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I

PHYSICAL PROPERTIES OF THE HALOGEN FLUORIDES AND OTHER COMPOUNDS OF FLUORINE

I The Construction and Operation of a Rayleigh Interferometer

II Refractive Indices and Molar Refractions of Some Halogen Fluorides and Some Fluorocarbon Derivatives in the Vapor State

III Refractive Indices and Molar Refractions of Some Complex Fluorides in Aqueous Solution

[redacted]

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II

INTERFEROMETRIC STUDIES OF THE REFRACTIVE INDICES OF SOME FLUORINE COMPOUNDS

By

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A THESIS

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* * *

IV

VITA

Jim Gorden Malik was born [redacted] He attended high school in East Chicago, Indiana and after graduation in 1946, enrolled at Wabash College in Crawfordsville, Indiana. He was graduated in 1950 with an A. B. degree in chemistry. He was a member of Lambda Chi Alpha holding the office of secretary, worked as a stockroom and laboratory assistant, and was the chemistry librarian.

He entered the Graduate School of Michigan State College in the fall of 1950 and was appointed a Graduate Teaching Assistant. After two years, he received the honor of outstanding assistant and then was selected to receive a grant from the Atomic Energy Commission working with several other graduate students as Special Graduate Research Assistants under the direction of Dr. Max T. Rogers.

He was honored by Sigma Pi Sigma, was selected to become a full member of the Society of the Sigma Xi, and is a member of the American Chemical Society. His first publication is entitled "An Interferometer" and was published in the Journal of Chemical Education, 1953. He will complete his work toward the Doctor of Philosophy degree the summer of 1954 majoring in physical chemistry and minoring in inorganic chemistry and physics.

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I. INTRODUCTION

All interferometers divide a beam of light into two or more parts which travel different paths then recombine to form interference fringes. The form of these fringes is determined by the difference in optical path travelled by successive beams. Thus interferometers measure primarily differences in optical path. But as the optical path is the product of the geometric path and the refractive index, an interferometer either measures differences of geometric path when the two beams travel in the same medium, or the difference of refractive index when the geometric paths are equal. Therefore, interferometers can be designed to measure the refractive indices of solids, liquids, solutions, and gases.

In measurements on solids and liquids, an interferometer has no great advantage over a precision refractometer. However, the interferometer is much better adapted to the measurement of the small difference between the refractive index of a pure solvent and that of a very dilute solution of a substance in that solvent. The interferometer is even able to detect these small differences when the substances to be dissolved are very slightly soluble. Only an interferometer will measure the refractive index of a gas with any accuracy.

It has been the object of this investigation to construct an interferometer of the Rayleigh type and adapt it for two purposes; first, the measurement of the refractive indices of gases by an absolute method and, second, the measurement of the refractive indices of very dilute solutions by the difference method.

An additive quantity, the molar refraction, can be computed from the measured refractive index and density of a substance. The molar refraction may also be obtained from empirically deduced atomic and structural refractive constants. A comparison of the values of molar refractions observed with those obtained from additive constants gives information concerning the structure of the substance. In this dissertation molar refraction data have been obtained by experiment and from literature sources for this comparison. The molar refractions of ionic and covalent fluorides have been discussed in detail.

II. HISTORICAL BACKGROUND

Refractive Index

When light passes from one medium into another medium it undergoes a change in velocity and, unless the beam is perpendicular to the boundary, also in direction. The change in direction is measured in terms of the angle of incidence i and the angle of refraction r which the incident and refracted beam make with the normal to the boundary (See Figure 1). Snell's law of refraction states that

$$n_1 \sin i = n_2 \sin r \qquad (1)$$

where n_1 is the index of refraction of the first medium, from which the angle of incidence (sin i) is measured, and n_2 is the index of refraction of the second medium, from which the angle of refraction (sin r) is measured. According to the wave theory of light,

$$n_1/n_2 = v_1/v_2 \qquad (2)$$

where v_1 and v_2 are the velocities of the light beam in the respective media.

When air, or more accurately vacuum, is the first medium, the equation reduces to

$$n = \sin i/\sin r = v_1/v_2. \qquad (3)$$

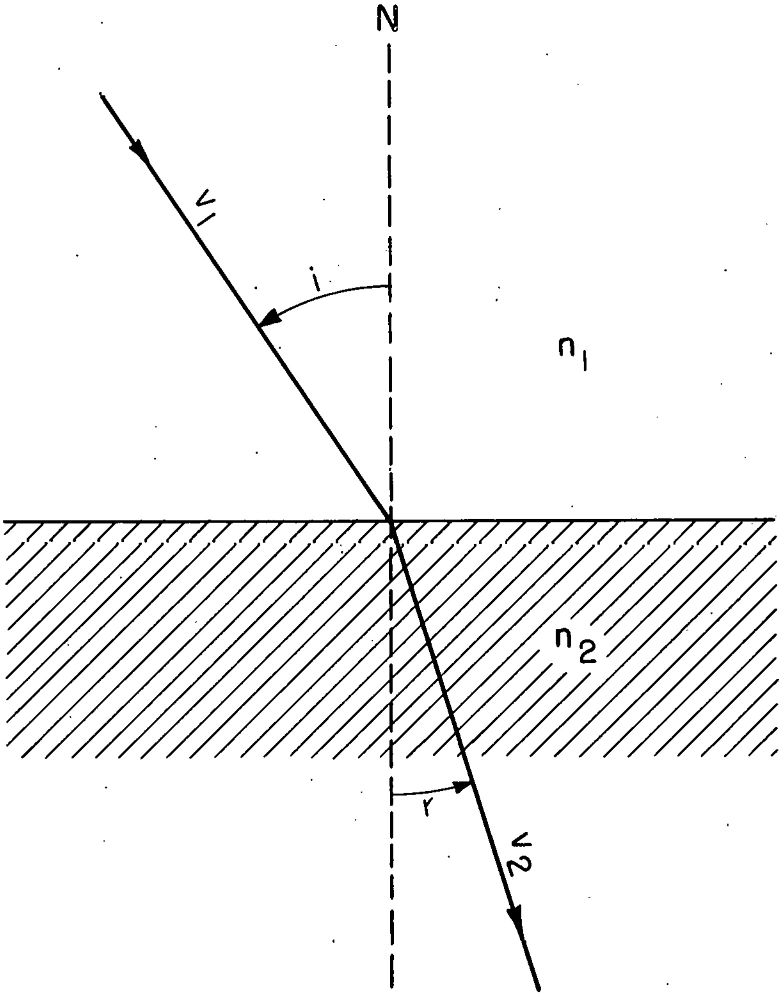

Figure 1. Refraction of light at a boundary

Thus the refractive index n is a dimensionless constant whose value, for light of a given wave-length, is determined by the nature and state of aggregation of the substance and of the reference (air or vacuum). If measurements of the refractive index are to be strictly comparable, it is evidently necessary to specify the reference medium as well as to control other variables which affect the velocity of light in the sample itself. Since the index of refraction of air at 0^oC is about 1.000297, depending upon the percentage of carbon dioxide in it, it is usually taken as unity in measurements on solids and liquids. The refractive indices of gases are usually referred to vacuum as the reference medium; this yields an absolute index of refraction characteristic of the substance.

The refractive index is of value in three respects. First, it serves as a means for the identification of a substance, for its quantitative analysis and as a criterion of its purity. The usefulness of the refractive index for these purposes is due to the ease and precision with which it can be determined. Second, knowledge of the refractive index is necessary for the evaluation of dipole moments of substances if the dielectric constant is measured at one temperature only. Third, certain functions of the refractive index, such as the molar refraction MR, are characteristic of a given molecule and indicative of its structure.

It is important to notice that the velocity of light in a medium depends on the wave-length, so rays of light with different wave-lengths are refracted differently and a composite ray is broken up by refraction into homogeneous rays of different wave-lengths. This effect is known as dispersion. Comparable values of refractive indices must, therefore, refer to the same wave-length. Very commonly the D line in the sodium spectrum, or selected lines of the hydrogen discharge or mercury arc spectra, are used.

The optical dispersion is expressed as $n\lambda_1 - n\lambda_2$ or as some simple function of it. Other expressions used are the "nu value",

$$\bar{v} = (n_D - 1)/(n_F - n_C), \qquad (4)$$

and the specific dispersion[1-4],

$$v = (n_D - n_C)/d. \qquad (5)$$

Here n_D, n_F, and n_C refer to the wave-lengths denoted by the Fraunhofer symbols[5]; C for H_α = 6563 Å, D for Na_D = 5893 Å, and F for H_β = 4861 Å. With the intense and convenient light sources now available the optical dispersion is readily measured and frequently used. It shows greater differences among closely related compounds than the refractive index itself and has been used to identify compounds of similar refractive index.

For a wide variety of liquids[6,7] an increase in temperature causes a decrease in the refractive index, but some liquids, especially at temperatures near the boiling point, have negative temperature coefficients. Thus it is necessary to specify the temperature and this is usually done by writing the temperature as a superscript, e.g., n^{25}. Most data are given for 15°C, 17.5°C, and 20°C, but to conform with other physico-chemical data measurements at 25°C are becoming increasingly desirable.

Pressure changes are usually neglected completely in liquid and solid refractive index measurements. Tilton[8] has shown that an increase in pressure of one atmosphere will increase the refractive index by about 3×10^{-6} so normal fluctuations of barometric pressure produce a negligible change during the measurement of a refractive index.

The refractive indices of solutions vary with concentration of solute and therefore may be used as a measure of concentration. The most reliable method utilizes interpolation from an empirical calibration curve made up using solutions of known concentration. In certain cases there exists a linear relationship between these two quantities but more generally the data are represented by a curve, the shape of which is influenced by the way in which the concentration is expressed; molarity M is more likely to give a nearly linear relationship than weight per cent p. For solutions in which the components undergo association, or in which the intermolecular forces are sufficiently different from those in the pure components, a maximum or minimum in the refractive index versus molarity curve may occur.

If it is necessary to predict a value of the refractive index of a solution of given concentration without use of a calibration curve one can often use equation (6), which is among the simplest

$$\frac{100(n-1)}{d} = \frac{p_1(n_1-1)}{d_1} + \frac{(100-p_1)(n_2-1)}{d_2} \qquad (6)$$

of the many functions proposed[9-12] for relating the refractive index, density, and composition of a mixture. The subscripts, one and two, distinguish the two components. This equation is based on the assumption that, for binary mixtures, the specific refraction r_G, calculated by the Gladstone-Dale formula, is a linear function of composition. A relation based on additivity of the Lorenz-Lorentz refraction is often used instead of this equation. Although the additivity of the Lorenz-Lorentz refraction for mixtures is not always as exact as that of other expressions for refraction, its application has an advantage in that the deviations from additivity are often related in a simple way to the forces within and between the molecules.

When determining the refractive index of a pure compound the amount of impurity in the material used is of utmost importance. Therefore it is of some advantage to be able to estimate how pure a sample should be to give the accuracy desired in the refractive index. The following formula[13], based on equation (6), is useful in certain cases in estimating the degree of purification necessary for measurements of a given accuracy.

$$n - n_0 = 0.01\, p_1 (n_1 - n_0) \tag{7}$$

The symbols n, n_0, and n_1 refer to the mixture, the pure substance, and the impurity, respectively, and p_1 is the weight percent impurity. It is assumed that the impurity is known and that the density of the impurity and of the pure compound are the same. It therefore applies best to solutions containing a small amount of a solute having physical and chemical properties closely similar to those of the solvent--a situation frequently encountered in the final purification of liquids. Volume percent may be used instead of weight percent in equation (7) with about equal success.

One should therefore estimate the precision with which one is justified in measuring the refractive index of a substance having a probable weight percent impurity p_1.

The Interferometer

As was noted in the introduction, the interferometer may measure differences in optical path, in length, or in refractive index. To this end there have been devised interferometers which fall into two general classifications--division of wave front requiring point or slit sources, and division of amplitude requiring broad or extended sources. Examples of the first class are the Fresnel biprism and Fresnel mirror, Lloyd's mirror, Billet's split lens, and Rayleigh's interferometer. In each case when the slit is too wide the fringes disappear. This disappearance of the fringes was actually used by Michelson in his method of measuring the angular diameter of stars and by Gerhardt in his adaptation of Michelson's method of obtaining the diameters of ultramicroscopic particles.

In the second class, where the beam is divided by partial reflection at a half-silvered mirror, there is a point-to-point correspondence between the wavefronts of the transmitted and reflected beams. This means that with division of amplitude extended light sources may be used. Examples of this class[14] are the interference effects of thin films and the interferometer systems of Jamin, Mach, Michelson, Fabry-Perot, and Lummer-Gehrcke. Since this work is concerned with refractive index measurement, no detailed mention shall be made of any or all of the various types of interferometers for other measurements than that of refractive index since they have been extensively reviewed by Candler.[15]

Perhaps the beginning of the interferometer should be traced back to the astronomers who for many centuries realized that the earth's atmosphere refracted the light passing through it and therefore that the position of a star is displaced. From the time of Tycho Brahe, when astronomical techniques first became sufficiently precise, attempts have been made to correct this deviation. In 1805 Delambre[16] used a large number of astronomical observations to determine the refractive index of air for white light. The first accurate laboratory measurement was made about the same time by Biot and Arago[16,17] who measured the deviation of white light passing through air enclosed in a hollow glass prism.

Grimaldi, who was the first to observe accurately and describe diffraction, or the bending of light around the edges of obstacles, reported as early as 1665 an experiment which he believed proved the interference of light. However, interference could not have occurred under the conditions of his experiment. A century later this experiment was modified by Young in trying to verify the principle of the interference of light, and true destructive interference of light was observed. Fresnel then carried this work further and produced interference without the diffraction effects observed by Young. The development of the various types and forms of interferometers followed this basic work.

The refractive indices of gases were first measured by the prism method[18] which is explained in some detail by Partington.[19] Observations are made using a hollow glass prism which is first evacuated and then filled with the pure dry gas to be measured. A prism constructed by Dulong[20] consisted of a wide glass tube with glass plates cemented on the ends.

Jamin in 1857 first used an interferometer to measure the refractive index of a gas. Taking advantage of the increased accuracy, Ketteler[21] measured the refractive index of air with the red, yellow, and green lines in the spectra of lithium, sodium, and thallium, respectively, and thus obtained a value for the dispersion of air. Since that date some forty measurements have been made on air. In measurements of wave-length the primary standard is the wave-length of the red cadmium radiation in standard air, but there has been a decided trend to adopt as a standard the green line of the mercury isotope of mass 198 because of its purity and availability.

Lord Rayleigh[22,23] designed an interferometer in 1896 when he wished to measure the refractive indices of the recently discovered gases, argon and helium. Refractive indices have usually been measured with his form of the interferometer, or the Jamin interferometer; however, many interferometers of other types have been, or could be, adapted. The Rayleigh interferometer is by far the most accurate and convenient means available for measuring small changes in refractive indices. It surpasses other interferential methods, such as that of Jamin, because the fiduciary system is a similar set of fringes and not a cross wire. This feature was introduced by Haber and Lowe.[24] Subsequently the Rayleigh interferometer has been extensively developed by Williams, Geffcken, Carl Zeiss, Inc., Adam Hilger & Co., and others. The problem of calibration has been discussed by Edwards[25,26] and by Adams,[27] who have also considered the errors due to dispersion.

A Rayleigh interferometer is, in principle, an instrument which divides a collimated beam of light from a single source into two parts by means of two adjacent slits. These travel different parallel paths and recombine to form vertical straight interference fringes. If the optical path of one of these divided interfering beams is changed there is a lateral shift of the whole fringe system. This shift is observed in a telescope and its magnitude is found in terms of the number of fringes displaced from the original position, and can be calibrated[28-33] in terms of the change in refractive index. A gas, liquid, or solution placed in one of the divided interfering beams will change the optical path of that beam and cause the fringes to be displaced appreciably.

If an interferometer is used to measure the refractive index of a liquid, it is not possible to count the number of fringes displaced and special methods are used, such as the compensating plates described by Candler[15] or a rotating chamber described by Geffcken.[34] These also result in greater convenience and accuracy with gaseous measurements.

The compensating plates are glass plates of equal thickness, ground flat to a quarter of a wave-length; one is introduced in each of the parallel light beams of the Rayleigh interferometer. They produce equal path lengths when parallel with one another, but if one is tilted slightly with respect to the other a difference in optical path length is introduced and the fringes displaced. If the fringes are displaced by the introduction of the substance to be measured they can be returned to the original position by rotating one compensating plate and the exact number of displaced fringes found. Hansen[35] has described five types of these compensators.

Low intensity is a major difficulty with the Rayleigh instrument, so a bright source is essential. A mercury arc with a green filter is a commonly used monochromatic source for work with gases. Usually the yellow sodium doublet has been used for liquid measurements. The low intensity is caused by the collimator slit, which must be narrow since an increase in width reduces the visibility of the fringes. One of the developments or modifications to meet this objection was that made by Williams[36] which allows a slit up to three times as wide as that permissible in the Rayleigh instrument. Williams introduced a second rhomb, referred to as an Albrecht rhomb, which takes the place of the double slit. About a twenty-fold gain in brightness is obtained, as a conservative estimate. The instrument has been used very little, perhaps because it is not easy to adjust.

The Rayleigh interferometer has been adapted to the measurement of the refractive index of crystals.[39] The precision of the measurement of the refractive index is $\pm 3 \times 10^{-5}$. For isotropic solids, the technique is simpler than with anisotropic solids. For the latter, the specimens must be examined under the polarizing microscope[37] to determine the orientation of the polarizability ellipsoid. The ordinary interferometer cells are replaced by a single vessel having parallel windows which are large enough to allow both beams to pass. The vessel is filled with an appropriate liquid whose index of refraction can be varied continuously. A single crystal fragment as small as 0.5 mm. in cross-section is immersed in the liquid and placed in the path of one of the beams. If the refractive index of the liquid differs slightly from that of the solid, the ordinary interference fringes appear distorted, having a V-shaped notch; however, when the refractive indices are equal, the fringes have sharp straight edges as if no crystal were in the beam at all. A measurement of the refractive index of the liquid gives the refractive index of the solid.

Kruis and Geffcken[38-40] have described the precautions and refinements in the usual instrument necessary to obtain an accuracy of ± 1 x 10^{-8} in the measurement of the refractive index using monochromatic light. An ingenious modification of the Rayleigh interferometer by Geffcken[41,42] eliminates the dispersion effect by using monochromatic light in conjunction with a rotating chamber. The fringe order is determined by counting the number of fringes which pass while the cells are slowly turned through a given angle with respect to the axis of the interferometer. This device is not yet available commercially. This is unfortunate for with it one would be able to make rapid precision measurements of even very large differences in refractive index, and also could measure the relative dispersion more conveniently. Measurements of absolute values of the refractive indices of liquid substances may also be made with the rotating chamber, but experimental details have not been published.

The Rayleigh interferometer is frequently used to determine a single varying component in a transparent mixture. This component may be solute or solvent, electrolyte or non-electrolyte or any substance which will not attack the cell. The analysis of aqueous solutions has been described by Adams,[43] Gans and Bose,[44] and by Barth.[45] A partial list of other applications for which the instrument has been used follows.[46] The analyses of the following have been carried out: smoke,[47] non-aqueous solutions,[48] flue gas,[49] beer,[50-51] milk,[52] soils,[52] colloids,[30, 50,52,53] river and well water,[52,54] mine air,[49,55-57] content of CO_2 in lungs,[58,59] CO_2 tension in venous blood (pregnancy test),[60,61] and gas and water purity.[45,54,62-66] It has been used as an interferential galvanometer,[67] to measure lengths,[68,69] coefficients of thermal expansion of metals,[67,70] percentages of peptone in serums in biological work,[71] in serological studies,[72,73] and in immunological studies.[74] It has been used as a precise pressure gage,[75-77] to measure wave-lengths,[78,79] in fermentation rate studies,[32] and in general kinetic rate studies.[80-82]

Refractivity Formulas

The refractive index for a given wave-length varies considerably with the physical state of a given substance, being much smaller for the gaseous than for the liquid state. It is to be anticipated that the variation of density is the main factor causing this change, and many attempts were made to connect the refractive index with the density. It was found that various functions of the refractive index, when divided by the density, had numerical values which were constant for a given substance, independent of temperature of pressure. The constant value obtained for a given substance is usually called the specific or molar refractivity of the substance, depending on whether one gram or one mole is chosen, and has the dimensions of volume. The first such function was deduced from Newton's corpuscular theory[83] of light by Laplace.[84-86] The corpuscles on entering a medium at an angle were supposed to be attracted by it, and hence the light-ray refracted. Newton showed empirically that $(n^2 - 1)/d$ is roughly the same in the liquid and vapor states for a number of substances. Hence,

$$(n^2 - 1)/d = 4\,k/c^2 = \text{const.} \qquad (8)$$

Here k is a constant which was taken to be a measure of the attraction of the light corpuscles by the medium.

