1942

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Recommended Citation

Plucknett, William Kennedy, "The effect of various organic radicals on the atomic refractivities of the halogens " (1942). *Retrospective Theses and Dissertations*. 12985.
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THE EFFECT OF VARIOUS ORGANIC RADICALS ON THE ATOMIC REFRACTIVITIES OF THE HALOGENS

by

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A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Plant Chemistry

Approved:

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Iowa State College
1942

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INTRODUCTION

Molar Refraction

The effect of chemical constitution on the refractive properties of compounds has been extensively studied since Gladstone and Dale (1) empirically established the formula which bears their name; namely,

$$\frac{n-1}{d} = r = \text{a constant,} \qquad (1)$$

where n is the refractive index, d is the density, and r is termed the specific refraction. Their studies, beginning in 1858, marked the first successful attempt to systematize refraction data of compounds. They succeeded in showing that r was reasonably constant for any one given compound over a range of temperatures. Since it is customary for the chemist to express constants in terms of gram-molecules, molecular refraction, obtained by multiplying the above constant by the molecular weight of the compound, largely replaced specific refraction.

The formula of Gladstone and Dale was extensively used until it was superseded by the theoretically deduced Lorentz (2) and Lorenz (3) formula,

$$\frac{n^2-1}{n^2+2}\,\frac{M}{d} = R \text{ (a constant)} \qquad (2)$$

This constant has proved to be independent of temperature and pressure and quite largely of physical state. It is not, however, independent of the wave-length of light used. This will be discussed later under Dispersion.

It was early recognized that molecular refraction is an additive property, as shown by the fact that isomers have the same or nearly the same constant. By comparing the molar refractions of a series of compounds with those of compounds differing by only one atom or group of atoms, the refractivities due to the atom or group can be calculated; for example, comparing ethers with hydrocarbons for oxygen, or successive members of an homologous series for the CH_2 group. In this way tables of atomic refractivities have been built up. Much of this early work was done by Brühl (4), but his tables have now been largely superseded by those of Auwers and Eisenlohr (5).

That molecular refraction is not entirely an additive property but also a constitutive property is made clear by noting the usually small, but occasionally large, discrepancies in the values calculated from the atomic refractivities and those actually observed. Certain constitutive features are sufficiently constant to allow definite values to be assigned to them; for example, the double and triple bonds; ring formation; primary, secondary, tertiary, and nitrile nitrogens; carbonyl, ether, and hydroxyl oxygens; etc. The constitutional effect on molar refraction has, in some cases, proved useful in establishing molecular structure.

Dispersion

As has been noted, the molecular refraction of a compound is not independent of the wave-length of light used. However, the value always varies in a regular manner with the wave-length. Korff and Breit (6) give an excellent review on optical dispersion, treating both the early theories and the modern quantum theory. Cauchy in 1836 deduced the equation,

$$n = a + \frac{b}{\lambda^2} + \frac{d}{\lambda^4} + \frac{f}{\lambda^6} + \cdots\cdots\cdots, \qquad (3)$$

where a, b, d, f, etc. are constants, on the basis of the elastic theory of ether. This equation serves reasonably well for most transparent substances, but fails to account for "anomalous" dispersion. It is observed experimentally that as one approaches an absorption line from the long wave-length side, the refractive index increases sharply, while approaching from the short wave-length side it decreases sharply. To account for this, Sellmeier (7) deduced the equation,

$$n^2 = 1 + \frac{a\ \lambda^2}{\lambda^2 - \lambda_0^2}, \qquad (4)$$

where λ_0 represents the absorption line concerned. Since most compounds have several absorption lines, the equation becomes,

$$n^2 = 1 + \Sigma\ \frac{a\ \lambda^2}{\lambda^2 - \lambda_0^2}, \qquad (5)$$

where the summation is taken over all the absorption lines. The Cauchy formula is seen to be a special case of this equation when far removed from absorption lines. The Sellmeier equation gives good results when not too near resonance. It is seen that this equation yields a discontinuity for the refractive index at the absorption line, while this is not true experimentally. Ketteler and Helmholtz introduced a "frictional" or "damping" term into the Sellmeier equation to avoid this discontinuity,

$$n^2 = 1 + \sum \frac{a\lambda^2}{\lambda^2 - \lambda_0^2 + b^2\lambda^2}. \qquad (6)$$

This equation fits dispersion curves within experimental error.

Drude and Voigt led the way to a new deduction, and Lorentz (8) made the rigorous development from classical mechanics of a dispersion equation relating refractive index to the absorption coefficient of the substance. He obtained,

$$n^2(1-ik)^2 = 1 + \sum \frac{N\frac{e^2}{m}}{\nu_0^2 - \nu^2 + iG\nu}, \qquad (7)$$

where k is the absorption coefficient, i is $\sqrt{-1}$, N is the number of dispersion electrons per unit volume, e is the charge on the electron, m is its mass, ν_0 is the absorption frequency, ν is the frequency of light used, and G is the damping constant. Assuming only one important absorption frequency and separating equation (7) into its real and imaginary parts, two equations are obtained,

$$n^2(1-k^2) = 1 + \frac{Ne^2}{2m} \cdot \frac{\nu_0^2 - \nu^2}{(\nu_0^2 - \nu^2)^2 + G^2\nu^2}, \qquad (8)$$

and

$$2n^2k = \frac{Ne^2}{2m} \cdot \frac{G\nu}{(\nu_0^2 - \nu^2)^2 + G^2\nu^2}. \qquad (9)$$

These equations may be solved for n and k and are found to agree excellently with the experimental values. However, these equations are rather cumbersome, and it is seen that if one neglects the damping factor, which is important only within the absorption line, equation (7) reduces to the Sellmeier equation.

Of the many dispersion equations which have appeared, Pickard and Hunter (9) have adopted a modified form of Sellmeier's equation as being most suitable for organic compounds,

$$n^2 = a^2 + \frac{b^2}{\nu_0^2 - \nu^2} . \tag{10}$$

By measuring the refractive index at three different wave-lengths the three constants may be evaluated.

The usual method of comparing refractivity of compounds is to choose some arbitrary wave-length, usually the Na D line, because of its easy availability, and to make all comparisons at this one point. A glance at the variety of dispersion curves exhibited by organic compounds should make clear the objection to such an arbitrary procedure. Any other spectral line selected would give different results because of the divergence of the dispersion curves. It would be a much sounder procedure to make comparisons at points on the dispersion curves which are equidistant from the nearest absorption band, or better yet, to extrapolate the curves to infinitely long wave-lengths where all would be equidistant from absorption bands. The same objections may be raised to selecting an arbitrary interval of wave-lengths for all compounds for the purpose of comparing "dispersivity" of these compounds.

Relation of Molar Refraction to Molar Polarization

When a dielectric is placed between the plates of a condenser, the capacity of the condenser increases due to the energy required to set up small dipoles in the dielectric. The dielectric constant is defined as the ratio of the capacity of the condenser with the dielectric between the plates to its capacity when the space is evacuated,

$$\epsilon = \frac{C_x}{C_v}. \qquad (11)$$

Molar polarization as defined by the Mosotti-Clausius equation,

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d}, \qquad (12)$$

is not entirely independent of temperature for polar compounds, and its dependence on temperature is expressed by the familiar Debye equation,

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = \frac{4}{3} \pi N \alpha + \frac{4}{3} \pi N \left(\frac{\mu^2}{3KT}\right). \qquad (13)$$

Where N is Avogadro's number, α is defined as polarizability, μ is dipole moment, k is Boltzmann's constant, and T is temperature. Polarizability, α, is defined as the ratio of the electric field strength acting on the molecule to the induced electrical moment in the molecule,

$$\alpha = \frac{F}{m}, \qquad (14)$$

and is, therefore, a measure of the deformability of the molecule.

If one examines the nature of the dipoles set up in the dielectric when under the influence of an electric field, it becomes clear why the molar polarization of polar molecules is dependent on temperature. The dipoles are of two types, induced and permanent. The permanent dipoles tend to line up under the influence of an electric field, but this is opposed by the kinetic action of the molecules which, of course, varies with the temperature.

The total polarization, then, is made up of two parts, that due to orientation, the second term in the Debye equation, and that due to distortion, the first term in the Debye equation,

$$P = P_d + P_o \,. \qquad (15)$$

If one examines the polarization due to distortion, one sees that it can be further broken down to that due to electron displacement, P_e, and that due to atom displacement, P_a,

$$P_d = P_e + P_a = \tfrac{4}{3}\pi N\alpha. \qquad (16)$$

The molar refraction of light, which is an oscillating electric field, in the ultra-violet and visible regions is a measure of the deformability of the electron shell, but is no measure of the atomic polarization, because the atoms are too sluggish to react to such high frequency oscillations. However, molar refraction measured in the infra-red region is a measure of the distortion polarization due to both. If it is measured through the infra-red region and extrapolated to infinitely long waves, it is identical with the distortion polarization; thus,

$$R_\infty = \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \frac{M}{d} = P_d = \tfrac{4}{3}\pi N \alpha . \qquad (17)$$

This fact is utilized in measuring the dipole moments of compounds. In actual practice it is difficult to measure refractive index in the infra-red, and the usual procedure is to get the molar refraction for the Na D line and arbitrarily add five percent for the atomic polarization (10).

It might be well at this point to say a word concerning the physical interpretation of molar refraction. A glance at the Lorentz-Lorenz formula shows that its units are cubic centimeters. This suggests that it may be the actual volume occupied by the molecules themselves in a mole. That this is a legitimate interpretation is borne out by the fact that ionic radii calculated on this basis by Fajans (11) are of the same order of magnitude as those found by experimental methods such as electron diffraction (12).

Studies on Inconstancies of Atomic Refraction

Not much has been published on attempts to systematize inconstancies of atomic refractions. Krause and co-workers have published several papers on changes in refractivities of the metal atoms in some series of organometallics. Their studies include compounds of zinc (13), tin (14), lead (15), silicon (16), cadmium (17), and mercury (18). They used the H_α and the Na D lines for illumination. To obtain the refractivity of the metal atoms, they subtracted the molar refractions of the substituted groups as calculated from Eisenlohr's table of atomic refractivities from the molar refractions of the compounds. Their results for the Na D line are summarized in table I. They concluded that the mass of the substituted groups was the important factor in influencing the atomic refractivity of the metal atom. In all cases they found the atomic refractivity increases as the molecular weight of the compound increases.

