THE ADDITIVE PROPERTIES OF THE CHLORBENZENES AND THEIR ELECTRONIC FORMULAS

MOLECULAR REFRACTIVITIES AND MOLECULAR VOLUMES

A Thesis

by

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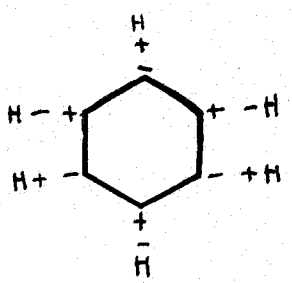
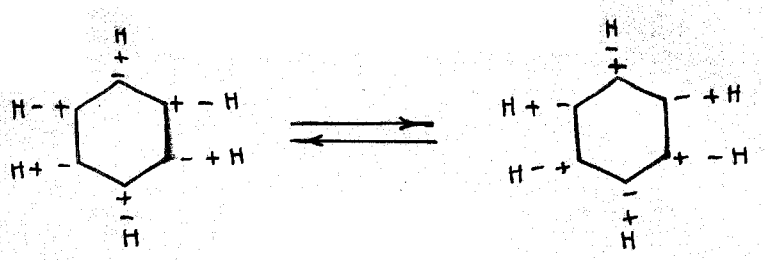
Introduction

The electronic theory of valency which has been developed so extensively since the discovery of the electron and the phenomena of radioactive disintegration has been applied by H. S. Fry[1] in a remarkably adaptable theory of substitution. Assuming that the atoms can either give up or absorb electrons, consequently functioning either with positive or negative valencies, and considering the atoms in the molecule to be bound by this opposition of electronic characters, the following electronic formula for benzene has been proposed:



Benzene is represented by a ring of six carbon atoms bearing alternately positive and negative charges, by means of which are linked hydrogen atoms with negative and positive valencies respectively. A form of dynamic change within the molecule, termed electronic tautomerism, is supposed to be continually taking place in which the valencies undergo reversal, the positive valences of carbon and of the positive hydrogen atoms becoming negative, and the negative valences becoming positive, as follows:



For any substitution product of benzene, obviously, two such electronic modifications may be assumed to be present. It is to be expected, though, that the groups substituted for hydrogen will be either dominantly positive or negative, so that one electronic modification or the other will be the relatively stable form. That electronic formulas can be assigned to benzene derivatives is borne out by regularities in the molecular volumes[2] of the chlorbenzenes, which seem to indicate that when the chlorine atom functions positively, it has a different atomic volume than when it functions as a negative substituent.

Other additive physical properties might be expected to show similar regularities. The purpose of this investigation was to prepare in a state of guaranteed purity as many chlor-substituted derivatives of benzene as time would permit and to determine, in all cases in which data was not available, the values of the two additive properties - molecular volumes and molecular refractivities - and to calculate from these the atomic volumes and atomic refractivities of chlorine in the various compounds. It was hoped that any regularities observed could be correlated with the electronic formula for benzene of H. S. Fry.

Historical

Molecular volumes

The quotient of molecular weight divided by the density of a substance expresses the volume occupied by one gram molecule of the substance.

$$V_{molecular} = \frac{\text{mol. wt.}}{\text{density}}$$

We may suppose the space occupied by the molecule as a whole to be the sum of the volumes occupied by the atoms.

$$V_m = \sum V_a$$

A volume effect for each atom may be assigned by comparisons made between pairs of substances having the same differences of composition, and the molecular volume can be reconstructed from these atomic volumes. The degree of constancy of the atomic volumes deduced in various ways and the accuracy with which molecular volumes are reproduced are measures of the additive character of this property.

As early as 1855 Kopp[3] showed that the numbers obtained by dividing the molecular weights of members of an homologous series of carbon compounds by their respective densities at the boiling points showed a regular increase. In making these first investigations, Kopp was quite aware of the disturbing influence of temperature, and recognized the extreme importance of securing comparable conditions. He adopted the boiling points at atmospheric pressure (temperatures of equal vapor pressures for all liquids); a

particularly happy choice, for it was later shown by Guldberg[4] that the absolute boiling points of most liquids are approximately two thirds of their absolute critical temperatures, so that the substances are virtually in "corresponding states". Other methods have since been recommended and give interesting results, but since the method of Kopp is supported by theoretical reasons, it is generally accepted as the best. The experimental procedure was to determine the boiling point accurately, to obtain the density of the liquid at some fixed temperature, then to calculate from these data and the experimentally determined coefficient of expansion the volume at the boiling point. The process gave good results but was tedious and required complicated apparatus.

In order to simplify the determination of densities, Ramsay[5] devised a process for determining directly the weight of a known volume of liquid at its boiling point. A thin glass bulb shaped like a lemon and having at the upper end a capillary tube bent in the form of a hook was used to contain the liquid. The bulb nearly filled with the liquid under observation was suspended in the vapor of another portion of the same liquid which was kept boiling in a flask. After complete equilibrium was attained, the bulb was allowed to cool and was then weighed. A correction was applied for the expansion of the glass and the difference between the temperature of the liquid in the bulb and its real boiling point, and the molecular volume of the liquid was then calculated. On the whole, the results were remarkably in concordance with

those obtained by Kopp. Anomalous results were ascribed by Ramsay to the following causes:

First. The substances examined may not have been quite pure.

Second. The boiling point may not be a fit point of comparison.

Third. The elements may not possess the same value in different compounds.

For many substances, an expression of the form

$$mc + nh + po$$

was found to give the molecular volumes of a series of substances $C_mH_nO_p$ with great accuracy. In other cases the error was greater than could be attributed to experimental error, and could only be ascribed to the influence of constitution, or arrangement of atoms within the molecule. Kopp showed that a similar expression could be applied if account was taken of the position of oxygen - whether it were carbonyl or hydroxyl oxygen.

Table I

Atomic Volumes of the Elements[6]

	Atomic volume
Carbon	11
Hydrogen	5.5
Oxygen (carbonyl)	12.2
Oxygen (hydroxyl)	7.8
Sulphur	22.6
Chlorine	22.8
Bromine	27.8
Iodine	37.5
Nitrogen (ammonia)	2.3
Cyanide radical	28
Nitro group	33

The last three values in the above table for nitrogen and its compounds cannot be reconciled with the values of carbon, hydrogen and oxygen. Kopp did not decide whether the nitrogen atom alone was responsible for these variations or whether the carbon atom also varied.

For a compound of the type $C_mH_nO_pO'_q$ in which O represents carbonyl oxygen and O' hydroxyl oxygen, the molecular volume is given by the following:

$$V_{mol.} = 11.0m + 5.5n + 12.2p + 7.8q.$$

A great variety of materials were investigated, and in no case did the difference exceed 4% of the sum of the atomic volumes. Kopp also introduced the idea that the atomic volumes of the elements were approximately integral multiples of a universal constant, the value of which varied between 5.1 and 5.9.

Buff[7] proposed the hypothesis that the carbon atom in the unsaturated compounds possessed a greater value than in the saturated ones, for the values were uniformly higher than the calculated ones. The differences, however, were so small as to lie within the limits of experimental error, so the direction of the variation only was indicated. The atomic volumes, he thought, depended on the valence.

Thorpe[8] determined the boiling points, specific volumes and coefficients of expansion of a great number of materials. He used the experimental method of Kopp with many refinements of procedure. Other investigators: Lossen[9], L. Meyer[10] and Schiff[11], contributed a large quantity of data. Lossen con-

cluded that Kopp's additive rule could be applied to any single class of bodies if the constants for that class were determined. Schiff confirmed Buff's view in regard to the increased value of the ethenoid linkage, and calculated that the increase for single unsaturation was 4.0 units approximately. LeBas[12] has published a monograph on the subject, and finds that using the new numbers which he has calculated, unsaturation is responsible for no special effect!

Traube[13] has ascribed the non-application of the rules of Kopp to association of molecules in the liquid state. He developed the idea of the "co-volume" which was an additional space occupied and defended by the vibrations of the molecule. This molecular co-volume for many substances appeared to be a nearly constant quantity and by its means molecular weights could be selected. Traube worked out a series of constants which must be deducted to allow for ring formation and for double and treble linking. Traube's theory has not been very successful, and apparently has not led to any extensive results. The experimental results show that no constant values can be assigned to the elements, and it seems impossible to derive molecular volumes from the summation of atomic volumes. The only profitable method seems to be a comparison only of similarly constituted compounds in which the elements bear the same relation to each other. This is true of the series of chlorbenzenes, and if any regularities exist, they should be detectable in these compounds.

LeBas has attempted to apply the theory of molecular volumes to a study of the constitutions of organic compounds. He points out that it is just these limitations of the additive rule in most physical properties which have been so useful in working out details of structure, and indicate the keen need for a unifying principle.

Perhaps the fact that the molecular volume is so sensitive to constitutive influences can be traced to the electronic functions of the atoms and correlated with the electronic formulas of the compounds. Compounds of the type of o, m and p dihalogen benzene derivatives, and the tri-substituted derivatives, have not yet been systematically investigated, and it is to these types of compounds that this investigation has been directed.

Jungfleisch's[14] data for the volume changes on the gradual chlorination of the benzene molecule has been interpreted by H. S. Fry[15] from the point of view of his electronic formula of benzene. In the present work, the attempt is made to extend this point of view to include the molecular volumes of other chlorine substituted benzene derivatives.

