Fig XIV) which eliminated all errors due to evaporation. It is similar to that used by Ismardi (277) and described by Smyth and Morgan (157). Williams used an Ostwald-Sprengel pycnometer. The bottle was thoroughly cleaned, evacuated, dried and weighed. It was standardized with water at 25° ± 0.05°. The density of water was taken as 0.997073 from the I.C. Tables. Air was not removed from the water as Frivold (278) showed the difference in density between air-free and air-saturated water was only 19.02×10^{-7} at 15.6°C. The method was the same as used for vinyl acetate, with the usual corrections. The density of pure benzene from several measurements was 0.8734 ± 0.0002, which compares well with other values.

In measuring the densities of solutions, the only extra precaution was to prevent evaporation of the solvent in the case of the glycol mono-esters, as the latter are non-volatile. Any lost solvent was replaced by pure benzene.

XI. Final Experimental Results

The experimental results used in determining the electric moments are given in Table V. An example of the calculation using equation (29) and following equations will be given.

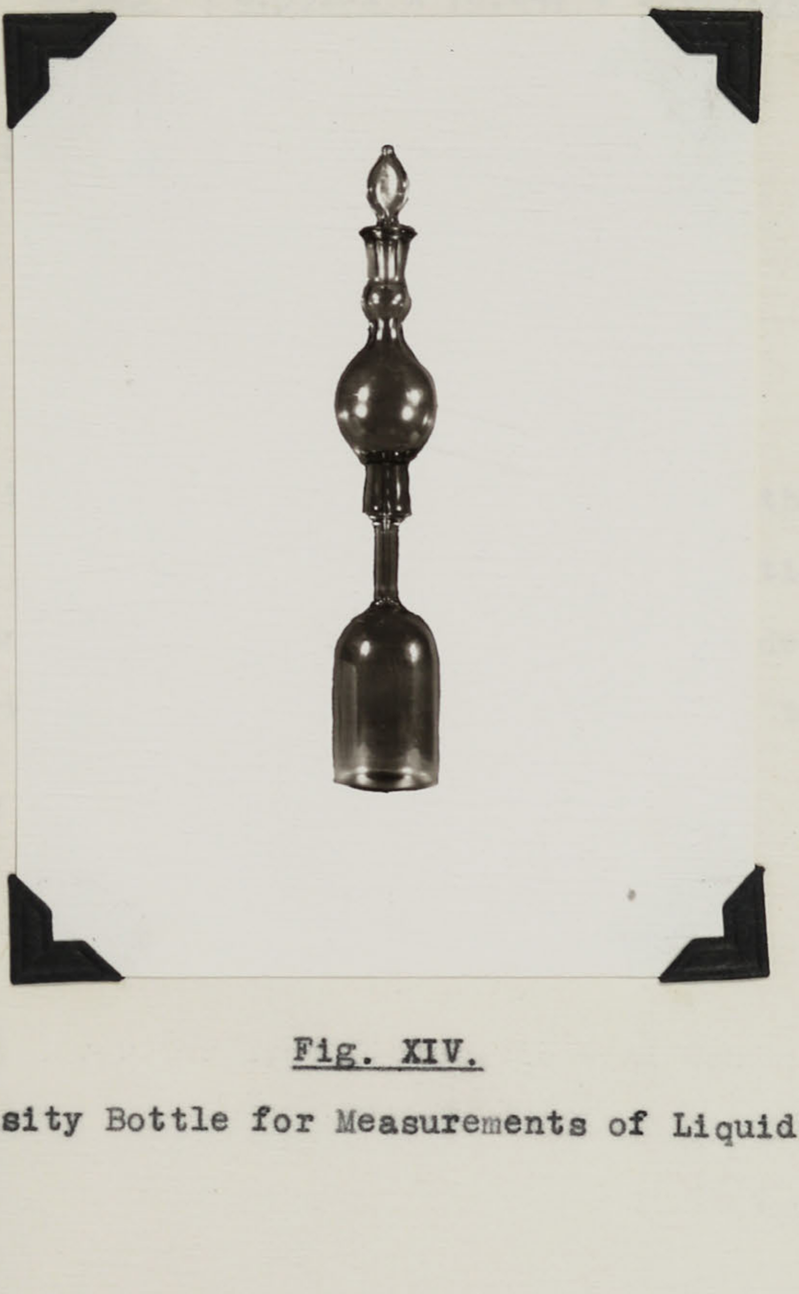


Fig. XIV.

Density Bottle for Measurements of Liquids.

$P_{1,2}$ and P_2 for solution $f_2 = 0.8191\%$ (propylene oxide)

$$d_4^{25} = 0.8731 \qquad \epsilon = 2.315$$

$$P_{1,2} = \frac{1.315}{4.315}\left(\frac{0.99181 \times 78.047 + 0.008191 \times 58.047}{0.8731}\right)$$

$$= 27.185 \text{ cc.}$$

$$P_2 = \frac{27.185 - 0.99181 \times 26.68}{0.008191}$$

$$= 88.4 \text{ cc.}$$

In Table V the first column f_2 gives the mole fraction (in %) of the polar substance in benzene solution, and succeeding columns give the dielectric constant and density at 25°, the polarization $P_{1,2}$ of the mixture, and the total polarization P_2 of the polar solute.

TABLE V

Dielectric Constants, Densities and Polarizations

$f_2\%$	ϵ	d_4^{25}	$P_{1,2}$(cc.)	P_2(cc.)
		Glycol Monochloroacetate		
0.0000	2.275	0.8733	(26.661 = P_1 of benzene)	
.0873	2.334	.8746	27.53	330.6
.4501	2.359	.8753	27.90	306.7
.8233	2.420	.8772	28.76	283.1
.9220	2.432	.8776	28.94	280.9
1.0581	2.449	.8785	29.17	264.5
		Glycol Dichloroacetate		
0.0000	2.275	0.8733	(26.654 = P of benzene)	
.1701	2.300	.8741	27.05	261.3
.2089	2.306	.8747	27.14	250.7
.2163	2.306	.8745	27.14	251.4
.2610	2.315	.8754	27.26	259.3
.3484	2.322	.8756	27.38	234.1
.3658	2.330	.8758	27.49	256.2
.5019	2.347	.8768	27.75	245.1
.6818	2.373	.8782	28.14	244.2
.7899	2.389	.8790	28.36	243.7
1.0020	2.443	.8807	29.13	274.0
		Propylene Oxide		
0.0000	2.276	0.8734	(26.68 = P_1)	90.1
.5593	2.303	.8732	27.02	88.2
.8191	2.315	.8731	27.18	88.4
2.1318	2.373	.8725	27.94	85.6
2.5055	2.383	.8724	28.04	80.0
5.7758	2.519	.8711	29.67	78.5
		Trimethylene Oxide		
0.0000	2.2760	0.8734	(26.68=P_2 of C_6H_6)	100.0
.3072	2.2945	.8734	26.91	100.9
.3759	2.2970	.8734	26.94	97.3
.8023	2.3194	.8735	27.27	96.0
		Tetrahydropyran (Pentamethylene oxide)		
0.0000	2.276	0.8734	(26.68 = P_1)	96.0
.3788	2.294	.8735	26.94	95.2
.6560	2.306	.8736	27.11	92.7
2.0463	2.355	.8739	27.85	83.6
3.1684	2.406	.8742	28.59	86.9
3.1776	2.407	.8742	28.61	87.0

The first column of Table VI gives the compound, and the polarization, P_∞, at infinite dilution ($f_2 = 0$), the molar refraction ($MR_D = P_E$), the orientation polarization ($P_\infty - MR_D = P_M$) and the electric moment ($\mu \times 10^{18}$) follow in order. The absolute values of the moments are a little high because of the neglect of the atomic polarization P_A.

TABLE VI

Refractions, Orientation Polarizations and Electric Moments

Compound	P (cc.)	P_E (cc)	P_M (cc)	$\mu \times 10^{18}$(e.s.u.)
Glycol mono-chloroacetate	352.0	28.92	323.1	3.94
Glycol dichloro-acetate	266.6	33.21	233.4	3.35
Ethylene oxide	-	-	-	1.88[a]
Propylene oxide	90.1	16.29	73.8	1.88
Trimethylene oxide	100	16.06	84	2.01
Tetrahydrofuran	80.7	19.76	60.9	1.71[a]
Tetrahydropyran	96.0	22.84	73.1	1.87

[a] These values are included for comparison

DISCUSSION OF RESULTS.

This discussion falls naturally into two sections:

1. The examination of the glycol monoesters to find an explanation for the observed difference in the experimental values of their moments, and to attempt a calculation of the moments according to the rules of vector addition; and
2. The evaluation of the oxygen valence angles in the isomeric ring form of glycol dichloroacetate, to explain the stability of the structure; a test of this hypothesis by measuring the electric moment of a strainless ring; and the relation of the "normal" oxygen valence angle of this compound (tetra-hydropyran) to other ring compounds. The proposed theory is then applied to the elucidation of the structure of other oxygen compounds and a correlation between the theory and the chemistry of these compounds is made.

I Preliminary.

The relationships stated to exist between the electric moment and molecular structure are as follows:

(1) The hydrocarbons have zero electric moment.

(2) If a hydrogen atom in a molecule is replaced by another atom or radical, a moment is produced which is a characteristic of the substance in question, called the

group moment. The group moment varies somewhat depending on whether the substituent is attached to an alkyl or aryl residue.

(3) The moments of the group substituents may be regarded as vectors. If a molecule contains several substituents, the moments of the molecule may be calculated from the rules of vector addition.

While the first rule seems to be without exception, the last two did not appear to hold except qualitatively. Quantitative results seemed to be out of the question, until it was shown that such groups, as hydroxyl, were complex groups of two dipoles, of which the resultant moment could be resolved at an angle inclined to the moment of the remaining part of the molecule. In this connection the value of the oxygen valence angle is very important.