Carr (19) determined the atomic refraction of mercury in a series of R-Hg-CN compounds and in a series of R-Hg-R compounds in acetone solutions, since most of the compounds are solids. He obtained the value for the mercury atom by subtracting the measured value of the molar refractions of the R-CN and R-R compounds from that of the corresponding mercury compounds. He found a correlation between the atomic refraction of mercury and the decomposition temperature of the compound. Those compounds having a value for mercury approaching the value found for free mercury vapor have a low decomposition temperature. His results are summarized in table II. The accuracy of these determinations is limited since they were made with very dilute solutions, and small

Table I. Refractions of the metal atoms for the Na D line in some organometallic compounds.

Compound	At. ref. of metal	Compound	At. ref. of metal
Zinc		**Lead**	
$(C_2H_5)Zn(n\text{-}C_3H_7)$	9.004	$(CH_3)_4Pb$	17.31
$(n\text{-}C_3H_7)_2Zn$	9.352	$(C_2H_5)_4Pb$	18.10
$(C_2H_5)Zn(i\text{-}C_4H_9)$	9.365	$(C_3H_7)_4Pb$	18.78
$(n\text{-}C_3H_7)Zn(i\text{-}C_4H_9)$	9.529	$(i\text{-}C_4H_9)_4Pb$	19.12
$(i\text{-}C_4H_9)_2Zn$	9.640		
		Cadmium	
$(i\text{-}C_4H_9)Zn(i\text{-}C_5H_{11})$	9.757	$(CH_3)_2Cd$	12.61
$(i\text{-}C_5H_{11})_2Zn$	9.825	$(C_2H_5)_2Cd$	13.00
		$(n\text{-}C_3H_7)_2Cd$	13.21
Silicon			
$(C_2H_5)_3SiC_6H_4Cl$	7.74	$(C_4H_9)_2Cd$	13.21
$(C_2H_5)_3SiC_6H_4Br$	8.32	$(i\text{-}C_5H_{11})_2Cd$	13.33
$(C_2H_5)_3SiC_6H_4I$	9.89		
		Mercury	
$(n\text{-}C_3H_7)_3SiC_6H_4Cl$	8.26	$(CH_3)_2Hg$	12.282
		$(C_2H_5)_2Hg$	12.591

Table II. The atomic refractivity of mercury and decomposition temperature for some organomercurials.

Compound	Decomposition temperature (degrees)	Atomic refraction of Hg
CH_3HgCN	260-270	10.19
C_2H_5HgCN	245-265	11.53
$C_6H_5CH_2HgCN$	208-216	13.07
o-$ClC_6H_4CH_2HgCN$	210-215	13.07
C_6H_5HgCN	above 250	10.58
p-$CH_3C_6H_4HgCN$	above 250	9.35
$(C_3H_7)_2Hg$	190	12.25
$(C_6H_5CH_2)_2Hg$	170	13.81
$(C_6H_5)_2Hg$	300	11.42
Hg vapor		13.95

errors in refractive index and density measurements would be greatly magnified in the values of the molar refractions of the mercury compounds obtained. However, the trend is significant.

Decker (20) calculated the atomic refraction of mercury in di-methyl mercury and di-ethyl mercury from measurements in the gaseous phase made by means of an interferometer. He subtracted the measured molar refractions of ethane and butane, respectively, from those of the mercury compounds. He obtained a value of 12.95 for the mercury atom in di-methyl mercury, and a surprising value of 14.93 in di-ethyl mercury.

Johnson (21) determined the atomic refraction of phosphorus for the Na D line in various aliphatic and aromatic substituted compounds by subtracting the values of the substituted groups, calculated from atomic refractivities, from the molar refraction of the compounds. The series of compounds used to determine the value for phosphorus varied in more than one substituent simultaneously, and thus have very little comparative value for determining the effect of any individual substituent group. For the aliphatic substituted compounds he obtained values ranging from 6.84 for P in $(C_2H_5.O)_3P$ to 8.67 in $(C_2H_5)_3P$. The refraction of P in his aromatic compounds ranged from 9.87 to 10.65. It is interesting to note that compounds containing the $\equiv P=O$ group gave values for this group that were lower than the values for P itself in the corresponding compounds without the semi-polar bonded oxygen. For example, the value for the $\equiv P=O$ group in $(C_2H_5.O)_3P=O$ was found to be 5.93 compared to the value of 8.67 for P in $(C_2H_5.O)P$.

Johnson (21) summarizes values obtained for As by Gryszkiewicz-Trochimowski and Sikorski in a similar manner. Only one constituent is varied in this series and thus it has some value in determining the effect of specific substituent groups. These data are presented in table III.

Stevels (22) made an intensive study of the refraction data of halogenated methane derivatives. He came to the

Table III. The atomic refractivity of arsenic in some organo-arsenicals.

Compound	Atomic refraction of As
Phenyl-dichlorarsine	11.36
m-Chlorophenyl-dichlorarsine	11.49
p-Bromophenyl-dichlorarsine	11.75
m-Bromophenyl-dichlorarsine	11.36
β-Chlorovinyl-dichlorarsine	11.49
β,β′-Dichlor-divinyl-chlorarsine	12.20
β,β′,β″-Trichlor-trivinyl-arsine	12.47

conclusion that successively substituting halogen atoms on methane for hydrogen atoms caused appreciable increases in the bond refractivities of both the C-H and C-X bonds. He further concluded that the C-H bonds in CH_3X increase in refractivity as the atomic weight of X becomes larger. Some of his data are summarized in table IV.

Table IV. The refractivities of C-H and C-X bonds in some halo-substituted methanes.

Substance	Ref. of C-H	Ref. of C-X	Substance	Ref. of C-H	Ref. of C-X
CH_4	1.65	--	CH_4	1.65	--
CH_3Cl	1.77	6.19	CH_3F	1.76	1.65
CH_2Cl_2	1.89	6.33	CH_3Cl	1.77	6.19
$CHCl_3$	2.01	6.47	CH_3Br	1.93	8.19
CCl_4	--	6.61	CH_3I	1.95	13.26

However, values he found for some of the compounds differ markedly from those found by other careful investigators.

It is noted that most investigators in studying inconstancies of the refraction of any given atom obtain their values for that atom by subtracting values of the substituted groups, as calculated from atomic refractivity tables, from the molar refractions of the compounds containing the given atom. It would seem to the author to be a much sounder procedure to measure the molar refraction of the parent hydrocarbon and subtract this from the value for the compound containing the atom in question, making allowance for the hydrogen atom or atoms replaced. Atomic refractivity tables are admittedly only average values; constitutional environment does make small differences in all of them. By the former method, all these deviations from the average are thrown into the value calculated for the atom in question. By the latter method, nearly all these deviations would cancel out, and a more significant value should be obtained for the given atom.

Atoms of high atomic weight are much more highly polarizable than those of lower atomic weights and should be much more sensitive to effects of substituted groups. It was thought by the author that the iodine atom with an atomic refractivity given by Auwers and Eisenlohr (5) of 13.900 should serve to register these effects with measureable differences in its refraction. It was thought further that any series arranged on this basis should be capable of being checked by corresponding series of bromides and chlorides. Preliminary calculations made from the values given by the International Critical Tables for the organic halides failed to give any regularity when effects on the iodide, bromide, and chloride atoms were compared, although appreciable variations in the atomic refractivity values were found in all three cases. However, literature values of refractive indices and densities of even the fairly common compounds differ so markedly that it would seem necessary for all measurements to be made by the same observer and with the same instruments if they are to have any comparative value.

STATEMENT OF THE PROBLEM

A series of organic iodides, bromides, chlorides, and hydrocarbons were chosen for refractometric studies in order to ascertain whether the varying of the organic radical causes measureable variations in the atomic refractions of the halogens, and if such measureable variations are found, to determine if the radicals when arranged in order of effect on one halogen atom retain the same order with the other halogens.

It was further sought to determine if measureable differences in effect are observable between isomeric ortho- and meta-substituted halobenzenes.

It was also desired to obtain the molar refractions of the compounds for various spectral lines in the visible region in order to determine the effect of wave-length on the order of the organic radicals in their effects on the atomic refractions. Dispersion equations for each compound were desired in order to extrapolate the molar refractions to infinitely long wave-length for comparative purposes.

EXPERIMENTAL

General Methods

Purification of Compounds

The most important prerequisite to measuring physical constants of compounds is to secure the compounds in a high degree of purity. All compounds used were Eastman C. P. chemicals except dioxane, Carbide and Carbon U. S. P. grade; p-bromotoluene, made by Dr. Theodor Schuchard for the Henry Heil Chemical Co.; and benzyl chloride, a Baker's Analyzed grade.

Liquids:--A special fractionating column was designed and made for the liquids. The column was made of Pyrex glass and measured 60 cm. from the base to the outlet arm. The outside diameter of the column was 28 mm. A Hopkins-type reflux condenser was sealed into the upper 16 cm. of the column in order to control the reflux ratio. The rest of the column consisted of a 12 mm. tube sealed coaxially into the outer tube. The inner surface of this outer jacket was silvered by the usual method, and the space evacuated to a fraction of a millimeter pressure by means of a mercury pump. The whole column was then insulated with a one-half inch steam-pipe insulation. The inner tube was packed with one-eighth inch, single-turn, glass spirals. The outlet tube consisted of an 8 mm. tube which extended out perpendicularly from the column for about 1 cm., then turned upward, expanded into a 12 mm. tube for a length of 2 cm. to serve as a bath for a thermometer bulb, then contracted back to 8 mm. and extended upward about 30 cm. to serve as a sheath for the thermometer. The upper end was again expanded to accommodate a rubber stopper for the thermometer. At the upper end of the lower expansion bulb was sealed a 1 cm. tube which extended downward at an angle and sealed to a Liebig-type condenser. The lower end of the condenser was anchored to the base of the column by means of a glass rod sealed at both ends. The column was made with glass seals throughout to permit vacuum distillation.

The liquids to be distilled were placed in a 250 ml. round-bottomed flask packed with glass wool to prevent bumping.. The flask was connected to the base of the column by means of a well-rolled, charred, cork stopper. The receiving flasks were 125 ml. Erlenmeyer flasks fitted with side arms near the neck of the flasks. These were connected to the condenser by means of a rubber stopper.

The liquids were heated by means of an oil bath, and the vapors allowed to reflux in the column for two hours to bring the column to equilibrium conditions. The reflux was controlled by blowing compressed air through the reflux condenser. After the column had reached equilibrium, the rate of air flow through the reflux condenser was reduced to permit one drop of distillate to form for about fifteen to twenty drops of reflux return. The distillations were carried on at a slow pace, one drop of distillate condensing every ten to fifteen seconds. The middle one-third of the distillate was saved, and re-distilled, and about the middle three-fifths of this distillate was saved for the physical measurements. In most cases, two distillations were considered sufficient. In no case did the temperature range of the distillate exceed two-tenths of a degree, and in most cases no change in the temperature readings could be noticed at all. However, changing the rate of distillation did have some effect on the temperature. Rapid distillation would cause a rise of one to two degrees. A calibrated Wilkens-Anderson 360° thermometer was used.