This equation was thought to be confirmed by experiments on gases by Biot and Arago[17,87-91] but more accurate measurements by Arago and Petit ten years later showed marked deviations, the value of $(n^2 - 1)/d$ being much less for a vapor than for the corresponding liquid substance whereas the change in density should have compensated the change in the square of the refractive index.

The Newton-Laplace equation gave way to a very simple formula

$$(n - 1)/d = k, \qquad (9)$$

proposed empirically by Beer,[92] and by Gladstone and Dale.[93-95] This formula holds very well for a particular state, gaseous or liquid. A deduction of it is given by Dufet[96] and Sutherland.[97]

A more precise relation was derived independently by Lorenz and Lorentz from entirely different assumptions. Lorenz considered the passage of light through spherical molecules immersed in an elastic ether with the assumption that the velocity of light in a substance is an average between the value in free space and in the molecules themselves. Lorentz deduced it from Maxwell's electromagnetic theory of light. For light of a given frequency passing through a substance, their relationship takes the form

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} = \text{constant} \tag{10}$$

Various workers have found that one or another of the formulas work well for certain classes of compounds but not as well for others. It appears that a single formula cannot satisfactorily represent the effects of changing temperature, density, and refractive index.

The Lorenz-Lorentz formula has been derived theoretically. It reduces to the Newton-Laplace and Gladstone-Dale equations as the limiting case for gases. Thus, starting with the Lorenz-Lorentz equation, since

$$(n^2 - 1) = (n - 1)(n + 1)$$

it follows that when the refractive index is nearly unity, then

$$r_L = \frac{(n + 1)(n - 1)}{(n^2 + 2)} \cdot \frac{1}{d} = \frac{2}{3} \frac{n - 1}{d} \tag{11}$$

or, rearranging the constants,

$$\frac{3}{2} r_L = \frac{n - 1}{d} = r_G \tag{12}$$

which is the Gladstone-Dale equation. Similarly,

$$r_L = \frac{(n^2 - 1)}{(n^2 + 2)} \cdot \frac{1}{d} = \frac{(n^2 - 1)}{3} \cdot \frac{1}{d} \qquad (13)$$

or, rearranging the constants,

$$3\,r_L = (n^2 - 1) \cdot \frac{1}{d} = r_N \qquad (14)$$

which is the Newton-Laplace equation. Hence these three formulas for specific refraction differ only by a constant factor for gases.

For liquids the Gladstone-Dale and the Lorenz-Lorentz equations are usually nearly equally satisfactory,[98-104] but when the same substance is compared in the gaseous and liquid states the second is decidedly superior. Workers have extensively tested both formulas for effects of changes of state, pressure, temperature, and concentration changes; each claims that one or the other is better for a certain type of substance under their particular conditions. However, there seems to be only one formula that is extremely consistent and precise, that of Eykmann.

$$\frac{n^2 - 1}{n^2 + 0.4} \cdot \frac{1}{d} = \text{const.} \qquad (15)$$

This empirical formula of Eykmann[105] is the most successful in all respects. Eisenlohr[106] stated that Eykmann's function is nearly independent of temperature over a wide range. Many others have found that their results agree only with Eykmann's equation.[107] However, his equation has not yet been blessed by a theoretical deduction, and therefore seems destined to lie dormant for awhile. Partington says that "... unlike so many formulae which are useless for practical application, (this) is one which deserves to be kept in mind in the laboratory...." Many other formulas have been proposed[108-110] but are not in common use.

A precision technique for measuring the molar refraction of solutes has been developed by Kohner,[111] Geffcken,[112-115] and Kruis[116-118] for aqueous solutions. Geffcken and Kruis emphasize the importance of differential measurements. The reliability of the results depends on the following precautions: (1) The solution and solvent should be compared under identical conditions. (2) The measurements of the refractive indices of the solution and solvent should be made on the same samples as those used for determination of the densities. (3) The solvent used for reference and that used in preparing the solution should come from the same source. (4) Special devices and precautions should be taken for transferring and storing the liquids to prevent any change of concentration by evaporation. (5) All aliquots should be made up from a single stock solution, preferably using weight burettes.

The molar refraction of a solute is obtained from that of the solution by assuming that the total molar refraction of the solution is the sum of the molar refractions of the pure solute and solvent, each multiplied by its respective mole fraction in the solution, $N_1(MR)_1 + N_2(MR)_2 = MR$. The molar refraction of the solution MR is defined by the expression

$$MR = \frac{n^2 - 1}{n^2 + 2} \frac{(N_1M_1 + N_2M_2)}{d} \qquad (16)$$

where M_1, M_2, N_1, and N_2 are the molecular weights and mole fractions of the solvent and solute respectively. The Lorenz-Lorentz molar refraction MR, the density d, and the refractive index n refer to the solution.

Before considering in detail the Lorenz-Lorentz relation between refractive index and density, it should prove of some interest to consider some other relationships of various properties to that of refractive index or molar refraction. Several such empirical relationships are listed in Table I.

The Lorenz-Lorentz molar refraction equation has been, and probably will continue to be, used the most and so it will be of some interest here to discuss it further. In the derivation of the Lorenz-Lorentz equation one must first find the relation between the dielectric constant k and the refractive index n. From Maxwell's electromagnetic equations for the case of a non-conducting, isotropic medium with plane waves traveling in the x direction and with wave fronts parallel to the yz plane, it can be shown that the following differential equations of the wave motion result.

$$\partial^2 \vec{E}_y / \partial t^2 = (c^2/uk)\, \partial^2 \vec{E}_y / \partial x^2 \qquad (17)$$

and

$$\partial^2 \vec{H}_z / \partial t^2 = (c^2/uk)\, \partial^2 \vec{H}_z / \partial x^2 \qquad (18)$$

where $\vec{H}$ is the magnetic field, $\vec{E}$ the electric intensity, c the velocity of light in vacuo, u the magnetic permeability, and k the dielectric constant. Then, by taking the general equation of plane waves and

TABLE I

EMPIRICAL RELATIONSHIPS OF REFRACTIVE INDEX AND MOLAR REFRACTION TO OTHER PROPERTIES

Relationship	Remarks	Reference
$b = k R$	$k = 4.03$ for most substances	Guye[119-122]
$1.8\ T_c/p_c = R$	The factor 1.8 is an average of values ranging from 1.6-2.0	Guye[123-126]
$T_c = k_1R + k_2$	k_1 and k_2 are constants	Wan[127]
$bT_b + c = R$	b and c are constants	Livingston[128,129]
$b = 4\ r_L$		Traube[130]
$R\ \sigma_b/T_b$ = constant	The constant varies from 1.20-1.25	Walden[131,132]
$M\ l_e/R = 310$		Walden[133]
$n_o = \left[\frac{(M + 2d_oR)}{(M - d_oR)}\right]^{\frac{1}{2}}$		Herz[134]
$n_o/n_c = 1.11$		Herz[134]
$M/d_o = V_o = 3R$		Lorenz and Herz[135-137]
$M/d_b = V_b = 5R$		Herz[134]
$M\ l_e/R = 8\ p_c$		Herz[138,139]
$[F] = -[P]\log(n^{20} - 1)$		Joshi and Tuli[140]

Key to symbols:

b - Van der Waal's coefficient
R - Lorenz-Lorentz molar refraction
p_c - Critical pressure
T_c - Critical temperature
r_L - Lorenz-Lorentz specific refraction
σ_b - Surface tension at the boiling point
T_b - Boiling point, degrees Kelvin
l_e - Latent heat of evaporation per gram
M - Molecular weight
n_o - Refractive index at $0^{\circ}K$
d_o - Density at absolute zero
V_o - Molar volume at $0^{\circ}K$
V_b - Molar volume at the boiling point
d_b - Density at the boiling point
$[P]$- Parachor
$[F]$- Refrachor
n^{20}- Refractive index of sodium D line at $20^{\circ}C$

differentiating twice with respect to x, and then twice with respect to time t, the result is:

$$\partial^2\vec{E}_y/\partial t^2 = v^2 \partial^2\vec{E}_y/\partial x^2 \qquad (19)$$

and

$$\partial^2\vec{H}_z/\partial t^2 = v^2 \partial^2\vec{H}_z/\partial x^2 . \qquad (20)$$

It is seen from these equations that the velocity of the waves is

$$v = c/(uk)^{\frac{1}{2}} . \qquad (21)$$

For two isotropic non-conducting media in which the velocities of light are v' and v'', the relation becomes

$$v'/v'' = (u''k''/u'k')^{\frac{1}{2}} . \qquad (22)$$

But v'/v'' equals n''/n' and if one medium is vacuum, both u and k for that medium become unity, hence

$$n = (uk)^{\frac{1}{2}} . \qquad (23)$$

For non-polar molecules u can be taken as unity and we have

$$k = n^2. \qquad (24)$$

This is a consequence of Maxwell's theory and has been verified experimentally.

In considering the optical properties of a dielectric, Lorentz[19,141] calculated the local electric field which polarizes a single atom or molecule of a dielectric by substituting a very small spherical cavity in place of the atom or molecule with the unchanged continuous dielectric on all sides of the cavity. This field $\vec{F}$ is usually called the Lorenz field and is given by

$$\vec{F} = \vec{E} + (4\pi/3)\vec{P} \qquad (25)$$

where $\vec{E}$ is the applied or external electric intensity and $\vec{P}$ the polarization. It can also be shown that the effect of the atoms or molecules which are removed in forming the cavity is zero. Lorentz then assumed that if there are N' molecules in the unit volume, it is possible to assign to each an average induced moment $\bar{m}$, which is proportional to the field $\vec{F}$, such that

$$\bar{m} = \vec{P}/N' = \alpha\vec{F} \qquad (26)$$

where α is the atomic polarizability. From equations (25), (26), and the definition of the electric displacement $\vec{D}$,

$$\vec{D} = \vec{E} + 4\pi\vec{P}, \qquad (27)$$

one has

$$(\vec{D}/\vec{E} - 1)(1 - 4\pi N'\alpha/3) = 4\pi N'\alpha \,. \qquad (28)$$

In the presence of a dielectric,

$$\vec{D} = k\vec{E} \qquad (29)$$

and by substitution in equation (28)

$$k - 1 = 4\pi N'\alpha/(1 - 4\pi N'\alpha/3). \qquad (30)$$

and also

$$k + 2 = 3/(1 - 4\pi N'\alpha/3) \qquad (31)$$

Dividing equation (30) by equation (31), the result is

$$(k - 1)/(k + 2) = (4\pi/3) N' \alpha . \qquad (32)$$

If this is then divided by d, the density of the dielectric, and N'/d set equal to N", which is the number of molecules in a unit mass of the dielectric, one obtains

$$(k - 1)/(k + 2)d = (4\pi/3)N'' \alpha . \qquad (33)$$

If M is the molecular weight of the dielectric, MN" equals the number of molecules per mole, or Avogadro's number N; hence,

$$(M/d)(k - 1)/(k + 2) = (4\pi/3) N \alpha = P_m \quad (34)$$

where P_m is the molar induced polarization. As was previously shown, if n is the refractive index of the medium for very long waves,*

$$k = n^2, \qquad (24)$$

and so

$$\frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2} = MR \qquad (35)$$

where MR is the molar refraction. This then is the Lorenz-Lorentz equation for the special case of light of a given frequency.

The molar refraction MR is a property characteristic of a given molecule and indicative of its structure. For a long time the term "characteristic of the molecule" was understood to mean that the value

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* The nuclei are not able to respond to the high frequencies of visible light so the refractive index does not include the atomic polarizability.

of the molar refraction is independent of temperature and pressure whether the substance is present in the gaseous, liquid, or solid state. "Indicative of the molecular structure" was understood to mean that the molar refraction of a molecule is a property which can be additively composed of increments assigned to atoms or groups present in the molecule, or to constitutive factors. There has been some criticism of the application of the molar refraction values and so the source of these values should be examined more thoroughly.

The experimental foundation for the application of the principle of additivity is the approximate constancy of the difference between the molar refractions of adjacent members of a homologous series. If atomic refractions are used, the increment MR_{CH_2} may be expressed by

$$MR_{CH_2} = MR_C + 2\,MR_H. \qquad (36)$$

Therefore, by taking the difference between the molar refraction values for several saturated hydrocarbons differing by CH_2 in composition, the value of MR_{CH_2} may be found. Considering the right-hand side of equation (36), the molar refraction values of carbon and hydrogen can be determined by finding directly the molar refractions of diamond and hydrogen. But despite the fact that these molar refraction values can be determined accurately to four figures, the values of the molar refraction increment for CH_2 from the two sources do not agree. In fact, in the saturated hydrocarbon series itself, the specific refraction increases with molecular weight, but the increase for each addition CH_2 decreases on ascending the series. This type of error is not serious if it is realized that it is present. However, for olefins and acetylenes, the calculated molar refraction values are so different from the experimental values that constant increments for the double and triple bonds must be assigned. Also different values must be assigned to oxygen and nitrogen in different homologous series and values may be assigned in different ways. This criticism should not impair the use of a table of increments of atomic refractions as long as the number and nature of the constants chosen are adequate and consistent and the conclusions drawn do not go beyond the limitations of the system.

Lack of exact additivity stems from several sources. The influence of conjugation results in both positive and negative deviations. Therefore it is not possible to use a single constant increment for conjugation since the exaltation depends on the molecule. This exaltation is not limited to conjugated double bonds but has been observed in other instances, e.g., the value for chlorine in acid chlorides is always somewhat higher than the normal value. Another source is the influence of ring structures. Here values have been observed which are higher, lower, and exactly the same as the predicted molar refraction.

Not only isomerism but even mere association of neutral molecules can lead to large changes of molar refraction. Also, seemingly valid conclusions regarding the value of dimers can lead to error. Thus, while one would be inclined to assume that the value for acetic acid[13] in the liquid state should be intermediate between the observed values of the monomer and dimer, the molar refraction of the liquid is lower than that of either.

Since substitution of a given atom in two different molecules cannot be expected to place it in an identical environment, an identical effect on the molar refraction cannot be expected and constant increments are not found.[142] Extensive experimental evidence concerning the molar refractions of inorganic and organic substances[143] leads to the conclusion that deviations from additivity of the Lorenz-Lorentz equation can be considered as an indication and measure of changes in the electronic systems involved. These changes are due to intra- and intermolecular electric interactions between the parts of the system.

The Lorenz-Lorentz molar refraction for infinitely long waves is considered a measure of the electronic polarizability of the molecule, i.e., of the looseness of its electronic system. There is a good reason[141-146] to believe that the increase of the molar refraction which usually accompanies an increase of temperature of a liquid, or accompanies its vaporization, is a real indication of the loosening of the electronic shell due to the increase in distance between the molecules.

A list of the atomic refractions that have been considered in the discussion is given in Table II. These are the values calculated by Vogel[19,147,148] for the sodium D line.

A second method of using molar refraction values is by use of the so-called bond refractions.[149,150] These seek to take into account the cond character or electron configurations of the atoms concerned by use of additive bond refraction values. Various increments are assigned to the bonds between atoms.

TABLE II

ATOMIC REFRACTIONS

Atom	Value
C	2.591
H	1.028
O (ether)	1.643
F	0.8
Cl	5.844
Br	8.741
I	13.954
C=C (double bond only)	1.575
N (tertiary aliphatic)	2.941

According to Fajans and Knoor,[151,152] the ordinary atomic refractions have no simple physical significance but the bond refractions may be regarded as measuring the polarizability or deformability of the electron groups in an external electric field, or in the field produced by strongly polar groups in the molecule itself. Denbigh,[153] and Warrick,[154] found the bond refractivities to be additive with a deviation of less than 0.7 percent. However, averages still must be taken to obtain a particular bond refraction. For example, the conjugated double bond varies from 1.14 to 1.58, the average being 1.29.

III. THEORY OF THE RAYLEIGH INTERFEROMETER

In the Rayleigh interferometer light from a narrow slit is collimated by a lens and passed through a double slit. One of the divided beams passes through the reference cell, the other through the solution to be compared. The emergent beams recombine to form interference fringes in the focal plane of a telescope. Thus, in principle, the Rayleigh interferometer may be regarded as a diffraction grating with only two openings, Although, as in the case of the usual diffraction grating, it is not the diffraction effects at each slit that give it its important properties, but the interference effects of the beams diffracted at the two apertures. We will, therefore, briefly investigate the shape and intensity distribution of the fringes produced by this double slit.

The intensity and distribution of the fringes may be found through a detailed derivation of the double-slit diffraction phenomenon. The resulting equation is

$$I \cong 4 R_0^2 \frac{\sin^2 \beta}{\beta^2} \cos^2 \gamma \ , \qquad (37)$$

which states that the intensity is proportional to the square of the amplitude. The factor $\sin^2 \beta / \beta^2$ is that derived for a single slit of width a, and the quantity β is a variable which signifies one-half the phase difference in radians between the contributions from opposite edges of any one slit. The second factor $\cos^2 \gamma$ is characteristic of the interference pattern produced by the two beams of equal intensity but with phase differences δ ; it signifies one-half of the phase difference from corresponding points in the two adjacent slits. The resultant intensity will be zero when either of the two factors is zero. For the first factor this will occur when $\beta = \pi$, 2π, 3π, ..., and for the second factor when $\gamma = \pi/2, 3\pi/2, 5\pi/2, \ldots$. The two variables β and γ are not independent. The difference in path from the two edges of a given slit to the screen is a sin θ. The corresponding phase difference is $(2\pi/\lambda)$ a sin θ, which equals 2β . The path difference from any two corresponding points in the two slits is d sin θ as illustrated in Figure 2 for the two points at the lower edges of the slits, and the phase difference is $(2\pi/\lambda)$ d sin θ which equals 2γ . Therefore, in terms of the dimensions of the slits,

$$\frac{\delta}{2\beta} = \frac{\gamma}{\beta} = \frac{d}{a}. \qquad (38)$$

A study of Figure 3 reveals that certain orders are missing, or at least one reduced to two maxima of very low intensity. These so-called missing orders occur where the condition for a maximum of the interference, and for a minimum of the diffraction, are both fulfilled for the same value of θ, that is, for

$$d \sin\theta = m\lambda \quad \text{and} \quad a \sin\theta = p\lambda \qquad (39)$$

so that

$$d/a = m/p. \qquad (40)$$

The physical picture of the cause of missing orders is as follows.

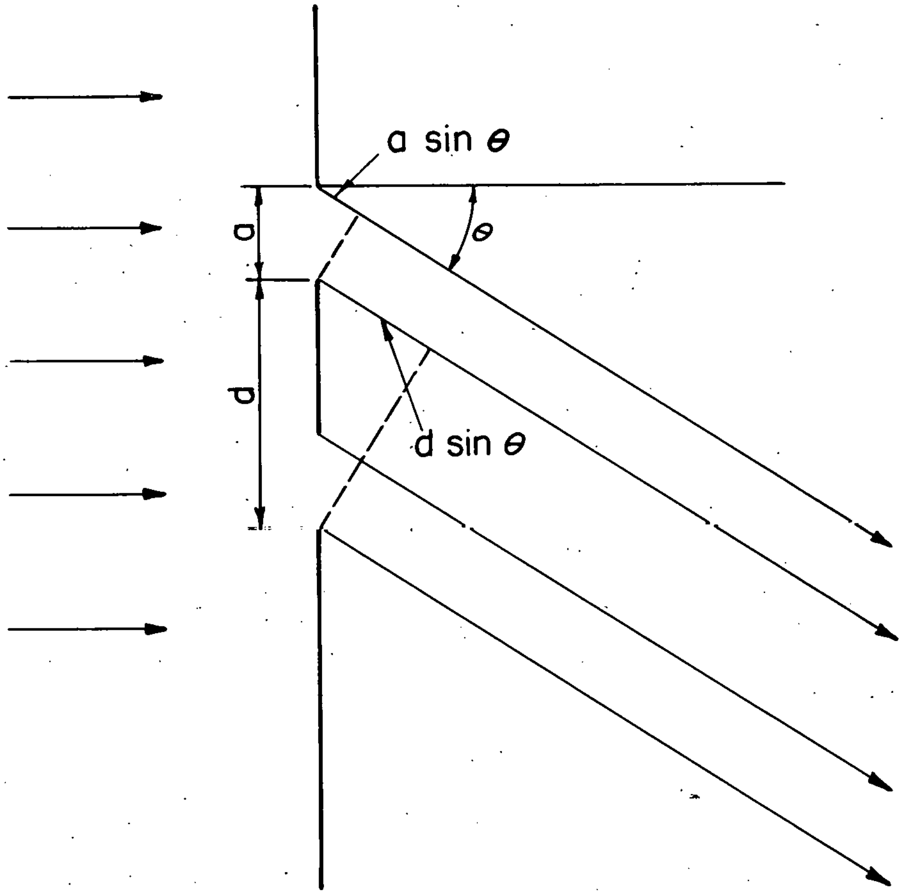

Figure 2. Illustration of the path difference of parallel rays.