It had also been noticed that in certain homologous series, the moments of the molecules either decreased or increased as we ascended the series and three explanations for the variations observed were forthcoming, all based on an alteration of the relative effective positions of the two (or more) doublets in the molecule. Since $\mu = ea$, it was expected that the hydrogen halides should show an increase in moment, as we passed from Chlorine to iodine, due to increasing separation of the atomic nuclei. Actually a decrease is found which can only be explained by distortion of the halogen molecule, due to the strong attraction of the electrons by the attached proton. This distortion, shown most conspicuously in such too close approaches of large electronegative atoms is called the polarizability. Similarly we should expect a larger moment for hydrogen sulphide than for water, but the reverse is true, due to the large polarizability of the sulphur atom.

If a table of moments of the alkyl halides is examined, it is observed that the magnitude of the moments varies according to the position of the halogen in the molecule. Tables VII and VIII give the moments for some alkyl chlorides.

Table VII

Moments of Alkyl Chlorides(x 10^{18}).

	Cl	A	B
Methyl	CH_3 -	1.85	
Ethyl	C_2H_5 -	1.99	
n-Propyl	C_3H_7 -	2.04	
n-Butyl	C_4H_9 -	1.97	1.90
iso. Butyl	$(CH_3)_2\,CHCH_2$	1.96	1.9
sec. Butyl	$C_2H_5\,CHCH_3$	2.09	2.1
tert. Butyl	$(CH_3)_3\,C$ -	2.15	2.14
n. Heptyl	C_7H_{15} -	1.85	
2- — heptane	$CH_3(CH_2)_4\,CHCH_3$	2.03	
3- — heptane	$CH_3(CH_2)_3\,CHCH_2CH_3$	2.04	
4- — heptane	$CH_3(CH_2)_2\,CH(CH_2)_2CH_3$	2.04	

The values for the butyl halides in Column A are those of Parts (260) given here for comparison by one method of determination. The values in Column B are the best values in the literature given by Smyth (94).

Table VIII

Moments of dihalogenated hydrocarbons (x 10^{-18})

Methylene chloride	CH_2Cl_2	1.6
1.1 - Dichloroethane	$CH_3CH\ Cl_2$	2.01
1.1 - Dichloropropane	$CH_3CH_2CHCl_2$	2.06
2.2 - Dichloropropane	$CH_2CCI_2CH_3$	2.18

Table IX

Differences in Moments for one or two Cl atoms in Molecule μ (x10^{-18})

			Difference
Methyl chloride	CH_3Cl	1.85	
Methylene chloride	CH_2Cl_2	1.60	~~+~~0.25
Ethyl chloride	CH_3CH_2Cl	1.99	- 0.02
1.1 Dichloro ethane	CH_3CHCl_2	2.01	
n-Propyl chloride	$CH_3CH_2CH_2Cl$	2.0	
1.1 Dichloropropane	$CH_3CH_2CHCI_2$	2.06	- 0.06

From Table IX it will be noted that the differences vary considerably, depending on whether we consider the first members of the series, which are usually abnormal both physically and chemically, or higher members of the series, which are more nearly alike in properties. The differences of the last two pairs are not significant.

In Table VII there is an increase in moment from methyl to ethyl and a slight increase from ethyl to propyl, after which the values of the straight chain chlorides are sensibly constant. This increase has been attributed to induction of the alkyl group by the chlorine atom, an effect which extends noticeably to the second carbon atom and possibly to the third, although the effect would be very slight in the latter case due to bending of the carbon chain. When the chlorine atom is located as in tertiary butyl chloride, a maximum value for the moment is obtained. In Table VIII the marked increase in 2-2' - dichloropropane will be noted.

In a few cases, induction will cause a decrease in the value of the moment as was observed for the o-dichlorobenzenes. In this instance, the mutual induction of the two chlorine atoms caused the observed decrease below the calculated value.

In an homologous series of ethers, as shown in Table X, a decrease in moment is noticed with increase in size of the alkyl group. In this Table, values of the moments of other compounds which will be needed in this discussion have been included.

Table X.

Electric Moments (x 10^{18})

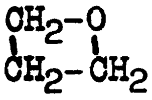
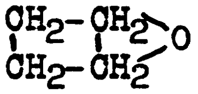
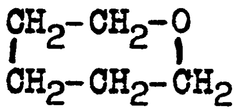
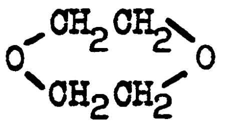
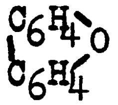
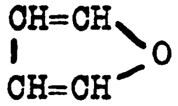
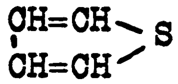
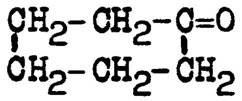
Divinyl ether	$(CH_2{=}CH)_2O$	1.06	(122)
Methyl ether	$(CH_3)_2O$	1.29	
Ethyl ether	$(CH_3CH_2)_2O$	1.12	
Propyl ether	$(CH_3CH_2CH_2)_2O$	0.86 1.16	(261)
Ethyl isoamyl ether	$C_2H_5O(CH_3)_2CH(CH_2)_2$	1.2	
Isoamyl ether	$[(CH_3)_2CH(CH_2)_2]_2O$	1.0	
Anisole	$C_6H_5OCH_3$	1.2	
Phenetole	$C_6H_5OC_2H_5$	1.0	
Phenyl ether	$(C_6H_5)_2O$	1.05	
Ethylene oxide		1.88	
Propylene oxide		1.88	
Trimethylene oxide		2.01	
Tetrahydrofuran		1.71	
Tetrahydropyran		1.87	

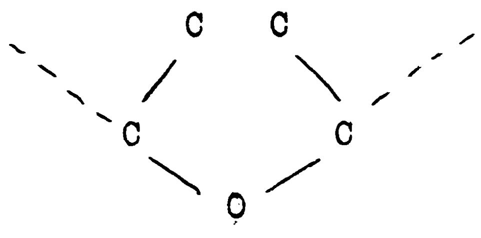
Table X (continued)

1.4-Dioxan		0.4	
Diphenylene oxide		0.9	
Water	H_2O	1.85	
Hydrogen sulphide	H_2S	0.95	
Methyl alcohol	CH_3OH	1.68	
Ethyl alcohol	C_2H_5OH	1.70	
Ethyl mercaptan	C_2H_5SH	1.39	(262)
Ethyl ether	$(C_2H_5)_2O$	1.12	
Ethyl sulphide	$(C_2H_5)_2S$	1.57	(262)
Phenyl ether	$(C_6H_5)_2O$	1.05	
Phenyl sulphide	$(C_6H_5)_2S$	1.47	
Furan		0.7 0.63	(262)
Thiophene		0.6	
Diethyl ketone	$(C_2H_5)_2C=O$	2.72	
Cyclohexanone		2.75	

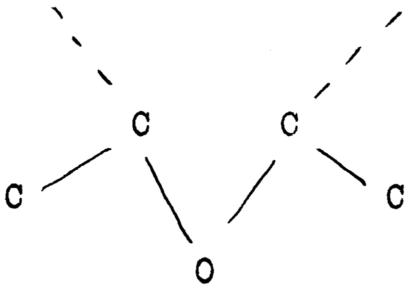
The electric moment of the water molecule is 1.85, If one of the hydrogen atoms is replaced by a methyl group, the distance a between the ends of the CH_3--O doublet is greater than the H--O in water, and an increase in moment is expected from this consideration. Another factor, however, appears and it is apparent that the resultant of the two doublets makes a considerable angle with the CH_3--O line, which reduces any inductive effect upon the CH_3 group. Thus the moments of ethyl and methyl alcohol are identical, in contrast with the chlorides and so it is concluded that the -OH group produces no effect by induction of adjacent carbon atoms. This statement is supported by the fact that the electric moments of heptanol -1, -2, -3 and -4 are identical. A slight increase in polarizability of the oxygen atom could explain the difference of the moments of water and methyl alcohol, but this is very doubtful. Why, then, is a decrease noted, on passing from water to the alcohols? It may be presumed that the increase in size of the substituent group produces a widening of the oxygen valence angle. Since the methyl group is known to have but a small polarity, this increasing repulsion due to its introduction must be due to steric effects almost entirely.

When the second hydrogen atom of water is replaced by a methyl group to give methyl ether, the increased size of the methyl group causes greater widening of the oxygen valence angle than in the case of methyl alcohol, and the moment decreases from 1.68 to 1.29. When methyl is replaced by ethyl the increased size of the alkyl group perhaps causes a slight increase in repulsion, although this effect is rather ill-defined. In n- propyl ether it would appear that there was a considerable further increase in angle between the doublets to cause the observed decrease in moment from ethyl, 1.12, to propyl, 0.86. This latter value is open to question. In a recent publication, Meyer and Büchner (261) point out certain errors in the data employed by Sänger in the calculation of the first value in the table, and with more accuracy, assign the value 1.16 ± 0.05 to n- propyl ether. This agrees with the moment of ethyl ether, and it is concluded that all the lower aliphatic ethers have the same oxygen valence angle. This statement seems to be supported by the moments of ethyl isoamyl ether and isoamyl ether. The former would be expected to have a moment of the same magnitude as ethyl ether, which is true. But the moment of iso- amyl ether on the basis of the first arguments should be lower than that of n- propyl ether, and it is actually larger, if we use for the latter the value 0.86.

In the ethyl ether molecule, two extreme positions (a) and (b) may be assumed by the second carbon atom relative to the C--O linkage.



(a)



(b)

Type (a) would necessitate considerable repulsion between the alkyl groups, and (b) would not. The moment of divinyl ether seems to support the suggestion that (b) would be the more favored configuration, and the mean effective position of the ethyl group would be indicated by the dotted line. The contribution of the double bond to the electric moment is usually small, as the moments of α-butylene ($CH_2 = CH\ C_2H_5$) and $1.1'$ - diphenyl ethylene ($(C_6H_5)_2C = CH_2$) are only 0.37 and 0.5. The real value may be taken as 0.3. The moments of ethyl ether and divinyl ether are identical which would also exclude formula (a) as a possibility, and favor (b). For the structure (a), there would be observed a decrease in moment (about 0.4) as the electrons of the double bond, as shown by the high refraction associated with them, are more mobile than those of a single bond. A molecular structure for divinyl ether is thus rendered more probable in which the $CH_2 = CH$ doublet is almost perpendicular to the bisector of the oxygen valence angle, in which position the $CH_2 = CH$ contribution to the moment would be zero.