All the liquids were dried at least forty-eight hours over sodium wire, anhydrone, or sodium sulphate before distillation as is indicated for each compound.

Solids.--All the solids were purified by successive recrystallizations from absolute alcohol. A sharp melting point was taken as the criterion of purity. In some cases, two recrystallizations were sufficient, and in others, as many as five or six were required. Melting points were taken on the standard micro melting point aparatus consisting of an electrically heated aluminum block in which is imbedded the bulb of a thermometer.

All compounds were dried over $CaCl_2$ at least forty-eight hours in a vacuum desiccator, evacuated to one to five millimeters.

Measurement of Density

All density measurements were made with two capillary pycnometers of about 10 and 14 ml. capacities blown from Pyrex capillary tubing of about 1mm. bore. The necks were about 65 mm. long and fitted with ground glass caps. They contained about five-tenths ml. expansion bulbs just beneath the caps, and were marked about half way up with a sharp ring by means of a carborundum crystal.

The pycnometers were filled by means of a capillary funnel drawn from 20 mm. glass tubing. They were filled above the mark and placed in a constant temperature water bath held at 20.00° C. After remaining in the bath for one-half hour, the excess liquid was drawn out with a capillary glass pipette; the walls were allowed to drain for ten minutes, and the finaladjustment made with a fine capillary glass tube. They were then taken from the bath, rinsed with distilled water, wiped thoroughly dry with a clean linen towel, and set in the balance case for one-half hour to allow them to reach equilibrium. A third pycnometer, which was always used as a tare, was rinsed with distilled water, wiped thoroughly dry, and set in the balance case beside the filled pycnometer.

All weighings were made on a Christian Becker, four-place chainomatic balance by the method of swings. The sensitivity of the balance was about four-tenths of a milligram per scale division. The weights were calibrated by substitution on the same balance against a set of weights that had been calibrated by the Bureau of Standards. The chain was calibrated at ten milligram intervals. The corrections on the weights were used throughout.

The constant temperature bath consisted of a five-gallon crock filled with distilled water and fitted with an efficient stirrer. The thermo-regulator was of the mercury expansion type, number TR-10 made by the H. B. Instrument Co. This controlled a relay on which was attached a glass tube through which a stream of water from the tap was constantly running. When the electrical circuit was closed, the glass tube directed the stream of water through a copper coil placed in the bath. When the circuit was open, the stream of water was directed into the sink. The temperature of the bath did not vary over two-hundredths of a degree. It was measured by means of a Wilkens-Anderson 50-degree range, tenth-degree thermometer which had been checked against a Fisher Scientific Co. 10-degree range, tenth-degree, precision thermometer.

After each usage, the pycnometers were rinsed several times with acetone and placed in a 110° oven. While they were in the oven a stream of compressed air was blown through them by means of a capillary tube.

They were calibrated with freshly prepared conductivity water made by the usual permanganate method. Weighings were corrected to vacuum in the manner given under the section on Calculations. The density of water was taken as 0.998203 at 20.0° as given by the Chemical Rubber Co.'s *Handbook of Chem-*

istry and Physics. The data obtained in calibrating the pycnometers are given in table V. The weights given are in addition to the tare. These values were checked from time to time throughout the course of the investigation.

Table V. Calibration of the pycnometers.

Pycnometer #1		Pycnometer #2	
Weight of empty pyc.	Weight of pyc. + water	Weight of empty pyc.	Weight of pyc. + water
5.9549 gm.	16.0116 gm.	2.4836 gm.	16.7974 gm.
5.9548	16.0116	2.4835	16.7976
5.9548	16.0116	2.4836	16.7975
5.9551			
5.9550			
Av. 5.9549	16.0116	2.4836	16.7975
Wt. H_2O in air = 10.0567 gm.		Wt. H_2O in air = 14.3139 gm.	
Wt. H_2O in vac.= 10.0674		Wt. H_2O in vac.= 14.3291	
Volume = 10.0855 cc.		Volume = 14.3549 cc.	

Measurement of Refractive Index

General:--There are four common types of instruments designed to measure the refractive index of liquids to a high degree of precision, the Abbè refractometer, the immersion refractometer, the Pulfrich refractometer, and the spectrometer fitted with a hollow prism. Of these, only the last two are capable of measuring dispersion. Since it was one of the objectives of the author to measure dispersion, and since a Pulfrich refractometer was not available, the spectrometer and hollow prism method was chosen.

The Spectrometer:--A Gaertner type L4020 spectrometer was generously loaned by the Physics Department. The telescope was attached to a movable, calibrated, circular base 14 cm. in diameter. The scale was fitted with a vernier which enabled one to read angles to twenty seconds. As originally designed, the table of the instrument could not be rotated by fine adjustment independently of the scale. This was an objectionable feature since it was necessary to set the prism at the angle of minimum deviation for each spectral line, and a new zero reading for each line would have been necessitated if the table could not have been rotated independently of the scale. The instrument was redesigned, the inner scale anchored to the collimator support, and the table anchored to an arm which was fitted with a fine adjustment screw. This enabled the table to be finely adjusted independently of the scale.

The telescope was adjusted for parallel light by focusing it on a distant object. It was then replaced on the instrument, lined up with the collimator, and the collimator adjusted for parallel light as determined by the sharpness of the image of the slit when viewed through the telescope. The telescope was made perpendicular to the axis of the rotation of the table by placing a plane, parallel glass plate upright on the table, setting the telescope perpendicular to it as determined by the coincidence of the reflected image of the cross-hairs and the cross-hairs themselves as obtained by use of the Gauss eye-piece, then rotating the table through an angle of 180° and again observing the position of the image of the reflected cross-hairs with respect to the cross-hairs themselves. If they did not coincide, both the level of the telescope and the level of the table were adjusted to bring them into coincidence. The table was then rotated to its original position and the image and the cross-hairs again brought into coincidence by adjusting both levels. This process was repeated until coincidence was observed without readjustment by rotation of either the telescope or the table through an angle of 180°. The collimator was made perpendicular with the axis of rotation of the table by covering the upper half of the slit, and adjusting its level until the line of demarcation on the slit made by the covering appeared in the center of the field as viewed through the telescope.

In order to maintain a constant temperature on the spectrometer table, a tin can 11 cm. in diameter and 20 cm. high with the bottom removed and fitted with a tight lid was placed over the table. A hole was cut in the side of the can for the collimator tube, and a slit 3 cm. wide and extending through an angle of 75° was cut for the telescope. This slit was fitted with a sliding door in which was cut a hole the size of the telescope tube. The inside of the can was lined with close-fitting coils of 3 mm. brass tubing. The coils were separated by 2 cm. at the level of the telescope and collimator. The outside of the can was covered with asbestos paper. The temperature could quite easily be maintained at 20.0° by regulating a slow stream of tap water through the coils. It was measured with a Fisher Scientific Co., 10-degree range, tenth-degree, precision thermometer which was tightly stoppered in a hole in the lid of the can. The bulb of the thermometer was placed about half way up the prism and removed from it about 5 mm.

The prism was held in place on the table by a triangular hole cut in a one-eighth inch rubber mat glued to the table.

The Prism:--Being unable to obtain a small hollow prism from any of the scientific instrument companies, the author constructed one. A small glass-stoppered bottle of about 4 ml. capacity was selected. Two sides were ground off the bottle to make an angle of about 60° by means of a cast iron wheel with 60-mesh carborundum.

A plane, parallel microscope slide was used for the windows. The slide was tested for parallelism by placing it upright on the spectrometer table and, by means of the Gauss eye-piece, viewing the images of the reflected cross-hairs from the two sides of the slide. If the two images were far enough apart to be measureable on the spectrometer (corresponding to about 10" of non-parallelism), the slide was rejected. The slide was tested for optical clarity by setting it upright on the table and viewing the transmitted image of the slit through the telescope. If the image was not sharp, the slide was rejected. Out of a box of 100 slides only three were found to pass the above tests. The edges of the windows were roughened and cemented onto the prism with water glass.

In grinding the bottle, no special pains were taken to make the sides exactly perpendicular to the base of the bottle, since it is only necessary that the faces be in a perpendicular position when on the spectrometer, and the table of the spectrometer could easily be adjusted to provide for this. After the telescope and the collimator had been adjusted perpendicular to the axis of rotation of the table by the method previously described, the prism was put in place on the table and the level of the table adjusted until both sides were perpendicular as determined by the Gauss eye-piece. Since the prism was always put on the table in the same position, one adjustment was all that was necessary.

In finding the prism angle, two methods were used, the usual Gauss eye-piece method for the two sides, and that of measuring the angle of deviation of light by the prism when filled with standard liquids. The refractive indices of the reference liquids used were measured with a Bausch and Lomb dipping refractometer illuminated with the Na D line. The average value for the prism angle was found to be 64° 37' 32". The substances used and the values of the angle obtained are given in table VI. The refractive index of air was taken into account in obtaining these values and was taken as 1.00027 as given by the International Critical Tables. The manner of correcting for the refractive index of air is given in the section on Calculations.

Table VI. Calibration of prism angle.

Substance	Ref. Index	Prism Angle		
		°	'	"
Dioxane + Eth. Acet.	1.40427	64	37	30
Dioxane	1.42238	64	37	48
CCl_4	1.46024	64	37	42
C_6H_6	1.49952	64	37	18
	Gauss eye-piece method	64	37	32
	Average	64	37	32

After each use the prism was rinsed several times and placed on top of an oven for several hours to dry.

<u>The Light Source</u>:--Seven spectral lines, covering the visible region, were used for all compounds. The seven lines used and their wave-lengths in Ångstrom units were:

H α	6563	H β	4861
Na D	5893	Hg blue	4358
Hg yel.	5770	Hg viol.	4047
Hg grn.	5461		

In certain cases, the Hg blue-green line, 4960, was used in addition.

The hydrogen lines were obtained by means of a discharge tube made from Pyrex glass. It consisted of a capillary tube of 2 mm. inside diameter and 35 mm. long on the ends of which were sealed 12 mm. glass tubings 4 cm. long. The electrodes consisted of seven or eight turns of closely coiled number 14 aluminum wire which were pinched onto tungsten wires sealed through the ends of the tube with nonex glass. The distance between the electrodes was approximately 8 cm. On the side of one of the ends was sealed a glass tube, which was in turn sealed to about a 50 ml. expansion bulb. On this was sealed a tube containing a stopcock. The expansion bulb served to keep the pressure fairly constant in the tube as it heated up due to discharge.