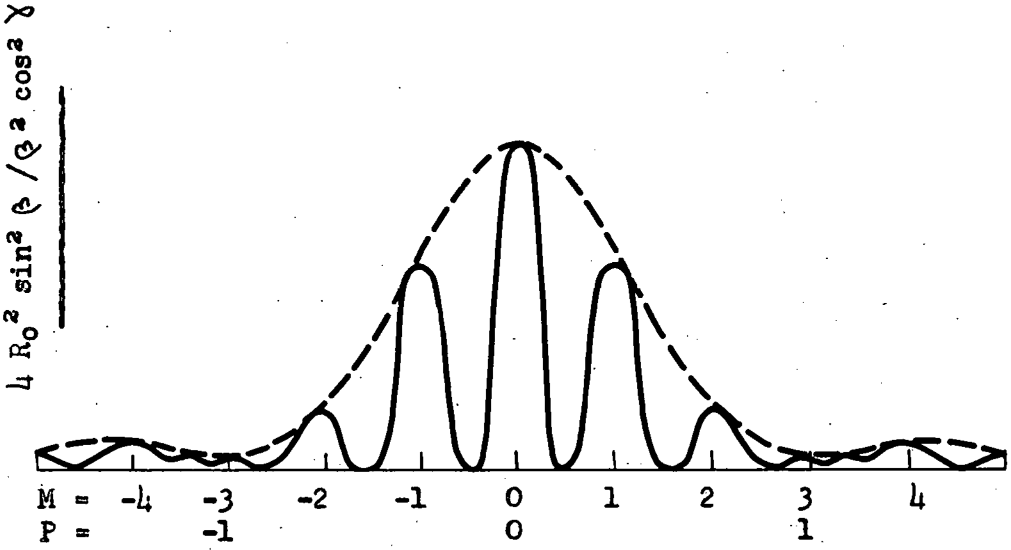

Figure 3. Pattern for a double slit.
The broken line envelope designates the diffraction pattern.
The solid line designates the interference pattern.

The point on the screen where the missing order, $m = \pm 3$ (Figure 3), occurs is just three wave-lengths farther from the center of one slit than from the center of the other. Hence we might expect the waves from the two slits to arrive in phase and to produce a maximum. However, this point is at the same time one wave-length farther from the edge of one slit than from the other edge of that slit. Addition of the secondary wavelets from one slit gives zero intensity under these conditions. The same holds true for either slit so that, although we may add the contributions from the two slits, both contributions are zero and must therefore give zero resultant.

An important aspect of the optical parts of the instrument is that there are criteria as to how flat the flat surfaces must be. If the flat surfaces of an optical part, such as the end plates of the cells, or the compensating plates, are not flat to within a quarter of a wave-length, then the fringes will be distorted in some manner. This criterion of a quarter of a wave-length can be arrived at by considering a surface of varying thickness. If the surface is not plane-parallel, so that one part makes an appreciable angle with another, the interfering rays do not enter the eye parallel to each other, but appear to diverge from a point near the surface. This will result in curved fringes or complete lack of fringes if the path difference is large. We can apply the equation

$$2\,nd \cos \phi = (m + \tfrac{1}{2}) \lambda , \qquad (41)$$

for bright fringes, as given by films of varying thickness. If $\cos \phi$

equals unity, i.e., observations are made normal to the field, then for the number of fringes m equal to zero,

$$nd = \lambda/4 \qquad (42)$$

where nd is the optical path. So it is seen that, for zero fringe movement, the optical path should differ by a quarter of a wave-length or less and the surface of a flat plate should be ground to a quarter of a wave-length.

IV. APPARATUS AND METHOD

Construction of the Interferometer

The Rayleigh interferometer illustrated in Figure 6 consists essentially of a light source, a single slit, a double slit, a double cell for the sample and standard substance, two thin movable glass plates inclined in the optical path and controlled by movement of a calibrated dial, and a telescope to observe the fringes. The source is focused on the single slit by means of a lens, and a filter is mounted in front of the slit to provide monochromatic light. An achromatic objective lens makes the light parallel and a deviation prism brings the two sets of fringes together for easier matching.

The general construction, materials, and over-all plan of the instrument are now described along with details of the construction of each of the parts. For this purpose, it will be of value to refer often to the schematic diagram of the interferometer (Figure 4) and the photographs (Figures 5 and 6).

The support upon which all the carriages rested was an optical bench consisting of two bars each two meters long, one a round rod and the other a beveled square bar, supported by four posts. These posts are seen in Figure 6, and it is to be noted that each of the four have two leveling screws so that the whole system could be accurately leveled. A series of carriages were machined from aluminum and served to support the various parts of the interferometer. A knurled hand screw passes

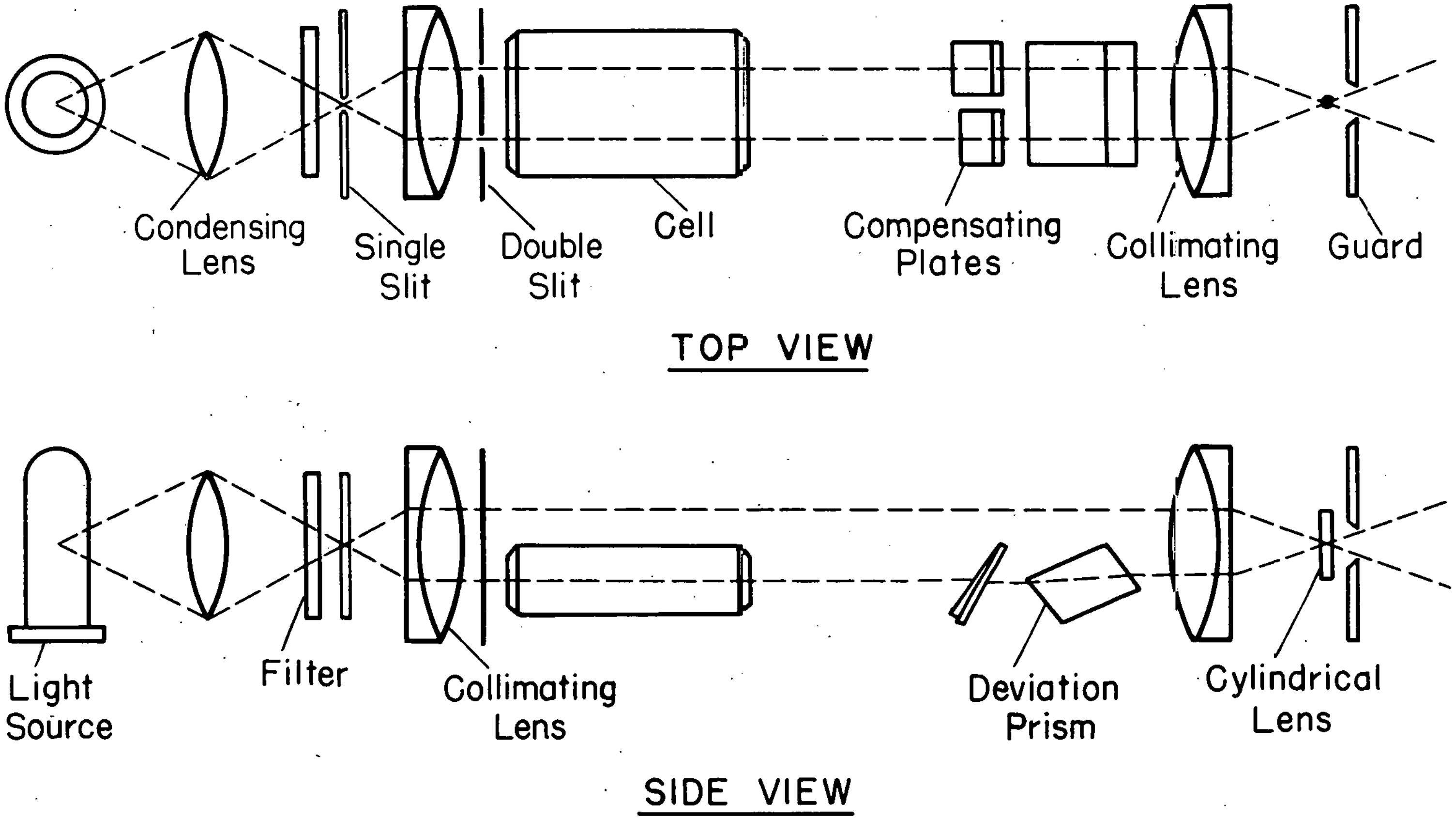

Figure 4. Schematic Diagram of the Interferometer

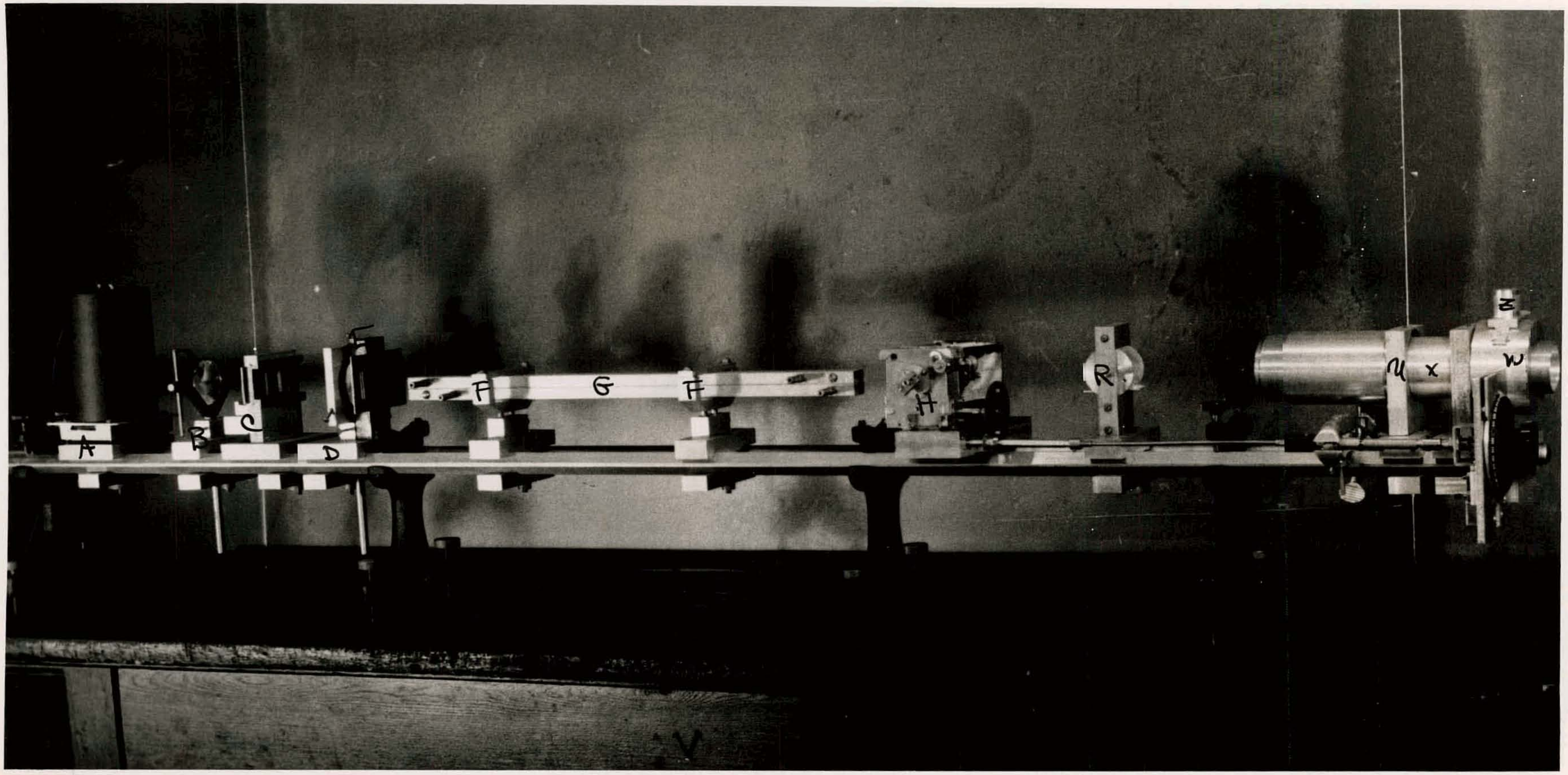

Figure 5. The Interferometer (side view)

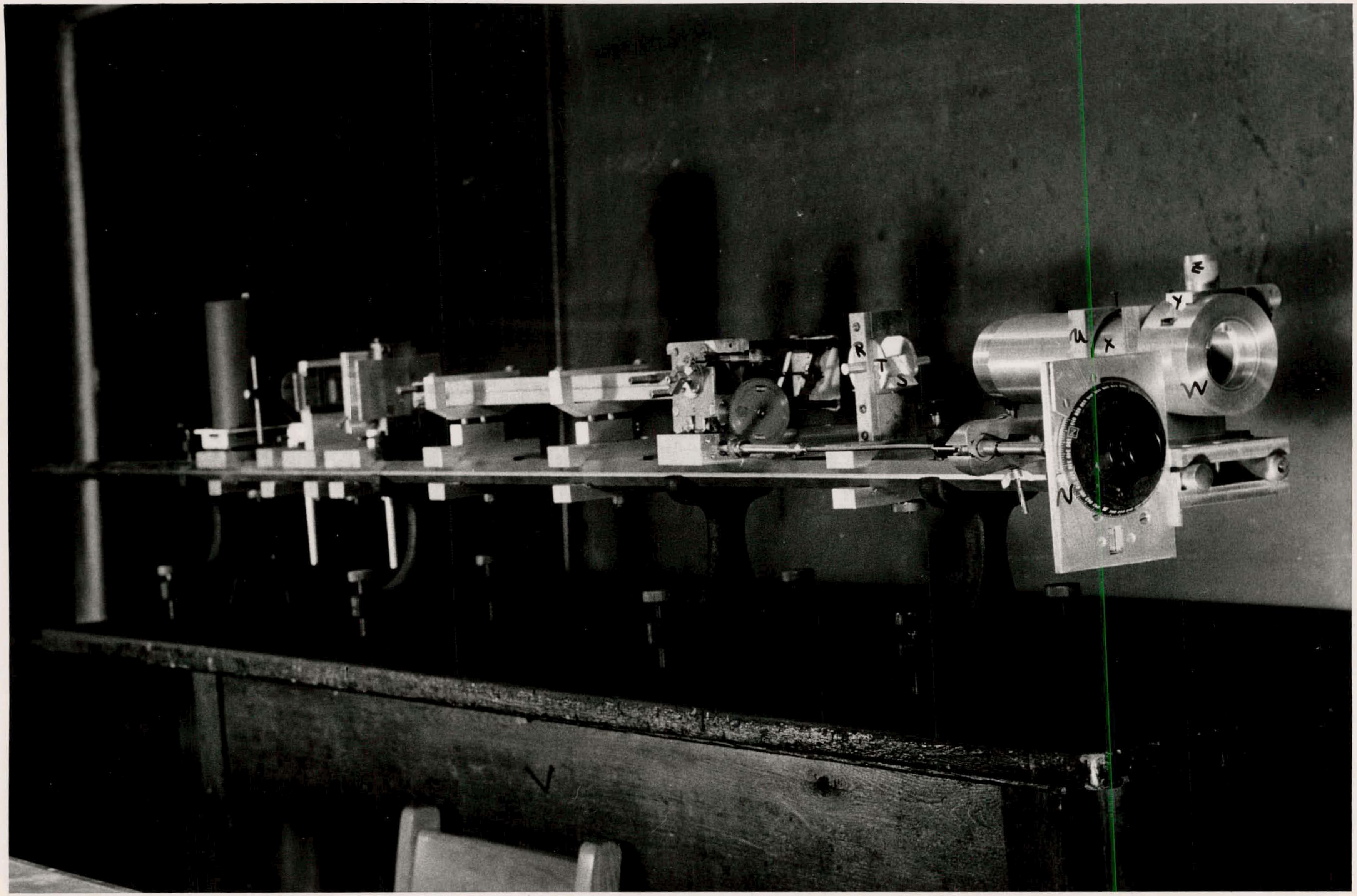

Figure 6. The Interferometer (end view).

through both the base of each carriage and a matching block beneath so that tightening the screw locked the carriage in place; the design of the pieces prevented twisting.

A mercury-arc source* was enclosed in a special housing A mounted on the optical bench. A magnifying lens of 6" focal length is held in a standard lens-holder B (see Figures 5 and 6) which can be rotated, moved up and down, or moved laterally. This makes it possible to focus light exactly on the single slit.

An upright holder C is used to hold the filter and single slit in place; both may be moved laterally in grooves in the holder. The center of the single slit was fixed at a position 2.5" above the carriage. This determined the level at which the other pieces were set.

The next carriage D supports both a 2" diameter achromatic lens of 7" focal length and the double slit. The lens holder which held the achromatic lens could be moved laterally or rotate. Next to the lens holder was a vertical upright E which held two clamps similar to those used on a microscope stage, enabling the double slit to be adjusted. The double slit was milled from aluminum, one edge of a 60° dovetail cutter being used to obtain a uniform slit aperture 0.5 mm. wide and 4 cm. long; the distance between slits was 1 cm.

The supports for the gas cells F could be moved laterally by moving the aluminum blocks G in a slot milled in the carriage.

Originally four 50 cm. tubes, each 1 cm. x 1 cm. in cross-section, were to be boxed together. If the diagonally opposite tubes are filled

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* General Electric Co., Type AH-4

with the same gas and the other set of diagonally opposite tubes are evacuated, the combination acts the same as two tubes each twice as long. This arrangement of the gas cells G can be seen in Figure 5. The mechanical system for the compensating plates H was made to hold the four plates for the four-tube cell. The object of the device containing the compensating plates is to enable two pieces of glass J,J in diagonally opposite corners to be rotated by turning shaft K through a measurable angle, independently of the pair L,L (Figure 7). The latter pair can be rotated through any desired angle by turning shaft M, which is coaxial with shaft K; this angle of rotation need not be measured. In operation light passing through one diagonally opposed pair of cells passes through plates J,J and light from the other pair through plates L,L. The position of the latter pair is fixed in any given series of measurements but may be changed when it is desired to alter the sensitivity of the instrument. The sensitivity is least when plates L,L are at an angle to the beam and greatest when plates L,L are perpendicular to the beam. An extremely small rotation of the compensating plates J,J must correspond to a large rotation of the dial so that up to 1/100 of a fringe may be detected. The glass plates were cemented to a framework (P and Q) which was substituted for the plates of a precision radio condenser. The spindle of the framework Q, which held one set of plates, was rotated by a set of anti-backlash gears with a 1:10,000 ratio and the angle of rotation was read on a dial N. A compass dial divided accurately into 360 degree divisions (Figure 6) was used for the dial. A counter was attached through a system of gears so each complete rotation of the dial would

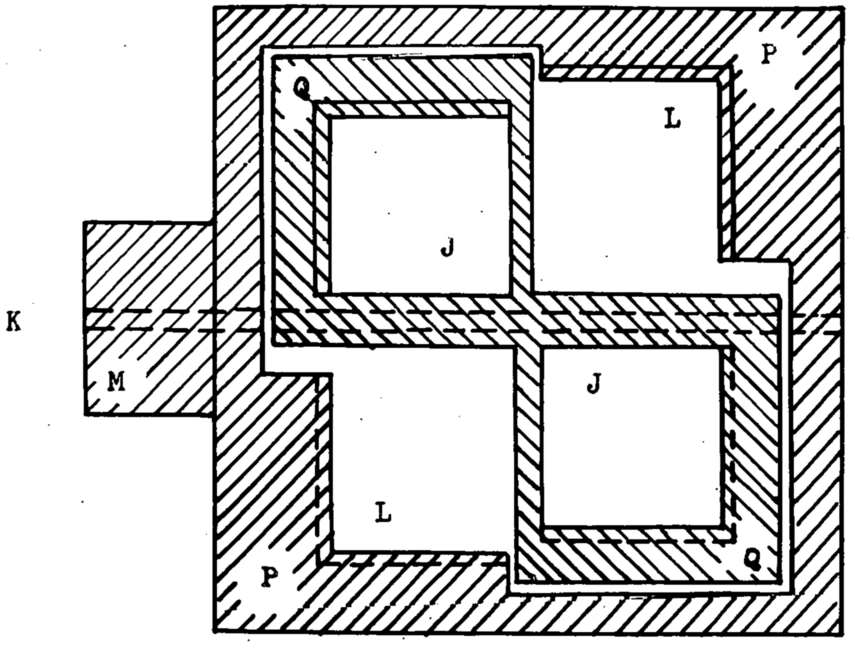

Figure 7. Framework to hold the compensating plates.

register a mark. The other set of compensating plates were placed in the frame P illustrated in Figure 7. This piece was large enough to allow the framework Q to rotate inside it and was shaped to hold the plates parallel to each other and even with the other set when one wished to place the two in coincidence to observe the white light fringes. In actual practice, only the bottom two glass plates were used; the upper two were omitted because of the difficulty in adjusting the four compensating plates; also, this gave stationary fringes which acted as the reference set.