In the mixed alkyl-aryl ethers, the difference between anisole and phenetole would be explained by analogy with methyl and ethyl ether. Approximately the same value for phenyl and ethyl ether would suggest the same value for the oxygen valence angle for the two molecules, although a marked increase in repulsion might be expected. The aryl group, however, seldom produces the same effect on the moment as an alkyl group, hence some type of compensation effect must be introduced in the phenyl compounds. In the higher ethers it would appear that any differences in repulsive effects are obscured by experimental errors.

It has been shown that an increase in polarizability of an atom would account for an observed decrease in moment. As the differences for the ethers are not large, small increases in polarizability could conceivably account for the observed variations. The effect of polarizability would be small.

It has been stated that the moment of hydrogen sulphide was lower than that of water because of the increased polarizability of the sulphur atom. The same explanation holds for ethyl alcohol and ethyl mercaptan although it is evident that substitution of hydrogen by an alkyl group increases the moment for a sulphur compound, while the opposite effect was noticed for the oxygen compounds. It would appear that the effect of increased polarizability was not so great in this case. Thus we see in diethyl sulphide that the second alkyl group causes an increase in moment, again unlike the oxygen compound. The same is true for the aryl sulphides and ethers to a like extent, which suggests that this change in the relative magnitude of the moments is due to an inherent property of the sulphur atom. Rather strangely, the moments of furan and thiophene are identical, a fact which Smyth and Walls (122) explain by assuming a sulphur valence angle for thiophene of possibly 140° or more, and this could only be true when the polarizability effect is absent. In the dialkyl sulphides then, polarizability effects are almost, if not entirely, negligible, and as these effects are not noticeable in simple oxygen compounds, but are very marked in H_2S and C_2H_5SH, it is evident that polarizability will not be a contributing factor to the moment even of the higher ethers.

From these considerations, it may be reasonably concluded that all the lower aliphatic ethers have oxygen valence angles of the same magnitude and that the value for methyl ether is an exception, comparable with other exceptional physical and chemical properties, usually associated with the first members of homologous series.

We may then summarize the explanations offered for variations in the observed moments of related compounds:

1. An increase in moment, ceteris paribus, is explained by the induction of two unlike atoms, exemplified by the alkyl chlorides. The effect is transmitted to the second

carbon atom. A decrease in the "effective" angle, or the real angle, between two doublets offers a second explanation of an observed increase in moment.

2. A decrease in moment is explained by an increase in polarizability of a single atom, or in two similar series of compounds (eg. oxygen and sulphur derivatives) by an increase in polarizability of the larger electronegative atom. A decrease in magnitude of the valence angle between two linkages, as in the oxygen atom, also accounts for an observed decrease in moment.

With regard then to the rule of vector addition, calculations of the electric moment of more complex compounds may be made with a fair degree of accuracy if we take into account the stereo-chemistry of the atoms involved. On this basis, in the absence of either confirmatory or contradictory evidence other than that presented here, the "normal" oxygen valence angle for the aliphatic cyclic and chain ethers will be taken as 90°. The "normal" angle is defined as the angle which will be made by the two oxygen valence bonds when the oxygen atom is part of a "strainless" ring, such as tetrahydropyran, or is a constituent of a simple ether, aliphatic or aromatic, in which the interaction of adjacent groups is negligibly small.

In brief, the normal angle is that assumed by the valence bonds under ideal <u>intramolecular</u> conditions.

Since the effects of induction and polarizability can be neglected for oxygen compounds, any variation from the calculated values must be explained by variations in the oxygen valence angle.

II. The Glycol Monoesters.

Glycol monochloroacetate, the half-ester, has an electric moment of 3.94. All chemical evidence points to the fact that this compound has an open chain structure. In the preparation, the reaction mixture was kept at 10° C so that if a ring could possibly form, the temperature might not be too high to prevent its formation. The ring isomer would be expected to have a lower boiling point than the chain compound and could possibly be obtained if distillation were carried out in a molecular still.

The preparation of the dioxelane compound III, isomeric with glycol monodichloroacetate from ethylene oxide and dichloroacetic acid, would lead one to expect an open chain product, whereas apparently the ring isomer, 2 hydroxy-2'-dichloromethyl-1.3.-dioxolane, alone was formed. Evidence for the stability of this ring has already been outlined. Its method of preparation by isomerization of the expected open chain compound would suggest that the ring possessed considerable stability. It may be assumed to have an increased stability over the unsubstituted 1.3-dioxolane, because of the stabilizing influence of the two substituent groups or C_2.

In the series of glycol monoesters such as glycol monoacetate; glycol monochloroacetate; glycol monodichloroacetate and glycol monotrichloroacetate, which was studied with Hibbert and Greig, they predicted (126) that the tendency toward cyclisation would increase in the order mentioned, and stated that this tendency and ease of ring formation would be dependent on: (a) the relatively labile character of the hydrogen attached to the hydroxyl group, (b) the negative polarity of carbonyl group in the acyl radical and (c) the spatial relationship of the migratory hydrogen atom with reference to the carbonyl group of the first factor we know comparatively little, and with reference to the third, space relations appear to be nearly perfect in the chain formula on the basis of any theory of ring structure if we assume free rotation of the hydrogen atom and the substituted group about the C--O linkages.

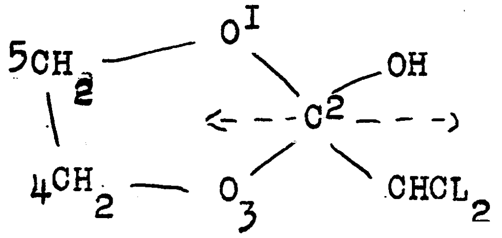
With regard to postulate (b), it is impossible to make definite statements, considering the fact that the word "polarity" is used with regard to what is normally called the electronegative character or the group moment of the carbonyl group. When the acetyl group is progressively substituted by chlorine atoms, it can be shown theoretically, since the open-chain glycol dichloroacetate was not obtained, that glycol monochloroacetate and dichloroacetate have the same electric moment. The only effect, in this case, could be a distortion of the electronic arrangement of the carbonyl group, due to an electrostatic field within the molecule which may arise from the presence of free electric charges, such as are found in the anions of acid esters. It would appear, as a result of the cyclization of glycol monodichloroacetate, that the energy of activation of the carbonyl group is decreased in some manner.

If we consider the constitution of the two glycol esters as open-chain compounds, it will be noted the only difference is that one hydrogen atom in the monochloroacetate has been replaced by a chlorine atom. If this were the only difference between the two compounds, we might expect that their difference in electric moment would be comparable to the difference in moment of other compounds which differ in constitution in the same way, such as methyl chloride and methylene chloride (1.1 dichloromethane); ethyl chloride and 1.1 dichloroethane, etc. A short review of the moments of such compounds has been made. From these differences, we should establish at least a qualitative relation with the difference of 0.60 x 10^{-18} e.s.u. between glycol monochloroacetate and "glycol monodichloroacetate." If the compounds are considered as derivatives of alkyl chlorides, should they be considered then (1) as compounds of the nature of methyl and methylene chloride; or (2) of the nature of ethyl chloride and 1.1 dichloroethane. In the latter case, would the mutual induction of the doubly bound oxygen or hydroxyl group as the case may be, counterbalance the induction of the chlorine atoms on the same #2 carbon atom? We can only approximate an answer to any of these questions, as each one is probably to some extent true. In the first case, the difference is 0.25×10^{-18} e.s.u. while that reported here is 2.4 times as great. In the second case, differences are not even comparable, so we must account for the whole difference of 0.60×10^{-18} e.s.u. by other than constitutive factors.

It has been shown that the hydroxyl group produces no inductive effects, and the same is true for the carbonyl group. As the inductive effect of Chlorine atoms extends to the second carbon atom, these compounds will be considered as if they were derivatives of ethyl chloride and 1.1'-dichloroethane. The moment of the glycol monodichloroacetate may now be calculated, assuming that it has the dioxolane ring structure.

III. Assumptions Involved in Calculation of the Electric Moment of 2 Hydroxy- 2'- dichloromethyl - 1.3 - Dioxolane.

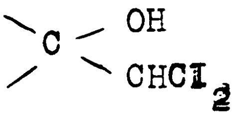
The dioxolane derivative (II) has the following formula:



(II)

In this formula, the C_2 carbon atom does not lie in the same plane as the rest of the molecule, with the result that the O--C--O linkage may make an angle with the rest of the plane of about 90°. The -OH and $-CHCl_2$ groups are perpendicular to this vertical plane, as indicated by the arrows. If the angle at C_4 and C_5 are tetrahedral, the distance O_1--O_3 = 2.37A. If C_2 is a tetrahedral angle, O_1--O_3 = 2.03A. It is evident that when this ring is formed, the angles at C_4 and C_5 decrease, and the angle at C_2 increases. If the O--C--O linkage stands at right angles to the plane of the rest of the molecule, the angle C_2--O_3--C_4 is about 85°, which could conceivably be the oxygen valence angle in this dioxolane ring.
In the calculation of the moment of (II) it is necessary to assume group moments for the substituent groups, and the C--O--C linkages of the ring.

(1) Calculation of the resultant and direction of the moment of the $>C<^{OH}_{CHCI_2}$ grouping.