Water vapor was used in the tube instead of hydrogen gas in order to keep the band spectra at a minimum. A few drops of water were placed in the tube and the tube evacuated with an oil pump to a fraction of a millimeter until the lines reached a maximum brightness. The stopcock was then closed.

A Sola gas-tube transformer number R330 with a secondary voltage of 3000 was used for the excitation.

The sodium line was obtained from an electric sodium vapor light made by Franz Schmidt in Germany. This burned out during the course of these experiments, and a new source was devised by supporting a sodium chloride impregnated asbestos pad on a Bunsen burner with a nichrome wire. This served very well.

The mercury lines were furnished by a 100-watt, General Electric type H4 mercury vapor lamp. The lines were extremely bright.

The Readings:--After the prism had been filled with the liquid to be measured, it was placed on the spectrometer table. The table was turned to the approximate minimum deviation angle for sodium light, and then the lid placed on the constant temperature bath. The temperature was brought to 20.0° and held there for one-half hour before any readings were taken. It was not allowed to fluctuate more than .05 of a degree during the readings.

After the prism had reached equilibrium, the readings were taken. The cross-hairs were always set on the stationary side of the slit image. Before taking any readings on each line, the table was rotated by means of the fine-adjustment screw until the prism was set at the angle of minimum deviation for that line. Two or three readings were considered sufficient for each line if they did not vary over 20", as close as the spectrometer could be read. After a series of readings had been taken on each line, they were all gone over once more as a check. If this last value checked within 20" of the first readings, no more readings were taken, but if the variation was greater than that, several more were taken. After all the readings had been taken and checked, the prism was removed and the zero reading checked three or four times. The angle of deviation was obtained by subtracting the zero reading from the average of the other readings for each line. The method of calculating the refractive index from this is discussed under the section on Calculations.

Preparation of Solutions

For substances whose molar refractions were measured in solution, two concentrations were used, 0.2 mol fraction and

0.4 mol fraction. The solute was weighed in a weighing bottle in which was kept a short stirring rod throughout all the weighings. The approximate calculated weight of solvent was added and the solute allowed to dissolve with occasional stirring with the stirring rod. After the solute was all dissolved, the solution was allowed ten minutes to reach room temperature, since the solution usually cooled during the dissolving due to the heat of solution. The solution was vigorously stirred and an accurate weighing made to obtain the exact amount of solvent. The solution was quickly poured into the capillary funnel used to fill the pycnometers, and the top of the funnel was covered. While the solution was draining into the pycnometer, enough of it was withdrawn from the funnel by means of an eye-dropper to fill the prism. The eye-dropper was dipped at least one centimeter below the surface of the solution in the funnel each time to avoid having the concentration changed by evaporation from the surface. Enough of the solution was always made up so that four or five milliliters remained in the funnel when the pycnometer was filled. This prevented the solution that went into the pycnometer from changing concentration due to evaporation at the surface of the solution in the funnel. It required three or four minutes to fill the pycnometer.

All weights were reduced to vacuum by the methods indicated in the section on Calculations. The densities of the solids needed in these calculations were estimated by extrapolating the densities of the two solutions taken at the two concentrations to a mol fraction of one. This was sufficiently accurate for this purpose.

Calculations

Correction of Weights to Vacuum:--The true weight of a body calculated to a vacuum is given by the expression (23)

$$W_v = W_a(1 + \frac{0.0012}{d} - \frac{0.0012}{8.5}) \, , \qquad (18)$$

where W_v is the weight in vacuum, W_r is the weight in air, d is density of the body being weighed, 0.0012 is the average density of air, and 8.5 is the density of brass weights. By taking extreme cases, the fluctuations in the density of the air due to changes in humidity and barometric pressure were found to be insignificant.

Combining the first and last terms of equation (18),

$$W_v = W_a(0.99986 + \frac{0.0012}{d}) \, . \qquad (19)$$

For a density of about 1.8, the highest density of any of the compounds or solutions used, the correction on the true density proves to be about five parts in ten thousand.

Refractive Index:--The relation between the refractive index and the angle of minimum deviation with a prism is given by

$$n_1 = \frac{\sin \frac{A + D}{2}}{\sin \frac{A}{2}} \qquad (20)$$

where A is the prism angle, and D is the angle of minimum deviation for the particular line in question. This, however, is not the true refractive index, but only the refractive index as compared to that of air. The true value, that is, compared to a vacuum, is given by

$$n = n_a n_1 \tag{21}$$

where n_a is the refractive index of air, 1.00027. Taking the prism angle as 64° 37' 32", the value of $\frac{n_a}{\sin(A/2)}$ is 0.187127. Therefore, the refractive index for any spectral line of wavelength λ for any given substance is given by

$$n_\lambda = 0.187127 \sin \frac{A + D_\lambda}{2}. \tag{22}$$

Six-place sines were taken from tables compiled by Gifford (24).

Molar Refraction:--Molar refractions of pure compounds were calculated by means of the Lorentz-Lorenz formula,

$$R_\lambda = \frac{n_\lambda^2 - 1}{n_\lambda^2 + 2} \frac{M}{d}, \tag{23}$$

where M is the molecular weight of the compound calculated from the 1941 values of the International Atomic Weights, and d is the density of the compound recalculated to a vacuum.

The molar refraction of a solution of x_1 and x_2 mol fractions, respectively, of two substances of molecular weights M_1 and M_2 is defined as (25)

$$(R)_{1,2} = \frac{n_{1,2}^2 - 1}{n_{1,2}^2 + 2} \frac{x_1 M_1 + x_2 M_2}{d_{1,2}} \tag{24}$$

and is related to the individual refractions by

$$(R)_{1,2} = x_1R_1 + x_2R_2. \qquad (25)$$

Thus, if the molar refraction of the solution be measured and the molar refraction of one of the components be known, the molar refraction of the other component can be calculated from the composition of the solution.

If equation (25) be solved for R_2 and $\frac{x_1M_1}{x_2}$ set equal to G, equation (26) is obtained,

$$R_2 = \frac{n_{1,2}^2 - 1}{n_{1,2}^2 + 2}\,\frac{G + M_2}{d_{1,2}} - \frac{n_1^2 - 1}{n_1^2 + 2}\,\frac{G}{d_1}. \qquad (26)$$

It is seen that G is the number of grams of the solvent associated with one mole of the solute, and can be calculated from $G = \frac{g_1M_2}{g_2}$, where g_1 and g_2 are the grams of the solvent and solute, respectively, used in making the solution. With dioxane as a solvent the values of G for concentrations of exactly 0.2 and 0.4 mol fractions are 264.312 and 132.156 gm., respectively.

Equation (26) is the form used by Fajans (26) in determining ionic refractions in solution. It is also the form used by the author in calculating the molar refractions from solutions.

<u>Dispersion and R_∞</u>:--A dispersion equation was fitted to each compound and solution. The form of the Sellmeier equation adopted by Pickard and Hunter (9),

$$n_i^2 = a + \frac{b}{c - \nu_i^2}, \qquad (27)$$

was chosen as being the most suitable. By choosing three lines of frequencies ν_i, and the three corresponding values of n^2, the three constants can be evaluated. The three lines, H_α, 6563 Å, Hg green, 5461 Å, and Hg blue, 4358 Å, were chosen because they were sharply defined and they represent a wide spread in the visible region.

Solving these three equations for c, one obtains

$$c = \frac{\nu_1^2\nu_2^2 n_2^2 - \nu_1^2\nu_2^2 n_1^2 + \nu_1^2\nu_3^2 n_1^2 - \nu_1^2\nu_3^2 n_3^2 + \nu_2^2\nu_3^2 n_3^2 - \nu_2^2\nu_3^2 n_2^2}{\nu_1^2 n_2^2 - \nu_1^2 n_3^2 + \nu_2^2 n_3^2 - \nu_2^2 n_1^2 + \nu_3^2 n_1^2 - \nu_3^2 n_2^2}, \quad (28)$$

and solving for a in terms of c,

$$a = \frac{(c - \nu_1^2)n_1^2 - (c - \nu_2^2)n_2^2}{\nu_2^2 - \nu_1^2}. \quad (29)$$

Similarly, b expressed in terms of a and c is

$$b = (c - \nu_2^2)n_2^2 - ca + a\nu_2^2. \quad (30)$$

The squares of the frequencies, ν_i^2, given by $\frac{c^2}{\lambda_i^2}$ where this c is the velocity of light, 2.99796×10^{10} cm./sec., for these three lines are 2.0866×10^{29}, 3.0137×10^{29}, and 4.7324×10^{29}, respectively.

With these constants for the dispersion equations determined, R_∞ is calculated by setting ν equal to zero. These constants, the values of n^2 observed and calculated by using the dispersion equations, and the values of R_∞ are tabulated for the compounds in the section on Compounds and Their Physical Constants.

<u>Compounds and Their Physical Constants</u>:

In this section, the method of purification, the boiling and/or melting points, the boiling range of the distillate saved if not constant, the density at 20° calculated to a vacuum, the molecular weight, and the values of the dispersion equation constants are tabulated. In addition, the average values of the angle of deviation measured on the spectrometer, the refractive index, the value of n^2 calculated from the dispersion equation, its observed value, the difference, and the value of the molar refraction are given for each spectral line used.

The value of G is given for each solution, and values of $R_{1,2}/x_2$ and G x r, which are equal to the first and second terms, respectively, in equation (26), r being the specific refraction of dioxane, are given for each spectral line.

<u>Benzene</u>:--Dried over Na wire; fractionated twice under atmospheric pressure; b. p., 79.8°/743 mm.; d, 0.87774; M, 78.108; a, 0.72700; b, 79.084 x 10^{29}; c, 54.400 x 10^{29}.

Table VII. Dispersion of benzene.

λ	D			n	n^2	n^2	dif.	R
	°	'	"		(obs)	(calc)		
6563	41	33	25	1.49625	2.2388	2.2387	0.0001	26.003
5893	42	03	25	1.50114	2.2534	2.2534	0.0000	26.220
5770	42.	09	25	1.50211	2.2563	2.2567	-0.0004	26.262
5461	42	29	15	1.50533	2.2660	2.2660	0.0000	26.405
4861	43	18	00	1.51317	2.2897	2.2900	-0.0003	26.750
4358	44	19	20	1.52293	2.3193	2.3193	0.0000	27.177
4047	45	14	50	1.53165	2.3660	2.3439	0.0021	27.556
∞						2.1808		25.129

<u>Chlorobenzene</u>:--Dried over anhydrone; fractionated twice under atmospheric pressure; b. p., 131.0-.1/739 mm.; d, 1.10648 M, 112.557; a, 1.70532; b, 13.003 x 10^{29}; c, 23.661 x 10^{29}.