Molecular refractivity

Molecular refractivity of liquids has likewise been applied as an additive and a constitutive property to the determination of structure somewhat in the same way as molecular volume. The refractive index of a substance varies with the

temperature; the density also varies, and several formulae have been proposed to connect the refractive index with the temperature. Molecular refractivity becomes a quantity independent of the temperature, and in this respect it is superior to molecular volume which is arbitrarily measured at the boiling point.

The relation between refractive index and density, known as the "specific refractivity" may be expressed in several ways:

1. The formula of Laplace[16] $\frac{n^2 - 1}{d} = r' = \text{constant.}$

2. The expression of Gladstone and Dale[17]

$$\frac{n - 1}{d} = r'' = \text{constant.}$$

3. That of Lorentz and Lorenz[18]

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} = r''' = \text{constant.}$$

The formula of Laplace, based on the emission theory of light, did not agree very well with experimental data and has been discarded. Berthelot[19] made use of it in calculating molecular refractivity increases in homologous series.

The simple formula of Gladstone and Dale was proposed as an empirical relation in 1858 and has given quite satisfactory results. The Lorentz-Lorenz formula was advanced, on theoretical grounds, almost simultaneously by the two authors and has been extensively applied. Neither expression is absolutely accurate.

The product of the specific refractivity and the molecular weight is called the molecular refractivity. It has been possible to represent the molecular refractivity as the sum of the refractive effects of the component atoms, modifying the atomic value according to the mode of linkage of the atom. Gladstone and Dale stated that "every liquid has a specific refractive energy composed of the specific refractive energies of its component elements modified by the manner of combination". They published a very comprehensive table of experimental results.[20] Berthelot[19] had shown that using the Laplace formula and multiplying by the molecular weight, a quantity was obtained which showed a constant difference corresponding to a constant difference in composition of the material under observation. Landolt[21] undertook a systematic investigation of the relation between refractive index and chemical composition. He introduced further the quantity which we call molecular refractivity, obtained by multiplying the specific refractivity calculated from the Gladstone-Dale formula by the molecular weight of the substance. He showed that isomers have nearly the same molecular refractivity, even though the refractive indices and the densities are quite different. Similar differences of composition bring about similar differences of molecular refractivity, and the average value of the refractive effect of the CH_2 group was 7.60.

Landolt proposed that the refraction equivalent of a compound was the sum of the refraction equivalents of its constituent elements. He calculated the refraction equiva-

lents of some of the elements, for example:

Table II

Carbon	5.00
Hydrogen	1.30
Oxygen	3.00

and used these to calculate molecular refractivities from the formula

$$R_m = m(5.00) + n(1.30) + p(3.00)$$

where m = no. of carbon atoms,

n = no. of hydrogen atoms

p = no. of oxygen atoms.

The calculated and experimental refraction equivalents were almost identical for a large number of liquids containing C, H and O and he proposed this as a method of quantitative analysis applicable to many mixtures.

From old observations, Gladstone agreed that C might be taken as 5.0 and H at 1.3, and this being settled, he calculated values[22] for chlorine, bromine, iodine, tin and a number of other elements. Some fifty compounds which had not previously been examined, showed a remarkable agreement with the calculated values. The whole group of aromatic hydrocarbons and their derivatives (about fifty were examined) were cited as exceptions , giving results from 6 - 9 above calculated values. Gladstone attributed this to the constitution of the nucleus of the whole group. His first suggestion was that the hydrogen atom in benzene should be 3.5 instead of 1.3 as in hydrogen chloride, hydrogen bromide and hydrogen

iodide. The hydrogen remaining unchanged in all these derivatives was sufficient to account for the high value, so he carried out measurements on chlorhydranil,[23] a compound in which all the hydrogen atoms have been substituted by other atoms or groups, and found even here results exceeding the calculated values by the same amount.

The refraction equivalents of the elements for the A line of the solar spectrum were tabulated. Regarding the constitutive nature of the property, Gladstone[24] wrote: "It will be seen that many of these elements have a double value. This is a source of difficulty, but the disadvantage is far more than counterbalanced by the promise it holds out of throwing new light on the constitution of bodies. If an element had always the same refraction equivalent in whatever way it might be combined, the determination of the numbers would be very easy, and there might be some curious relations between them, but beyond that they could have little interest for the chemical philosopher. If, on the contrary, every difference in the manner of combination were to affect the the rate at which light is propagated by an element, the problem would be very complex and valuable deductions would be almost hopeless. The fact, however, is intermediate between these; an element usually exerts the same influence on transmitted rays in all analogous compounds, and in many that are not analogous, but there are differences of composition which do affect this quality, and in some cases at least these are coincident with a change of atomicity."

For ten years very little progress was made with the subject. Brühl[25] again called attention to the subject by means of a series of papers, contributing largely to the number of good observations. He pointed out especially that there was a great increase of refraction, not only in the aromatic group, as was previously known, but wherever the carbon atoms were supposed to be united b y double bonds; so he attributed to each carbon atom in such a case the refraction equivalent, not of 5.0 but of 6.1. He also came to the conclusion that oxygen has also two values, according to whether it is combined singly or doubly.

The deductions of Brühl led Gladstone to take up the matter again, and the result was a long contribution of experimental results[26] from which he deduced atomic refractivities for the elements depending on their mode of combination. In many cases the calculated values agreed with the observed values; very often they did not, and Gladstone recommended this problem to the consideration of inquiring chemists.

Brühl contributed a large amount of experimental data and advanced the subject very much.

A summary of the calculations of the refractivities of the elements and a list of references to the original literature will be found in Smiles: "The Relation between Chemical Constitution and some Physical Properties."

The modern development of the relations between refractivity and the problems of structure has not been so extremely

extensive. Measurements of refractivity have been applied to the determination of the presence and number of ethenoid linkages in a substance[27]; to the constitution of benzene[28]; to determining the position of unsaturated groups[29], and to determining the constitution of tautomeric substances and the conditions under which tautomeric changes take place.[30]

Like molecular volumes, the molecular refractivities of compounds of the type of o, m and p dihalogen benzene derivatives and the trisubstituted chlorbenzenes have not before been investigated. In the present investigation some of these have been determined, and a comparison of values attempted.

Electronic Conception of Valency

The process of electrolysis gave rise to the first electrochemical theories of valency. According to Berzelius,[31] the elements could be arranged in a series with oxygen, the most electronegative element, at one end and the alkali metals at the other. Each atom of an element was supposed to have opposite electrical poles with different quantities of electricity so that there would be an excess of one or other kind of charge. The metals were strongly electropositive, so that the lower oxides retained a residual positive polarity while the non-metallic oxides were electronegative. By virtue of these opposite polarities, a salt was formed of two oxides of opposite polarity.

A more quantitative relationship could be expressed

after the doctrine of valency had been developed. The amount of electricity carried by the ion is constant for each unit of valency, and Helmholtz[32], reviewing Faraday's convictions on the subject, proposed that the forces termed chemical affinity and electricity are one and the same. In the modern theory of valency, every unit of affinity of every atom is connected with one and only one other unit of another atom. Most elementary substances have molecules composed of two atoms and it is probable that even in such cases the combination of the atoms results from electrical neutralization of unlike charges.

Not only has valency been interpreted from the electronic point of view, but the structure of the atom itself has been assumed[33] to be merely an arrangement of electrons about a positively charged nucleus. The electrons are supposed to be divided up into a series of spherical layers, the outer ring of which may tend to lose or gain electrons, and the number of electrons which it can gain or lose is the same as the valence. Valency is regarded as a tube of force issuing from a valency electron, and terminating on the positive charge of another atom.

Many other modifications of this electronic theory of valency have been suggested, but the general form is very much the same. The essential difference between the chemical theory and the electronic theory can probably best be given in the words of J. J. Thomson:[34]

> "the symbol indicating a bond on the chemical theory is not regarded as having direction; no difference is

made on this theory between one end of a bond and the other. On the electrical theory, however, there is a difference between the ends, as one end corresponds to a positive, the other to a negative charge."

H. S. Fry[35] illustrates this view of J. J. Thomson as follows:

"The conceptions presented in the foregoing quotation may be illustrated and amplified by applying them to the combination of two univalent atoms, X and Y, of such nature that X tends to lose a corpuscle, or electron, which Y tends to acquire. Through the loss of one electron, i.e., one negative charge,(represented by the symbol $\ominus$), X functions positively; thus, $X - \ominus \rightarrow X^+$. Through the acquisition of this electron, Y functions negatively; thus, $Y + \ominus \rightarrow Y^-$.

Accordingly the electronic formula of the resultant compound, XY, from the union of X^+ and Y^-, is written $X^+—^-Y$ which indicates the polarities of the bond of attraction or Faraday tube of force between X and Y."

"A survey of these hypotheses leads to the conclusion, which is becoming more general, that, if the forces which hold the atoms together in electrolytes are electrical, then the same forces must also be assumed to hold in combination the atoms constituting the molecules of non-electrolytes. Hence, it may be maintained that chemical reactions which involve the dissociation of molecules either of electrolytes or of non-eledtrolytes are, let us say, <u>electronic</u>."

In substitution reactions, diatomic molecules take part. Helmholtz was the first to apply the conception of electro-dualism to the constitution of elementary molecules. W. A. Noyes[36] has stated this conception as follows:

"If we suppose what seems not to be improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of of the molecules, it would follow that elementary molecules as well may ionize into positive and negative parts."