Free rotation is assumed about the C--O and C--C linkages, and thus the moments of these groups will act approximately in the direction of these bonds. M(C--OH) is taken from the value for methyl alcohol, μ = 1.68. M(C--$CHCI_2$) is taken from the value of 1.1'- dichloroethane, μ = 2.01, rather than from methylene chloride, μ = 1.6 as the

$-CHCl_2$ group would cause induction in the 2-carbon atom. The moment of the 2.2' - dichloroethyl alcohol has not been measured, but Smyth & Walls have measured 2 - chloroethyl alcohol (ethylene chlorohydrin), $\mu = 2.0$. If we assign the value of the moment of ethyl chloride to $M(C{-}{-}CHCl_2) = 1.99$, and calculate θ from equation (33), $\theta = 115^\circ$. Since $-CHCl_2$ would cause slightly greater repulsion of -OH than $-CH_2Cl$, the angle between these doublets would be greater than 115°, possibly 120° - 125°.

The resultant moment from Equation 33 is

$$r = \sqrt{(2.01)^2 + (1.68)^2 + 2(2.01)+(1.68) \cos 121^\circ}$$
$$= 1.84$$

The direction of the doublet will make an angle of 7°-8° with the bisector of the angle between the two groups. In the formation of this ring (<u>II</u>), closure could take place so that either the -OH or $-CHCl_2$ groups would be on the same side of C_2 as the $C_4{-}{-}C_5$ linkage. The two possible compounds would form in a 1:1 ratio, since any other ratio would be potentially an assymmetric synthesis, which is highly improbable. The net result will be that the above resultant will act along the bisector of the angle between the two groups.

(2) <u>Calculation of the Resultant of the moments of the two C--O--C linkages.</u>

The C--O--C linkages are assigned the values of two ether linkages from the value for methyl ether, $\mu = 1.29$.

These two moments will bisect the C--O--C angles and make an angle of 85° each with one another. Thus:

$$r = 1.29\sqrt{2(1+\cos 85^\circ)}$$
$$= 1.90$$

This resultant will make an angle of 45° (or larger, being half the angle between the two planes of the molecule) with the former resultant, $r = 1.84$

$$\text{Hence } \mu = \sqrt{(1.84)+(1.90)+2(1.84)(1.90)\ \cos 45^\circ}$$
$$= 3.45$$

a result based on the assumption that the oxygen valance angle is 85°.

In view of the approximations made in this calculation, the value $\mu = 3.45$ agrees exceptionally well with the measured value of $\mu = 3.35$. It thus appears that 85° or some value only slightly greater than this angle, is the correct one for the oxygen valence angle in the dioxolane ring. For any angle slightly larger than 85° the calculated moment will decrease and become identical with the experimental value, an agreement which is impossible. Using the tetrahedral value for oxygen, the calculated moment is not greater than 3.0. This supports the hypothesis that the normal oxygen valence angle is about 90° rather than a higher value, and the fact that this system is a stable, and almost strainless diplanar ring follows logically from this hypothesis.

A Calculation of the moment of glycol monochloroacetate on similar assumptions gives a value greater than $\mu = 4.0$. The experimental value is 3.94. Since the values of the moments of ethyl chloride and 1.1'-dichloroethane are equal, the calculated value of the chain structure of glycol monodichloroacetate will also be greater than 4.0. Comparison with the experimentally found value immediately eliminates this structure, and shows that the latter compound is a closed ring, which agrees with the same conclusion based upon organo-chemical evidence. The measurement of the electric moment has thus distinguished which of two possible isomers is formed in a reaction, and the difference in moment of 0.60 is due to ring closure alone.

Almost two years ago (279) it was stated: "The electric moment ought to be governed by two factors: (a) length of the chain, if such is formed, or (b) whether the polymer is a circular configuration spiral or is a true closed ring. In this connection, therefore, different results should be expected from (a) and (b), and we may be able to indicate whether a given polymer possesses a long open chain structure or is closed in a ring." In this case, we have obtained definite indications that this is true for two molecules of the glycol monoester type and so for the first time it appears that another physical measurement, dipolar moments, may serve as at least a confirmatory test of ring or chain structure in organic molecules.

IV. Interatomic or Internuclear Separation.

In all calculations, the following values, are used for the internuclear separations: C--C = 1.54 A (263) and C==C = 1.33 A in aliphatic compounds (264,265); C--C = 1.42A (266) in aromatic compounds; C--H = 1.08A (269) and C--O = 1.24 ± 0.04 (268) with a maximum value of about 1.37.

The value assigned to C--O is open to question, and a variety of figures appear in the liberature with little to choose between most of them. Smyth has used the value 1.43A given by Pauling (267) and on this basis calculates values for the oxygen valence angle in different compounds. Pauling has formulated tables of radii for use in crystals containing electron-pair bonds and with the use of these tables has constructed a table of radii (Table XI) non-metallic atoms in covalent molecules.

Table XI.

Normal Electron-Pair-Bond Radii of Atoms in A.

Single Bond Radii

H
0.29A° (0.375 A in H_2)

C	N	O	F
0.77	0.70	0.66	0.64

Double Bond Radii

C	N	O
0.69	0.63	0.59

Triple Bond Radii

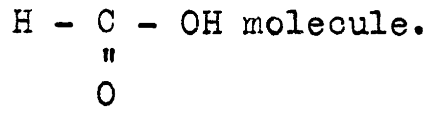
C	N	O
0.61	0.55	0.52

All the bond radii except C and H were obtained by interpolation with the aid of crystal data. The triple bond radii were obtained by multiplying the single bond radii by the factor 0.79, which gives agreement with the accurately known C≡N distance in HCN. The factor for double bond radii was taken as 0.90. The conclusion is drawn that resonance between two or more structures leads to interatomic distances nearly as small as the smallest of those for the individual structures. Two possible structures of the bonds in carbon monoxide, nitrous oxide, carbon dioxide, benzene, and the nitrates and carbonate ions as discussed in support of the resonance hypothesis. The agreement is usually good, but the use of values (as for C—C in the examination of benzene) which are greater than any experimentally measured separation makes the agreement only apparent in some cases. The value 1.43A, even as a maximum, is believed to be too high. It is an open question whether values of atomic separations determined for the solid state can be applied to other states. Many molecules may well have, in the liquid state and in gases, shapes which are very different from those found to prevail when they solidify.

Ebert $\left(^{103}_{P.66}\right)$ regards the assumption that the distances between centres of gravity of the atoms in large organic molecules are nearly constant as a sound approximation. Wycoff (263) states that the radius of a particular atom is not constant but depends on its environment. The atom becomes smaller as it loses electrons as the resultant field becomes more intense, and therefore an ion is larger than a neutral atom. All gradations exist between purely polar (inorganic) and non-polar (organic) bonds. It is concluded that carbon, oxygen and nitrogen atoms cannot be taken as spheres.

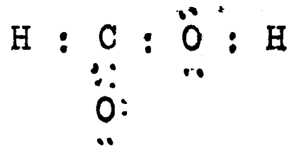
It would appear that the values assumed by Pauling are not conclusive, and that the intrapolation may not be justifiable. Other C--O separations given by Pauling disagree with experimental results. $C=O$ is calculated 1.28A for formaldehyde and experiment gives 1.2A (270) a difference which cannot be explained in terms of the resonance hypothesis. The separations in nitrous oxide agree only if N-N and N-O in the structure N.N.O. behave like triple bonds. A discrepancy in the application of the theory to benzene is noted, and the observed aromatic C--C separation is actually only half as small as the smallest of the two possible values. The agreement is good for carbonates and nitrates as it is from just these compounds that the interpolated values of the normal electron-pair-bond radii were obtained. For $CO_3^{=}$ the observed separation is not <u>nearly as small</u> as the smallest distance calculated by Pauling, but is actually less.

The experimental value used here was measured by Hengstenberg (268) for the $H - \underset{\overset{\|}{O}}{C} - OH$ molecule.



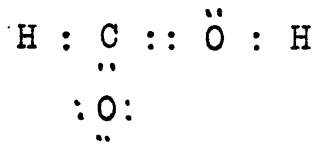
$$H - \underset{\overset{\|}{O}}{C} - OH$$

The work of this investigator is usually reliable. The value obtained for the C--C separation in acetone is slightly high. Also the measurements were made by electron diffraction in the gaseous state, which would indicate that the value C--O = 1.24, was certainly not too high. In this molecule the C--O and C = O periods were found to be equal. Pauling's resonance theory would explain this fact by the postulation of resonance between the two forms



$\mathrm{H : \underset{\ddot{O}:}{C} : \ddot{O} : H}$

and



$\mathrm{H : \underset{:\ddot{O}:}{C} :: \ddot{O} : H}$

In any case, the observed value would be less instead of greater than the C::O calculated value, 1.28.

If there is any relation between force constants (S and B) and interatomic distances, an examination of these factors indicates a maximum value of C--O = 1.3A. If the value C==O = 1.24A is really the value of the carbonyl group in formic acid, and the conversion factor, 0.90, used for a double bond, is applied to this experimental value, a maximum of 1.37A is given for the C--O separation.

From the above reasoning the value assigned to the C--O separation of 1.43A appears to be too large, due to the large value assigned to the radius of the oxygen atom. In view of these facts, the experimental value C--O = 1.24A is used in preference to other values based on theoretical considerations.

V. Bond Moments.

The values which are used for bond moments in the following calculations are: M(H--O) = 1.09; M(CH_3--) = 1.20 and M(H--C) = 0.2 - 0.4. Some evidence in support of of the selection of values for the first two group moments in preference to the values of Eucken and Meyer has been given. If the internuclear separations are constant, the oxygen valence angle in ethylene oxide is 77°, and the carbon angles are 51.5°. This gives $M(CH_3{-}{-}O) = 1.20$ from equation (34).

Since the moments of ethylene oxide and water are equal, it might be expected that the oxygen valence angle in both cases would have the same value, ca. 77°. This is not the case, as in water the H--O internuclear separation is calculated by Debye as $\underline{a} = 1.07$ or 1.02×10^{-8} cm. if the oxygen valence angle is 64° or 109° 28'. The value for the C--O distance is 1.24. Smyth uses the value 1.43. If there is any connection between the relative magnitudes of the internuclear separation and the bond moments, then $M(H{-}{-}O)$ is less than $M(CH_3{-}{-}O)$ which supports the selection of $M(H{-}{-}O) = 1.09$, whether the value $M(CH_3{-}{-}O) = 1.20$ or 1.12 is accepted. Thus the value of 64° for the oxygen valence angle is rendered very probable.