Table VIII. Dispersion of chlorobenzene.

λ	D			n	n^2 (obs)	n^2 (calc)	dif.	R
	°	'	"					
6563	43	56	00	1.51924	2.3081	2.3080	0.0001	30.887
5893	44	28	35	1.52440	2.3238	2.3224	0.0014	31.144
5770	44	33	56	1.52524	2.3264	2.3256	0.0008	31.186
5461	44	53	30	1.52813	2.3352	2.3351	0.0001	31.330
4861	44	45	20	1.53642	2.3606	2.3601	0.0005	31.740
4358	46	52	10	1.54673	2.3924	2.3922	0.0002	32.246
4047	47	50	25	1.55560	2.4199	2.4208	0.0009	32.679
∞						2.2549		30.002

<u>Bromobenzene</u>:--Dried over Na_2SO_4; fractionated twice under atmospheric pressure; b. p., 156.0/740 mm.; d, 1.49543; M, 157.016; a, 1.2771; b, 38.367 x 10^{29}; c, 35.809 x 10^{29}.

Table IX. Dispersion of bromobenzene.

λ	D			n	n^2 (obs)	n^2 (calc)	dif.	R
	°	'	"					
6563	56	08	39	1.55398	2.4149	2.4148	0.0001	33.649
5893	55	26	51	1.55948	2.4320	2.4320	0.0000	33.925
5770	56	31	21	1.56083	2.4362	2.4359	0.0003	33.992
5461	56	42	57	1.56430	2.4470	2.4470	0.0000	34.165
4861	57	12	49	1.57317	2.4749	2.4759	-0.0010	34.606
4358	57	52	42	1.58482	2.5117	2.5117	0.0000	35.180
4047	58	26	51	1.59462	2.5428	2.5425	0.0003	35.659
∞						2.3485		32.561

Iodobenzene:--Dried over Na_2SO_4; fract. twice under red. pres.; b. p., 63.7-.9/10 mm., 188.0/737 mm.; d, 1.82903; M, 204.020; a, 1.3990; b, 32.364 x 10^{29}; c, 28.951 x 10^{29}.

Table X. Dispersion of iodobenzene.

λ	D			n	n^2	n^2	dif.	R
	°	'	"		(obs)	(calc)		
6563	54	31	40	1.61361	2.6037	2.6037	0.0000	38.857
5893	55	24	35	1.62086	2.6272	2.6266	0.0006	39.226
5770	55	35	00	1.62227	2.6318	2.6319	-0.0001	39.297
5461	56	09	15	1.62690	2.6468	2.6468	0.0000	39.531
4861	57	37	40	1.63865	2.6852	2.6860	-0.0008	40.121
4358	59	35	45	1.65393	2.7355	2.7353	0.0002	40.879
4047	61	24	05	1.66751	2.7806	2.7784	0.0032	41.546
∞						2.5169		37.460

n-Heptane:--Dried over Na wire; fractionated twice under atmospheric pressure; b. p., 97.5/734 mm.; d, 0.68380; M, 100.198; a, 1.0926; b, 65.101 x 10^{29}; c, 80.667 x 10^{29}.

Table XI. Dispersion of n-heptane.

λ	D			n	n^2	n^2	dif.	R
	°	'	"		(obs)	(calc)		
6563	30	57	15	1.38603	1.9211	1.9211	0.0000	34.421
5893	31	08	25	1.38807	1.9267	1.9264	0.0003	34.582
5770	31	10	25	1.38843	1.9277	1.9276	0.0001	34.611
5461	31	16	45	1.38959	1.9310	1.9310	0.0000	34.703
4861	31	34	25	1.39280	1.9399	1.9396	0.0003	34.956
4358	31	54	35	1.39646	1.9501	1.9499	0.0002	35.245
4047	32	13	00	1.39979	1.9594	1.9585	0.0009	35.506
∞						1.8996		33.803

n-Heptyl bromide:--Dried over Na_2SO_4; fract. twice under red. pres.; b. p., 37.2/3 mm.; d, 1.13910; M, 179.106; a, 1.1951; b, 54.523 x 10^{29}; c, 62.636 x 10^{29}.

Table XII. Dispersion of n-heptyl bromide.

λ		D		n	n^2	n^2	dif.	R
	°	'	"		(obs)	(calc)		
6563	36	43	50	1.44761	2.0956	2.0956	0.0000	42.061
5893	36	59	15	1.45027	2.1033	2.1031	0.0002	42.277
5770	37	03	15	1.45096	2.1053	2.1048	0.0005	42.333
5461	37	11	55	1.45244	2.1096	2.1096	0.0000	42.453
4861	37	34	35	1.45633	2.1209	2.1219	-0.0010	42.769
4358	38	06	30	1.46176	2.1367	2.1367	0.0000	43.207
4047	38	31	10	1.46594	2.1490	2.1492	-0.0002	43.543
∞						2.0656		41.211

n-Heptyl iodide:--Dried over Na_2SO_4; fract. twice under red. pres.; b. p., 77.8/10mm., 203.4/739mm.; d, 1.38001; M, 226.110; a, 1.3418; b, 37.055 x 10^{29}; c, 44.682 x 10^{29}.

Table XIII. Dispersion of n-heptyl iodide.

λ		D		n	n^2	n^2	dif.	R
	°	'	"		(obs)	(calc)		
6563	40	38	15	1.48719	2.2117	2.2117	0.0000	47.139
5893	41	00	25	1.49085	2.2226	2.2221	0.0005	47.441
5770	41	04	30	1.49151	2.2246	2.2244	0.0002	47.495
5461	41	17	40	1.49368	2.2311	2.2311	0.0000	47.673
4861	41	41	30	1.49757	2.2427	2.2483	-0.0056	47.992
4358	42	36	00	1.50642	2.2693	2.2693	0.0000	48.713
4047	43	14	15	1.51258	2.2879	2.2872	0.0007	49.213
∞						2.1711		46.003

Toluene:--Dried over Na wire; fract. twice under atmospheric pressure; b. p., 109.9/742 mm.; d, 0.86591; M, 92.134; a, 1.1066; b, 45.838 x 10^{29}; c, 42.968 x 10^{29}.

Table XIV. Dispersion of toluene.

λ	D			n	n^2	n^2	dif.	R
	°	'	"		(obs)	(calc)		
6563	41	11	05	1.49260	2.2279	2.2279	0.0000	30.901
5893	41	38	40	1.49711	2.2413	2.2418	-0.0005	31.141
5770	41	45	45	1.49827	2.2448	2.2449	-0.0001	31.203
5461	42	04	20	1.50129	2.2539	2.2539	0.0000	31.363
4861	42	50	25	1.50875	2.2763	2.2770	-0.0007	31.757
4358	43	50	40	1.51839	2.3055	2.3054	0.0001	32.263
4047	44	43	20	1.52672	2.3309	2.3296	0.0013	32.697
∞						2.1734		29.916

p-Chlorotoluene:--Dried over Na_2SO_4; fractionated twice under atmospheric pressure; b. p., 160.7/736 mm.; d, 1.06930; M, 126.583; a, 1.4971; b, 22.478 x 10^{29}; c, 30.200 x 10^{29}.

Table XV. Dispersion of p-chlorotoluene.

λ	D			n	n^2	n^2	dif.	R
	°	'	"		(obs)	(calc)		
6563	43	32	20	1.51547	2.2967	2.2967	0.0000	35.725
5893	44	03	45	1.52047	2.3118	2.3112	0.0006	36.016
5770	44	10	10	1.52148	2.3149	2.3145	0.0004	36.074
5461	44	28	50	1.52444	2.3239	2.3239	0.0000	36.246
4861	45	18	15	1.53220	2.3476	2.3487	-0.0011	36.694
4358	46	24	30	1.54248	2.3792	2.3797	-0.0005	37.283
4047	47	19	55	1.55097	2.4055	2.4067	-0.0012	37.767
∞						2.2414		34.648

<u>p-Bromotoluene</u>:--Dried over Na_2SO_4; fract. twice under red. pres.; b. p., 60.0/10 mm., 184.0/743 mm.; d, at 30°, 1.39296; M, 171.042; a, 1.3590; b, 32.682×10^{29}; c, 34.128×10^{29}.

Table XVI. Dispersion of p-bromotoluene.

λ		D		n	n^2	n^2	dif.	R
	°	'	"		(obs)	(calc)		
6563	46	24	00	1.54240	2.3790	2.3790	0.0000	38.668
5893	46	57	05	1.54748	2.3947	2.3952	-0.0005	38.968
5770	47	06	00	1.54884	2.3989	2.3989	0.0000	39.049
5461	47	28	10	1.55222	2.4094	2.4094	0.0000	39.248
4861	48	25	15	1.56085	2.4363	2.4368	-0.0005	39.754
4358	49	39	20	1.57187	2.4708	2.4708	0.0000	40.395
4047	50	46	00	1.58165	2.5016	2.5001	0.0015	40.959
∞						2.3166		37.452

<u>p-Iodotoluene</u>:--Dried over Na_2SO_4; fract. twice under red. pres.; b. p., 64.0/3 mm., 210.7/735 mm.; d, at 40°, 1.67267; M, 218.046; a, 1.7689; b, 14.553×10^{29}; c, 21.365×10^{29}.

Table XVII. Dispersion of p-iodotoluene.

λ		D		n	n^2	n^2	dif.	R
	°	'	"		(obs)	(calc)		
6563	51	34	35	1.58867	2.5239	2.5241	-0.0002	43.911
5893	52	19	25	1.59509	2.5443	2.5439	0.0004	44.300
5770	52	29	55	1.59658	2.5491	2.5486	0.0005	44.390
5461	52	58	30	1.60062	2.5620	2.5619	0.0001	44.633
4861	54	19	20	1.61191	2.5983	2.5976	0.0007	45.310
4358	56	02	20	1.62597	2.6438	2.6438	0.0000	46.143
4047	57	37	15	1.63860	2.6850	2.6855	-0.0005	46.885
∞						2.4416		42.310

<u>Benzyl chloride</u>:--Dried over Na_2SO_4; fract. twice under red. pres.; b. p., 53.0/9 mm., 177.7/741 mm.; d, 1.09921; M, 126.583; a, 1.5241; b, 23.198 x 10^{29}; c, 30.078 x 10^{29}.