For any compound XY, two different electronic formulae may be written, namely, $X^+—^-Y$ and $X^-—^+Y$. For this new

type of isomer, H. S. Fry[37] has proposed the term "electronic isomer" or "electromer". Even if such isomers were stable, though, they would possess very different degrees of stability, and consequently there would be a tendency for the unstable one to pass over into the stable form. This dynamic instability results in what is called "electronic tautomerism", which signifies an equilibrium mixture of two electromers in the sense that one electromer may be assumed to revert to another electromer through the transposition of valence electrons.

The benzene nucleus presents a particularly difficult problem in the development of a complete theory of valency. Since Kekule proposed the first structural formula for benzene, a great variety of other benzene formulae have appeared. The application of the electronic conception of positive and negative valences to the benzene formula is a very interesting recent development. Reviewing the history of the subject, the plane formulae of Kekule,[38] Dewar,[39] Claus,[40] Ladenburg,[41] Armstrong[42] and Baeyer[43] may be cited as the most important contributions.

The modern tendency has been to ascribe space formulae to benzene. These are of the dynamic type; fixed three dimensional formulae being excluded for these would require molecular asymmetry in the substitution products.

The Collie[44] formula arranges the system of carbon atoms in such a way that movement can take place:

1. Each carbon atom (represented by a tetrahedron) rotates about its center.

2. All the tetrahedra rotate about the center of gravity of the whole system.

The various phases of the configuration include both the Kekule and the Centric formula, these being convertible each into the other, and it is perfectly in accord with the formulae of Ladenburg and of Claus. It offers probably the most satisfactory interpretation for benzene, in its reactions, does not behave like "one particular substance which can be represented at all times and under all conditions by the same rigid formula".[45] However, none of the proposed formulae can be accepted as complete, for in any theory of the constitution of the benzene nucleus, substitution and all the anomalous reactions of benzene and its derivatives must be explained. The direction, by a group, of substituents to the para- ortho or meta positions is the most fundamental of all these unsolved problems.

The deficiencies of the older formulae in this respect have been corrected by an electronic formula for benzene derived by H. S. Fry[1] and proposed as a means of interpreting and correlating the reactions of the benzene nucleus.

The essential features of this electronic formula have already been described. The hydrogen atoms in positions 1,3,5 and those in positions 2,4,6 are of unlike polarity: consequently if a given hydrogen atom or substituent is negative, then the hydrogen atoms or substituents ortho and para

to it are negative, while that one meta to it is positive. The following substitution rule is developed:[46]

> "When substituents are of the same sign or polarity they will occupy positions meta to each other; if two substituents are of opposite sign or polarity they will occupy positions either ortho or para to each other."

In substitution a positive group will take the place of a positive hydrogen attaching itself to a C^- atom and a negative group will become attached to a C^+ atom. After the group has become attached to the ring it may either preserve the electronic sign which it had when substituting hydrogen or electronic tautomerism may result in part or all of the molecules being converted into the electronic isomer in which the group bears the sign opposite to that which it possessed when it became attached to the ring. The material is supposed eventually to consist chiefly of that electronic isomer in which the tendencies of each of the groups and hydrogen atoms in the molecule to be dominantly electro-positive or electro-negative in character are best satisfied. The bulk of the material will consist then of that electronic isomer which possesses the least internal energy per molecules, or, if the two isomers have more nearly equal molecular internal energies, of an equilibrium mixture of the two in more nearly equal quantities.

In the formation of di-substitution derivatives of benzene, the meta compound will be formed if the second

group entering possesses the same sign as the group already joined to the ring, while if the two groups are of opposite sign, the product will be the ortho or para compounds or a mixture of the two.

Theoretical

The formation of higher substitution products proceeds in an analogous way and one can tabulate for the entire series of substitution products of benzene the arrangement of electronic characters which must exist among the substituted groups in the molecule in order to agree with this formula for benzene.

Table 3

Position of Groups	Signs of Groups	
1	+	or -
1,2	+,-	or -,+
1,3	+,+	or -,-
1,4	+,-	or -,+
1,2,3	+,-,+	or -,+,-
1,2,4	+,-,-	or -,+,+
1,3,5	+,+,+	or -,-,-
1,2,3,4	+,-,+,-	or -,+,-,+
1,2,3,5	+,-,+,+	or -,+,-,-
1,2,4,5	+,-,-,+	or -,+,+,-
1,2,3,4,5	+,-,+,-,+	or -,+,-,+,-
1,2,3,4,5,6	+,-,+,-,+,-	or -,+,-,+,-,+

The actual electronic formulas will depend on the electro-positive or electro-negative nature of the groups in positions 1,3,5 and 2,4,6 respectively and it would be

exceedingly difficult to determine from the constitutional formula alone in the case of a complicated benzene derivative of which of the isomers the material chiefly consists. We could reason qualitatively from the known electro-chemical nature of the groups in their chemical relations, but attachment to the benzene nucleus, proximity to other strongly charged groups and perhaps even temperature changes might alter their electrochemical natures.

If the groups are all of the same chemical constitution the problem is much more simple. Each group will tend to possess that electronic character in the molecule which agrees with its electro-chemical nature. All the groups cannot be of the same sign, however, except in the case of the meta disubstituted and the symmetrical trisubstituted derivatives, and so it is a question of the relative number of groups which can satisfy this tendency. In the halogen substitution products of benzene, for example, the halogen will presumably tend to function negatively and the molecule will presumably take that form in which the greatest number of halogen atoms are negative. The free halogen, for example, chlorine, supposedly consists of a positive atom of chlorine and a negative atom of chlorine held together by mutual attraction of these opposite electronic characters and undergoing tautomeric reversal of electronic characters within the molecule also. This can be represented by the following electronic formula:

$$Cl^{+}—Cl^{-} \rightleftharpoons Cl^{-}—Cl^{+}$$

In substitution hydrogen chloride is formed. The chlorine in hydrogen chloride is unquestionably negative and the hydrogen equally certainly is positive, so substitution in the ring by chlorine apparently consists of the removal of a positive hydrogen from the ring, the positive chlorine atom taking its place, and the remaining negative chlorine atom forming with the displaced positive hydrogen atom molecular hydrogen chloride.

The chlorine atom attached to the ring then undergoes a reversal of charge and becomes presumably negative. This is shown by the fact that disubstitution gives ortho and para and not meta dichlorbenzene, indicating that the chlorine atom already attached to the ring and the second chlorine atom to substitute hydrogen bear unlike charges. It may be that the mechanism is just the opposite of that outlined above, i.e., negative hydrogen may leave the ring, negative chlorine take its place, negative hydrogen and positive chlorine form the electronic isomer of hydrochloric acid which instantly goes over into the common $H^{+}—^{-}Cl$ form, and the negative chlorine attached to the ring reverses to positive chlorine. However, we are not concerned with the question as to whether the chlorine atom which substitutes hydrogen is positive or negative, since whichever it is, the mechanism will be consistent throughout a series of consecutive substitutions.

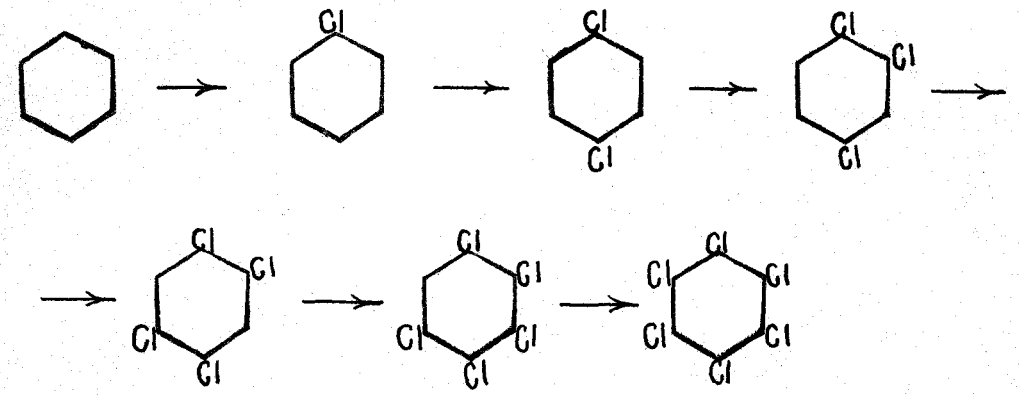
In the following, we are concerned only with the relative numbers of atoms which are of opposite electronic characters, and it will be assumed for the sake of simplicity that the substituting chlorine atom is positive.

In certain compounds, the positive chlorine which joins to the ring in substitution does not undergo reversal of charge according to this theory, in others it must. The first type of substitution corresponds to adding to the molecule a positive chlorine atom and taking away a positive hydrogen atom, and the second type of substitution results in the addition of a negative chlorine atom and a decrease in the number of negative hydrogen atoms by one. It is reasonable to expect that the additive properties of a compound should have their numerical values changed differently by these two types of substitution. Evidence that this is the case has been pointed out by H. S. Fry[2] in the molecular volumes of the chlorbenzenes formed by progressive chlorination of benzene, and an interesting statement in the literature has been given an explanation.

Where the theory leads one to expect that the substituted chlorine atom remains positive, the molecular volume is changed by a different increment than is found where theory demands that the chlorine atom be negative but the increments within either class are constant. It appears, then, that positive chlorine atoms and negative chlorine atoms have respectively different atomic volumes. Since it is this correspondence between a physical property .

and the theoretical electronic formulas which suggested the present line of research, a brief outline of the subject will be necessary.