If the new values for $M(CH_3{-}{-}O)$ and $M(H{-}{-}O)$ are used, we find for methyl alcohol that the oxygen valence angle, $\theta = 86°$. For methyl ether, $\theta = 115°$ and other aliphatic ethers are about the same value. For ethylene oxide, using the bond moment data, $\theta = 77°$, the same value as was calculated using the internuclear distances. In ethylene oxide, the structure is comparatively rigid, and the valence angles have a quite definite angle. The magnitude of the oxygen valence angle, and of the carbon angles, is fixed if the C--C and C--O internuclear separations are fixed. This value for oxygen is the minimum for any C--O--C linkage, and has been shown to be 77°.

Suppose that the following values of Eucken and Meyer, which are based on the assumption of a tetrahedral oxygen valence angle, are assumed to be correct: $M(H\text{--}O) = 1.6$; $M(CH_3\text{--}O) = 1.12$. θ for methyl alcohol is then 106°, which agrees with the assumption of a tetrahedral oxygen valence angle. If, however, θ is calculated for ethylene oxide, the C--O--C angle is found to be 65°, which is impossible, unless an inconsistent value is assumed for the C--O separation.

The value of $M(H\text{--}C)$ is very small, but not negligible, as will be shown later. It is usually assigned the value $M(H\text{--}C) = 0.4$. Calculations of the moments of methylene chloride and chloroform suggest the value $M(H\text{--}C) = 0.15 - 0.2$, but the problem is complicated by the chlorine atoms. Values of the Kerr (124) constant of toluene show that this bond moment has a finite value. The fact that the moments of diethyl ketone and cyclohexanone are identical would appear to be evidence against assigning any group moment to the H--C bonds in cyclic structures. As cyclohexanone exists as a puckered ring, there will be a sufficiently large angle between the carbonyl group moment and the resultant moment of the H--C bonds, to nullify the effect of the latter, regardless of the value of M(H--C) unless it were very large.

VI. Heterocyclic Rings - Cyclic Oxides.

In proving the ring structure and isomeric nature of glycol monodichloracetate, an evaluation of the oxygen valence angle was necessary to calculate the electric moments of three possible structures. This angle was shown to be about 90° rather than the tetrahedral angle. Ebert states that "it must be emphasized, however, that any deviation, even if small in amount, of the actual valency configuration from the angles, (i.e. from the symmetry) of the regular tetrahedron puts the heuristic importance of this model for chemical purposes in a different position from that associated with the ideas of classical stereochemistry." In view of the remarkable implications of the result that an oxygen valence angle of 90° was rendered probable, the electric moment of tetrahydropyran was measured, $\mu = 1.87$. The absolute value is a little high due to neglect of the atomic polarization. Previous to the determination of the moment of this compound the value was calculated assuming that the oxygen valence angle is 90°, and $M(H{-}{-}C) = 0.4$. The calculated moment for this geometrical structure is 1.91, in remarkable agreement with the experimental result. If the oxygen valence angle is calculated using the values given for the internuclear separations, $\theta = 85^{\circ}$. Using this value of θ, and M(H--C) = 0.2, the calculated moment is 1.77. This value is lower than the value 1.91 previously calculated due largely to the smaller value assigned to M(H--C). If, as has been suggested, the (H--C) group moment is not taken into account, all experimental values of the electric moments must be explained on the basis of a smaller oxygen valence angle than is suggested here, as the polarizability of the oxygen atom in all ethers is about the same, and it has been shown that the effects of induction are negligible. The results indicate without the slightest doubt, that the oxygen valence angle in tetrahydropyran is not greater than 90°. This result gives to our best knowledge, the first and only experimental confirmation, by electric moment measurements, of the value of 90° assigned to the normal oxygen valence angle from the quantum mechanical consideration of directed bond eigenfunctions, by Pauling.

The electric moments of propylene oxide and ethylene oxide are identical as might have been predicted by analogy of the moments of the alcohols, where substitution of a hydrogen atom by a methyl group causes no alteration in the value of the moment. This result confirms the conclusion that the moments of adjacent members of certain homologous series are identical. The oxygen valence angles in propylene oxide and ethylene oxide are also the same, in this case, about 77°.

Since the triangular structure for ethylene oxide sets a minimum value for the oxygen valence angle, it is impossible for any electric moment of a cyclic ether to be greater than that of ethylene oxide, unless other factors contributing to the moment are assumed. In the absence of induction and polarizability effects, this necessitates the conclusion that the H--C bond moments in a plane heterocyclic structure must contribute something to the electric moment. For trimethylene oxide, using M(H--C) = 04, this contribution is 0.46 for the two H--C bonds opposite the oxygen atom. Since $\mu = 2.01$, this still leaves a contribution of 1.55 for the two CH_2 --O linkages.

The electric moment of trimethylene oxide would almost appear to be too high. It was somewhat greater than expected. The only possible impurity would have been allyl bromide which has a smaller moment than trimethylene oxide. In the measurement of P1,2 (Table V) the low concentrations employed may cause an error of about 3 c.c. in P_∞ , which would lower the moment to 1.97. In the cyclopropane ring, the C_1 -- C_3 distance is 2.48A, exactly twice the value of the C--O separation and the oxygen valence angle would be 180°. This angle calculated from the moment of trimethylene oxide is about 102°. If we consider the cyclobutane molecule, the carbon valence angles are apparently 90°. If now one $-CH_2-$ is mechanically replaced by -O-, the result will be, on the basis of this hypothesis, the substitution of a "strained" atom by a normal, "unstrained" atom. The carbon angles could then increase in magnitude to decrease their "strain" and the oxygen valence angle would increase with increasing "strain", equilibrium being attained when the opposing forces are balanced. It must be remembered that the C--O separation is less than the C--C separation, so that any variations in the angles will be multiplied for the oxygen valence bonds. It is also highly probable that there is some stretching of the bonds.

The highly speculative nature of this treatment is fully realized, but the consideration of the structure of this molecule indicates how greatly "expected" results are modified, and may even be entirely altered, according to the perspective of the investigator. The magnitude of the oxygen valence angle in trimethylene oxide suggests very interesting and important possibilities. A very careful investigation of the chemistry of trimethylene oxide appears to be long overdue on this compound about which comparatively little is known. The oxygen valence angles obtained for the cyclic ethers may be tabulated.

Table XII.

Oxygen Valence Angles in Cyclic Ethers.

Compound	Moment ($X10^{18}$)	Oxygen Valence Angle
Ethylene oxide	1.88	77° 65° .. a.
Propylene oxide	1.88	77°
Trimethylene oxide	2.01	102°
Tetrahydrofuran	1.71	105° ca. 100° .. a.
Tetrahydropyron	1.87	88°

a. Data of Dr. C.P. Smyth.

VII. Applications of the Theory.

The theory that the oxygen valence angle is 90° rather than 109° 28' has been applied to numerous oxygen compounds, and certain discrepancies in behavior based on the tetrahedral theory have disappeared as a result. The most important of these is the fact that a pyranose ring is more stable than a furanose ring in carbohydrates and polysaccharides. For furanose derivatives the theory shows that this ring is planar and strained. Since the internuclear distances are C--C = 1.54 A and C--O = 1.24 A, and the oxygen valence angle is less than the tetrahedral angle, it is evident that these two factors both contribute to the consequent instability of the resultant ring, though this ring may be more stable through the influence of the many substituents found in a furanose-ring type of polysaccharide.

A consideration of the same factors for the pyranose ring shows that this ring is a diplanar, and hence strainless structure. This result is in complete agreement with the conclusions of Haworth (248) based on physical and chemical data, of Cox (248) from X-ray investigations, and many others. The high degree of substitution of the "pyranose-ring" type of sugar would in no way affect the stability or fundamental nature of this type of ring, substitution usually causing <u>increased</u> stability of a ring, and, consequently, only further puckering of the system would be expected. The possible exception noted by

Linnell and Melhuish (253) in their study of aceto-propyl and -butyl alcohols is not fully proved.

The theory explains why the polymethylene dials of Franke (254) form 1.5- oxido compounds rather than the 1-4 oxide compound which would be expected on the assumption of classical stereochemistry.

For the observed differences in stability of cyclopropane (trimethylene), ethylene oxide, and their substitution products, it is only necessary to point out that in the former there are three atoms whose valence angles are very different from the normal value. In the latter case, the oxygen atom is normal and the two carbon atoms are not normal.

The formation of the dioxolane ring and the confirmation of the proof of the ring structure assigned to it by Hibbert and Greig (136) show that the compound is quite stable. The carbon atoms are slightly strained although the vertical plane of the ring may move in the direction of the arrows. (See II, page 187.) In explanation of the stability of the dioxolane ring formed in the de-acetylation of the methyl acetyl-rhamnosides and-mannosides observed by Haworth (233) and Freudenberg (235) is thus offered. By analogy, this dioxolane ring is supposed to be a typical form of all such rings which are postulated as intermediates in certain well-known molecular rearrangements and group migrations, and explains the facility with which these transitions occur.

The relative stability of γ - and δ - lactones would appear to be definitely an exception to this rule. Evidence is at present being accumulated which points to the fact that the carbon valence angle in the carbonyl group of ketones is about 132°. If this is so, then the greater stability of γ-lactones is nicely explained as the increased magnitude of the carbon valence angle is conteracted by the 90° value of the oxygen valence angle. This suggestion, however, does not explain the relative instability of δ- lactones any more than the Sachse-Mohr theory. A plausible explanation has been offered by Carothers (3) in connection with the remarkable polymerization of six-membered cyclic esters.

It would appear that many of the properties of the oxide rings of carbohydrates and polysaccharides with relation to stability, ease of formation, and interconvertibility, can be explained on the same basis as has been employed in connection with the above simple heterocyclic rings. This conclusion is based on the theory postulated as a result of electric moment measurements in which the normal oxygen valence angle is shown to be 90°.