Table XVIII. Dispersion of benzyl chloride.

λ	D			n	n^2	n^2	dif.	R
	°	'	"		(obs)	(calc)		
6563	45	29	15	1.53392	2.3529	2.3529	0.0000	35.792
5893	46	01	50	1.53879	2.3679	2.3680	-0.0001	36.064
5770	46	08	40	1.54003	2.3717	2.3714	0.0003	36.133
5461	46	28	50	1.54314	2.3813	2.3813	0.0000	36.306
4861	47	23	05	1.55145	2.4070	2.4070	0.0000	36.766
4358	48	32	05	1.56187	2.4394	2.4394	0.0000	37.339
4047	49	33	10	1.57096	2.4679	2.4675	0.0004	37.835
∞						2.2954		34.729

<u>Benzyl bromide</u>:--Dried over Na_2SO_4; fract. twice under red. pres.; b. p., 48.0/1 mm., 197.0/734 mm.; d, 1.43845; M, 171.042; a, 1.1563; b, 45.436 x 10^{29}; c, 36.765 x 10^{29}.

Table XIX. Dispersion of benzyl bromide.

λ	D			n	n^2	n^2	dif.	R
	°	'	"		(obs)	(calc)		
6563	49	32	10	1.57052	2.4665	2.4665	0.0000	39.042
5893	50	12	10	1.57671	2.4860	2.4857	0.0003	39.388
5770	50	21	30	1.57807	2.4903	2.4901	0.0002	39.464
5461	50	47	55	1.58193	2.5025	2.5025	0.0000	39.680
4861	51	55	55	1.59173	2.5336	2.5348	-0.0012	40.223
4358	53	26	35	1.60457	2.5746	2.5747	-0.0001	40.929
4047	54	47	20	1.61576	2.6107	2.6090	0.0017	41.539
∞						2.3921		37.689

Nitrobenzene:--Dried over Na_2SO_4; fractionated twice under atmospheric pressure; b. p., 209.1/740 mm.; d, 1.20306; M, 123.100; a, 1.8110; b, 8.178 x 10^{29}; c, 16.270 x 10^{29}.

Table XX. Dispersion of nitrobenzene.

λ	D °	'	"	n	n^2 (obs)	n^2 (calc)	dif.	R
6563	46	42	15	1.54521	2.3877	2.3876	0.0001	32.361
5893	47	26	55	1.55203	2.4088	2.4087	0.0001	32.696
5770	47	37	25	1.55363	2.4138	2.4137	0.0001	32.775
5461	48	07	35	1.55819	2.4280	2.4279	0.0001	32.998
4960	49	21	05	1.56918	2.4623	2.4626	-0.0003	33.531
4861	49	29	05	1.57036	2.4660	2.4670	-0.0010	33.588
4358	51	25	45	1.58740	2.5198	2.5198	0.0000	34.407
∞						2.3136		31.160

Dioxane:--Dried over Na wire; fractionated twice under atmospheric pressure; b. p., 101.2-.3/740 mm.; d, 1.03386; M, 88.104; a, 1.2523; b, 50.221 x 10^{29}; c, 67.750 x 10^{29}.

Table XXI. Dispersion of dioxane.

λ	D °	'	"	n	n^2 (obs)	n^2 (calc)	dif.	spec. ref.
6563	34	07	25	1.42026	2.0170	2.0170	0.0000	0.244908
5893	34	19	25	1.42239	2.0232	2.0230	0.0002	0.245994
5770	34	22	20	1.42290	2.0246	2.0243	0.0003	0.246254
5461	34	29	10	1.42411	2.0281	2.0281	0.0000	0.246871
4960	34	46	30	1.42716	2.0368	2.0358	0.0010	0.248424
4861	34	48	20	1.42748	2.0377	2.0377	0.0000	0.248586
4358	35	11	35	1.43157	2.0494	2.0492	0.0002	0.250661
∞						1.9936		0.24065

Solutions

m-Chloronitrobenzene:--Recrystallized twice from absolute alcohol; m. p. 45.0°; M, 157.549. 0.2 mol fraction--g_1, 13.4338; g_2, 8.0162; G, 264.026; $d_{1,2}$, 1.13930; a, 0.9168; b, 68.233 x 10^{29}; c, 57.500 x 10^{29}. 0.4 mol fraction--g_1, 8.3351; g_2, 8.6385; G, 152,016; $d_{1,2}$, 1.18243; a, 1.5920; b, 15.185 x 10^{29}; c, 26.939 x 10^{29}.

Table XXII. Dispersion of m-chloronitrobenzene solutions.
0.2 mol fraction.

λ		D		n^2 (obs)	$n2$ (calc)	dif.	$R_{1,2}/x_2$	Gr	R_2
	°	'	"						
6563	38	29	30	2.1482	2.1482	0.0000	102.420	64.662	37.758
5893	38	52	35	2.1596	2.1594	0.0002	103.157	64.949	38.208
5770	38	57	20	2.1620	2.1619	0.0001	103.307	65.017	38.290
5461	39	11	45	2.1691	2.1691	0.0000	103.765	65.180	38.585
4960	39	43	55	2.1850	2.1840	0.0010	104.775	65.590	39.185
4861	39	45	25	2.1857	2.1875	-0.0028	104.822	65.633	39.189
4358	40	34	20	2.2098	2.2099	-0.0001	106.338	66.181	40.157
∞					2.1035		99.508	63.538	35.970
0.4 mol fraction.									
6563	40	20	35	2.2031	2.2030	0.0001	74.937	37.230	37.707
5893	40	46	50	2.2154	2.2156	-0.0002	75.484	37.395	38.089
5770	40	52	15	2.2186	2.2185	0.0001	75.626	37.435	38.191
5461	41	08	45	2.2267	2.2267	0.0000	75.983	37.528	38.455
4960	41	46	30	2.2452	2.2441	0.0011	76.791	37.764	39.027
4861	42	19	05	2.2611	2.2484	0.0127	77.482	37.789	39.693
4358	42	50	05	2.2762	2.2758	0.0004	78.131	38.104	40.027
∞					2.1557		72.808	36.583	36.225

m-Bromonitrobenzene:--Recrystallized twice from absolute alcohol; m. p., 55.5°; M, 202.008. 0.2 mol fraction--g_1 13.8046; g_2, 10.5219; G, 265.032; $d_{1,2}$, 1.24509; a, 1.5381; b, 18.509 x 10^{29}; c, 31.194 x 10^{29}. 0.4 mol fraction--g_1, 8.5179; g_2, 13.0211; G, 132.146; $d_{1,2}$, 1.35521; a, 1.6319; b, 14.454 x 10^{29}; c, 25.136 x 10^{29}.

Table XXIII. Dispersion of m-bromonitrobenzene.

λ	D			n^2 (obs)	n^2 (calc)	dif.	$R_{1,2}/x_2$	G x r	R_2
	°	'	"						
0.2 mol fraction.									
6563	39	21	45	2.1740	2.1740	0.0000	105.506	64.908	40.598
5893	39	44	40	2.1853	2.1851	0.0002	106.234	65.196	41.038
5770	39	49	35	2.1878	2.1877	0.0001	106.390	65.265	41.125
5461	40	04	10	2.1949	2.1949	0.0000	106.849	65.429	41.420
4960	40	36	45	2.2110	2.2102	0.0008	107.872	65.840	42.032
4861	40	40	20	2.2128	2.2139	-0.0011	107.984	65.883	42.101
4358	41	31	00	2.2376	2.2376	0.0000	109.550	66.433	43.117
∞					2.1315		102.730	63.780	38.950
0.4 mol fraction.									
6563	42	14	50	2.2590	2.2590	0.0000	72.889	32.364	40.525
5893	42	43	55	2.2732	2.2729	0.0003	73.464	32.507	40.957
5770	42	50	05	2.2762	2.2761	0.0001	73.585	32.541	41.044
5461	43	08	55	2.2853	2.2853	0.0000	73.954	32.623	41.331
4960	43	41	25	2.3011	2.3047	-0.0036	74.586	32.828	41.758
4861	43	57	05	2.3086	2.3095	-0.0009	74.888	32.850	42.038
4358	45	03	35	2.3406	2.3403	0.0003	76.153	33.124	43.029
∞					2.2069		70.738	31.801	38.937

m-Iodonitrobenzene:--Recrystallized twice from absolute alcohol; m.p., 37.7-38.0°; M, 249.012. 0.2 mol fraction-- g_1, 10.6440; g_2, 10.0128; G, 264.710; $d_{1,2}$, 1.34977; a, 1.7851; b, 8.330 x 10^{29}; c, 20.831 x 10^{29}. 0.4 mol fraction-- g_1, 7.4438; g_2, 14.0196; G, 132.215; $d_{1,2}$, 1.51023; a, 1.6039; b, 16.721 x 10^{29}; c, 24.789 x 10^{29}.

Table XXIV. Dispersion of m-iodonitrobenzene.

λ	D °	'	"	n^2 (obs)	n^2 (calc)	dif.	$R_{1,2}/x_2$	G x r	R_2
0.2 mol fraction									
6563	41	14	25	2.2295	2.2295	0.0000	110.639	64.830	45.809
5893	41	38	50	2.2414	2.2417	-0.0003	111.398	65.117	46.281
5770	41	45	45	2.2448	2.2445	0.0003	111.613	65.186	46.427
5461	42	01	45	2.2526	2.2526	0.0000	112.106	65.349	46.757
4960	42	41	15	2.2719	2.2700	0.0019	113.316	65.760	47.556
4861	42	45	10	2.2738	2.2743	-0.0005	113.435	65.803	47.632
4358	43	44	10	2.3024	2.3025	-0.0001	115.212	66.352	48.860
∞					2.1850		107.767	63.702	44.065
0.4 mol fraction									
6563	45	03	15	2.3404	2.3404	0.0000	77.957	32.381	45.576
5893	45	37	30	2.3568	2.3571	-0.0003	78.614	32.524	46.090
5770	45	46	05	2.3610	2.3609	0.0001	78.778	32.558	46.220
5461	46	08	50	2.3718	2.3718	0.0000	79.208	32.640	46.568
4960	46	59	10	2.3957	2.3975	-0.0018	80.150	32.845	47.305
4861	47	11	10	2.4014	2.4007	0.0007	80.371	32.867	47.504
4358	48	27	55	2.4375	2.4376	-0.0001	81.773	33.141	48.632
∞					2.2784		75.426	31.818	43.608

o-Chloronitrobenzene:--Recrystallized twice from absolute alcohol; m. p., 31.7-.9°; M, 157.549. *0.2 mol fraction*--g_1, 16.7721; g_2, 10.0079; G, 264.034; $d_{1,2}$, 1.13849; a, 1.2976; b, 33.968 x 10^{29}; c, 42.292 x 10^{29}. *0.4 mol fraction*--g_1, 10.0573; g_2, 12.0131; G, 131.899; $d_{1,2}$, 1.19373; a, 1.8218; b, 6.495 x 10^{29}; c, 18.849 x 10^{29}.