When benzene is progressively chlorinated, the reactions proceed as follows:



Jungfleisch[14] determined the molecular volumes of each of these compounds, their constitutional formulas at the time being of course uncertain, and pointed out the fact that the changes in the molecular volume produced by the entrance of the first, third and fifth chlorine atom were larger than the increments produced by the even numbered atoms; i.e., second, fourth and sixth.

Table 4

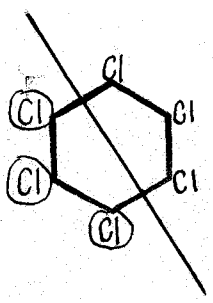
	Molecular volume	Difference
C_6H_6	96.059 cc.	
		18.736 cc.
C_6H_5Cl	114.795 "	
		16.104 "
$C_6H_4Cl_2$	130.899 "	
		17.022 "
$C_6H_3Cl_3$	147.921 "	
		16.337 "
$C_6H_2Cl_4$	164.258 "	
		18.588 "
C_6HCl_5	182.846 "	
		15.070 "
C_6Cl_6	197.916	

LeBas[47] recalculated the molecular volumes of the compounds from the data of Jungfleisch. The molecular volume of C_6H_6 is 96.0 and every atom of hydrogen subtracted involves a loss in volume of 3.2. The facts brought out may be tabulated as follows:

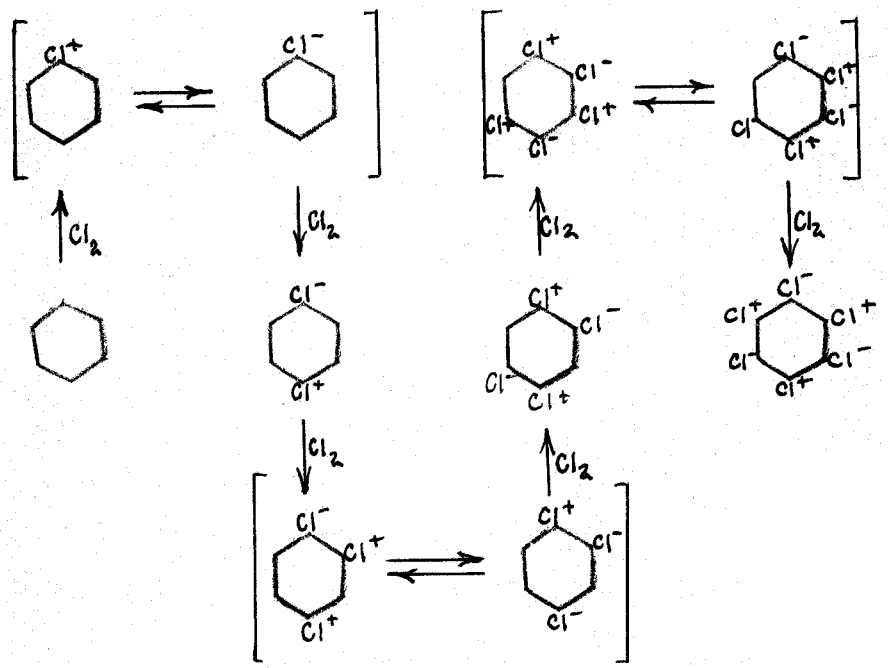
Table 5

	Normal Atomic	Abnormal Volume of Cl	
Cl = C_6H_5Cl - C_6H_5 = 114.6 - 92.8 = 21.8	21.8		odd
	=	19.5	even
Cl_2= $C_6H_4Cl_2$ - C_6H_4 = 130.9 - 89.6 = 41.3			
=	21.4		odd
Cl_3= $C_6H_3Cl_3$ - C_6H_3 = 149.1 - 86.4 = 62.7			
=		18.9	even
Cl_4 = $C_6H_2Cl_4$ - C_6H_2 = 164.8 - 83.2 = 81.6			
=	22.3		odd
Cl_5 = C_6HCl_5 - C_6H = 183.9 - 80.0 = 103.9			
=		19.3	even
Cl_6 = C_6Cl_6 - C_6 = 200.0 - 76.8 = 123.2			

The smaller values apply to the Cl atom marked (Cl) in the drawing and the apparent result is that one-half the chlorine atoms differ from the other half.

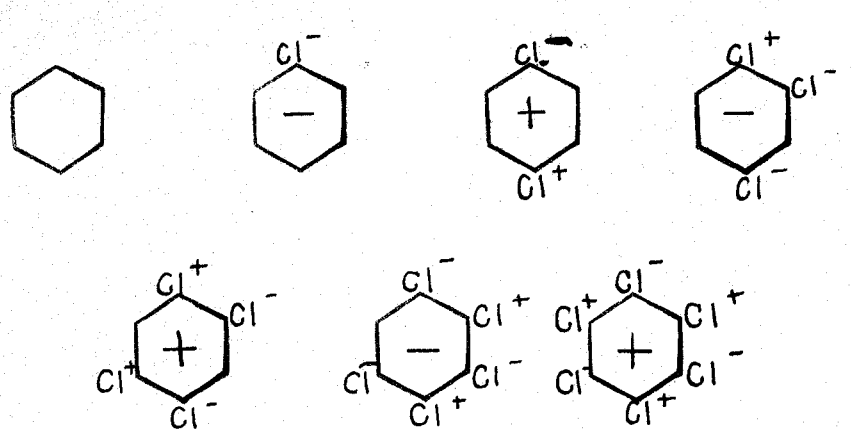


H. S. Fry[48] proposed the hypothesis that differences in the relative atomic volumes of the halogen atoms are directly related to differences in polarity. It will benoted that p-dichlorbenzene, 1,2,4,5 tetrachlorbenzene and hexachlorbenzene have no electromers; that is, the electronic isomers formed by electronic tautomerism are identical with the original. The scheme for the progressive chlorination appears, then, as follows:[49]



The electronic formulas of the six chlorbenzenes, (assuming for simplicity, as previously stated, that the substituting chlorine atom is positive and that after substitution the chlorine atom, if it can, becomes negative due to the predominantly electronegative character of chlorine) then, may

be arranged as follows, and the polarity of the entering chlorine atom indicated.



The simultaneous variation in polarity and atomic volume is apparent.

Table 6.

	Relative position	Polarity	Atomic Vol. negative	At.Vol. positive
1st chlorine atom	1	-	21.8	
2nd chlorine atom	4	+		19.5
3rd chlorine atom	2	-	21.4	
4th chlorine atom	5	+		18.9
5th chlorine atom	3	-	22.3	
6th chlorine atom	6	+		19.3

There is, evidently, a marked difference between the atomic volumes of the chlorine atoms in positions 1,3,5 and 2,4,6 respectively which parallels the theoretical opposition of polarity of the atoms in these two groups of positions.

It appeared desirable consequently to make a systematic study of the additive properties of the entire series of chlorbenzenes, including all the isomers, examining them with respect to the information their physical properties might give as to their electronic formulas. The data on molecular volumes was to be made complete by measuring those of the isomers other than the ones formed by direct chlorination and the molecular refractivities of all the members were to be measured. For this latter purpose it was proposed to use the Pulfrich (Hilger) refractometer making the calculations of the molecular refractivities from the Gladstone-Dale formula. It seemed probable that the values for the atomic volumes which apparently represent positive and negative chlorine would hold consistently throughout the series and that a correspondence between the molecular volumes and electronic formulas could be traced throughout. The same thing was to be done with the refractivities, for it seemed probable that the different types of valency represented by positive and negative chlorine should give rise to different atomic refractivities.

Conclusions

The refractive indices found for the various liquid chlorbenzenes are tabulated on page 53, and on the following page the corresponding densities are given. The interpolated values of these quantities at even temperatures and the corresponding specific and molecular refractivities are shown on page 55. The specific and molecular dispersions calculated from the dispersion data are presented on page 56. Dispersions were measured to the fifth decimal place. The accuracy of the data in this part of the work is much greater than that which follows for molecular volumes, and unquestionably is well within the limit set by the purity of the specimens. For convenience in examining the molecular refractivity data, the table on page 57 was constructed. The change in molecular refractivity produced by the entrance of chlorine in any given position is about constant for that position at the four temperatures tabulated; the average values of the differences being as follows:

Table 7
Differences in Molecular Refractivities

	D	C	F
Benzene			
Chlorbenzene	8.88	8.81	9.07
Dichlorbenzene (ortho	8.76	8.68	8.96
Dichlorbenzene (meta	8.93	8.85	9.13
Dichlorbenzene (para	9.08	8.98	9.31
Trichlorbenzene - 1,2,4	9.05 (8.98)	8.95 (8.89)	9.28 (9.21)

The deviations of the experimental values from the mean are all very small except in the case of trichlorbenzene, for which only two values can be calculated. Examination of the collected data will show a general trend of each of the molecular refractivities to decrease with rising temperature, so the values for trichlorbenzene at 50° are probably somewhat in error. Estimating from the rest of the data for this temperature, the most probable values for the mean difference are given in the brackets in the table.