While an attempt has been made to be as definite as possible, consistent with experimental facts, mathematical values given to the valence angles are not to be considered as rigid, but are suggested as a mean value for the compound to which they are assigned. In all cases, it must be remembered that the systems are definitely kinetic, not static, though the ring compounds may represent more closely defined geometrical structures.

SUMMARY

1. A heterodyne beat apparatus for the accurate measurement of dielectric constants has been constructed.

2. Glycol monochloroacetate and the isomer of glycol monodichloroacetate 2-Hydroxyl-2'-dichloromethyl-1.3-dioxolane have been prepared for the first time and their dielectric constants and densities of their dilute benzene solutions have been measured. The electric moments are 3.94 and 3.35 x 10^{-18} e.s.u. respectively. The difference in the observed moments is explained by the formation of the dioxolane ring. An oxygen valence angle of about 90° is suggested for this compound. Electric moment measurements are thus used for the first time to finally prove the existence of a ring in possible ring-chain isomerism.

3. Trimethylene oxide and tetrahydropyran have been prepared, and their densities and dielectric constants of their dilute solutions, and those of propylene oxide have been measured. The electric moments are 2.01, 1.87 and 1.88 x 10^{18} e.s.u. respectively. All electric moment measurements have been made for the first time. The predicted value of the electric moment of tetrahydropyran agrees within experimental error of the measured value.

4. The "normal" oxygen valence angle has been determined for tetrahydropyran as 90° ± 5°. This value is the first experimental confirmation, by electric moment measurements, of the same angle suggested by the theoretical considerations of Pauling.

5. The value of the moment of propylene oxide supports the

conclusions that substitution of a hydrogen atom by a methyl group causes no change in moment in certain homologous series.

6. The values of the oxygen valence angle in some heterocyclic rings have been calculated and tabulated.

7. A review of investigations conducted by various workers on the structure of the water molecule is given, and it is concluded that in this molecule the angle between the two oxygen valence bonds is either 64° as suggested by Debye, or slightly larger. This value is based on the analogy of the electric moment of ethylene oxide with that of the water molecule.

8. Newer and more consistent values are suggested for the linkage moments of the H--O and (CH_3--O) groups, and a minimum value is fixed for the oxygen valence angle in any C--O--C linkage. These values would seem to provide for the first time quantitative data in support of Smyth's qualitative predictions concerning the oxygen valence angle in water, methyl alcohol, methyl ether, and ethylene oxide molecules. The use of values previously assigned to these linkage moments leads to an impossible conclusion insofar as the ethylene oxide molecule is concerned.

9. The oxygen valence angle theory is applied to the pyranose and furanose rings in carbohydrates and polysaccharides, and their relative stability explained, in agreement with other

experimental data. The application is also extended to explain the formation of 1.5 - oxide compounds from polymethylene diols. The correlation of the theory and the properties of γ and δ lactones is satisfactory, and certain limitations are noted.

10. The commonly accepted assumption of a tetrahedral structure for the oxygen atom provides no explanation of the well-known difference in properties and stability of the cyclopropane and ethylene oxide rings respectively, or of their derivatives. A suggestion accounting for same is to be found on the basis of the foregoing theory.

11. It is shown from the above reasoning that the pyranose ring of carbohydrates and related polysaccharides represents a strainless puckered ring system in which the carbon-valence linkages are tetrahedral while the oxygen valence angle is approximately 90°.

On the other hand, the furanose ring structure of similar compounds represents a strained flat-ring in which both the carbon and oxygen valence angles are distorted.

The amount of the distortion undergone by the carbon and oxygen atoms respectively cannot be stated at present in the absence of sufficient experimental data.

It is this condition of strain brought about by the replacement of a carbon by an oxygen atom which gives rise to the well-known and characteristic instability of all furanose rings as compared with the corresponding isomeric pyranose structures.

BIBLIOGRAPHY

1. Meerwein, H. Houben's "Methoden der Organischen Chemie," Vol. 2, Leipzig, 1925, p.595.

2. Hess, K. "Die Chemie der Zellulose," Akad. Verlagsges. Leipsic, 1928, p. 574.

3. Carothers, W.H. Chem. Reviews 8, 406 (1931.)

4. Conant, J.B. and Peterson, W.R., J.A.C.S. 54, 628 (1932).

5. Matheson, H.W. and Skirrow, F.W., U.S.Pat. 1,746,665, Feb. 11th, (1930.)

6. Wagner-Jauregg, W. Ber. 63B, 3213 (1930).

7. Sheppard, S.E., Neitz, A.H. and Keenan, R.L., J.I.E.C. 21, 126, (1929.)

8. Carothers, W.H., J.A.C.S. 51, 2548, (1929.)

9. Levene, P.A. and Walti, A.,J.Biol.Chem. 77, 685, (1928.)

10. Manly, J.J. Phil. Mag. 13, 249 (1932).

11. Thiele, J. Ann. 306, 92, (1899.)

12. Rohm, Dissertation, Tübingen, (1901.)

13. Schroeter, G. Ber. 49, 2697, (1916); ibid. 53, 1917, (1920.)

14. Abderhalden, E. Naturwiss. 12, 716 (1924); Hess, K. Ann. 435, 1, (1924) et seq.; Bergmann, M. Ber. 59, 2973, (1926) et seq. Pringsheim, Naturwiss. 13, 1045 (1925) et seq.; Karrer, P. Polymere Kohlenhydrate, Leipzig, (1925).

15. Wagner-Jauregg, T. Ann. 488, 176 (1931.)

16. Staudinger, H. Z. angew. Chem., 45, 276, (1932).

17. Ostromuislenski, I.I. J. Russ. Phys. Chem. Soc. 47, 1928 (1915.)

18. Aschan, O. Ann. 461, 1, (1928.)

19. Krämer, G. and Spilker, A. Ber. 29, 552 (1896); Staudinger, H. and Bruson, H., Ann. 477, 97, (1926.)

20. Tilitschejew, M., J. Russ. Phys. Chem. Soc. 57, 143 (1925); Chem. Zentr. 1926, 1, 2667.

21. Ibid., 58, 477, (1926). C.A. 21, 3558, (1927)

22. Lycan, W.H. and Adams, R., J.A.C.S. 51, 625, 3450, (1929).

23. Drew, H.D.K. and Haworth, W.N., J.C.S. 1927, 775; Haworth, W.N., "Constitution of Sugars," London, 1929, p.78

24. Carothers, W.H., Dorough, G.L. and Van Natta, F.J., J.A.C.S. 54, 761, (1932).

25. Mohr, E., J. Prakt. Chem. 98, 315, (1918.)

26. Hibbert, H., Unpublished data.

27. Staudinger, H. et al., Helv. Chim. Acta, 8, 41, (1925) et seq.; Haworth, W.N. et al., Ref. 23, et seq.; Freudenberg, K. and Braun, E., Ann. 460, 288 (1928) et seq.; Meyer, K.H. and Mark, H., Ber. 61, 593, (1928) et seq.; Sponsler and Dore, Colloid Symposium Monograph, Chemical Catalog Co., New York (1926), p.176; Carothers, W.H. et al, Ref. 8, et seq.

28. Chem. Fabrik Griesheim-Elektron. Germ. Pat. 271,381, June 22nd, 1912; Brit. Pat. 14, 246, June 19th, 1913; U.S.Pat. 1,084,581, January 13th, 1914.

29. Ibid.; Germ. Pat. 281,687, July 4th, 1913; 281,688, April 2nd, 1914; Klatte, F. and Rollett, A., U.S.Pat. 1,241,738, October 2nd, 1918.