Table XXV. Dispersion of o-chloronitrobenzene.

λ	D °	'	"	n^2 (obs)	n^2 (calc)	dif.	$R_{1,2}/x_2$	G x r	R_2
0.2 mol fraction									
6563	38	18	05	2.1425	2.1425	0.0000	102.127	64.664	37.463
5893	38	40	40	2.1537	2.1531	0.0006	102.850	64.951	37.899
5770	38	46	05	2.1564	2.1556	0.0008	103.023	65.019	38.004
5461	38	58	15	2.1624	2.1624	0.0000	103.411	65.182	38.229
4960	39	29	05	2.1776	2.1782	-0.0006	104.383	65.592	38.791
4861	39	32	35	2.1794	2.1802	-0.0008	104.494	65.635	38.859
4358	40	18	10	2.2018	2.2020	-0.0002	105.916	66.183	39.733
∞					2.1008		99.403	63.540	35.863
0.4 mol fraction									
6563	40	33	20	2.2094	2.2093	0.0001	69.664	32.303	37.361
5893	40	58	10	2.2205	2.2212	-0.0007	70.120	32.446	37.674
5770	41	03	25	2.2241	2.2240	0.0001	70.265	32.481	37.784
5461	41	19	35	2.2320	2.2320	0.0000	70.588	32.562	38.026
4960	41	57	40	2.2506	2.2511	-0.0005	71.340	32.767	38.573
4861	42	04	40	2.2540	2.2535	0.0005	71.478	32.788	38.690
4358	43	01	55	2.2819	2.2819	0.0000	72.590	33.062	39.528
∞					2.1664		67.881	31.741	36.140

<u>o-Bromonitrobenzene</u>:--Recrystallized five times from absolute alcohol; m. p., 38.5-39.0°; M, 202.008; <u>0.2 mol fraction</u>--g_1, 15.7540; g_2, 12.0252; G, 264.647; $d_{1,2}$, 1.24685; a, 1.3828; b, 27.696 x 10^{29}; c, 37.230 x 10^{29}. <u>0.4 mol fraction</u>--g_1, 9.1613; g_2, 14.0096; G, 132.099; $d_{1,2}$, 1.35764; a, 1.0862; b, 47.075 x 10^{29}; c, 42.485 x 10^{29}.

Table XXVI. Dispersion of o-bromonitrobenzene.

λ		D		n^2	n^2	dif.	$R_{1,2}/x_2$	G x r	R_2
	°	'	"	(obs)	(calc)				
<u>0.2 mol fraction</u>									
6563	39	15	30	2.1709	2.1709	0.0000	105.071	64.814	40.257
5893	39	40	25	2.1833	2.1823	0.0010	105.864	65.102	40.762
5770	39	45	50	2.1846	2.1849	-0.0003	105.950	65.170	40.780
5461	39	58	45	2.1923	2.1922	0.0001	106.442	65.334	41.108
4960	40	29	20	2.2074	2.2077	-0.0003	107.401	65.745	41.656
4861	40	32	40	2.2090	2.2114	-0.0024	107.505	65.788	41.717
4358	41	26	05	2.2352	2.2350	0.0002	109.155	66.337	42.818
∞					2.1267		102.186	63.687	38.499
<u>0.4 mol fraction</u>									
6563	41	59	25	2.2515	2.2515	0.0000	72.442	32.352	40.090
5893	42	31	55	2.2673	2.2661	0.0012	73.085	32.496	40.589
5770	42	37	30	2.2700	2.2694	0.0006	73.195	32.530	40.665
5461	42	55	40	2.2789	2.2788	0.0001	73.552	32.611	40.941
4960	43	35	30	2.2982	2.2985	-0.0003	74.328	32.817	41.511
4861	43	38	35	2.2997	2.3032	-0.0035	74.388	32.838	41.550
4358	44	48	05	2.3332	2.3331	0.0001	75.715	33.112	42.603
∞					2.1942		70.070	31.790	38.280

<u>o-Iodonitrobenzene</u>:--Recrystallized four times from absolute alcohol; m. p., 49.0-.2°; M, 249.012. <u>0.2 mol fraction</u>--g_1, 12.7743; g_2, 12.0009; G, 265.060; $d_{1,2}$, 1.35119; a* 3.4584; b, 58.045 x 10^{29}; c, -45.000 x 10^{29}. <u>0.4 mol fraction</u>--g_1, 7.4973; g_2, 14.0126; G, 133.231; $d_{1,2}$, 1.51100; a* 2.9935; b, 12.601 x 10^{29}; c, -17.000 x 10^{29}.

Table XXVII. Dispersion of o-iodonitrobenzene.

λ	D			n^2	n^2	dif.	$R_{1,2}/x_2$	G x r	R_2
	°	'	"	(obs)	(calc)				
0.2 mol fraction									
6563	41	06	40	2.2256	2.2257	-0.0001	110.352	64.915	45.437
5893	41	31	20	2.2377	2.2387	-0.0010	111.121	65.203	45.918
5770	41	39	00	2.2415	2.2415	0.0000	111.361	65.272	46.089
5461	41	55	30	2.2496	2.2495	0.0001	111.871	65.436	46.435
4960	42	32	05	2.2674	2.2654	0.0020	112.993	65.847	47.146
Ø									
∞					2.1685		106.650	63.787	42.863
0.4 mol fraction									
6563	44	48	20	2.3333	2.3333	0.0000	77.835	32.629	45.206
5893	45	20	30	2.3487	2.3502	-0.0015	78.456	32.774	45.682
5770	45	31	15	2.3538	2.3539	-0.0001	78.663	32.807	45.856
5461	45	52	25	2.3639	2.3639	0.0000	79.067	32.891	46.176
4960	46	40	45	2.3869	2.3834	0.0035	79.978	33.098	46.880
Ø									
∞					2.2523		74.501	32.062	42.439

* Dispersion equation constants calculated from the 6563, 5770, and 5461 lines.

Ø The 4861 line was very faint, the 4358 line was absorbed.

Nitrobenzene:--Dried over Na_2SO_4; fract. twice under atm. pres.; b. p., 209.1/740 mm.; M, 123.100. 0.2 mol fraction--g_1, 15.0594; g_2, 7.0176; G, 264.166; $d_{1,2}$, 1.08280; a, 1.8239; b, 4.748 x 10^{29}; c, 17.969 x 10^{29}. 0.4 mol fraction--g_1, 10.7451; g_2, 10.0079; G, 132.167; $d_{1,2}$, 1.10993; a, 1.4065; b, 23.262 x 10^{29}; c, 32.098 x 10^{29}.

Table XXVIII. Dispersion of nitrobenzene in solution.

λ	D			n^2	n^2	dif.	$R_{1,2}/x_2$	G x r	R_2
	°	'	"	(obs)	(calc)				
0.2 mol fraction									
6563	37	38	35	2.1229	2.1229	0.0000	97.408	64.696	32.712
5893	38	00	30	2.1338	2.1326	0.0012	98.092	64.983	33.109
5770	38	05	40	2.1363	2.1349	0.0014	98.254	65.052	33.202
5461	38	17	55	2.1414	2.1414	0.0000	98.573	65.215	33.358
4960	38	48	35	2.1576	2.1571	0.0005	99.584	65.625	33.959
4861	38	52	45	2.1597	2.1591	0.0006	99.711	65.668	34.043
4358	39	39	25	2.1828	2.1826	0.0002	101.134	66.216	34.918
∞					2.0881		95.193	63.572	31.621
0.4 mol fraction									
6563	39	37	10	2.1817	2.1816	0.0001	64.989	32.369	32.620
5893	40	04	15	2.1922	2.1948	-0.0026	65.406	32.512	32.894
5770	40	09	25	2.1976	2.1978	-0.0002	65.616	32.547	33.069
5461	40	27	15	2.2063	2.2063	0.0000	65.957	32.628	33.329
4960	41	05	05	2.2249	2.2262	-0.0013	66.678	32.833	33.845
4861	41	11	20	2.2280	2.2287	-0.0007	66.797	32.855	33.942
4358	42	09	40	2.2565	2.2565	0.0000	67.890	33.129	34.761
∞					2.1312		62.974	31.806	31.168

DISCUSSION OF RESULTS

Precision of Measurements

As has been noted, the spectrometer scale was calibrated such that it could be read to the nearest twenty seconds of arc. In most cases the readings for each line were exactly the same, and in no case did the deviation of any reading from the mean exceed twenty seconds. The average deviation from the mean was about five seconds. Occasionally the Hα and the Hg violet lines were not particularly sharp, as was also sometimes the case with the Hg blue-green line when it was used. However, the deviations of successive readings for these lines did not exceed the above-mentioned limits. In these cases, however, the accuracy may not have been as great as this would lead one to believe, since two observers might not have chosen exactly the same point on the dim edges of these lines for measurement, while it would be possible for each observer to check his own readings closely. It can be noted in the preceding tables that when there was an appreciable difference in the observed values of n^2 and those obtained from the dispersion equation, it was usually for one of these three lines. The other lines were so sharply defined that there was no question concerning the exact positions of their edges.

An error of 20" in the angle of deviation produces an error of 3 parts in the third decimal of the molar refraction of iodobenzene, the compound with the highest refractive index measured in these experiments, and it produces an error of 4 parts in the third decimal with n-heptane, the compound with the lowest refractive index measured.

It was found in calibrating the pycnometers that the maximum deviation from the mean of successive weighings, even when the pycnometers were emptied and refilled, was 0.0002 gm., while the average deviation was 0.0001 gm. Allowing an error of 0.0003 in each of the three weighings involved in a density measurement, and assuming them to be all in the same direction, a maximum error of about one part in the fourth decimal would result with a 10 ml. pycnometer. An error of this magnitude in the density of either iodobenzene or n-heptane, the most and least dense compounds measured, respectively, would cause an error of 5 parts in the third decimal of their respective molar refractions.