Examining the differences between ortho, meta and para dichlorbenzenes and chlorbenzene, it is quite apparent that the ortho and para compounds differ considerably in molecular refractivity. We must conclude, then, that if the electronic formula for benzene of H. S. Fry is correct, the atomic refractivities of chlorine and of hydrogen (and probably all elements) depend upon other things than their electronegative or electropositive functions; probably chiefly upon position and proximity of other atoms or groups/ It has been impossible to assign distinct values to the atomic refractivities of positive and negative chlorine respectively. One point of interest, though, is that the differences in going from benzene to chlorbenzene and from chlorbenzene to metadichlorbenzene are almost the same, and one might conclude that the two chlorine atoms in metadichlorbenzene are very much like each other, and function the same way within the molecule as does the chlorine atom

in chlorbenzene. Another interesting but probably accidental relationship is that the difference between metadichlorbenzene and chlorbenzene is almost exactly the mean of the corresponding differences for ortho and para dichlorbenzenes for each of the three wave lengths.

Considering now the values for trichlorbenzene, the differences between trichlorbenzene and paradichlorbenzene are not the same as those between chlorbenzene and benzene for each wave length, which is what the theory demands if atomic refractivity depends on the electronic function of the atom only. There is a periodicity, however, in that the increments for the first and third chlorine atoms (negative) are both less than the increment for the second (p) chlorine atom added, which, according to the theory, is positive. Another interesting relationship may be developed: the change in molecular refractivity going from chlorbenzene to trichlorbenzene is almost the same as the change from benzene to paradichlorbenzene. In both cases, according to the theory, a positive and a negative chlorine atom are added. The data as a whole, though, indicates that it is unlikely that atomic refractivities can be assigned to positive and negative chlorine without any modification based on position within the molecule.

Taking up the molecular volumes data which is presented on page 58 , it should be stated that the order of accuracy is probably considerably less than that of the pre-

ceding refractivities data. The experimental determination of density at the boiling point is not so easily carried out. Nevertheless, the deviations between the data obtained and that of Jungfleisch are so astonishing that a thorough revision of the whole subject ought to be made. Jungfleisch's specimens were obtained by successive chlorination and were purified by freezing and fractionation[50]; it seems hardly probable that such samples would be as nearly pure as material prepared indirectly in more modern ways from derivatives. In the molecular volumes calculated, there is no periodicity, such as Jungfleisch found, observable. A partial check on the method is given by the fact that the molecular volumes found for benzene and chlorbenzene agree fairly well with those of Jungfleisch, considering the difficulty of fixing the density of benzene at its boiling point, upon which the calculations depend. Lachowicz[51] gives 0.81196 at 80.4° referred to water at 4°, while interpolating Sydney Young's[52] data the value .81407 under the same conditions is obtained. Basing the calibration of the pyknometers upon the data of Young, (tables pages 36,58) the molecular volumes are uniformly 0.26% lower than those calculated from the value determined by Lachowicz.

For convenience, the two sets of figures together with those recalculated from Jungfleisch's data using the present atomic weights may be tabulated as follows:

Table 8 (see table 15)

Molecular Volumes of the Chlorbenzenes

	Jungfleisch			Using the density of benzene determined by: Lachowicz			Young		
	Densi-ty	Mol. Vol.	Diff.	Densi-ty	Mol. Vol.	Diff.	Densi-ty	Mol. Vol.	Diff.
Benzene	.812	96.16		.8120	96.16		.8141	95.91	
Chlor-benzene	.980	114.83	18.67	.9797	114.87	18.71	.9822	114.57	18.66
Orthodi-chlorbenzene				1.1169	131.60	16.73	1.1198	131.26	16.69
Metadi-chlorbenzene				1.1060	132.90	18.03	1.1089	132.55	17.98
Paradi-chlorbenzene	1.123	130.88	16.05	1.1051	133.00	18.13	1.1080	132.65	18.08
1,2,4 Tri-chlorbenzene	1.227	147.87	16.99	1.2143	149.42	16.42	1.2175	149.03	16.38

LeBas has recalculated the values from Jungfleisch's data (see page 28) and gives substantially the same values as in the preceding table (Jungfleisch) with the exception of 1,2,4 trichlorbenzene. For this compound Jungfleisch gives 206° as the boiling point. Le Bas appears to have extrapolated the density to 213°, the accepted boiling point. The validity of such an extrapolation is questionable; one might rather question the purity of the sample or the accuracy of the thermometry. The original data of Jungfleisch in comparison shows only slight periodicity. The molecular volume determined in the present investigation for trichlorbenzene (149.03) is in better agreement, though, with the recalculated value of Le Bas (149.1) than with that of Jungfleisch.

In order finally to decide which set of data most nearly represents the facts, an independent determination of the densities of paradichlorbenzene and trichlorbenzene at their boiling points should be undertaken. If Jungfleisch's relationship is true of the chlorbenzenes, one would expect it to hold for analogous series, and the generality ought to be investigated by measurements on the brombenzenes, for example.

However, if the conflict noted above is due to the method of heating and not the specimens themselves, it should not interfere appreciably with the prime purpose of this investigation; a comparison of the molecular volumes of ortho, meta and paradichlorbenzenes. The experimental conditions surrounding each of these measurements were the same, for the temperatures of boiling lie very near each other. The agreement among a number of weighings for each specimen was all that could be expected; the greatest deviations from the means in a total of twenty one weighings being almost uniformly .008% and the average deviation from the means .004%. It is apparent that ortho and para dichlorbenzenes do not have the same molecular volume, just as with molecular refractivities the values increase in the order: ortho, meta, para. The increases are less uniform than with refractivities, the meta and para values being almost the same. Consequently, it is quite impossible to assign definite increments in molecular volume based on the electronic functions of the chlorine atoms only, and the conclusion must be drawn

that atomic volumes like atomic refractivities, are constitutive and depend upon the configuration of the molecule.

Experimental

I. Materials

Benzene

The sample of benzene used was prepared from Kahlbaum's (K) Thiophene-free benzene for molecular weight determination. Two different lots of the material were subjected to slow freezing, allowing about one third to solidify. The solid portions were collected, combined, and fractionated with a Hempel two-bulb column into four portions, the boiling point showing no observable change as the fractionation proceeded. The first and last portions were rejected. The two intermediate fractions were fractionated once more and the first and last fractions again rejected. The boiling point range of the two intermediate fractions was less than one hundredth of one degree so they were combined and kept over sodium wire.

Chlorbenzene

Starting with about one kilogram of dry Eimer and Amend chlorbenzene, five consecutive fractionations with a two bulb Hempel column were made, rejecting the first fifth and the last fifth in each case. The boiling point of the product was constant within one hundredth of one degree. Boiling point 130.4° at 735.9 mm. corrected. The sample was preserved over fused calcium chloride.

Orthodichlorbenzene

Starting with about two hundred grams of orthodichlorbenzene from the Eastman Kodak Research laboratory, a

product was obtained after eight successive fractionations (rejecting in each the first and last portions) which boiled within a range of one tenth degree.

Metadichlorbenzene

The sample was prepared from recrystallized metanitraniline by consecutive Sandmeyer reactions. The metachlornitrobenzene prepared was purified by distillation with superheated steam, reduced with tin and hydrochloric acid, the mixture made alkaline, and the metachloraniline distilled with steam. The oil was converted into the hydrochloride and fractionally crystallized several times. The product was diazotized, treated with cuprous chloride solution, and the metadichlorbenzene distilled with steam. The dried material was distilled through a two-bulb Hempel column, rejecting the first and last portions. The boiling point remained practically constant, and a second distillation gave a product which showed no observable variation of boiling point.

Paradichlorbenzene

About one kilogram of solid obtained from the Eimer and Amend Company was melted and the fused material fractionally crystallized. This process was repeated with the intermediate portions. The fractions obtained from the second crystallization were dissolved in alcohol and allowed to cool slowly, crystallizing in fractions from the solvent. This was repeated with the intermediate portions,

The purest crystals were washed with alcohol, dried, and fractionally distilled several times, rejecting the first and last portions. The boiling point of the product showed a range less than one tenth degree.

1,2,4 Trichlorbenzene

This compound was prepared by nitration of paradichlorbenzene, fractional crystallization of the carefully washed dichlornitrobenzene, reduction and distillation with steam, fractional crystallization of the aniline and hydrochloride of the aniline, diazotization and decomposition with cuprous chloride and distillation of the product twice with steam. An ice funnel was constructed and the trichlorbenzene repeatedly fractionally crystallized. The final product showed no observable freezing point range.

1,3,5 Trichlorbenzene

This material was prepared by dichlorination of acetanilide, hydrolysis and steam distillation of the dichloraniline, chlorination of the dried aniline suspended in dry carbon tetrachloride with gaseous chlorine, and conversion of the steam distilled trichloraniline into trichlorbenzene by diazotization in alcoholic solution. The product was distilled repeatedly with steam, recrystallized several times from alcohol and finally was distilled. The amount of material was too small to obtain a steady reading of the thermometer during distillation.

II. Apparatus and Procedure

(a) Determination of Densities at low temperatures

The densities of the liquids were determined up to temperatures around thirty degrees (the maximum range of the instrument) by means of a Becker Chainomatic Specific Gravity Balance. The liquid was placed in a small test tube and immersed in a beaker of water at room temperature. The float thermometer was compared and readings adjusted throughout its range with a recently certified thermometer used with the Pulfrich Refractometer for refractivity measurements. For readings above room temperature the liquid was warmed by means of an electrically heated spiral of chromel ribbon, wrapped on an air-jacketed glass cylinder. Temperatures could be held constant for an hour at a time without any difficulty whatever, and the high degree of heat insulation afforded by the wide air jacket insured the absence of appreciable convection currents of air. A series of readings indentical to one ten thousandth of a unit could easily be obtained, but temperature readings were subject to an error of about one tenth degree.