30. Taylor, H.S. and Vernon, A.A., J.A.C.S. 53, 2527, (1931).

31. Skirrow, F.W., U.S.Pat. 1,746,615, February 11th, 1930; Canadian Pat. 287,496, February 26th, 1929.

32. Consortium für elektrochem. Ind. Brit. Pat. 261,406, November 14th, 1925.

33. Hermann, W.O. and Baum, E., U.S. Pat. 1,586,803, June 1st, 1926; Can.Pat. 257,808, February 2nd, 1926.

34. I.G. Farbenind. A.-G., Fr. Pat. 656,151, June 30th, 1928.

35. Young, C.O. and Douglas, S.D., U.S.Pat. 1,775,882, September 16th, 1930.

36. Engler, C. and Weissberg, J., Kritische Studien über die Vorgängen der Autoxydation, Braimschweig, 1904.

37. Stobbe and Posnjak, Ann. 371, 259, (1909).

38. Heinemann, A., Brit. Pat. 14,041 (1910); Ger.Pat. 276,678 (1915); U.S.Pat. 1,146,253 (1915).

39. Moureau, C. and Dufraisse, C., Bull.Soc.Chim. 31, 1152, (1922); 35, 1564, (1924).

40. Moureau, C. and Dufraisse, C., and Badoche, M., ibid. 35, 1591, (1924).

41. Milas, N.A., Proc.Nat. Acad. Sci. 14, 844, (1928.)

42. Conant, J.B. and Tongberg, C.O., J.A.C.S. 52, 1659, (1930).

43. Staudinger, H. and Lautenschlager, L., Ann. 488, 1, (1931).

44. Houtz, R.C. and Adkins, H., J.A.C.S. 53, 1058 (1931).

45. Ref. 4, p. 630.

46. Milas, N.A., J.A.C.S. 52, 739, (1930).

47. Starkweather, H.W. and Taylor, G.B., J.A.C.S. 52, 4708, (1930.)

48. Milas, N.A., Chem.Reviews, 10, 324, (1932.)

49. Christiansen, J.A., J. Phys. Chem. 28, 145, (1924.)

50. Semenoff, N., Chem. Reviews, 6, 215, (1929).

51. Roithner, Monatsh. 15, 665, (1894.)

52. Staudinger, H., Ber. 58, 1075, (1925.)

53. Staudinger, H., and Schwalbach, A., Ann. 488, 8, (1931).

54. Ref. 47, p. 4714.

55. Blaikie, K.G., Can.Pat. 282,860, August 28th, 1928.

56. Skirrow, F.W., U.S. Pat. 1,746,665, February 11th, 1930.

57. Klatte, F. and Zimmermann, A., Ger.Pat. November 8th, 1928.

58. Luther, R. Z. physik. Chem. 45, 662, (1903.)

59. Milas, N.A., Chem. Reviews 10, 295 (1932).

60. Alyea and Bläckström, J.A.C.S. 51, 90, (1929).

61. Skrabal, A. and Zahorka, A., Monatsh 48, 459, (1927).

62. Staudinger, H., Ber. 59-B, 3019 (1926).

63. Hermann, W.O. and Haehnel, W., Ber. 60-B, 1658 (1927.)

64. Staudinger, H., Ber. 60-B, 1782 (1927.)

65. Lebedev and Merezhkovskii, Journ. Russ. Phys. Chem. Soc. 47, 1927, (1915).

66. Whitby, G.S. and Katz, M., J.A.C.S. 50, 1160, (1928).

67. Whitby, G.S., and Crozier, Can. Journ. Research, 6, 203, (1932.)

68. Whitby, G.S., McNally, J.C. and Gallay, W., Trans. Roy. Soc. Can. 22, 27, (1928).

69. Tamman, G. and Pape, A. Z. anorg. Allgem. Chem. 210, 113, (1931).

70. Gallay, W., Kolloid - Z, 57, 1, (1931).

71. Jahn, E.C., Thesis, (Ph.D.) McGill University (1929).

72. Rider, T.H. and Hill, A.J., J.A.C.S., 52, 1521,(1930).

73. Hibbert, H., Perry, S.Z., and Taylor, K.A., J.A.C.S. 51, 1551, (1929).

74. Ruigh, W.L. and Major, R.T., J.A.C.S. 53, 2662, (1931).

75. Bates, and Taylor, H.S., J.A.C.S. 49, 2438 (1927).

76. Linton, E.P. and Maass, O., J.A.C.S., 54 1863, (1932).

77. Mosotti, Mem. soc. ital. sci. Modena, 14, 49, (1850).

78. Clausius, "Die Mechanische Wärmetheorie," Vuiveg (1879) Vol. 2, p. 94.

79. Bigot, Ann. Chem. Phys (6), 22, 433 (1891).

80. Nivière, Bull. Soc. Chim. (4) 15, 464, (1914).

81. Prileschajew, Ber. 42, 4811 (1909).

82. Hibbert, H. and Burt, P., J.A.C.S. 47, 2240, (1925).

83. Smyth, C.P. and Walls, W.S., J.A.C.S. 53, 527 (1931).

84. Findlay, "Practical Physical Chemistry," 4th. Ed. Longmans, 1923, pp. 24,38.

85. Debye, P. Phys. Zeit. 13, 97, (1912).

86. Williams, J.W., Chem. Reviews 6, 589, (1929).

87. Sutton, L.E., Proc. Roy. Soc. A. 133, 668, (1931).

88. Hammick, D.L; New, B.G.A. and Sutton, L.E., J.C.S. 1932, 742; Sigdwick, N.V. and Bowen, E.J., Ann. Reports Chem. Soc. (London) 28, 393, (1931).

89. Errera, J., J. Phys. Radium, (6) 5, 304, (1924).

90. Pauling, L., J.A.C.S. 53, 1367, (1931).

91. Slater, J.C., . Phys. Rev. 37, 481 (1931); 38, 1109 (1931)

92. Stuart, H.A., ibid. 1372 (1931).

93. Zahn, C.T., Phys. Rev. 40, 291, (1932) and previous papers.

94. Smyth, C.P., "Dielectric Constant and Molecular Structure", Chemical Catalog Co., Inc., New York, 1931.

95. Ebert, L., see Ref. 103, P. 68.

96. Bergmann, E., and Engel, L. Z. Phys. Chem., 15B, 85, (1931).

97. Errera, J., see Ref. 103, P. 101.

98. Hückel, W., ibid. P. 79.

99. Waters, W.A., Phil. Mag. (7), 8, 436, (1929).

100. Kerr, R.N., J.C.S. , 1929, 239.

101. Pratesi P. Atti. Accad. Lincei. 13, 779 (1931; C.A. 26 1235.

102. Report of the Committee on Electrical Insulation, National Research Council (Wash) 1930, et seq.

103. Debye, P., "Polar Molecules" Chemical Catalog Co. Inc., New York, (1929).

. ibid., "The Dipole Moment and Chemical Structure", Blackie and Son, London, 1931.