The deviation prism R was placed in an upright holder. The exact height of this prism had to be quite carefully set so that a slight tilt of the prism would raise the lower fringes and cut out the view of the obstructions (Figure 8). The prism S (Figure 6) was placed in a cylindrical holder T, the center axis of which extended through two holes in the upright and allowed the prism to be rotated.

The telescope arrangement is best described in two parts. The first part holds the achromatic collimating lens which focuses the parallel light on the cylindrical lens, and the second part is the mechanism holding the cylindrical lens. The whole telescope was held in position by two large uprights U and V. The holes in these were somewhat larger than the actual size of the tubing of the telescope so that, by means of positioning pins and springs, the telescope could be moved some distance up and down at both uprights. This is illustrated in Figure 9 which also shows the method by which rotation of the focusing sleeve will move the lens parallel to the light beam but will not rotate the lens or any

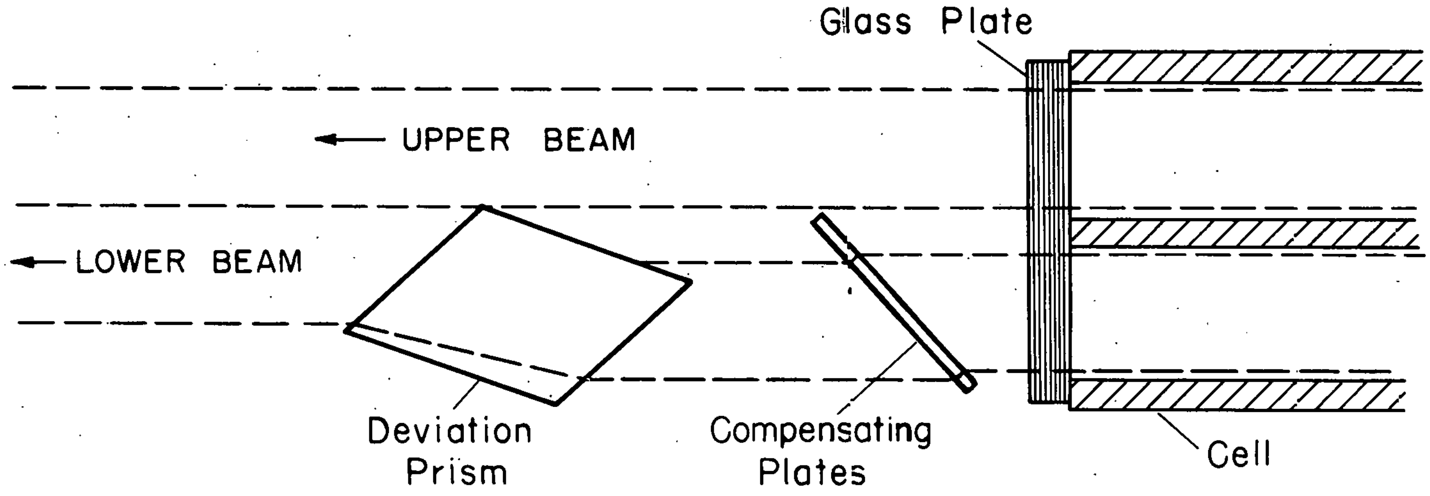

Figure 8. Diagram illustrating the action of the deviation prism.

other part of the system. Figure 10 illustrates the second part of this system. The large cylindrical block W, as seen in Figure 10, fitted closely into the aluminum tube X and could rotate. The block W held a piece of aluminum Y, which could be moved laterally in a slot by means of a screw. In the sliding piece Y a vertical circular hole holds a knurled knob Z which extends down into the large opening of the cylindrical block and holds the cylindrical lens, which was simply a piece of thin stirring rod. A one-eighth inch in diameter hole was cut in the center of a circular piece of thin aluminum and placed in a threaded ring to serve as an aperture; it could be rotated in and out of the cylindrical block.

The Cells

The cells for use with liquids were cut from a block of Monel and the faces were machined flat. Two cells were made, both 1.17" wide and 1.15" high. The small cell was 0.9611 cm. in length and the large cell 2.3706 cm. in length. These lengths were determined by a traveling microscope. Two troughs were machined in the piece, each 0.860" deep, leaving a middle partition 0.120" wide. Glass plates, optically flat to one-quarter wave-length, were cemented on the ends with optical wax.*
A cover was used to prevent evaporation. In operation these cells were placed in a block of aluminum (7" long by 5" wide by 3" high) which had a trough cut down the center just wide enough to contain the cell and

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* Equal parts of beeswax and rosin.

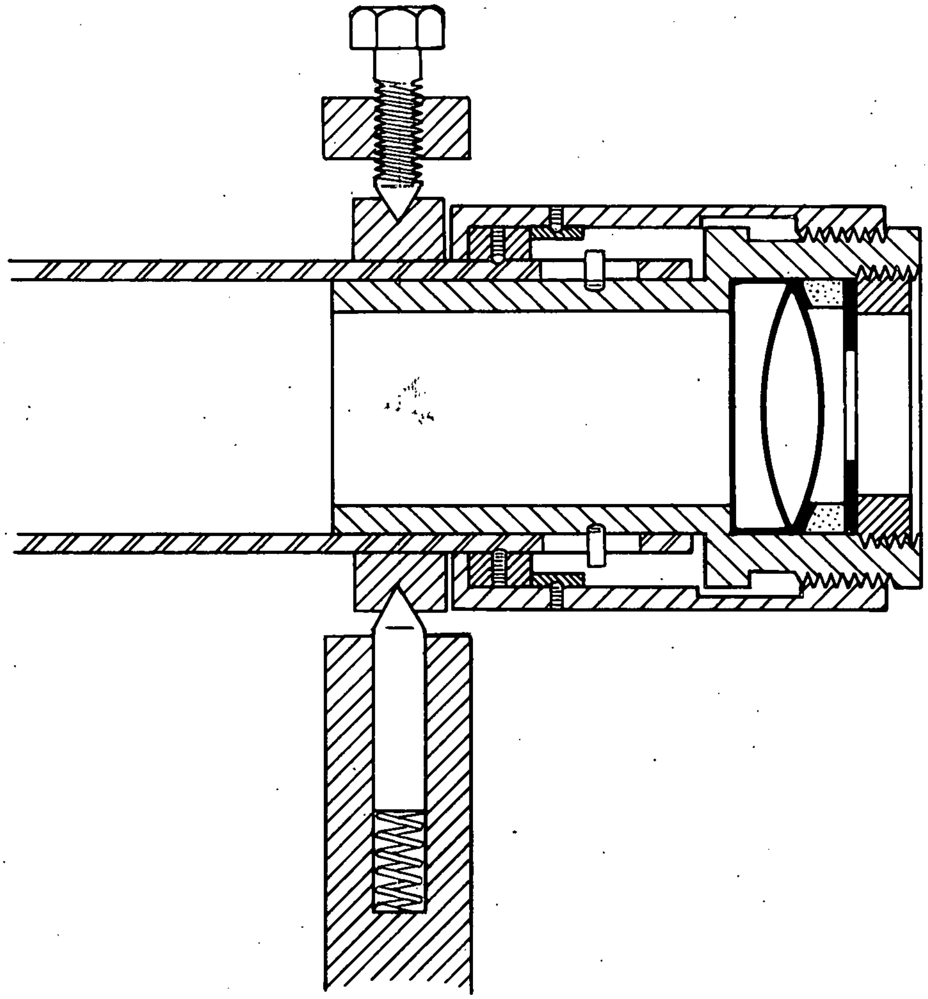

Figure 9. Mechanism for adjustment of the focusing lens of telescope.

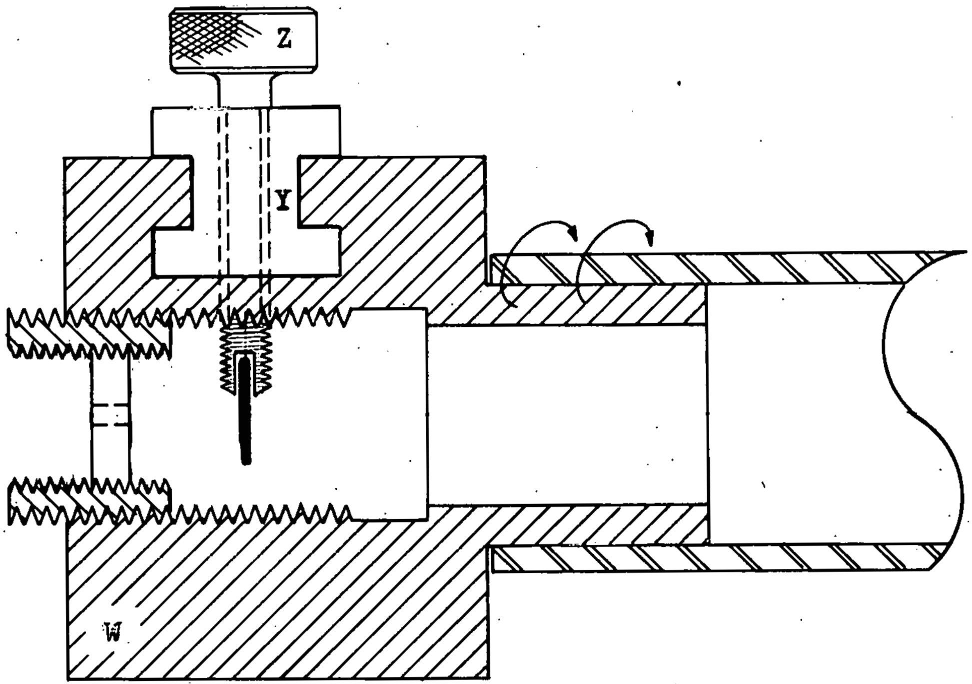

Figure 10. Cylindrical lens holder.

provide good thermal contact. A cover one inch thick was then placed over this. The block had been so constructed that water could be circulated through it and the cover to keep the cell at a constant temperature. All the solutions to be measured were kept in a large constant-temperature bath. A pump circulated water from this bath to the cooling system for the cells. The solutions were thus at the same temperature as the cell and thermal equilibrium was usually reached in ten minutes or less. Variations of ± 0.10°C in the bath temperature rarely affected the cell temperature over ± 0.01°C since the Monel cell block responded slowly to a change in temperature.

The gas cells consisted of two copper-plated brass tubes three-eighths of an inch square and 102.08 cm. long, which were soldered together. The ends were milled flat and quartz plates attached using fluorothene wax. (This cell was to be used with halogen fluorides.) There was one opening in each tube through which the gas was introduced or removed. A water jacket surrounded the tubes except for the ends. It was constructed with a space above the cells so the upper beam, which provided the reference fringes, would be present. Silver solder was used wherever it would be in contact with the gas to be measured. The cells and windows were intended for use with the highly corrosive halogen fluorides but were suitable for any gas.

Operation

Solutions

The system is first aligned by removing the cells, deviation prism, and compensating plates, and obtaining good sharp fringes. This is done in the following manner. The first lens B is made to focus the light directly on the single slit, which has been previously located in the center of the system. With the light on, the first collimating lens (Figure 5) is placed in position at exactly its focal length away from the single slit. This is accomplished by placing a mirror in the light beam and reflecting the parallel light from the collimating lens back through the lens and forming the image of the single slit just next to the actual slit. By moving the collimating lens along the optical bench, the slit image will be seen to be wide and indistinct, then narrow and clear, and once again indistinct. The position for the sharpest image possible is located and the lens fixed there. The telescope is next inserted with only the focusing lens in place and the parallel light and focusing lens are centered. The double-slit is then fixed in place and moved laterally so that the middle of the two parallel, vertical beams of light from the double-slit is in the exact center of the focusing lens. This may be observed from either side of the telescope. The cylindrical lens is then put in place and moved laterally, or rotated by rotating the cylindrical block W, to locate the fringes. It was also occasionally necessary to rotate the cylindrical lens about its axis to obtain satisfactory fringes. After the fringes have been found minute variations in the adjustments can be made to increase their brightness and sharpness. The focusing lens might be moved parallel to the light beam by turning the focusing sleeve, the collimating lens may be twisted slightly in position, and cylindrical lenses of different sizes may be used. After this, the cells are put in place, one beam passing through one side, the other through the other side. The compensating plates are put in place and adjusted so the fringes are not distorted. The deviation prism is next added to remove the effect of the obstructions by raising the lower beam (see Figures 11a and 11b).

The constant-temperature water bath is connected and water is circulated through the cooling block around the cell. The solvent to be used in the measurements is placed in the cell and thermal equilibrium established. Temperature gradients in the liquid are shown by weaving, curving, and other motions of the fringes. Any air current, caused by a fan, heat, person breathing close to the instrument, etc., will cause this shimmy of the fringes.

The mercury light is then replaced by a white light source. A very few strongly colored fringes are seen in the upper reference set. The compensating plates are rotated by the dial until the lower fringes come into view and are made coincident with the reference set. The filter is removed for this operation. One then switches back to the green mercury light and, remembering which fringe is which, the zero position is approached from both directions and the average reading taken for the position of the zero-order fringe.

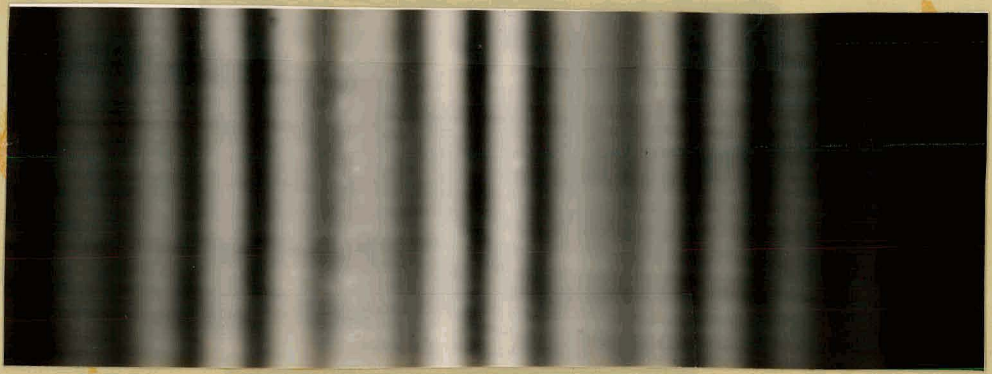

Figure 11a. Monochromatic light fringes

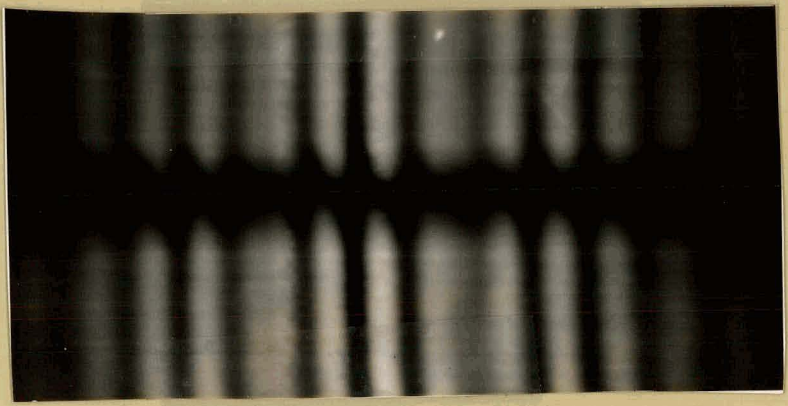

Figure 11b. Fringes with obstructions

The solution is now placed in one side of the cell, allowed to come to thermal equilibrium, and white light substituted again. The dial is rotated until the white light fringes are again coincident with the reference set. The mercury light is again used to obtain the average reading of the position of the zero-order fringe because fringes obtained with monochromatic light are so much sharper. The solution is removed, the cell rinsed thoroughly with distilled water and the zero-order fringe reading checked as before. The cell is then rinsed with the next solution and filled again. This rinsing is always a necessary precaution because the dilution of the solution by the water remaining in the cells causes an error, especially with very dilute solutions. Drying the cell did not prove practical because it disturbed the cell position and changed the zero point. It also proved unsatisfactory with more concentrated solutions since appreciable amounts of salt remained.

The solutions were added with a pipette which was first rinsed with the solution; they were taken out by an eye-dropper. The solutions were made up from the same batch of water that was used for the standard reference liquid, and the rinsing liquid was the same.

The procedure for the calibration and sample calculations are given in Section V.

The refractive indices of the solutions of the two salts, potassium ferrocyanide and potassium ferricyanide, were measured with the Dipping Refractometer made by Bausch and Lomb Company. The measurements were made using only prism A and were made with the yellow sodium doublet radiation as a light source.

Gases

The system was aligned as described in the previous section on solutions. The gas cells were then placed in the system and the deviation prism adjusted in place. The cells were raised or lowered until the fringes appeared sharpest and brightest. The compensating plates may or may not be used. If not, the water bath was connected to the water jacket of the tubes, and both cells were connected to the vacuum line and evacuated. The whole system must, of course, be devoid of leaks. Using the mercury light source, and watching the fringes, the gas to be measured is slowly let in one side of the cell. After a number of fringes have passed the valve is shut off and the pressure recorded from the nercury manometer. These two quantities are all that is necessary to calculate the refractive index. The fringes should be watched carefully before introduction of the gas and after. A slow movement in either direction indicates a leak, reaction, adsorption, etc. The fringes should start perfectly matched with the reference set and end in the same way to eliminate estimating fractions of a fringe. The fringes can be matched with a precision of about one-tenth of a fringe. If the gas may be condensed by use of a Dry Ice-isopropanol bath or a liquid nitrogen bath, it is wise to count the fringes and read the pressure as the gas is removed from the cells. If the values obtained are not the same, then some difficulty is present which must be located. Impurity of gases can cause a great amount of trouble. A small percentage of impurity, even if only slightly more volatile, will tend to go into the cells first and give a greater percentage of impurity in the first few measurements. This is overcome by calculating the values as one makes the measurements and continuing to make measurements with fresh samples of gas until constant values of the refractive index are obtained.

A second method, using the compensating plates, eliminates the necessity of allowing only an integral number of fringes to pass. The exact fraction of a fringe can be found in the manner illustrated by the following typical example. The fringes are set in exact coincidence when the cells are evacuated. If about 140.5 fringes have passed when the valve is shut off, then readings are taken of the 140th and 141st fringe. If the reading for the 140th fringe reading was 220.0, that for the 141st 240.0, and the initial reading 228.5, then the fraction of a fringe is

$$\frac{228.5 - 220.0}{240.0 - 220.0} \quad \text{or } 0.425.$$

Details of the actual handling of the gases are given in the following section which describes the gas-handling system. The methods of calibration and calculation have been described in Section VI.

Gas Handling Equipment

Vacuum Line

The cells were to be used for both unreactive gases and the reactive halogen fluorides and the vacuum system was built so that both could be handled. Halogen fluorides react with glass, mercury, etc., and so must be handled only in a special all-metal system. To this end, valves A, B, and C in Figure 12 are metal with brass bellows and all connections to them and to the cell are copper tubing, silvered-soldered in place. Closing valve B shuts off passage to the Bourdon gage but not to the cell. Likewise, when valve C is closed to the sample container, passage from B to the Bourdon gage remains open. The rest of the system was constructed of Pyrex glass, using vacuum stopcocks. The two three-way stopcocks E and G, and those on the manometer, were always kept open during measurements.