Observed readings were corrected for the change in volume of the float due to thermal expansion. This correction was made as follows:

Let V_{15} be the volume of the float at 15°C (the reference temperature of the float).

Let V_t be the volume of the float at any temperature t.

Then $V_t = V_{15}\left[1 + k(t-15)\right]$ where k is the coefficient of cubical expansion of the glass, and t = Centigrade temperature. At temperatures above 15°, V_t will be larger than V_{15}, and the observed density will be larger in the same proportion. The observed density d_t can be corrected, therefore, by multiplying by the ratio $\frac{V_{15}}{V_t}$.

Let d'_t be the density corrected in this way for expansion of the float.

$$d'_t = \frac{V_{15}}{V_t}(d_t)$$

$$d'_t = \frac{1}{1 + k(t-15)}\ d_t$$

Since k is so extremely small and (t-15) is also small,

$\frac{1}{1 + k(t-15)} = 1 - k(t-15)$ (approx.).

Then $d'_t = \left[1 - k(t-15)\right]\ d_t$

and $d'_t = d_t - kd_t(t-15°)$

The value of k was taken as 0.000025 (the value for ordinary glass) and a graph was constructed in which the value of $kd_t(t-15)$ for a series of densities was plotted against temperature. The correction to be subtracted from the observed density couldthen be read off directly.

The instrument was calibrated with boiled distilled water and with the purified benzene prepared as described above, referring all readings to water at 4°C. Practically the same factor for the instrument was found in both sets of readings, the average factor for water being .99931 and that for benzene .99924; the average of the two, .99928 was used.

The following table shows the densities obtained for benzene compared with those interpolated from Perkin's data.[53]

Table 9
Density of Benzene

Temp.	Density- Perkin	Density - observed
21.6	.8777	.8779
25.2	.8740	.8741
25.4	.8738	.8739
28.0	.8710	.8710
28.6	.8704	.8704
28.8	.8702	.8701

The agreement is quite satisfactory. Both sets of values refer to water at 4°C.

(b) Densities at temperature higher than 30°C and lower than the boiling points

The densities of the liquid chlorbenzenes were determined in the usual manner with Ostwald-Sprengel pyknometers, using a water-bath which could be kept within one hundredth degree of a constant temperature. The usual corrections for buoyancy of the air were made, and the densities refer to water at 4°C.

(c) Densities at the Boiling points

The first plan that suggested itself was to use a U-shaped device of the expansimeter type, made of a pipette with capillary tubing, one tube of which was bent through an angle of 180°. The capillary tubing available, however, was far from uniform in bore and too much difficulty was experienced in calibration. A second method based on the flotation of little bulblets of Pyrex glass was found to

require more preliminary work and accurate temperature data than circumstances allowed, so finally the densities were determined directly with tiny pyknometers of Pyrex glass which were heated to the boiling point by vapor of the liquid under observation in an airjacketed Beckmann boiling tube.

The usual type of boiling tube about 3 cm. diameter with a platinum wire sealed in the bottom was fastened in the center of a glass tube about 4.5 cm diameter and 14 cm. length by means of two stoppers at top and bottom made of strips of asbestos paper cemented together with sodium silicate. A small condenser was attached to the side arm of the boiling tube and a portion of about 20 cc. of the liquid under observation boiled gently by means of a small gas flame, shielding the apparatus from the flame with a perforated screen of asbestos board. The pyknometers, of Pyrex glass with single delivery tubes bent through an angle of 180° and terminating in hooks under the bulbs, were suspended one at a time in the vapor by means of a platinum wire loop passing through the cork. The pyknometers were filled by placing them in a test tube with the delivery tube under the surface of the liquid and alternately applying suction and opening to the air. They were emptied in the same fashion but with the pyknometer inverted. The nearly filled pyknometers were then suspended in the tube and heated by condensation of the vapor. When vapor no

longer appeared to be condensing on the pyknometer in appreciable quantity, (shown by the absence of drops of condensed vapor) the pyknometer was removed for weighing. The liquid withim the pyknometer expands and the excess escapes through the delivery tube. No drying of the pyknometers was needed for the liquids evaporated sufficiently rapidly from the hot surfaces during cooling.

The densities were calculated from the following formula which takes into account the buoyancy of air and the expansion of the glass:

$$d_{4^\circ}^{t^\circ} = \frac{W'D}{W} - \frac{0.0012(W'-W)}{W} + \frac{W'D}{W} \times 0.0000096(t-t')$$

in which

W is the apparent weight of benzene in air at the temperature t,

W' is the apparent weight of the liquid in air at the temperature t',

D is the density of benzene at the temperature t.

(0.0000096 was taken as the coefficient of cubical expansion of the Pyrex glass, and 0.0012 as the mean density of air.)

The average apparent weights and the corresponding barometric pressures are tabulated in table 15. The densities are calculated corresponding to these pressures. For the comparisons it was necessary to have the densities for all the materials boiling under the same pressure (760 mm.). The small changes of density corresponding to this reduction to standard pressure were calculated with quite sufficient

accuracy by means of two general expressions:

(1) Ramsay and Young's[54] expression for correction of boiling point to 760 mm. pressure;

$$\Delta t = 0.000120\ (\Delta p)(T)$$

in which Δp is the difference between the observed barometric pressure and 760 mm., T is the absolute boiling point of the liquid and Δt the desired boiling point correction. The value of the constant 0.000120 is that for benzene, fluorbenzene, chlorbenzene, brombenzene and iodbenzene. The calculated temperature corrections are all about 1°, so the corresponding density corrections are very small.

(2) A modification of LeBas'[55] formula for extrapolating densities at the boiling point. LeBas' equation is:

$$\frac{d_0}{d_t} = 1 + C\left(1 - \frac{273}{B.P.}\right)$$

in which

d_0 = density at 0°

d_t = density at the boiling point

c = a constant (for benzene = 0.47)

Rearranging

$$\frac{d_0 - d_t}{d_t} = c\,\frac{T - 273}{T}$$

in which T = absolute boiling point. This states that the relative change of density is proportional to the relative change of temperature from the boiling point. Using a simpler notation, and arranging the expression for extrapolation from any temperature to T_b, we have

$$\frac{\Delta d}{d_b} = c \frac{\Delta t}{T_b}$$

Then $\Delta d = c.d_b.\frac{\Delta t}{T_b}$

The value c = 0.47 for benzene was used. The mean value of c for a variety of organic compounds is 0.463. As explained above, Δ t was calculated from Young's formula.

From the above expression, the density corrections were calculated for the changes of boiling point Δ t corresponding to the observed barometric pressures. Instead of d_b, the observed densities were used; the error due to this substitution is insignificant. Obviously, since the extrapolation is carried out only over about 1° change of temperature, the corrections could be very much more approximate without seriously changing the accuracy of the molecular volumes.

The corrected densities and the molecular volumes calculated from them at the boiling points at 760 mm. pressure are tabulated in table 15. The discussion of the collected data will be found on page 34.

(d) Measurements of Refractivities

The indices of refraction of the liquid compounds were measured with a Pulfrich Refractometer of Hilger make. The wave lengths used were those of the sodium flame and the C and F lines of the hydrogen tube spectrum. Constant temperature was maintained by a stream of water from a large well stirred constant temperature bath circulating

about the prism and through the plunger immersed in the liquid. At high temperatures it was found advantageous to surround the cell and cover the prism with batting to minimize any irregular cooling due to draughts. Dispersions were read on the micrometer drum and calculated to the fifth decimal and consequently differ somewhat from the dispersions obtained by subtraction which give only the fourth decimal.

A modification of the equations usually used with the Pulfrich instrument was made. The refractive index for the sodium line is ordinarily obtained from the angle of the refracted ray by means of a table, adding a correction for the effect of temperature change on the prism obtained from another table:

$$[n_r]_D^t = [\mu_D]_D + [\Delta_D]_t \Delta t \qquad (1)$$

in which

$[n_r]_D^t$ = refractive index for the D line at a temperature t.

$[\mu_D]_D$ = refractive index for the D line uncorrected for temperature (table).

Δ_D = coefficient for temperature correction of the refractivity μ_D for the D line (table)

Δt = rise of temperature above 20°C.

For the refractive index for the C line, we have:

$$[n_r]_c^t = [\mu_D]_c - P_c + [\Delta_c]_t \Delta t \qquad (2)$$

in which

$[n_r]_c^t$ = refractive index for the C line at a temperature t.

$[\mu_D]_c$ = refractive index for the C line uncorrected for temperature and for the prism used. (table)

P_c = prism correction for the C line. (table)

$[\Delta c]_t$ = coefficient for temperature correction for the C line. (table)

Δt = rise of temperature above 20°C.

Likewise, for the F line we have:

$$[n_r]_F^t = [\mu_D]_F + P_F + [\Delta_F]_t \Delta t \qquad (3)$$

in which the symbols have the corresponding meanings for the F line.