104. Smyth, C.P., and co-workers, Phi. Mag. 1923-24, J.A.C.S. 1924-32.

105. Williams, J.W. and co-workers, "Phys. Zeit. 1928-30", J.A.C.S., 1927-31.

106. Smyth, C.P., J.A.C.S. 46, 2151, (1924).

107. Williams, J.W., Physik J. 29, 174, (1928).

108. Müller, H. and Sack, H., ibid. 31, 815 (1930)

109. Ebert, L., Eisenschitz, and v.Hartel, Z. Phys. Chem. 1B, 97, (1928.)

110. Weissenberg, Ber. 59, 1526 (1926), Naturwiss, 15, 662, (1927); Physik. Z. 28, 829 (1927).

111. Højendahl, K., thesis, Copenhagen. (1928)

112. Williams, J.W., Physik. Z. 29, 683 (1928).

113. Sanger, R., Physik. Z. 27, 165 (1926)

114. Smyth, C.P. and Morgan, S.O., J.A.C.S. 49, 1030 (1927).

115. Smallwood, H.M. and Hertzfeld, K., ibid. 52, 1919 (1930)

116. Errera, J., Compt. rendu, 182, 1623 (1926); Physik. Z. 27, 764 (1926).

117. Sutton, L.E. and Taylor, T.W.J., J.C.S., 1931, 2190.

118. Sutton, L.E., Nature, 128, 638 (1931); unpublished measurements.

119. Bergmann, E. and Schutz, W., ibid. 128, 1077 (1931).

120. Estermann, I., Z. physik. Chem. 1B, 134 (1928).

121. Smyth, C.P., and Kamerling, S.E., J.A.C.S. 53, 2988, (1931).

122. Smyth, C.P., and Walls, W.S., ibid. 54, 1854, 3230, (1932)

123. Eucken, A. and Meyer, L., Physik. Z. 30, 397, (1929).

124. Wolf, K. L., Zeit phys. Chem. B3, 128, (1929).

125. Williams, J.W. and Fogelberg, J.M., J.A.C.S. 52, 1356, (1930).

126. Hibbert, H. and Greig, M.E., Can.Journ. Research, 4, 254 (1931).

127. Stuart, H. A., Z. Physik. 51, 490 (1928).

128. Smyth, C.P. and Stoops, W.N., J.A.C.S. 50, 1883 (1928)

129. Wolf, K.L. and Gross, W.J., Z. Phys.Chem. 14B, 305 (1931).

130. Haworth, W.N. "Constitution of Sugars," Arnold, London, 1929, Chap. 2.

131. Morgan, S.O. and Lowry, H.H., J. Phys. Chem. 34, 2385, (1930).

132. Loeb, L.B., "Kinetic Theory of Gases," McGraw-Hill, New York (1929), Chap. 10.

133. Debye, P. "Handbuch der Radiologie," 6, 633, (1925).

134. Sidgwick, N.V. "Electron Theory of Valency," Oxford, 1927, Chap. 8.

135. Staudinger, H., Z. angew. Chem. 42, 67 (1929).

136. Rolinski, Physik. Z. 29, 658 (1928).

137. Baedecker, K., Z. Physik. Chem. 36, 305 (1901).

138. Linton, E.P. and Maass, O., Can. Journ. Research, 7, 81, (1932).

139. Geiger and Scheel, "Handbuch der Physik," Springer, Berlin, Vol. 16, Chap. 19, 20. (1927).

140. Silow, Pogg., Ann. 156, 389 (1875); ibid. 158, 306 (1876).

141. Pirot, Compt. rend. 113, 415, (1891).

142. Carman, Phys. Rev. 24, 396 (1924); ibid 30, 922 (1927).

143. Cohn and Arons, Wied. Ann. 33, 13 (1888).

144. Quincke, Wied. Ann. 32, 529 (1887); ibid. 34, 401 (1888)

145. Michaud and Balloul, Ann. Phys. (9) 11, 295 (1919).

146. Furth, Z. Physik. 22, 98, (1924); Physik. Z. 25, 676, (1924).

147. Drude, P., Wied Ann. 55, 633,(1895); Z.Physi. Chem. 23, 267, (1897).

148. Holborn, Z. Physik. 6, 328 (1921.)

149. Mesny, L'Onde Electrique. (1924).

150. Wachsmuth, Verhand. deut. physik. Ges. 3, 7, (1922).

151. Devoto and Stevenson, Gazz. Chim. Ital. 60, 199 (1930).

152. Grechowa, Z. Physik, 38, 621, (1926).

153. Nernst, Z. Physik Chem. 14, 622 (1894).

154. Hertwig, Ann. Physik. 42, 1099 (1913).

155. Joachim, ibid. 60, 570 (1919).

156. Smythe, C.P., Morgan, S.O. and Boyce, J.A.C.S. 50, 1536 (1928).

157. Smythe, C.P., Morgan, S.O., ibid. 50, 1547 (1928).
Dornte, R.W. and Smythe, C.P., ibid. 52, 3546 (1930.)

158. Williams, J.W., Fortschritte Chem., Physik. physik. Chem. 20, No. 5, (1930).

159. Ball, J.C.S. 1930, 570.

160. Chrétien, Compt. rend. 192, 1385 (1931).

161. Lattey, Phil. Mag. 41, 829 (1921).

162. Walden, Ulich and Werner, Z. Phys. Chem. 115, 177, (1925); ibid. 116, 261 (1925).

163. Williams, J.W. and Krchma, I., J.A.C.S. 48, 1888 (1926).

164. Golubkov, Chem. Zentr. 1927, 1, 144.

165. Kniepkamp, Z. Physik. 51, 95, (1928).

166. Astin, A., Phys. Rev. 34, 300 (1929).

167. Wyman, J., Phys. Rev. 35, 623 (1930); J.A.C.S. 53, 3592, (1931).

168. Smith, J.W., Proc. Roy. Soc. London, A 136, 251 (1932)

169. Herweg, Verhandt, deut. phys. Ges. 21, 572, (1919); Z. Physik. 3, 36 (1920).

170. Whittington, Proc. Camb. Phil. Soc. 20, 445 (1931).

171. Isnardi, Z. Physik, 9, 152 (1922).

172. Grützmacher, ibid. 28, 342 (1924)

173. Stranathan, J.D., Phys. Rev. 31, 653 (1928.)

174. Williams, J.W. and Weissberger, A., J.A.C.S. 50, 2332 (1928).

175. Williams, J.W., ibid. 52, 1831 (1930).

176. Graffunder and Weber, Z. Physik. 65, 723 (1930).

177. Jona, Physik. Z. 20, 14 (1919).

178. Stuart, H., Z. Physik. 47, 457; 51, 490 (1928); 55, 358, (1929).

179. Sänger, R. and Steiger, O., Helv. Phys. Acta. 1, 369 (1928); 2, 136, (1929).

180. Zahn, C.T., Phys. Rev. 47, 457 (1924); ibid 40, 291, (1932).

181. Ghosh and Mahanti, Nature 124, 13 (1929).

182. Andrews, H.T., Physics 1, 366 (1931).

183. Williams, J.W., and Schwingel, C., Phys. Rev. 35, 855, (1930).

184. Hartshorn and Oliver, Proc. Roy. Soc. London, A.123, 664 (1929).

185. Sayce and Briscoe, ibid. 127, 315 (1925).

186. Williams, J.W., Z. phys. Chem. A 138, 75 (1928.)

187. Stuart, H.A., Phys. Rev. 38, 1372 (1931.)

188. Smyth, C.P. and Rogers, H.E., J.A.C.S. 52, 2227 (1930).

189. Timmermans, J. J. Chem. phys. 27, 65, (1930).

190. Wolf, K.L., Ref. 103, P.124.

191. Kossel, W., Ann. Physik, 49, 229 (1916.)

192. Langmuir, I., J.A.C.S., 41, 868 (1918).

193. Heisenberg, W., Z. Physik. 26, 196, (1924).

194. Hund, F., ibid. 31, 81 (1925; 32, 1, (1925);
Z. Physik. Chem. 73, 1, (1931).

195. Eucken, A., Z. Electrochem. 26, 377, (1920).

196. Pauling, L., J.A.C.S. 53, 1367 (1931).

197. Ewald, P.P. and Hermann, C., "Structurbericht."

198. Plyler, E.K., Phys. Rev. 38, 1784 (1931).

199. Slater, J.C., ibid. p. 1109.

200. Thomson, J.J., Phil. Mag. 46, 513 (1923).

201. Sidgwick, N.V., and Bowen, E.J., Ann. Rep. Chem.
Soc. 28, 389 (1931).

202. Pictet and Castan, Helv. Chem. Acta 3, 645, (1920);
cf 5, 884 (1922); Fortschritte der Chemie, 20, 11, (1929).

203. Brigl, P. and Schinle, R., Ber. 62, 1716, (1929).

204. Hickinbottom, J., J.C.S. 1928, 3140.

205. Bergmann, E. and Schotte, H., Ber. 54, 440, 1564 (1921).

206. Pauling, L. Proc. Nat. Acad. Sci. 18, 293, (1932).

207. Allen, J.S. and Hibbert, H., Berichte, in the press.

208. Vogel, Helv. Chem. Acta, 11, 422, 1210 (1928).

209. Schlubach and Elsner, Ber. 61, 2358, (1928);
65B, 579, (1932); Naturwiss. 16, 772 (1928).

210. Hibbert, H., Tipson, R.S. and Brauns, F., Can. Journ.
Research, 4, 221 (1931).

211. Hurd, C.O. and Isenhour, L.L., J.A.C.S. 54, 693 (1932).

212. Brookes, "Non-Benzenoid Hydrocarbons." Chemical Catalog
Co. Inc., New York, 1922. p. 341.

213. Derick, C.G. and Bissell, D.W., J.A.C.S. 38, 2478, (1916).

214. Smith, L., Wode, G., and Widhe, T., Z. Physik, Chem.
130, 154, (1927).

215. Meerwein, H., Ann. 455, 227 (1927); Ber. 61, 1840 (1928).

216. Sattler, L., J.A.C.S., 54, 831 (1932).

217. Aschan, Ber. 23, 1833 (1890).

218. Hübner and Müller, Ann. 159, 168, (1871.)

219. Tornöe, Ber. 24, 2674, (1891).

220. Horne, W.H. and Shriner, R.L., J.A.C.S. 54, 2925, (1932).

221. Meerwein, H., Bersin, T., and Bruneleit, W.,
Ber. 62B, 999, (1929).

222. Meerwein, H., and Hinz, G., Ann. 484, 1, (1931.)

223. Meerwein, H. and Maier-Hüser, H., J. prakt. chem.
134, 51, (1932).

224. Perkin, J.C.S. 1929, 1355.

225. Böeseken, J., Vermy, C.O.G., Bunge, H., and Van Meeuwen,C
Rev. trav. chim. 50, 1023 (1931).

226. Tiffeneau, M., et al, Bull. Soc. Chim. 49, 1840,(1932)
et seq.

227. Levy, J. and Sfiras, J., Cpmpt. rend. 191, 261, (1930).

228. Fischer, E., Ber. 53, 1621 (1920).

229. Meerwein, H. and Sonke, H., Ber 64B, 2375 (1931).

230. Greig, M.E. Report, Nat. Research Council of Canada, (1931).

231. Allen, J.S. ibid.

232. Hibbert, H. and Caster, N.M., J.A.C.S. 51, 1601 (1929).

233. Haworth, W.N., Hirst, E.L. and Millar, E.J.,
J.C.S. 1929, 2469.

234. Haworth, W.N., Hirst, E.L. and Samuels, H., ibid.
1931, 2861.

235. Freudenburg, K., Naturwiss, 18, 393, (1930).

236. cf Bertrand, 10^{ieme} Conference de L'Union Int. de Chim.
38, (1930).

237. Karrer, Helv. Chem. Acta. 7, 519, (1924).

238. Hibbert, H., and Anderson, C.G., Can. Journ. Research, 3, 306, (1930.)

239. Criegee, R., Ann. 495, 211, (1932).

240. Smolenski, K., Przemysl Chem. 11, 146 (1927); C.A. 23, 2930.

241. Tiffe~~r~~neau, M., Compt. rend. 159, 771 (1914).

242. Pogorzelski, Chem. Zentr. 1905, 1, 767.

243. Hassel, O., Z. Electrochem. 31, 540, (1931); A.1219.

244. Stoermer, R., and Keller, W. Ber. 64B, 2783, (1931).

245. Vogel, J.C.S. 1928, 2014.

246. Thorpe and Ingold, J.C.S. 1915 - 26.

247. Thorpe et al., ibid 1922, et seq.

248. Cox, E.G., J.C.S. 1931, 2313; 1932, 133.

249. Cox, E.G. and Goodwin, T.H., ibid. 1932, 1844.

250. Haworth, W.H., ibid, 1927, 3136.

251. Haworth and Porter, ibid, 1930, 649.

252. Haworth, Hirst and Webb, ibid, 1930, 651.

253. Linnell, W.H. and Melhuish, B.A., Quart.J.Pharm. Pharmacol. 3, 40 (1930)

254. Franke, A. and Gomolka, H., Monatsch. 53 and 54, 577-84 (1929).

255. Franke, A., and Kroupa, A., ibid. 56, 331 (1930).

256. Franke, A., Kroupa, A., and Panzer, T., ibid. 60, 106 (1932).

257. Hibbert, H., Platt, M.E., and Carter, R.M., J.A.C.S. 51, 3641, (1929).

258. Haworth, W.N., Ref. 130, Chaps. 4 and 5.

259. Irvine, J.C. and McGlynn, R.P., J.A.C.S. 54, 356 (1932).

260. Parts, Z. Phys. Chem. B7, 327, (1930).

261. Meyer, L. and Büchner, A., Physik. Z. 33, 390 (1932)

262. Hunter, E.C.E. and Partington, J.R., J.C.S. 1931, 2062

263. Wycoff, R.G. "Structure of Crystals", Ind. Ed. Chemical Catalog Co. N.Y., 1931, Chap.20; Sidgwick and Bowen, q.v.

264. Hengstenberg, J. and Mark, H., Z. Krist. 70, 283 (1929)

265. Meyer, K . and Mark, H., "Aufbau der hochpolymeren organischen Naturstoffe", Leipzig Akad. Verlagsges. 1930, p.17

266. Lonsdale, (Mrs.) K., Proc. Roy. Soc. 123, 494 (1929); Bannerjee, K . and Robertson, J.M., Nature 125, 456 (1930); Wierl, R., Ann. Physik, (5) 8, 521 (1931).

267. Pauling, L., Proc. Nat. Acad. Sci. 18, 293 (1932)

268. Hengstenberg, J. and Brú. Anales soc. españ. fés. quím. 30, 341 (1932)

269. Mecke, R., Leipziger Vorträge, 1931

270. Henri, V. and Schou, H., Z. Physik. 49, 774 (1928)

271. Noller, C.R., Unpublished

272. Bogert, M.T. and Slocum, E.J., J.A.C.S. 46, 763 (1924)

273. Dem'yanov, N.Y. J.Russ. Phys. Chem. Soc. 45, 169, C.A. 7, 2226.

274. Cuthbertson, A.C. and Maass, O., J.A.C.S. 52, 483 (1930)

275. Lyons, W., Private communication.

276. Oestling, J. C. S. 101, 467 (1912)

277. Isnardi, Z. Physik. 9, 153 (1922)

278. Frivold, Physik. Z. 21, 529 (1920)

279. Allen, J.S., Report Nat. Research Council of Canada, Feb. 1930