When an unreactive was to be measured, its container was attached to the open end of valve F. The containers were of glass and were sealed directly to the vacuum line while the materials were frozen out in a liquid nitrogen bath. Then valves D, F, and A are opened to the vacuum line, while valve B is shut. When the plug of the three-way stopcock F was rotated, it closed the connection to the vacuum line and opened the connection to the substance so there could be no accidental loss of the compound by pulling it through the vacuum line. As the gas slowly entered the cells the fringes were counted and the manometer read with a cathetometer. The substance may be condensed back in the container by cooling it, or merely pulled out through the vacuum line by turning stopcock F. Stopcock F is the only one that needs to be turned to allow the gas in and out of the cells and the manometer. It was placed within reach of the operator when observing the fringes. It is suggested that a hand tally always be used when counting the fringes as the mind tends

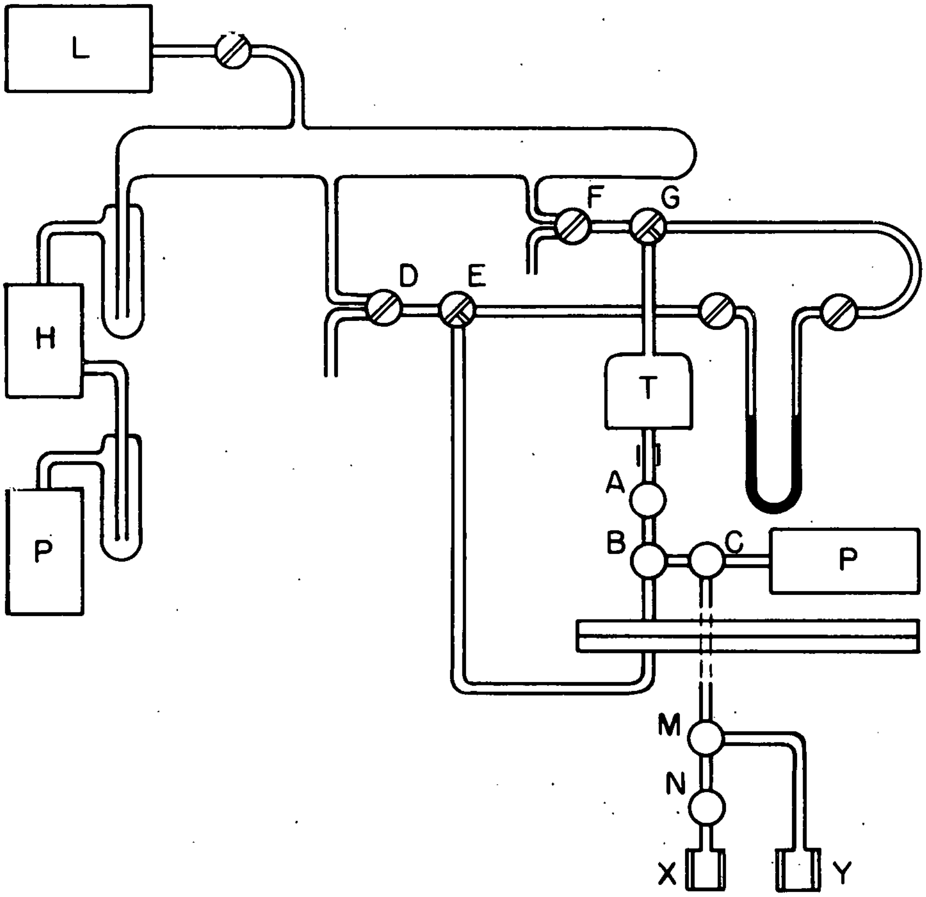

Figure 12. System for evacuating and filling the gas cells.

to wander and the count is easily lost, especially when several hundred fringes are to be counted.

For reactive compounds, both valve D and valve F were opened to the vacuum line. The sample tube and an empty Monel tube Y were connected to the vacuum line at C through Hoke bellows valves M and N. The sample has been placed in the container X and when connected valves M and C are opened. After evacuation to a suitably low pressure (about 0.1 micron), valves A and M are closed. Opening valve N allowed the gas to pass into the cell and the connecting Bourdon gage where the pressure was read and recorded. The fringes were counted as the gas entered. After closing valve N, valve M was opened and the gas condensed into sample tube Y which was surrounded by a Dry Ice-isopropanol mixture or by liquid nitrogen. A certain portion of the gas sometimes did not condense. Then the gas was pumped out, passing through the soda-lime trap, by closing valve M and opening valve A.

The purpose of the sample tube Y was to condense the gas, which may have reacted somewhat with the system, into a separate container and so not contaminate the sample in tube X. The specially purified halogen fluorides were stored in Monel tubes and had been handled only in a special all-metal vacuum line.

Measurement of the Pressure of the Halogen Fluorides

Since the halogen fluorides react with glass and mercury, the conventional pressure measuring devices such as were used for the other gases could not be utilized here. A method of measuring the pressure accurately over the range 0-760 mm. of Hg. was devised. Several Helicoid* gages were already in use and had an accuracy of ± 1 mm. at the best. The Helicoid mechanism was dismantled and a micrometer was attached to the Bourdon tube in such a way that the movements due to pressure changes, which expanded or contracted the tube, were detectable by it. The contact between the micrometer and the tube was detected by the opening or closing of a "magic-eye" tube. The electronic circuit used for this purpose is given in Figure 13. The micrometer was turned until the eye just opened (indicating contact) and the reading taken. These micrometer readings were calibrated against the mercury manometer. The precision of the readings on the micrometer was ± 0.0004 inches which corresponds to a pressure of ± 0.25 mm. of mercury. Since the calibration does vary with changes in temperature, the whole unit was enclosed in a constant temperature air bath. This used a light bulb as a heat source, a fan for circulation, and a bimetallic thermoregulator to maintain the temperature constant with 0.1°C.

Measurement of Densities of Solutions

All density measurements on the solutions were made in a modified Ostwald pycnometer.[156] The arms of the pycnometer were of equal and uniform bore and were calibrated to read directly the volume in each arm above the zero point. The volume of the pycnometer to the zero

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* American Chain and Cable Co., Helicoid Gage Division

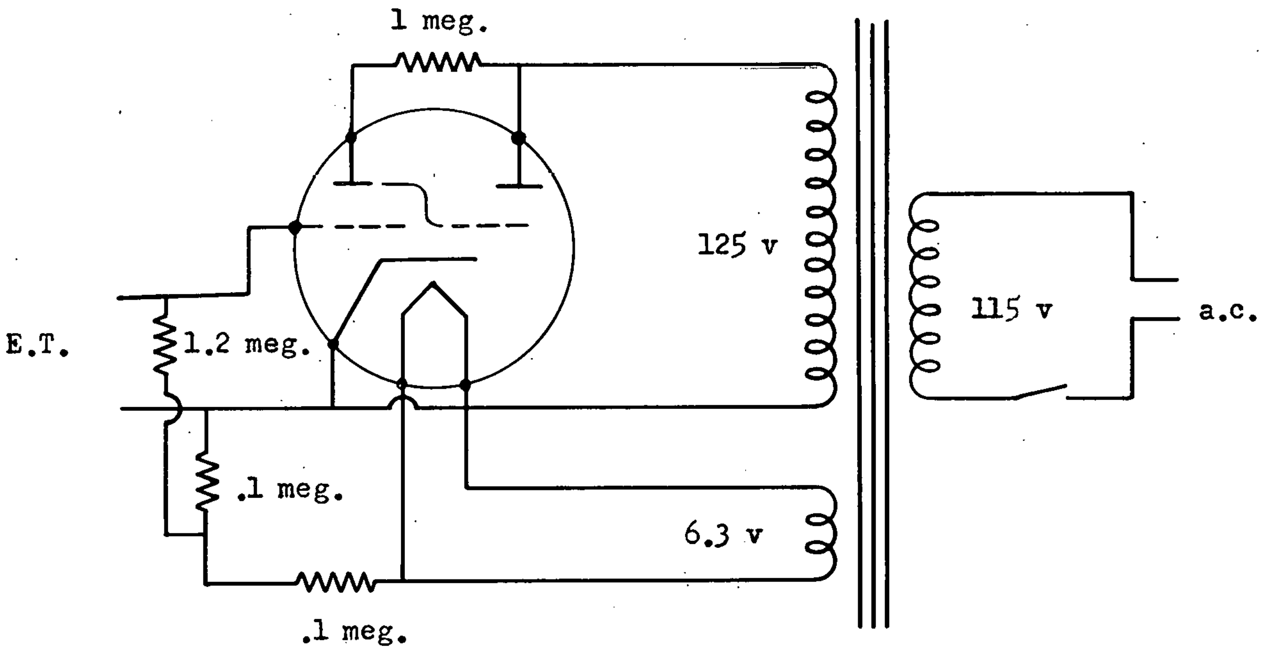

Figure 13. Electronic contact indicator for the pressure gage.

marks was determined by first weighing the pycnometer and then filling it with water to some level in the arms and reweighing. After a suitable period of waiting while the pycnometer was immersed in a constant temperature bath, the levels of the arms were read. The density of water is available in the literature so the volume could then be calculated. From this, the volume of the arms was subtracted, and hence, the volume of the pycnometer determined. This was repeated several times and an average value of 20.2611 accepted.

In the determination of the density of solutions, the same procedure was followed except that the experimentally determined weight was divided by the volume of the arms plus the zero volume (20.2611 cc.).

The usual precautions were observed, such as handling the pycnometer only with covered fingers, removing the static charge if any accumulates, rinsing thoroughly with water several times after a solution was removed, and then with acetone and ether rinse, and allowing the pycnometer to come to equilibrium with the moisture in the air before weighing. All weights were corrected for buoyancy.

A plot of the molarity of the solution versus the reciprocal of the density should give a straight line for dilute solutions. If any point was not on the line the density measurement was rechecked.

Materials

Halogen Fluorides

Chlorine monofluoride was prepared in a nickel system by mixing equal amounts of chlorine gas and chlorine trifluoride gas at about 200°C.

Both the chlorine and the chlorine trifluoride were previously purified by several distillations. The product was purified by trap-to-trap distillation. Its purity was checked by a determination of the spectrum. This indicated that traces of a chlorine oxide might be present.

The remaining halogen fluorides were purchased from Harshaw Chemical Company. These were each purified and the purity usually determined from freezing point curves. Iodine pentafluoride was purified by distillation in a Monel still. The molal concentration of impurities was found to be 0.0025. Bromine pentafluoride was purified by a similar distillation and the concentration of impurities found to be 0.02 molal. Bromine trifluoride and chlorine trifluoride were not obtained as pure as the other compounds. These were distilled from the iron shipping tank into a trap on an all-nickel vacuum line; three successive trap-to-trap distillations were made with the middle fraction taken for measurements. Probably no more than one to two mole percent of impurities were present.

Fluorocarbons

Purified samples of perfluoroethyl ether, 1,1,1,2,2,3,-heptafluoropropane, and perfluorotriethyl amine were furnished through the courtesy of W. H. Pearlson of the Minnesota Mining and Manufacturing Company. These compounds contained only traces of impurities.

The sample of purified chlorotrifluoroethylene was obtained from the Union Carbide and Carbon Corporation. This was purified by three trap-to-trap distillations.

Salts

Potassium chloride, sodium chloride, ammonium chloride, sodium silicofluoride, and potassium silicofluoride were Baker's Analyzed C. P. grade meeting the A.C.S. specifications. These were recrystallized four times using the same batch of water that was used to make the solutions and serve as the reference liquid.

The potassium bifluoride was Merck's pure grade and the sodium fluoride Merck's reagent grade. These were recrystallized as described above.

All the fluoborates were Baker and Adamson products, made by the General Chemical Division of Allied Chemical and Dye Corporation. The fluoboric acid was purified by the company and was said to contain 2.13% of meta-boric acid as an impurity. The others, potassium fluoborate, ammonium fluoborate, and sodium fluoborate were of technical grade and were recrystallized five times; water from the same batch that served as the reference liquid was used for the recrystallizations and was also used to make the solutions and diluted aliquots. Sublimation of ammonium fluoborate proved unsuccessful. Potassium fluotitanate was a student preparation and some care was taken in recrystallizing it to assure a fine product.

V. REFRACTIVE INDICES AND MOLAR REFRACTIONS OF SOLUTIONS

Theoretical

The insertion of a cell containing a pure liquid or a solution into the beam produces a discontinuous shift of the fringes so that the number of fringes displaced cannot be counted. This introduces a difficulty not encountered in the measurement of the refractive index of a gas, since gases can be introduced gradually into the light path by allowing them to flow into an evacuated tube, and the number of fringes displaced can be counted directly. Since, with monochromatic light, it is impossible to tell which fringe in the displaced set corresponds to a given one in the original set, white light is used to locate the so-called zero-order fringe. This is the particular fringe produced for exactly equal optical paths of the two beams. After location of this fringe, monochromatic light is used and the compensating plates are rotated until the zero-order fringe is brought back to alignment with the zero-order fringe of the fiduciary set of fixed fringes; the number of fringes displaced can then be counted.

It should be mentioned here that the interferometer is rarely used to measure the absolute refractive index of a pure liquid or solution. The number of fringes shifted by the introduction of the liquid is usually too great to count even if the change in optical path is not so great as to destroy the visibility of the fringes entirely. Usually, however, the fringes are destroyed and the interferometer must be used as a differential instrument. It therefore finds its greatest application in the measurement of refractive indices of dilute solutions or diluted aliquots of more concentrated solutions. Since the solutions that are to be compared are very close in composition and the method is a differential one, no special regulation of the temperature is required as both standard and solution will have the same temperature coefficient. With aqueous solutions a variation of ± 0.5°C is permissible even in very precise work.

We now discuss the white light fringes in greater detail since their use is essential. With monochromatic light there is one set of fringes for the particular wave-length used. Between the bright fringes there is destructive interference, i.e., dark fringes. With white light there is a different set of fringes for each wave-length of light present and so at certain intervals the fringes of one set overlap those of another. In the region of the zero-order fringes all the various wave-lengths are superimposed and result in a white fringe. It is bordered by a sharply defined black region. The first-order fringe, as the first fringe on either side of the zero-order fringe is called, will not have all the wave-lengths exactly superimposed. In fact it will have a blue edge on the side toward the zero-order fringe since the wave-length of the blue radiation is shorter, and will have a red edge toward the opposite side since the wave-length of the red radiation is longer. The first-order fringe has thus become spread somewhat and the dark fringe between the first-order and the second-order fringe has become smaller in width. This spreading of the fringes continues and even at a short distance from the zero-order fringe the overlapping has become so uniform the fringes can no longer be observed and white light results. This provides a method of locating the center as shown in Figure 14. The blue fringes of shorter wave-length (illustrated in Figure 14a), and the red fringes of longer wave-length (illustrated in Figure 14b), are superimposed with fringes of intermediate wave-length to form the pattern shown in Figure 14c. For purposes of illustration the red and blue bands have been chosen of convenient width and spacing such that only seven fringes are distinguishable in the superimposed pattern while actually perhaps twelve are distinguishable.

This method of locating the zero-order fringe gives rise to some complications. If the optical dispersion in the solution and the compensating plate differs too much from the optical dispersion in the reference liquid and the other compensating plate, the edges of the zero-order fringe become gradually colored, while one of the adjacent first-order fringes loses its usual color and becomes white. Thus the location of the zero-order fringe will be in error by one whole fringe because the reference set remains unchanged. For still greater differences in dispersion the adjacent second-order fringe becomes white, and so on.

One method of meeting this difficulty is to take readings at several closely spaced concentrations covering the region in which the shift occurs. Another method available is to calculate the chromatic aberration of the compensator and match it to that of the solution, for the wandering of the achromatic fringe is due to the different optical dispersions

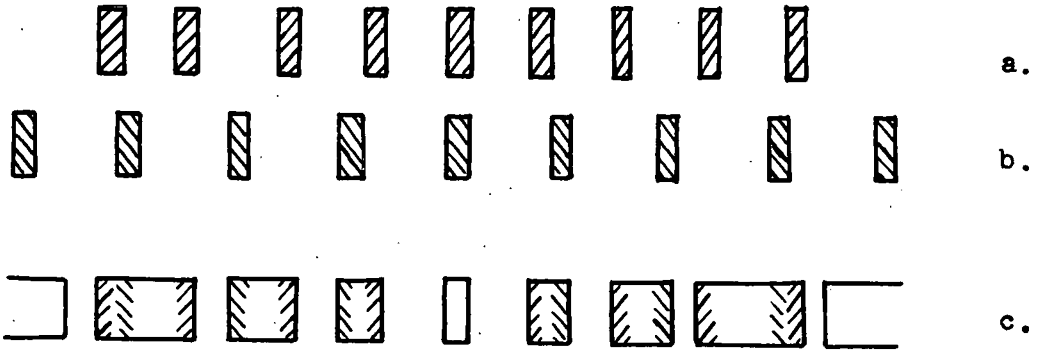

Figure 14. White light fringes

of the solution and water on the one hand, and of glass and air on the other. Or one may plot the concentrations of various diluted aliquots of the solution versus the interferometer reading and obtain a calibration curve. In the region of each shift of one fringe there will be a corresponding shift in the curve as shown in Figure 15. If the concentrations are dilute enough, the portions of the calibration curve are parallel and the sections which are different by one fringe, two fringes, etc., may be shifted the equivalent of that number of fringes on the graph. A straight line is obtained in this way and the correct concentration of an unknown solution may then be obtained by interpolation.

We can now investigate briefly the main types of compensators. Jamin[157] used two thick plates, which can be rotated about a common axis. One plate is in each beam of the interferometer and the common

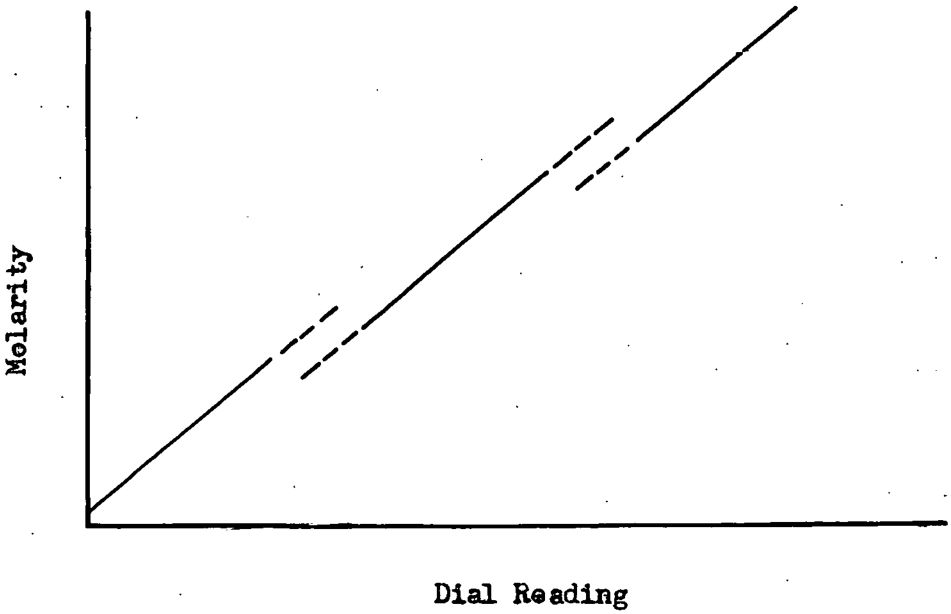

Figure 15. Typical calibration curve for solutions.

axis of rotation is perpendicular to the beam of light. If the two plates are set at a small angle to one another, a rotation of the combination alters the path difference, the change being roughly proportional to the angle between the plates and to the angle of rotation. The sensitivity can thus be varied over a wide range. A simple modification of the Jamin compensator, introduced by Lowe,[158] keeps one plate fixed while the other rotates; in the zero position the two plates are parallel to one another. In another method a thin glass prism, moved perpendicular to its refracting edge, introduces a path difference proportional to the displacement. Kosters modified this form and uses two prisms set in opposite directions which lie in one beam of the interferometer and may be moved relative to one another to change the optical path. A parallel-faced glass block of nearly equal optical path lies in the other beam. Both the prisms and the block should be made from the same melt.

An important fact which does not seem to be mentioned in articles concerning the optical parts of the interferometer is that each end plate of a gas or liquid cell should be made out of a single piece of glass (or whatever other material might be used). Also, the compensating plates should be cut from the same piece of material, marking their proper orientation. Despite the fact that glass is supposed to be isotropic, the strains that it is subjected to in its preparation are evidently enough to cause it to destroy the visibility of the fringes if the orientation of the plates is not the same as in the original piece. This means that, even though ground flat to a quarter of a wave-length and identical in thickness, two pieces of glass from different sources introduced one in each beam, as for compensating plates, will probably destroy the visibility of the fringes and be of no value. If one of these plates is held in one beam in a fixed position and the other rotated 90°, the fringes inspected, and this procedure repeated for the four orientations on one side of this second plate and then for the other four orientations on the opposite side of the plate, an orientation might be found where the fringes are visible and straight. If not, continue by rotating the first plate 90°, then repeating the above procedure to give a total of 64 orientations. Therefore, plates at each end of the cell should preferably be one piece of glass and the compensating plates should be cut from one piece of glass, marking the proper orientation beforehand.