Calculating the dispersions,

$$[n_r]_D^t - [n_r]_C^t = [\delta]_{D-C}^t$$

and

$$[n_r]_F^t - [n_r]_D^t = [\delta]_{F-D}^t$$

we have

$$[\delta]_{D-C}^t = ([\mu_D]_D - [\mu_D]_C) + P_C + [\Delta_D - \Delta_C]_t \Delta t \qquad (4)$$

and

$$[\delta]_{F-D}^t = ([\mu_D]_F - [\mu_D]_D) + P_F + [\Delta_F - \Delta_D]_t \Delta t \qquad (5)$$

Obviously,

$$[\delta]^t_{F-C} = [\delta]^t_{F-D} + [\delta]^t_{D-C} \qquad (6)$$

The three dispersions are easily calculated from these three expressions with much greater accuracy than by subtraction of the refractive indices, for the differences $\left([\mu_D]_D - [\mu_D]_F\right)$ and $\left([\mu_D]_F - [\mu_D]_D\right)$ can be obtained to the fifth decimal directly from the angular differences measured on the micrometer drum and the change $\Delta\mu$ per minute. $[\Delta_D - \Delta_C]_t$ and $[\Delta_F - \Delta_D]_t$ are, of course, directly obtainable from the tables.

To simplify the rather extensive calculations as much as possible, the refractive indices for the C and F lines were calculated from the dispersions and the mean refractive index of the D line. To decide more exactly on the position for the D line, the angle readings were weighted in the order of distinctness of line as follows:

D	x	3
C	x	2
F	x	1

and the mean position of the D line estimated from the dispersion angles and the various settings accordingly. About a half dozen settings for each line were made, and the average readings used. The refractive indices and the dispersions are collected in tables 10, 12, 13.

The refractive indices were plotted against temperatures and the values at even temperatures read from the

curves. The data for densities was likewise plotted, but since practically the same values for both sets of measurements are given by interpolation the curves are not included. The molecular refractivities and dispersions are based on the atomic weights for 1922. The discussion of the data will be found on page 32.

Table 10

REFRACTIVE INDICES OF THE LIQUID CHLORBENZENES

	Temp. t°	$(n_r)^{t°}_D$	$(n_r)^{t°}_C$	$(n_r)^{t°}_F$
Benzene	19.75°	1.5013	1.4966	1.5130
	35.4°	1.4914	1.4868	1.5031
	42.7°	1.4866	1.4819	1.4982
Chlor-benzene	22.9°	1.5230	1.5182	1.5352
	30.6°	1.5190	1.5142	1.5310
	39.7°	1.5142	1.5094	1.5261
	49.8°	1.5087	1.5041	1.5206
Ortho-dichlor-benzene	18.7°	1.5518	1.5468	1.5648
	30.45°	1.5463	1.5413	1.5591
	39.8°	1.5418	1.5368	1.5543
	39.5°	1.5419	1.5370	1.5545
	49.85°	1.5368	1.5319	1.5495
Meta-dichlor-benzene	20.2°	1.5463	1.5413	1.5591
	29.85°	1.5418	1.5368	1.5543
	39.8°	1.5370	1.5320	1.5493
	50.2°	1.5317	1.5269	---
Para-dichlor-benzene	54.1°	1.5307	1.5257	1.5433
	57.6°	1.5289	1.5239	1.5415
	62.7°	1.5263	1.5215	1.5389
1,2,4 Tri-chlor-benzene	32.6°	1.5656	1.5603	1.5791
	41.6°	1.5614	1.5562	1.5749
	50.8°	1.5578	1.5526	1.5712
	57.95°	1.5535	1.5483	1.5670
	65.3°	1.5495	1.5445	1.5624
1,3,5 Trichlor-benzene	65.2°	1.5447	1.5398	1.5576
	66.2°	1.5442	1.5391	1.5569

Table II

DENSITIES OF THE LIQUID CHLORBENZENES - $d_{4^\circ}^{t^\circ}$

Liquid	Temp.	Apparent Density	Correction for thermal expansion of float	Apparent density corrected for thermal expansion	Corrected density $d_{4^\circ}^{t^\circ}$
Water Calibration Data	25.8°	.99785	-.00027	.9976	.9969 *
	21.6	.8787	-.00014	.8786	.8779
	25.2	.8749	-.00022	.8747	.8741
	25.4	.8747	-.00022	.8745	.8739
Benzene	28.0	.8719	-.00028	.8716	.8710
	28.6	.8713	-.00029	.8710	.8704
	28.8	.8710	-.00030	.8707	.8701
	50.0	--	--	--	(.8474)**
	29.8	1.0972	.00041	1.0968	1.0960
	20.0	1.1082 $d_{20^\circ}^{20^\circ}$ ****	--	--	1.1063****
Chlor-	30.0	1.1004 $d_{30^\circ}^{30^\circ}$ ****	--	--	1.0957****
benzene	40.0	1.0934 $d_{40^\circ}^{40^\circ}$ ****	--	--	1.0851****
	50.0	1.0868 $d_{50^\circ}^{50^\circ}$ ****	--	--	1.0739****
	20.6	1.3052	-.00018	1.3050	1.3041
	20.7	1.3050	-.00019	1.3048	1.3039
	26.8	1.2986	-.00038	1.2982	1.2973
Ortho-	29.1	1.2962	-.00046	1.2957	1.2948
dichlor-	29.3	1.2959	-.00046	1.2954	1.2945
benzene	29.6	1.2957	-.00047	1.2952	1.2943
	30.0	1.2954	-.00049	1.2949	1.2941
	50.0	--	--	--	$(1.2709)\rho_{yK}$
	21.7	1.2888	-.00022	1.2886	1.2878
Meta-	29.3	1.2807	-.00046	1.2802	1.2793
dichlor-	29.4	1.2806	-.00047	1.2801	1.2792
benzene	50.0	--	--	--	$(1.2563)\rho_{yK}$
	55.0	1.2675 $d_{55^\circ}^{55^\circ}$ ****	--	--	1.2495****
Para-	60.0	1.2648 $d_{60^\circ}^{60^\circ}$ ****	--	--	1.2437****
dichlor-	65.0	1.2623 $d_{65^\circ}^{65^\circ}$ ****	--	--	1.2379****
benzene	19.9	1.4538	-.00018	1.4536	1.4526
	20.2	1.4537	-.00019	1.4535	1.4521
1,2,4	20.6	1.4526	-.00020	1.4524	1.4515
trichlor-	28.9	1.4435	-.00050	1.4430	1.4480
benzene	30.3	1.4420	-.00055	1.4415	1.4404
	50.0	--	--	--	$(1.4169)\rho_{yK}$

*Landolt-Börnstein Tables

**Perkin, J.C.S. 69, 1191

****Perkin, J.C.S. 69, 1202

Table 12

SPECIFIC AND MOLECULAR REFRACTIVITIES OF THE CHLORBENZENES

	Temp. t	Density d	Refr. Index D $(n_r)^t_D$	Spec. refr. $(r_G)^t_D$	Mol. refr. $(R_G)^t_D$	Refr. index C $(n_r)^t_C$	Spec. refr. $(r_G)^t_C$	Mol. refr. $(R_G)^t_C$	Refr. index F $(n_r)^t_F$	Spec. refr. $(r_G)^t_F$	Mol. refr. $(R_G)^t_F$
	20.0	.8795	1.5011	.5698	44.47	1.4965	.5645	44.06	1.5128	.5831	45.51
Benzene	30.0	.8689	1.4948	.5695	44.45	1.4901	.5640	44.02	1.5065	.5829	45.50
	40.0	.8582*	1.4883	.5691	44.41	1.4837	.5636	43.99	1.5000	.5826	45.47
	50.0	.8474*	1.4771	.5686	44.38	1.4818	.5630	43.94	1.4933	.5821	45.43
	20.0	1.1063*	1.5245	.4741	53.34	1.5196	.4697	52.84	1.5367	.4851	54.58
Chlor-	30.0	1.0957	1.5192	.4739	53.31	1.5145	.4696	52.83	1.5313	.4849	54.55
benzene	40.0	1.0851	1.5140	.4737	53.29	1.5092	.4693	52.79	1.5269	.4847	54.53
	50.0	1.0739*	1.5086	.4736	53.28	1.5039	.4692	52.79	1.5205	.4847	54.54
	20.0	1.3047	1.5512	.4225	62.07	1.5462	.4186	61.51	1.5640	.4323	63.51
Ortho-	30.0	1.2938	1.5464	.4223	62.05	1.5414	.4185	61.49	1.5592	.4322	63.50
dichlor-	40.0	1.2823	1.5416	.4224	62.06	1.5366	.4185	61.49	1.5543	.4323	63.51
benzene	50.0	1.2709	1.5368	.4224	62.06	1.5318	.4184	61.48	1.5494	.4323	63.51
	20.0	1.2895	1.5464	.4237	62.26	1.5414	.4199	61.69	1.5591	.4336	63.71
Meta-	30.0	1.2785	1.5416	.4236	62.24	1.5366	.4197	61.67	1.5542	.4335	63.69
dichlor-	40.0	1.2675	1.5369	.4236	62.24	1.5318	.4196	61.66	1.5492	.4333	63.67
benzene	50.0	1.2563	1.5318	.4233	62.19	1.5270	.4195	61.63	1.5442	.4332	63.64
	54.0	1.2507*	1.5307	.4243	62.34	1.5257	.4203	61.76	1.5433	.4344	63.82
Para-	55.0	1.2495	1.5302	.4243	62.34	1.5252	.4203	61.75	1.5428	.4344	63.83
dichlor-	60.0	1.2437	1.5276	.4242	62.33	1.5228	.4204	61.76	1.5403	.4344	63.83
benzene	65.0	1.2379*	1.5251	.4242	62.32	1.5203	.4203	61.75	1.5378	.4345	63.83
	20.0	1.4532	--	--	--	--	--	--	--	--	--
1,2,4	30.0	1.4408	1.5667	.3933	71.35	1.5614	.3896	70.67	1.5803	.4028	73.07
trichlor	40.0	1.4288	1.5621	.3934	71.36	1.5570	.3898	70.71	1.5756	.4029	73.09
benzene	50.0	1.4169	1.5581	.3939	71.46	1.5529	.3902	70.78	1.5715	.4034	73.18
	60.0	1.4051	1.5524	.3931	71.31	1.5472	.3894	70.64	1.5656	.4025	73.02
	64.4		1.5452			1.5403			1.5580		
1,3,5	65.0		1.5448			1.5399			1.5577		
trichlor	66.0		1.5442			1.5392			1.5570		
benzene	66.5		1.5439			1.5389			1.5567		