Assuming an error of 20" in the angle of deviation, 20" in the prism angle, and 1 part in the fourth decimal in the density, and assuming that all the errors are in the same direction, the maximum error in the molar refraction of heptyl iodide, the compound with the highest molar refraction, would be 9 parts in the third decimal. Similar errors for benzene, the compound with the lowest molar refraction, would produce a maximum error of 7 parts in the third decimal in its value.

Assuming the same errors in the angle readings and weighings given above, and assuming them all to be in the same direction, the maximum errors in the molar refractions of the solutes measured in 0.2 and 0.4 mol fraction solutions would be about 34 and 20 parts in the third decimal for these respective concentrations.

Comparison of Atomic Refractivities

In order to determine the refractivity of the halogen atom in the compounds studied, the molar refraction value of the substituted radical, obtained by subtracting the atomic refraction of hydrogen given by Auwers and Eisenlohr (5) from the measured molar refraction of the unsubstituted parent compound, was subtracted from the measured molar refraction of the halogen compound. That a very definite measureable variation in the atomic refractivities of the halogens does occur in a series of organic halides is made apparent by table XXX, which gives the values for the halogen atoms for the Na D line as well as the differences between the iodine and bromine, iodine and chlorine, and the bromine and chlorine within each series. The molecular refractions of the compounds and the calculated values for the radicals from which the atomic refractions are calculated are given in table XXIX. The atomic refraction of hydrogen for the Na D line was taken as 1.100. It is to be noted that the atomic refraction of each halogen decreases as one goes down the series of radicals, benzyl, p-tolyl, phenyl, and heptyl, with the one exception of chlorobenzene, and that this same order of radicals is retained when the differences between the halogens are compared.

Table XXIX. Molar refractions of the liquids for Na D line.

Radical	R-I	R-Br	R-Cl	R-H	R-
benzyl	--	39.388	36.064	31.140	30.040
p-tolyl	44.300	38.968	36.016	31.140	30.040
phenyl	39.226	33.925	31.144	26.220	25.120
n-heptyl	47.441	42.277	--	34.582	33.482

Table XXX. Atomic refractivities of the halogens and their differences.

Radical	I	Br	Cl	I-Br	I-Cl	Br-Cl
benzyl	--	9.348	6.024	--	--	3.324
p-tolyl	14.260	8.928	5.976	5.332	8.284	2.952
phenyl	14.106	8.805	6.024	5.301	8.082	2.781
n-heptyl	13.959	8.795	--	5.164	--	--

Any other line chosen for comparison yields the same order of radicals.

For reasons discussed in the introduction, it was desired to compare the molar refractions at infinite wave-length. These values, obtained in the manner specified in the section on Calculations, are given in table XXXI. The atomic refraction of hydrogen at infinite wave-length was estimated in the following manner: For heptane, R_D equals 34.582, while R_∞ equals 33.803. This latter value is 97.75 percent of the former. Since there are no highly polarizable bonds in heptane, it seems reasonable to assume that all will change about the same rate on being extrapolated to infinity. Making this assumption, the value of the atomic refraction of hydrogen at infinite wave-length would be 1.075.

The comparisons of the atomic refractivities of the halogens and their differences for infinite wave-length are given in table XXXII. It is seen that the same order of the radicals is retained here with the same exception of chlorobenzene and the additional exception of the difference between iodine and bromine in iodobenzene and bromobenzene.

Table XXXI. Mol. ref. of the liquids at infinite wave-length.

Radical	R-I	R-Br	R-Cl	R-H	R-
benzyl	--	37.689	34.729	29.916	28.841
p-tolyl	42.310	37.452	34.648	29.916	28.841
phenyl	37.460	32.561	30.002	25.129	24.054
n-heptyl	46.003	41.211	--	33.803	32.728

Table XXXII. Atomic refractivities of the halogens and their differences at infinite wave-length.

Radical	I	Br	Cl	I-Br	I-Cl	Br-Cl
benzyl	--	8.848	5.888	--	--	2.960
p-tolyl	13.469	8.611	5.807	4.858	7.662	2.804
phenyl	13.406	8.507	5.948	4.899	7.458	2.559
n-heptyl	13.275	8.483	--	4.792	--	--

Since the comparison of the atomic refractions at the Na D line proved valid in these cases as evidenced by the fact the order of the radicals obtained at this point was the same as the order obtained at infinite wave-length, it was thought a comparison of the dispersions for a definite interval in the visible range would also be valid. The interval chosen for this comparison was between the Hg blue line and the H_α line since these lines were sharp and the difference represents a wide spread of wave-lengths. The atomic dispersions for the halogens and their differences are given in table XXXIII. It is gratifying to note that the same order of radicals as found above is retained. Two values appear to be out of place, but in at least one of these cases the difference is so small that it probably does not exceed the experimental error.

Table XXXIII. Dispersion of atomic refractions between Hg blue and H_α lines of the halogen atoms and their differences.

Radical	I	Br	Cl	I-Br	I-Cl	Br-Cl
benzyl	--	0.555	0.215	--	--	0.340
p-tolyl	0.899	0.395	0.226	0.504	0.673	0.169
phenyl	0.878	0.387	0.215	0.491	0.663	0.172
n-heptyl	0.780	0.352	--	0.428	--	--

A comparison of the effects of the ortho- and meta-nitrophenyl radicals by molar refractions measured in solution shows that the atomic refractivities of the halogen atoms are invariably higher in the meta compounds than in the ortho. The data obtained with the Na D line are presented in tables XXXIV and XXXV. The value of the atomic refractivity of hydrogen is taken as 1.100.

The same order is retained when comparisons are made at infinitely long wave-length. These data are presented in tables XXXVI and XXXVII. The value of the atomic refractivity of hydrogen is taken as 1.075 as explained above.

Table XXXIV. Mol. ref. of the solids meas. in dioxane solutions with the Na D line.

Radical	R-I	R-Br	R-Cl	R-H	R-
0.2 mol fraction					
m-nitrophenyl	46.281	41.038	38.208	33.109	32.009
o-nitrophenyl	45.918	40.762	37.899	33.109	32.009
0.4 mol fraction					
m-nitrophenyl	46.090	40.957	38.089	32.894	31.794
o-nitrophenyl	45.682	40.589	37.674	32.894	31.794

Table XXXV. Atomic refractivities of the halogens and their differences with the Na D line.

Radical	I	Br	Cl	I-Br	I-Cl	Br-Cl
0.2 mol fraction						
m-nitrophenyl	14.272	9.029	6.199	5.243	8.073	2.830
o-nitrophenyl	13.909	8.753	5.890	5.156	8.019	2.863
0.4 mol fraction						
m-nitrophenyl	14.296	9.163	6.295	5.133	8.001	2.868
o-nitrophenyl	13.888	8.795	5.880	5.093	8.008	2.915

Table XXXVI. Mol. ref. of the solids meas. in dioxane solutions at infinite wave-length.

Radical	R-I	R-Br	R-Cl	R-H	R-
0.2 mol fraction					
m-nitrophenyl	44.065	38.950	35.970	31.621	30.546
o-nitrophenyl	42.863	38.499	35.863	31.621	30.546
0.4 mol fraction					
m-nitrophenyl	43.608	38.937	36.225	31.168	30.093
o-nitrophenyl	42.439	38.280	36.140	31.168	30.093

Table XXXVII. Atomic refractivities of the halogens and their differences at infinite wave-length.

Radical	I	Br	Cl	I-Br	I-Cl	Br-Cl
0.2 mol fraction						
m-nitrophenyl	13.519	8.404	5.424	5.115	8.095	2.980
o-nitrophenyl	12.317	7.953	5.317	4.364	7.000	2.636
0.4 mol fraction						
m-nitrophenyl	13.515	8.844	6.132	4.671	7.383	2.712
o-nitrophenyl	12.346	8.187	6.047	4.159	6.299	2.140

It is noted that the molar refractions of these compounds varied considerably with concentration. The more dilute solutions give the higher values for the molar refractions. In the case of nitrobenzene where the molar refraction was measured in the pure state as well as in solution, the values found in solution were higher than those for the pure compound. All comparisons were made by values found in the same mol fraction concentrations where they should retain their comparative values.

Although the order of the radicals based on the magnitude of the effects on the atomic refractions and dispersions of the halogen atoms seems clearly established, no logical explanation of this order is forthcoming. It is undoubtedly due to a complex combination of various factors acting with different force in opposing directions. Such factors as resonance and strength of bonds would certainly contribute to the effect. It can be pointed out that certain factors are not alone responsible for this order. There is clearly no correlation with molecular weight, "electron-sharing ability", Kharasch's series of radicals based on the irreversible splitting of organometallics, or reactivity.

Further insight into the problem could be obtained by extending the series to other compounds. It certainly seems that there should be an intimate relation between refraction and the chemical bond, inasmuch as both are concerned with the valence electrons. Further researches on atomic refractions should most certainly throw more light on the nature of the chemical bond.

SUMMARY

1. The refractive indices of ten liquid organic halides and three parent hydrocarbons have been measured for seven spectral lines in the visible region.
2. The densities of the above compounds have been accurately determined.
3. Their molar refractions have been calculated for each of the seven spectral lines.
4. A dispersion equation has been fitted to each compound.
5. The molar refraction extrapolated to infinitely long wave-length has been calculated.
6. The molar refractions of the six ortho- and meta-halonitrobenzenes as well as nitrobenzene have been measured in 0.2 and 0.4 mol fraction solutions in dioxane.
7. The atomic refractions for the Na D line and for infinitely long wave-length have been calculated and compared for the halogen of each compound.
8. The atomic dispersions of the halogens have been calculated and compared for each of the liquid halides.

CONCLUSIONS

1. The spectrometer fitted with a hollow prism is a satisfactory method of measuring refractive indices of liquids with precision.
2. The atomic refractions of the halogens in a series of organic halides vary sufficiently to permit measurement.
3. The atomic refractions of the halogens decrease progressively through the halides of the benzyl, p-tolyl, phenyl, and n-heptyl radicals.
4. The same order of these radicals is maintained in their effects on each halogen.
5. The same order is maintained in comparing the atomic dispersions of the halogens.
6. Extrapolation of the molar refractions to infinitely long wave-length gives the same comparative results as the molar refractions for any single line.
7. The m-halonitrobenzenes yield values for the atomic refractions of the halogens which are higher than those for the corresponding o-halonitrobenzenes.
8. The molar refractions of the halonitrobenzenes measured in dioxane solutions vary with the concentration, being higher for more dilute solutions.

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ACKNOWLEDGMENT

The writer wishes to express his appreciation to Dr. I. B. Johns for suggesting and aiding in the development of the problem.