Method of Calculation

The method of calculating the refractive indices of solutions measured by the differential method is described. Since all measurements were made in aqueous solutions at 20°C, the exact refractive index of water for 20°C was found from as many sources as possible in the literature.[159,160] Values at temperatures relatively close to 20°C were converted to that temperature using standard formulas for the temperature coefficient of the refractive index of water. The average value from these data for the refractive index of water at 20°C, and for the mercury green radiation of 5461 Å, is

$$n = 1.334468 \pm 0.000002$$

This is the important zero point upon which all the calculated values depend.

The equation

$$n_d = \Delta m \lambda / CL \qquad (43)$$

where Δm is the number of fringes, λ the wave-length, CL the length of the light path (cell length), and n_d the difference in the refractive index, was used to find the change in refractive index per single fringe, $\Delta n'$. The value found was

$$\Delta n' = 5681.7 \times 10^{-8}.$$

A calibration curve was then made by plotting graphically the reading of the compensating dial on the instrument as a function of the number of fringes. This was done by setting the zero-order fringe of the white light fringes in exact coincidence with the fixed fiduciary set of fringes. The mercury source was then substituted for the white light to obtain more distinct fringes. Several readings of the position of this coincidence were taken approaching from each direction; an average value was used for the position of the zero-order fringe. Then the dial was rotated until the first-order fringe to the left side was exactly in coincidence with the zero-order fringe of the fixed set. Again several readings were taken approaching from both sides. This was continued for 40 fringes to the left and repeated for 24 fringes to the right of the zero-order fringe. The precision of these fringe settings was calculated from the deviation of the dial readings when several settings were made on a particular fringe, and also from the deviation of the difference in the dial readings from fringe to fringe. In the region of the zero-order fringe the precision of the fringe alignment was 1.16% or approximately to 1/100 of a fringe. Toward the extremes of the range the precision of the settings decreased to 3.03% or approximately 1/33 of a fringe.

Since the change of the refractive index per fringe is known, the number of fringes was plotted as a function of both dial reading and refractive index on the same graph. Since each fringe corresponds to exactly the same change in the refractive index, the plot of number of fringes versus refractive index is a straight line. Rotation of the compensating plates through a given angle, by rotation of the dial by a definite increment, produces a larger change in optical path when the plates make a larger angle with the vertical direction. This results in a slightly curved line for the plot of number of fringes versus the dial reading. To find the refractive index of a solution from the experimentally determined dial reading the number of fringes corresponding to the dial reading is located on the appropriate curve, then a horizontal line through this point is drawn to the refractive index curve and the refractive index read from the graph (Figure 16).

A method of calculating the molar polarization of a solute at infinite dilution from the densities and dielectric constants of a series of dilute solutions has been devised by Halverstadt and Kumler.[161] The Maxwell relation $k = n^2$ suggested the substitution of the square of the refractive index n^2 for the dielectric constant k in their equations. This method has been used here to obtain the molar refraction of the solute from the refractive indices and densities of a series of dilute solutions. The specific volumes γ_{12} of the solutions are first plotted as a function of weight fraction w_2. The slope β and the intercept γ_1 at infinite dilution are found from the graph. If the values do not lie close to a straight line the measurements are repeated since the relationship should be linear for dilute solutions. Next the squares of the refractive indices of the solutions n^2 are plotted as a function of the weight fraction of solute w_2 and the slope α and intercept n_1^2 at infinite dilution are found from the graph; a linear relationship between the quantities is again assumed. The specific refraction r_2 is then found from the equation

$$r_2 = \frac{3\alpha\,\gamma_1}{(n^2+2)^2} + (\gamma_1 + \beta)\,\frac{n^2-1}{n^2+2} \,. \qquad (44)$$

TABLE III

NUMBER OF FRINGES VERSUS REFRACTIVE INDEX FOR CALIBRATION CURVE

Fringe Number	Refractive Index	Fringe Number	Refractive Index
40	1.336741	7	1.334866
39	1.336683	6	1.334809
38	1.336627	5	1.334752
37	1.336570	4	1.334695
36	1.336513	3	1.334638
35	1.336457	2	1.334582
34	1.336400	1	1.334525
33	1.336343	0	1.334468
32	1.336286	-1	1.334411
31	1.336229	-2	1.334354
30	1.336173	-3	1.334298
29	1.336116	-4	1.334241
28	1.336059	-5	1.334184
27	1.336002	-6	1.334127
26	1.335945	-7	1.334070
25	1.335888	-8	1.334013
24	1.335832	-9	1.333957
23	1.335775	-10	1.333900
22	1.335718	-11	1.333843
21	1.335661	-12	1.333786
20	1.335604	-13	1.333729
19	1.335548	-14	1.333673
18	1.335491	-15	1.333616
17	1.335434	-16	1.333559
16	1.335377	-17	1.333502
15	1.335320	-18	1.333445
14	1.335262	-19	1.333388
13	1.335207	-20	1.333332
12	1.335150	-21	1.333275
11	1.335093	-22	1.333218
10	1.335036	-23	1.333161
9	1.334979	-24	1.333104
8	1.334923		

TABLE IV

NUMBER OF FRINGES VERSUS DIAL READING FOR CALIBRATION CURVE

Fringe Number	Dial Reading	Fringe Number	Dial Reading
40	43.1	5	157.2
39	56.0	4	171.3
38	69.1	3	185.7
37	82.0	2	199.8
36	94.8	1	214.0
35	107.6	0	228.6
34	120.6	-1	243.7
33	133.5	-2	258.5
32	146.5	-3	273.0
31	159.5	-4	287.6
30	172.6	-5	302.5
29	186.0	-6	316.8
28	199.5	-7	331.2
27	213.0	-8	345.6
26	226.4	-9	360.0
25	240.0	-10	14.2
24	253.8	-11	28.4
23	267.6	-12	42.8
22	281.4	-13	57.2
21	295.1	-14	71.6
20	309.0	-15	86.3
19	322.6	-16	100.7
18	336.3	-17	115.4
17	350.2	-18	130.2
16	4.2	-19	144.8
15	17.8	-20	159.4
14	31.8	-21	173.8
13	45.7	-22	188.6
12	59.4	-23	203.7
11	73.1	-24	219.0
10	86.9		
9	100.8		
8	114.6		
7	128.8		
6	143.0		

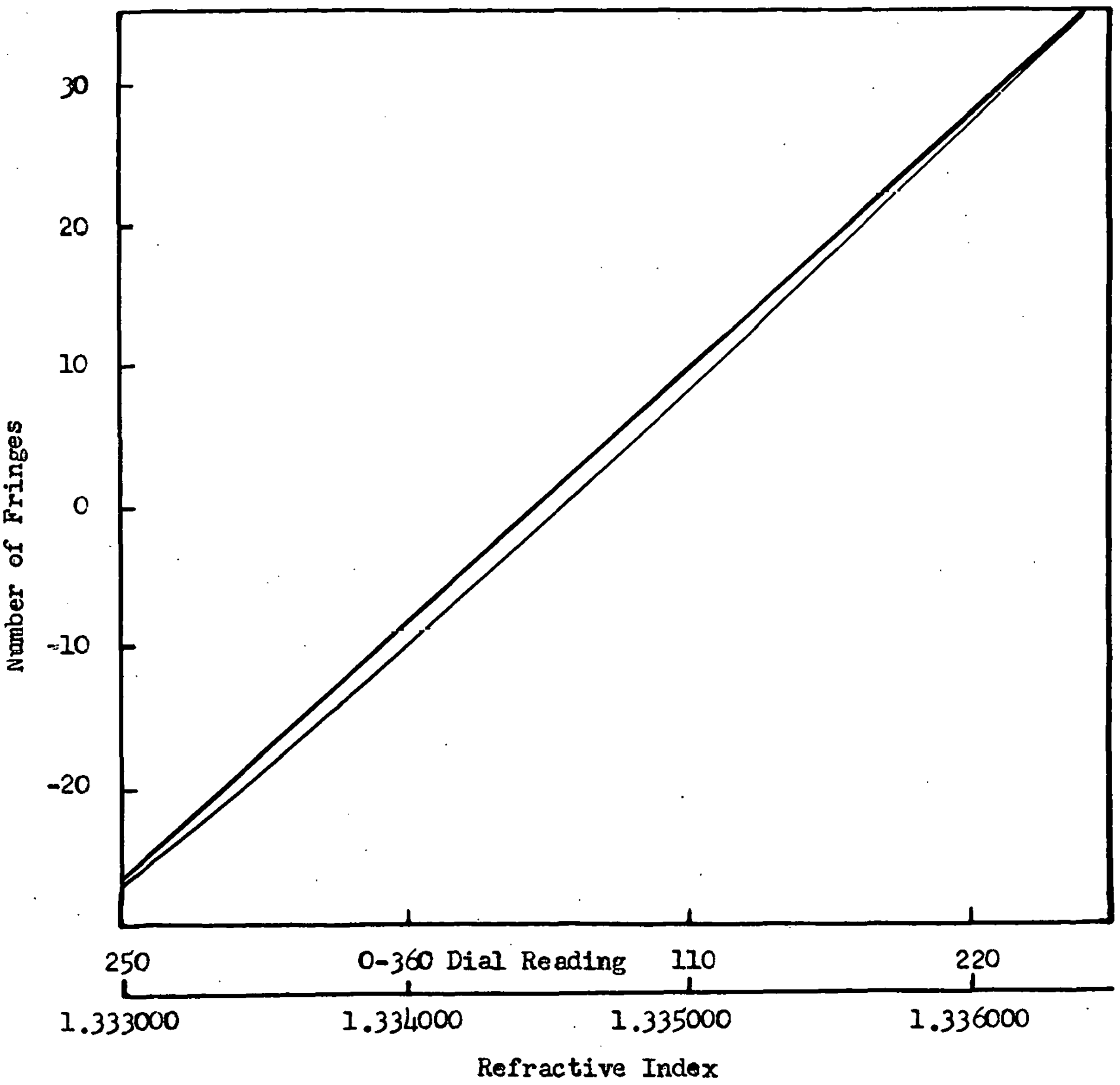

Figure 16. Calibration curve for conversion of dial readings to refractive index. The upper curve is a plot of number of fringes versus the dial reading. The lower curve is a plot of number of fringes versus the refractive index.

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The weight fraction w_2 is found from the relation

$$w_2 = \frac{(M)\ (MW)}{1000\ d} \quad , \qquad (45)$$

where M is the molarity of the solute, MW is the molecular weight of the solute, and d is the density of the solution.

The refractive index of the solution is obtained from a plot of molarity as a function of dial reading. If there is no zero-order fringe shift a single straight line is obtained; however, in many cases the dispersion is large enough that there are shifts in the zero-order fringe position. The plots of molarity versus dial reading then become broken lines of positive or negative slope depending on whether the solution has a higher or lower refractive index than the pure solvent. Examples of these are shown in Figure 17a and 17b and the method of computing refractive index from dial reading in these cases will now be described.

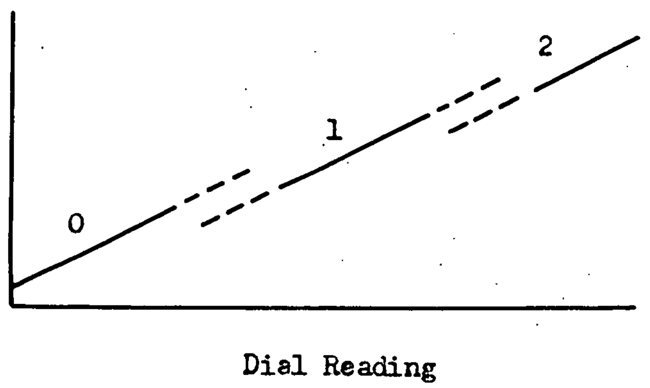

Figure 17a. Molar concentration of solute as a function of dial reading for solutions whose refractive index is larger than that of the pure solvent.

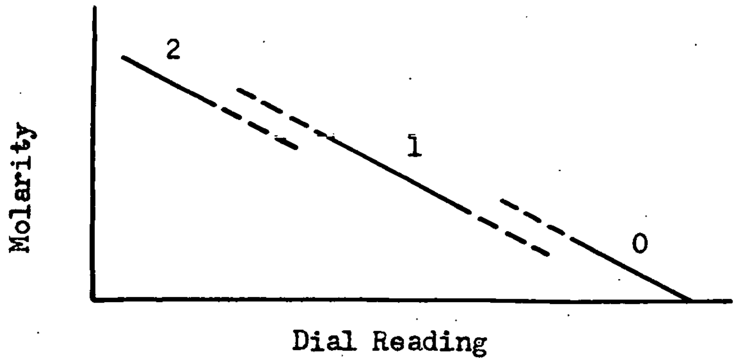

Figure 17b. Molar concentration of solute as a function of dial reading for solutions whose refractive index is smaller than that of the pure solvent.

All the dial readings whose abscissas will intersect on section 0 of either graph (Figure 17a and 17b) will give the correct refractive index as previously explained. Those which intersect on section 1 will be one fringe in error, those on section 2 will be two fringes in error, etc. The error in the number of fringes can then be determined from the molarity versus dial reading plot. To determine this number parallel straight lines are drawn for as many sections 0, 1, 2, etc., as may be needed noting that the width between the lines is one fringe (which, in turn, can be expressed in terms of dial reading using the original calibration curve). Any point not falling on one of the lines must be in error and should be rechecked or discarded.

The method of finding the refractive index in the above cases may be shown by an illustration in which the error, for example, is two fringes. For a salt of the first type such as potassium chloride in Figure 17a, point B in Figure 18, corresponding to a particular dial reading A, is located on the calibration curve. If this gives a reading of the number of fringes as 17.4 then, since there is an error of two fringes, two are subtracted and point C is found at 15.4 which, when extended to the left, intersects the refractive index curve at D. This gives the corrected refractive index reading at E.

For a salt of the second type such as sodium fluoborate in Figure 17b, the steps to locate A and B in Figure 19 are the same, but, since the fringe error is in the opposite direction, two fringes are added resulting in a point C higher than point B by exactly two fringes. The ordinate D corresponding to C give the corrected refractive index reading at point E.

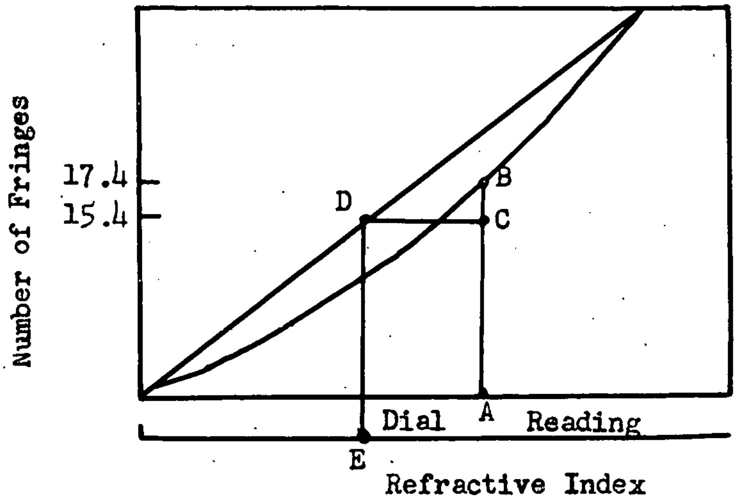

Figure 18. Method of using the calibration curve of Figure 16 when there is a zero-order fringe loss.

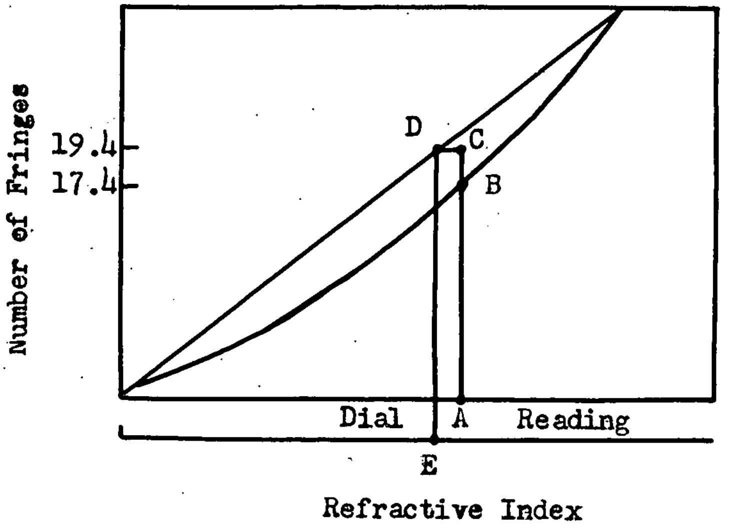

Figure 19. Method of using the calibration curve of Figure 16 when there is a zero-order fringe gain.

Results

Data and Calculations

A detailed calculation of the molecular refraction of sodium chloride from dilute solution measurements is now presented as an example of the procedure followed in every case.

Aliquots of an original solution of known concentration were diluted and the concentrations computed from the volumetric data. The densities of the solutions were determined as previously described. As a check on the precision of the density data the specific volumes γ_{12} of the solutions were plotted graphically as a function of the molarity (Figure 20) and any measurements which did not fall on the resulting straight line were repeated.

The dial readings on the interferometer necessary to restore the white light fringe to its initial position are measured upon introducing each solution into the cell. The molarities of the solutions were then plotted graphically as a function of dial reading (Figure 21) and a series of parallel straight lines obtained as described in the previous section for the example of potassium chloride. The fringe errors, if any, are now found from the graph and the refractive indices are obtained from the calibration curve. The data and results are shown in Table V. The molar refraction is now found by plotting graphically values of n^2 and γ_{12} versus weight fraction of solute w_2. From the slopes of these graphs (Figures 24 and 25), α and β, and the intercepts at infinite dilution,

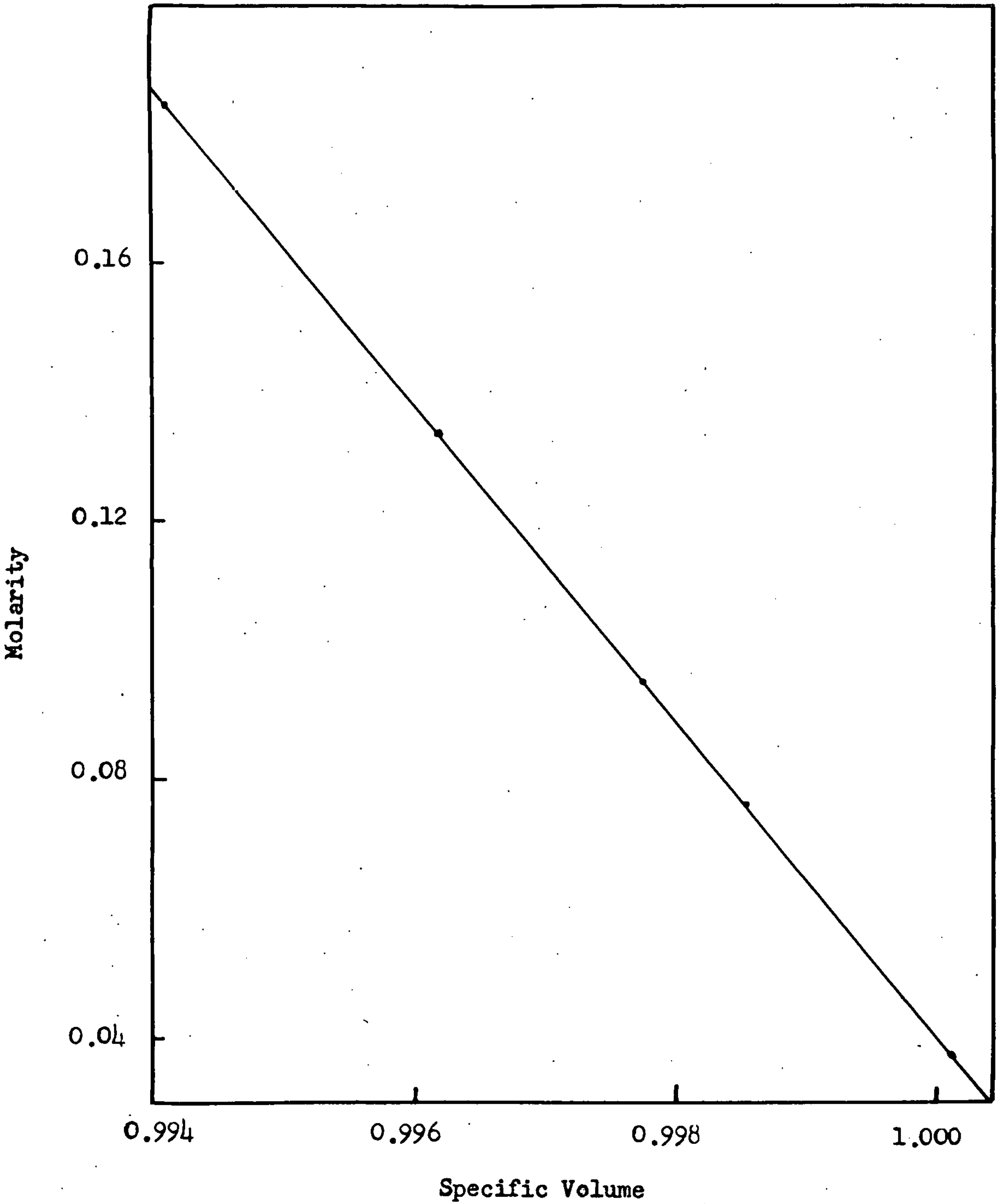

Figure 20. Molar concentration as a function of specific volume for sodium chloride.