*Perkin, J.C.S. 69, 1191, 1202

Table 13

SPECIFIC AND MOLECULAR DISPERSIONS OF THE CHLORBENZENES

	Temp. t	Density d		Dispersion C-D	Spec. Dis-persion C-D	Mol. Dis-persion C-D	Dis-persion C-F	Spec. Dis-persion C-F	Mol-Dis-persion C-F	Dis-persion D-F	Spec Dis persion D-F	Mol. Dis-persion D-F
	20.0	.8795		.00468	.00532	.4152	.01639	.01864	1.4548	.01172	.01333	1.0404
	30.0	.8689		.00462	.00532	.4152	.01631	.01877	1.4650	.01169	.01345	1.0497
Benzene	40.0	.8582	*	.00465	.00542	.4230	.01630	.01899	1.4821	.01164	.01356	1.0583
	50.0	.8474	*	.00464	.00548	.4277	.01625	.01918	1.4970	.01160	.01369	1.0685
	20.0	1.1063	*	.00479	.00433	.4871	.01709	.01545	1.7381	.01230	.01112	1.2510
Chlor-	30.0	1.0957	|	.00478	.00436	.4905	.01684	.01537	1.7281	.01206	.01101	1.2386
benzene	40.0	1.0851	|	.00483	.00445	.5006	.01670	.01539	1.7314	.01187	.01094	1.2308
	50.0	1.0739	*	.00472	.00440	.4950	.01654	.01540	1.7325	.01182	.01101	1.2386
	20.0	1.3047		.00504	.00386	.5671	.01797	.01377	2.0231	.01292	.00990	1.4545
Ortho-	30.0	1.2938		.00500	.00387	.5686	.01775	.01372	2.0158	.01275	.00986	1.4487
dichlor-	40.0	1.2823		.00496	.00387	.5686	.01757	.01370	2.0128	.01260	.00983	1.4443
benzene	50.0	1.2709		.00491	.00386	.5671	.01762	.01386	2.0364	.01271	.01000	1.4692
	20.0	1.2895		.00499	.00387	.5686	.01775	.01377	2.0231	.01276	.00990	1.4545
Meta-	30.0	1.2785		.00500	.00391	.5745	.01757	.01374	2.0187	.01257	.00983	1.4425
dichlor-	40.0	1.2675		.00503	.00397	.5833	.01739	.01372	2.0158	.01236	.00975	1.4325
benzene	50.0	1.2563		.00484	.00385	.5657	--	--	--	--	--	--
	54.0	1.2507	*	.00500	.00400	.5877	.01760	.01407	2.0672	.01260	.01007	1.4795
Para-	55.0	1.2495	|	.00498	.00399	.5862	.01760	.01409	2.0701	.01262	.01010	1.4839
dichlor-	60.0	1.2437	|	.00490	.00394	.5789	.01752	.01409	2.0701	.01262	.01015	1.4913
benzene	65.0	1.2379	*	.00484	.00391	.5745	.01733	.01400	2.0569	.01249	.01009	1.4825
	20.0	1.4522		--	--	--	--	--	--	--	--	--
1,2,4	30.0	1.4408		.00527	.00366	.6639	.01877	.01303	2.3646	.01351	.00938	1.7016
Trichlor-	40.0	1.4288		.00518	.00363	.6585	.01860	.01302	2.3619	.01347	.00943	1.7106
benzene	50.0	1.4169		.00524	.00370	.6712	.01865	.01316	2.3873	.01342	.00947	1.7179
	60.0	1.4051		.00513	.00365	.6621	.01837	.01307	2.3710	.01319	.00939	1.7034

* Perkin, J.C.S. 69, 1191, 1202

Table 14

Molecular Refractivity Increments

		D		C		F	
		Mol. Refr.	Diff.	Mol. Refr.	Diff.	Mol. Refr.	Diff.
Benzene	20°	44.47	-q	44.06	-	45.51	-
	30°	44.45	-	44.02	-	45.50	-
	40°	44.41	-	43.99	-	45.47	-
	50°	44.38	-	43.94	-	45.43	-
Chlor-	20°	53.34	8.87	52.84	8.78	54.58	9.07
benzene	30°	53.31	8.86	52.83	8.81	54.55	9.05
	40°	53.29	8.88	52.79	8.80	54.53	9.06
	50°	53.28	8.90	52.79	8.85	54.54	9.11
Ortho-	20°	62.07	8.73	61.51	8.67	63.51	8.93
dichlor-	30°	62.05	8.74	61.49	8.66	63.50	8.95
benzene	40°	62.06	8.77	61.49	8.70	63.51	8.98
	50°	62.06	8.78	61.48	8.69	63.51	8.97
Meta-	20°	62.26	8.92	61.69	8.85	63.71	9.13
dichlor-	30°	62.24	8.93	61.67	8.84	63.69	9.14
benzene	40°	62.24	8.95	61.66	8.87	63.67	9.14
	50°	62.19	8.91	61.63	8.84	63.64	9.10
Para- dichlor- benzene	50°	62.35	9.07	61.76	8.97	63.82	9.28
	60°	62.33	9.08	61.76	8.99	63.83	9.33
1,2,4	30°	71.35		70.67		73.07	
Tri-	40°	71.36		70.71		73.09	
chlor-	50°	71.46	9.11	70.78	9.02	73.18	9.36
benzene	60°	71.31	8.98	70.64	8.88	73.02	9.19

Table 15

Molecular Volumes of the Chlorbenzenes at their Boiling Points

	Average apparent wt.	Barometer corr.	Boiling Point corr.	Observed Density	Correction of density	Corrected Density*	Molecular wt.	Molecular Vol.	Difference
Benzene	1.5111	738.6	.91°	.8151 (Calc.)	-.00099	.8141*	78.08	95.91	
Chlor-Benzene	1.8246	738.7	1.03°	.9834	-.00118	.9822	112.53	114.57	18.66
Ortho-dichlor-benzene	2.0816	737.1	1.24°	1.1213	-.00145	1.1198	146.98	131.26	16.69
Meta-dichlor-benzene	2.0609	739.5	1.09°	1.1102	-.00128	1.1089	146.98	132.55	17.98
Para-dichlor-benzene	2.0592	739.7	1.08°	1.1093	-.00127	1.1080	146.98	132.65	18.08
1,2,4, Trichlor-benzene	2.2637	740.1	1.17°	1.2189	-.00137	1.2175	181.43	149.03	16.38

* Young, J.C.S. 55, 504

Summary

The object of this investigation was to determine the two additive properties - molecular volumes and molecular refractivities - for the liquid chlorbenzenes, and to interpret the data and correlate any observed regularities with the electronic formula for benzene of H. S. Fry. The assignment of distinct increments of molecular refractivity to positive and negative chlorine was hoped for, but not realized. The essential portions of the theory of additive properties, the electronic conception of valence, and the formula of benzene have been reviewed, and the molecular volumes determined by Jungfleisch for some of the chlorbenzenes and interpreted by LeBas and H. S. Fry summarized and recalculated. The densities and indices of refraction for the C, D and F lines have been determined (in some cases for the first time) for specially prepared and purified specimens of benzene, chlorbenzene, ortho, meta and para dichlorbenzenes and 1,2,4 and 1,3,5 trichlorbenzenes; the dispersions were measured and the molecular refractivities and molecular dispersions calculated and compared. Advantageous modifications of procedure and calculation are described. Ortho and para dichlorbenzenes are shown not to have the same molecular refractivity, contrary to what would be required if the electronic formula for benzene of H. S. Fry were correct and if atomic refractivities depended

only upon the electropositive and electronegative functions of the atoms. Definite increments of molecular refractivity could not be assigned to positive and negative chlorine, and no marked periodicity is observable. The molecular volumes at the boiling points of these chlorbenzenes have been determined and found to differ from those calculated by Jungfleisch and recalculated by LeBas sufficiently to remove the periodicity pointed out by these investigators. The regularities pointed out by Jungfleisch are not very striking and the validity of the recalculation of LeBas is questioned. The molecular volumes of ortho, meta and para dichlorbenzenes have been compared, and found to increase in this same order, just like molecular refractivities. The conclusion is drawn that it is not possible to assign definite increments in molecular volumes based on the electronic functions of the atoms only, and that configuration of the molecule must be the determining factor.

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