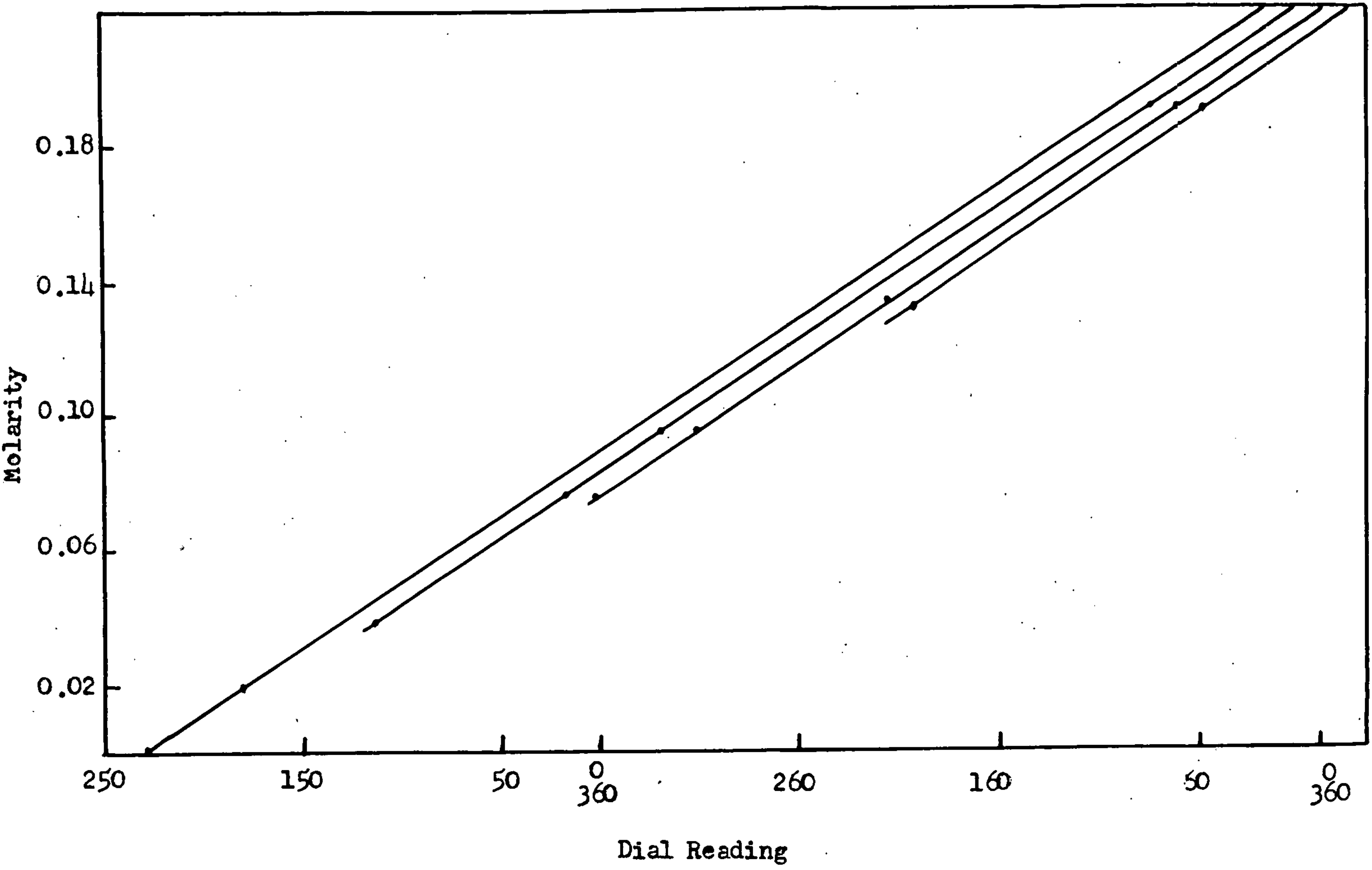

Figure 21. Molar concentration as a function of dial reading for sodium chloride.

n_1^2 and γ_1^o , the specific refraction r_2^o was calculated using equation (44).

$$r_2^o = \frac{3\,(0.4777)\,(1.00178)}{(1.780805 + 2)^2} + (1.00178 - 0.7092) \left[\frac{1.780805 - 1}{1.780805 + 2} \right] .$$

$$r_2^o = 0.16085$$

Then, from the equation

$$MR = MW\, r_2^o , \qquad (46)$$

we have

$$MR = 58.45\, r_2^o = 9.40$$

The data are summarized in the lower part of Table V. Data and results for the remaining compounds studied are presented in Tables VI to XVIII.

The greatest source of error in the determination of the molar refraction by this method is that of finding the slope of the lines. The maximum error in doing this is 0.9% which introduces a 2% error in the determination of the molar refraction. In some instances, the error is greater than this up to 4% if the plotted points did not fall exactly on a straight line. (See method of calculation).

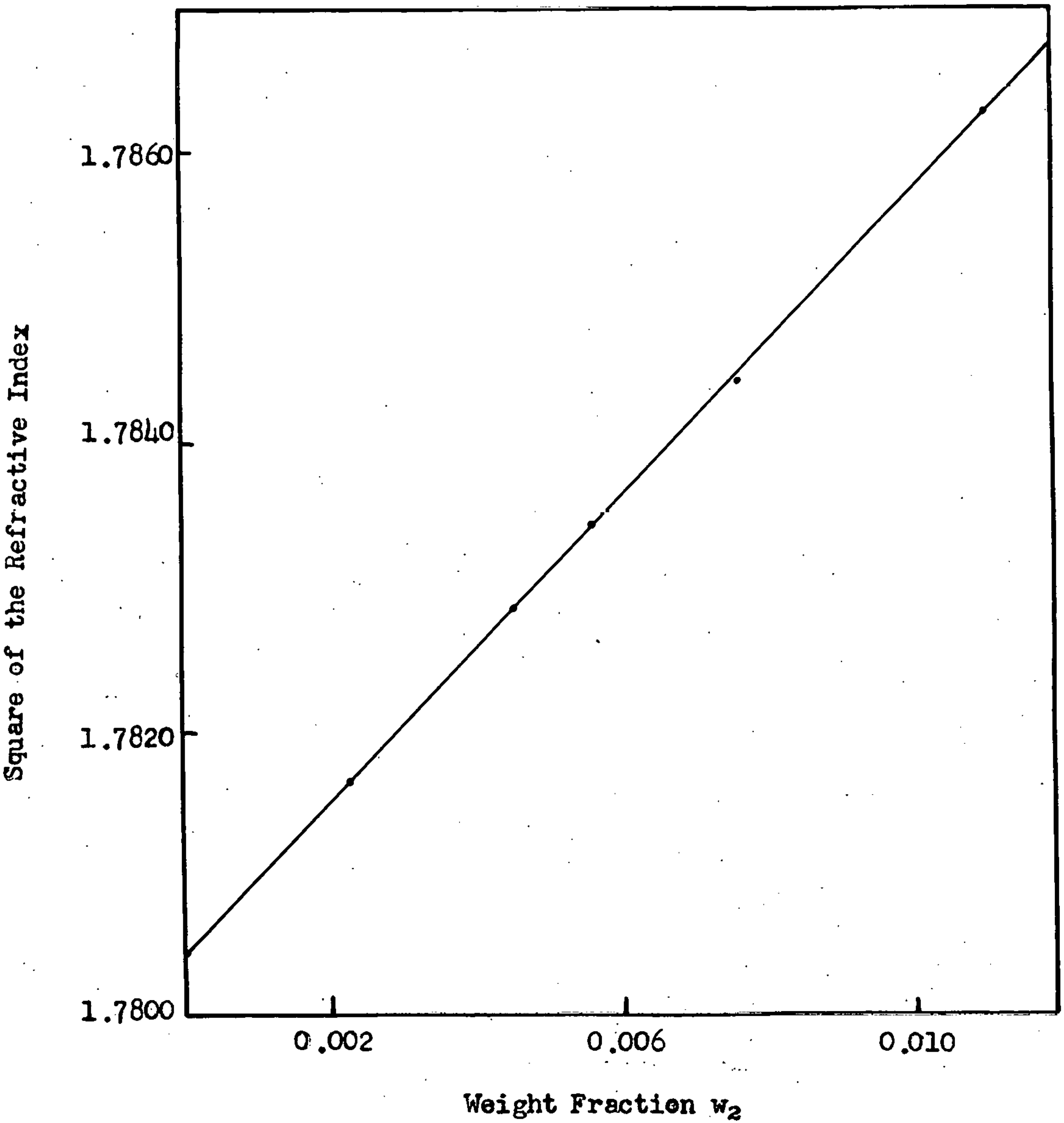

Figure 22. The square of the refractive index as a function of the weight fraction of sodium chloride.

0297 092

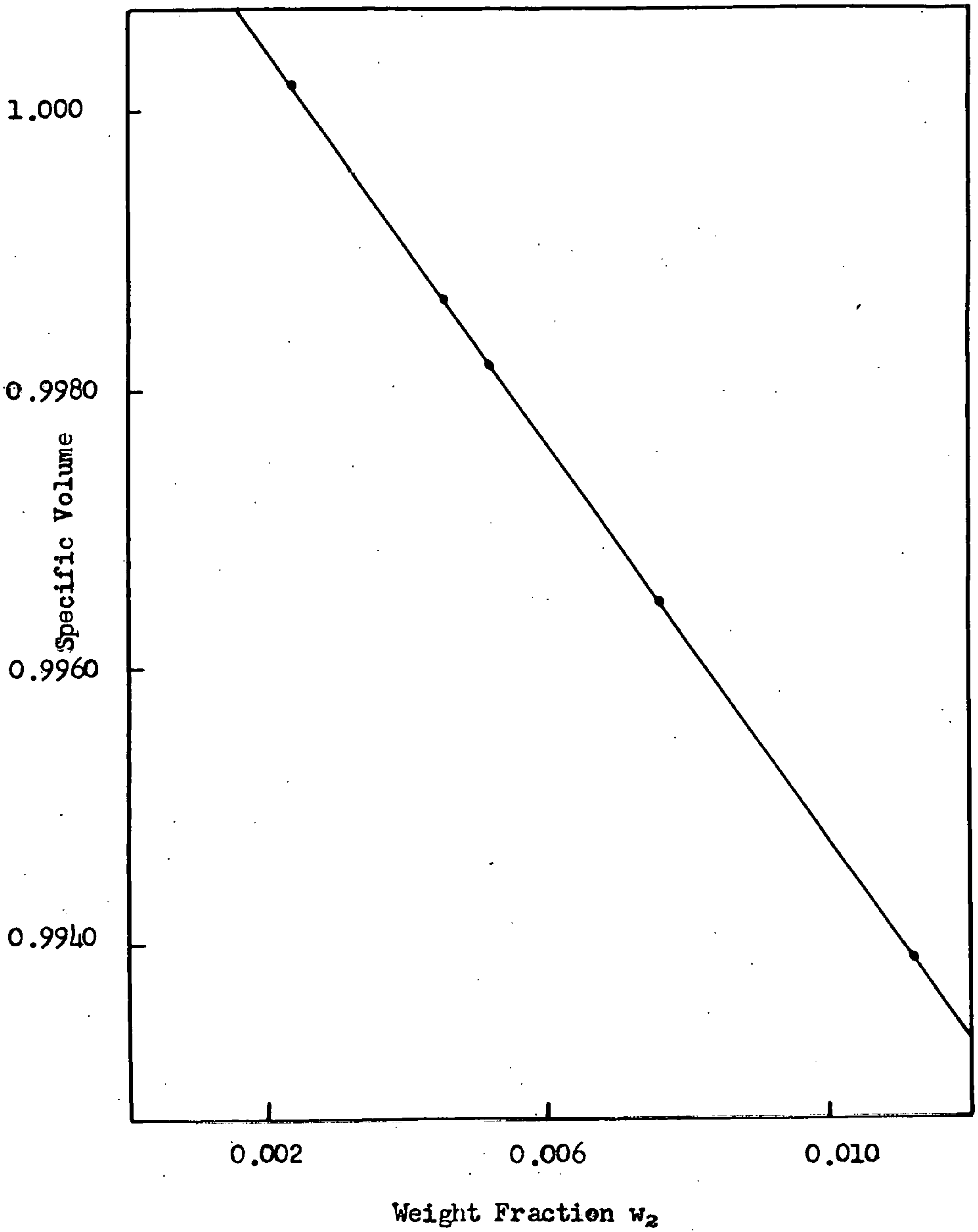

Figure 23. The specific volume as a function of the weight fraction of sodium chloride.

TABLE V

MOLAR REFRACTION OF SODIUM CHLORIDE

Molarity M	Density d	Weight Fraction w_2	Dial Reading	Fringe Loss	Refractive Index
0.00000	(1.00178)	0.000000	228.5		1.334468
0.01915	0.99888	0.001121	178.1		1.334665
0.03829	1.00138	0.002239	114.1	(-1)	1.334924
0.07658	1.00221	0.004470	17.1 3.7	(-1) (-2)	1.335263
0.09573	1.00221	0.005583	314.2 328.4	(-2) (-1)	1.335465
0.13402	1.00379	0.007804	219.0	(-2)	1.335818
0.19146	1.00612	0.011123	57.8 82.9 69.8	(-3) (-1) (-2)	1.336483

Values of the parameters in equation (44) as found from graphical plots of the above data:

$$n^2 = 1.780805$$
$$\gamma^0 = 1.00178$$

$$\alpha = 0.4777$$
$$\beta = -0.7092$$

Molar refraction calculated from equation (46):

$$MR = 9.40$$

TABLE VI

MOLAR REFRACTION OF POTASSIUM CHLORIDE

Molarity M	Density d	Weight Fraction w_2	Dial Reading	Refractive Index
0.00000	(1.00178)	0.000000	228.5	1.334468
0.02558	0.99940	0.001908	161.2	1.334735
0.07674	1.00183	0.005711	20.3	1.335300
0.12790	1.00427	0.009495	240.1	1.335830
0.19184	1.00721	0.014201	95.3	1.336508

Values of the parameters in equation (44) as found from graphical plots of the above data:

$n^2 = 1.780805$
$\gamma^o = 1.00178$

$\alpha = 0.3830$
$\beta = -0.6330$

Molar refraction calculated from equation (46):

$MR = 11.68$

TABLE VII

MOLAR REFRACTION OF AMMONIUM FLUOBORATE

Molarity M	Density d	Weight Fraction w_2	Dial Reading	Refractive Index
0.00000	(1.00178)	0.00000	228.5	1.334468
0.02725	0.99943	0.00286	244.8	1.334403
0.06813	1.00129	0.00714	269.9	1.334304
0.13626	1.00429	0.01423	310.4	1.334148
0.20439	1.00726	0.02128	350.5	1.333991

Values of the parameters in equation (44) as found from graphical plots of the above data:

$$n^2 = 1.780805$$
$$\gamma^0 = 1.00180$$

$$\alpha = -0.06077$$
$$\beta = -0.4280$$

Molar refraction calculated from equation (46):

$$MR = 11.08$$

TABLE VIII

MOLAR REFRACTION OF FLUOBORIC ACID

Molarity M	Density d	Weight Fraction w_2	Dial Reading	Fringe Gain	Refractive Index
0.00000	(1.00178)	0.000000	228.7		1.334468
0.04066	1.00061	0.003569	271.5	(-1)	1.334356
0.10164	1.00397	0.008892	316.4 330.4	(-1) (-2)	1.334184
0.20328	1.00916	0.017692	60.8 46.8	(-3) (-2)	1.333860
0.30492	1.01335	0.026430	156.6 144.0	(-3) (-2)	1.335508
0.40656	1.01839	0.035064	207.1 227.7	(-2) (-3)	1.333260

Values of the parameters in equation (44) as found from graphical plots of the above data:

$n^2 = 1.780805$
$\gamma^0 = 1.00164$

$\alpha = -0.0922$
$\beta = -0.569$

Molar refraction calculated from equation (46):

$MR = 6.14$

TABLE IX

MOLAR REFRACTION OF AMMONIUM CHLORIDE

Molarity M	Density d	Weight Fraction w_2	Dial Reading	Fringe Loss	Refractive Index
0.00000	(1.00178)	0.000000	228.7		1.334468
0.03543	0.99888	0.001899	118.3	(-2)	1.334794
0.05315	0.99913	0.002846	73.9	(-2)	1.334976
0.08858	0.99976	0.004740	328.5	(-4)	1.335293
0.17715	1.00127	0.009466	111.3	(-5)	1.336157

Values of the parameters in equation (44) as found from graphical plots of the above data:

$$n^2 = 1.780805$$

$$\gamma^0 = 1.00173$$

$$\alpha = 0.471$$

$$\beta = 0.316$$

Molar refraction calculated from equation (46):

$$MR = 12.86$$

TABLE X

MOLAR REFRACTION OF SODIUM FLUORIDE

Molarity M	Density d	Weight Fraction w_2	Dial Reading	Refractive Index
0.0000	(1.00178)	0.000000	228.7	1.334468
0.0221	0.99922	0.000945	195.4	1.334598
0.0344	0.99970	0.001417	179.3	1.334662
0.0562	1.00073	0.002360	46.5	1.334791
0.1120	1.00328	0.004708	68.8	1.335111
0.1691	1.00559	0.007043	354.7	1.335416

Values of the parameters in equation (44) as found from graphical plots of the above data:

$$n^2 = 1.780805$$
$$\gamma^0 = 1.00178$$

$$\alpha = 0.3645$$
$$\beta = -1.091$$

Molar refraction calculated from equation (46):

$$MR = 2.47$$

TABLE XI

MOLAR REFRACTION OF SODIUM SILICOFLUORIDE

Molarity M	Density d	Weight Fraction w_2	Dial Reading	Refractive Index
0.000000	(1.00178)	0.0000000	228.7	1.334468
0.002665	0.99871	0.0005018	220.6	1.334498
0.003998	0.99892	0.0007525	217.2	1.334513
0.006663	0.99932	0.0012537	210.0	1.334540
0.013330	1.00036	0.0025058	194.4	1.334603
0.019990	1.00143	0.0037537	178.7	1.334661

Values of the parameters in equation (44) as found from graphical plots of the above data:

$n^2 = 1.780805$
$\gamma^0 = 1.00171$

$\alpha = 0.1524$
$\beta = -0.817$

Molar refraction calculated from equation (46):

$MR = 13.20$

TABLE XII

MOLAR REFRACTION OF POTASSIUM SILICOFLUORIDE

Molarity M	Density d	Weight Fraction w_2	Dial Reading	Refractive Index
0.00000	(1.00178)	0.000000	228.7	1.334468
0.00125	0.99838	0.000277	224.4	1.334484
0.00250	0.99860	0.005514	221.05	1.334496
0.00250	0.99861	0.005514	221.05	1.334496
0.00375	0.99885	0.008269	217.5	1.334513
0.00500	0.99903	0.001102	215.2	1.334521

Values of the parameters in equation (44) as found from graphical plots of the above data:

$n^2 = 1.780805$
$\gamma^0 = 1.00181$

$\alpha = 0.1422$
$\beta = -0.767$

Molar refraction calculated from equation (46):

$MR = 17.40$

TABLE XIII

MOLAR REFRACTION OF SODIUM FLUOBORATE

Molarity M	Density d	Weight Fraction w_2	Dial Reading	Fringe Loss	Refractive Index
0.00000	(1.00178	0.00000	228.5		1.334468
0.04630	1.00141	0.00497	260.1	(-1)	1.334400
			277.9	(-2)	1.334400
0.06482	1.00265	0.00709	266.7	(-1)	1.334375
0.09261	1.00456	0.01012	292.6	(-2)	1.334334
0.11113	1.00589	0.1211	300.5	(-2)	1.334301
0.18321	1.01075	0.01989	340.7	(-3)	1.334200

Values of the parameters in equation (44) as found from graphical plots of the above data:

$n^2 = 1.780805$
$\gamma^o = 1.00178$

$\alpha = -0.0362$
$\beta = -0.6275$

Molar refraction calculated from equation (46):

MR = 7.63

TABLE XIV

MOLAR REFRACTION OF POTASSIUM FLUOTITANATE

Molarity M	Density d	Weight Fraction w_2	Dial Reading	Refractive Index
0.00000	(1.00178)	0.000000	228.7	1.334468
0.00864	0.99952	0.002075	199.5	1.334583
0.01080	0.99995	0.002593	190.6	1.334616
0.01728	1.00073	0.004146	174.5	1.334680
0.02161	1.00146	0.005179	159.9	1.334739

Values of the parameters in equation (44) as found from graphical plots of the above data:

$$n^2 = 1.780805$$
$$\gamma^0 = 1.00178$$

$$\alpha = 0.150$$
$$\beta = -0.618$$

Molar refraction calculated from equation (46):

$$MR = 26.68$$

TABLE XV

MOLAR REFRACTION OF POTASSIUM BIFLUORIDE

Molarity M	Density d	Weight Fraction w_2	Dial Reading	Refractive Index
0.00000	(1.00178)	0.000000	228.7	1.334468
0.01934	0.99941	0.001511	204.7	1.334560
0.02901	0.99950	0.002266	190.1	1.334615
0.04835	1.00108	0.003772	173.1	1.334685
0.09670	1.00386	0.007599	127.5	1.334868
0.14505	1.00630	0.011246	96.7	1.335051

Values of the parameters in equation (44) as found from graphical plots of the above data:

$$n^2 = 1.780805$$
$$\gamma^0 = 1.00178$$

$$\alpha = 0.1351$$
$$\beta = -0.7418$$

Molar refraction calculated from equation (46):

$$MR = 6.44$$

TABLE XVI

MOLAR REFRACTION OF POTASSIUM FERRICYANIDE

Molarity M	Density d	Weight Fraction w_2	Instrument Reading*	Refractive Index
0.00000	---	0.000000	14.90	1.333221
0.00494	1.00952	0.001610	23.10	1.336408
0.00997	1.02031	0.003185	31.58	1.340058
0.01479	1.03104	0.004728	39.79	1.342814
0.01974	1.04197	0.006238	48.21	1.345994

* Immersion refractometer

Values of the parameters in equation (44) as found from graphical plots of the above data:

$n^2 = 1.77748$
$\gamma^0 = 1.00129$

$\alpha = 0.5557$
$\beta = -0.6709$

Molar refraction calculated from equation (46):

$MR = 60.91$

TABLE XVII

MOLAR REFRACTION OF POTASSIUM FERROCYANIDE

Molarity M	Density d	Weight Fraction w_2	Instrument Reading*	Refractive Index
0.000000	---	0.000000	14.90	1.333221
0.004812	1.01013	0.001750	23.80	1.336674
0.009620	1.02137	0.003466	32.80	1.336674
0.014420	1.03262	0.005414	41.40	1.343422
0.019221	1.04385	0.006781	50.10	1.346707

* Immersion refractometer

Values of the parameters in equation (44) as found from graphical plots of the above data:

$$n^2 = 1.77748$$
$$\gamma^{o} = 1.00129$$

$$\alpha = 0.5318$$
$$\beta = -0.6341$$

Molar refraction calculated from equation (46):

$$MR = 69.06$$

TABLE XVIII

MOLAR REFRACTION OF POTASSIUM CHLORIDE*

gm. KCl / 100 gm. sol'n	gm. equiv. / liter	Refractive Index	Specific Volume
0.9466	0.1274	1.33376	0.9969
0.9769	0.1315	1.33380	0.9962
1.0013	0.1348	1.33388	0.9963
2.4297	0.3299	1.33577	0.9879
4.6474	0.6398	1.33871	0.9742
7.1636	1.0022	1.34215	0.9587
9.4579	1.3450	1.34523	0.9431

* Data from Landolt-Bornstein. Rf. 161

Values of the parameters in equation (44) as found from graphical plots of the above data:

$$n^2 = 1.7755$$
$$\gamma^0 = 1.0028$$

$$\alpha = 0.361$$
$$\beta = -0.616$$

Molar refraction calculated from equation (46):

$$MR = 11.59$$

VI. REFRACTIVE INDICES AND MOLAR REFRACTIONS OF GASES

Theoretical

If a thickness t of a substance having a refractive index n is introduced into the path of one of the beams in the interferometer, the optical path in this beam is increased because of the fact that light travels more slowly in the substance and consequently has a shorter wave-length. The optical path is now $n \cdot t$ through the medium, whereas it is t through a corresponding thickness of vacuum, and the increase in optical path due to insertion of the substance is $(n - 1)t$. This will introduce $(n - 1)t/\lambda$ extra waves in the path of one beam, so if we call Δm the number of fringes by which the fringe system is displaced when the substance is placed in the beam, we have

$$(n - 1)\,t = (\Delta m)\,\lambda . \qquad (47)$$

Thus a measurement of the number of fringes and the thickness of the sample gives a value of the refractive index of the substance when radiation of known wave-length is used.

Since the refractive index depends on the amount of gaseous substance in the cells, the practical formula becomes

$$\frac{\Delta m}{p}\,\frac{760\,\lambda}{t} = (n - 1) \qquad (48)$$

where p is the pressure of the gas in the cells. This then gives the refractive index at a standard pressure of one atmosphere.

Another variable is the temperature of the system. This was either controlled by circulating liquid from a thermostat through a jacket around the cells or else the system was allowed to come to room temperature. The latter can be done when conversion formulas are available to calculate the refractive index for 0°C, the usual temperature for comparing refractive indices. One such equation suitable for air, is

$$n_t - 1 = (n_0 - 1)/(1 + \alpha t) \qquad (49)$$

where n_t is the refractive index at a particular temperature t °C, n_0 is the refractive index at 0°C, and α is a constant characteristic of air and equal to 0.00367. This and other such equations are empirical.

A third factor is the wave-length of the radiation used in measuring the refractive index. The interferometer acts in the sense of a prism refracting light of various wave-lengths different amounts and will give a different refractive index for a different wave-length. To illustrate, the following table gives the values of the refractive indices at several wave-lengths. (See Table XIX).

A table like this allows one to set up an empirical general interpolation equation, as did Barrel and Sears for air, with the result

$$(n_{tp} - 1) = [A + \frac{B_2}{\lambda} + \frac{C_4}{\lambda}]\, P\, \frac{(1 + \beta P)}{(1 + \alpha T)} \qquad (50)$$

where P is the pressure in millimeters of mercury, T the temperature in degrees centigrade and the constants have the following values:

TABLE XIX

REFRACTIVE INDICES OF AIR FOR RADIATION OF VARIOUS WAVE-LENGTHS

Radiation	$(n - 1)10^6$
Cadmium red line 6440 Å	271.70
Mercury green line 5461 Å	273.19
Cadmium blue line 4801 Å	274.78
Mercury violet line 4359 Å	276.30

$A = 0.378153 \times 10^{-6}$ $\quad C = 17.59 \times 10^{-12}$

$B = 2.1442 \times 10^{-9}$ $\quad \alpha = 0.73 \times 10^{-6}$

$\beta = 0.73 \times 10^{-6}$

Cauchy's dispersion formula, which was mathematically derived, is essentially identical. It can have even more terms if necessary but a somewhat simpler form of it is usually sufficient:

$$n - 1 = A + B/\lambda^2, \qquad (51)$$

where A and B are constants which are different for every gas. These constants have been determined for approximately sixteen gases so the refractive indices for these gases may be found for any wave-length. The refractive index value should be corrected to a standardized wave-length, which is usually that of infinite wave-length. Many times the use to which the refractive indices are to be put is not such as to warrant this correction, and sometimes the data and conversion factors are just not available.

Investigation of the molar refraction values found for gases shows that, for some substances, the Lorenz-Lorentz values are constant to 7000 atmospheres. In other cases an increase in the molar refraction values with pressure was found at relatively low pressures. Many modifications of the molar refraction equations were attempted to correct for this change but none are satisfactory except perhaps for a few particular gases.

Finally, since the molar volume is involved in the molar refraction equation, different equations of state have been used to reduce the density to the ideal state. That is, assuming that a gas begins to deviate at higher pressures from the ideal gas equation,

$$PV = nRT. \qquad (52)$$

It is known, of course, that few gases obey the ideal gas equation strictly. It is usually assumed that if the refractive index of the gaseous substance is determined at a very low pressure, it probably follows the ideal gas law. This can be quite easily checked by finding the refractive index at several pressures differing by nearly equal increments and noting if there is a change of the refractive index. If so, this indicates some kind of non-ideal behavior.

Results

Data and Calculations

From the equation,

$$\frac{\Delta m}{p} \frac{760\ \lambda}{C.L.} = (n - 1) \qquad (48)$$

it is seen that only Δ m, the number of fringes, and p, the pressure, are variable in the determination of n, the refractive index. CL, the cell length, must first be determined before all the constants may be combined.

The cell length was determined by two methods. The first is an indirect method making use of the known refractive index value of nitrogen. The accepted value for the refractive index of nitrogen at 25°C is 1.0002767. When this gas was introduced into the interferometer, an average of 80.1 fringes passed for a pressure of 117.65 mm. Substituting these values in equation (48), one obtains a value of 102.07 cm. for the cell length. The second method to determine the cell length was to measure it directly using a standard meter bar for comparison. The value determined by this procedure was 102.08 cm.

Equation (48) now reduces to

$$\frac{406.56\ \Delta m}{p} = (n - 1) \qquad (53)$$

The average value of Δ m/p was found to calculate the refractive index of the gases. Then from the Lorenz-Lorentz equation,

$$\frac{n^2 - 1}{n^2 + 2} V = MR \qquad (54)$$

where V is the molar volume of the gas at a pressure of 760 mm., the molar refraction is calculated. The molar volume was calculated from the ideal gas equation (52) for the particular temperature at which the compound was run.

The first gas whose refractive index was determined was that of nitrogen. This served as a check on the accuracy of the instrument and gave experience in its operation. The values obtained are shown in Table XX along with values from the literature for comparison. The measured cell length was used in obtaining the observed refractive indices given in this table.

TABLE XX

DETERMINATION OF THE REFRACTIVE INDEX OF NITROGEN AT TWO DIFFERENT TEMPERATURES

Pressure	Number of Fringes	Temperature	$n_{obs.}$	n^*
104.45	70.0	25°C	1.0002720	1.0002720
117.65	80.1	20°C	1.0002766	1.0002768

* These values were obtained by converting the value at 0°C given in the literature to 20°C and 25°C.

The main source of error in the measurement of the refractive indices of the gases is that of the pressure measurements and exact number of fringes counted. Therefore, an estimate for each substance may be made by noting how the individual Δ m/p values vary from the average for each particular compound. This may then be found in terms of the refractive index or molar refraction.

The halogen fluorides which were measured were quite corrosive to glass and mercury, and therefore it was not possible to use an ordinary mercury manometer to measure the pressure. The pressure measuring system as described in Section IV was used. A calibration is needed to convert the pressure readings from the Bourdon pressure gage, which were in arbitrary units (distance measured with a micrometer) to millimeters of mercury. The data for this calibration is given in Table XXV. In the region of Bourdon gage readings from 416 to 409, the average slope is 6.43, while in the region from 409 to 400, the slope is 6.71. Only the first region was used in the measurements. Thus the equation to convert the pressure readings of the Bourdon gage to millimeters of mercury is

$$P_{mm} = 6.43\,\Delta \qquad (55)$$

where Δ is the difference in the Bourdon gage readings between vacuum and the pressure to be measured. Therefore, as a convenience, the average of the Bourdon gage readings was found and converted to millimeters of mercury pressure.

TABLE XXI

DETERMINATION OF THE MOLAR REFRACTION OF CHLOROTRIFLUOROETHYLENE

Fringes Displaced	Pressure (mm.)		Δ m/p
139.0	56.95		2.44
114.0	47.10		2.42
171.0	71.15		2.41
151.0	62.95		2.40
		Average	2.42

Calculated refractive index:

$n = 1.0009840$

Molar volume at 20°C:

$V_m = 24{,}035$ cc./mole

Calculated molar refraction:

MR = 15.77 cc./mole

TABLE XXII

DETERMINATION OF THE MOLAR REFRACTION OF PERFLUOROETHYL ETHER

Fringes Displaced	Pressure (mm.)	Δ m/p
220.0	62.5	3.52
65.5	18.35	3.57
100.0	28.25	3.54
66.0	18.75	3.52
180.0	50.85	3.54
101.0	28.70	3.52
149.0	41.80	3.56
409.0	114.10	3.58
	Average	3.55

Calculated refractive index:

$n = 1.0014396$

Molar volume at 25°C:

$V_m = 24{,}450$ cc./mole

Calculated molar refraction:

MR = 23.49 cc./mole

TABLE XXIII

DETERMINATION OF THE MOLAR REFRACTION OF 1,1,1,2,2,3,3--HEPTAFLUOROPROPANE

Fringes Displaced	Pressure (mm.)	Δ m/p
105.0	4.195	2.51
39.0	16.40	2.38
125.0	52.70	2.37
25.0	10.00	2.50
164.0	69.10	2.37
158.0	62.80	2.52
89.0	35.55	2.50
21.0	8.50	2.52
250.0	96.65	2.58
25.0	10.15	2.47
199.0	76.55	2.60
350.0	137.15	2.56
99.0	36.75	2.69
100.0	39.40	2.51
150.0	58.50	2.57
164.0	66.60	2.47
104.0	42.70	2.44
	Average	2.52

Calculated refractive index:

$n = 1.001023$

Molar volume at 25°C:

$V_m = 24{,}450$ cc./mole

Calculated molar refraction:

MR = 16.67 cc./mole

TABLE XXIV

DETERMINATION OF THE MOLAR REFRACTION OF PERFLUOROTRIETHYL AMINE

Fringes Displaced	Pressure (mm.)	Δ m/p	
50.0	9.65	5.181	28.0°C
50.0	9.90	5.051	
50.0	9.75	5.128	
25.0	4.85	5.154	
50.0	9.50	5.263	
50.0	9.30	5.376	
50.0	9.33	5.359	
50.0	9.20	5.435	
50.0	9.80	5.102	
50.0	9.70	5.155	
50.0	9.65	5.181	
50.0	9.70	5.155	
35.0	6.60	5.303	
	Average	5.209	
107.0	20.75	5.157	27.5°C
25.0	4.75	5.263	
25.0	4.75	5.263	
25.0	4.75	5.263	
133.0	26.20	5.225	
50.0	9.45	5.291	
50.0	9.70	5.154	
344.0	65.70	5.236	
50.0	9.60	5.222	
50.0	9.45	5.2388	
100.0	19.10	5.236	
	Average	5.233	

Calculated refractive index:
$n^{28.0}$ = 1.0021178
$n^{27.5}$ = 1.0021265
Molar volume at 28.0 °C: V_m = 24,697 cc./mole
Molar volume at 27.5 °C: V_m = 24,656 cc./mole
Calculated molar refraction: MR = 34.96 cc./mole (average)

TABLE XXV

CALIBRATION DATA FOR CONVERSION OF BOURDON GAGE READINGS TO PRESSURE

Bourdon Gage Reading	*	Pressure (mm.)	$\frac{\text{Column 3}}{\text{Column 2}}$
416.0	0.00	0.00	--
415.75	0.25	2.70	10.8
414.95	1.05	7.35	7.0
414.4	1.6	10.35	6.47
414.0	2.0	12.90	6.45
413.9	2.1	13.85	6.60
413.2	2.8	17.45	6.23
413.0	3.0	19.35	6.45
412.25	3.75	23.80	6.46
412.2	3.8	24.00	6.32
411.7	4.3	27.65	6.44
410.9	5.1	32.80	6.43
410.65	5.35	35.00	6.54
410.5	5.5	35.50	6.46
		Average	6.43
408.8	7.2	48.10	6.68
408.4	7.6	50.80	6.69
407.8	8.2	55.65	6.79
407.2	8.8	58.15	6.61
406.5	9.5	63.90	6.72
405.6	10.4	69.35	6.66
405.2	10.8	72.00	6.67
404.0	12.0	81.30	6.77
403.2	12.8	85.85	6.71
402.0	14.0	94.85	6.77
401.6	14.4	97.70	6.78
400.5	15.5	105.25	6.80
		Average	6.71

* is the difference between the reading for vacuum (416.0) and the reading at the given pressure.

TABLE XXVI

DATA FOR DETERMINATION OF THE MOLAR REFRACTION OF IODINE PENTAFLUORIDE

Pressure (Micrometer Reading)	Number of Fringes	Change in Pressure Per 10 Fringes
413.3	10	0.5
412.8		
414.2	20	0.5
413.2	10	0.5
412.7	9	0.55
412.2		
411.5	10	0.6
410.9	6	0.6
410.5		
414.1	10	0.6
413.5	10	0.5
413.0	10	0.6
412.4	10	0.5
411.9	10	0.6
411.3	8	0.5
410.9		
413.5	9	0.55
413.0	9	0.6
412.25	9	0.55
411.9	6	0.60
411.5		
414.0	10	0.6
413.4	9	0.5
413.0	8	0.6
412.5	9	0.55
412.0	10	1.0
411.0		
	Average	0.55

Using the average change in pressure per ten fringes (0.55) and the equation from Table XXVI,

$$P_{mm} \text{ of Hg} = 6.43\,\Delta \quad , \qquad (55)$$

the number of fringes per millimeter pressure change

$$\frac{\Delta m}{p} = \frac{10}{0.55 \times 6.43}$$

is found. Then, by use of equation 53,

$$\frac{\Delta m}{P} \times 406.56 = (n - 1)\,10^6 = \frac{10 \times 406.56}{0.55 \times 6.43} = 1156.0$$

and $n = 1.001156$

From the ideal gas law the molar volume

$$V_m = 24{,}780 \text{ cc./mole}$$

is calculated at 29°C and the molar refraction found using equation 54

$$MR = 19.17 \pm 0.27 \text{ cc./mole}$$

This is an example of the procedure used for the calculation of the molar refraction of the halogen fluorides, in this instance of iodine pentafluoride. The calibration data for the Bourdon gage reading to pressure conversion factor (equation 55) is given in Table XXV and explained on page 105.

TABLE XXVII

DATA FOR DETERMINATION OF THE MOLAR REFRACTION OF BROMINE PENTAFLUORIDE

Pressure (Micrometer Reading)	Number of Fringes	Change in Pressure Per 50 Fringes
409.0	24	3.13
410.6		
415.9	28	3.75
413.8		
415.9	70	3.86
410.5	41	3.54
413.4		
415.9	118	3.60
407.4	33	2.58
409.1	25	3.40
410.8		
415.9	142	3.59
405.7		
415.8	20	3.75
414.3	20	3.50
412.9	20	4.50
411.1	20	2.75
410.1	20	3.00
408.8	20	3.00
407.6	20	3.50
406.2	20	3.00
405.0	20	2.75
406.1	20	3.25
407.4	20	3.00
408.6	20	3.00
409.8		
409.9	5	3.50
410.25	5	4.50
410.7		

Continued next page

TABLE XXVII - Continued

Pressure (Micrometer Reading)	Number of Fringes	Change in Pressure Per 50 Fringes
410.7	4	2.50
410.9	5	4.00
411.3	6	2.50
411.6		
415.8	20	3.75
414.3	20	3.50
412.9	20	3.75
411.4		
411.5	20	4.00
409.9	20	2.50
408.9	20	2.75
407.8	20	3.50
406.4		
406.1	20	3.00
404.9	20	3.25
403.6	20	3.25
404.9	20	3.00
406.1	20.5	3.25
407.4	11.5	3.04
408.1		
415.8	20	3.50
414.4	20	3.50
413.0	20	3.75
411.5	20	3.25
410.2	20	3.00
409.0	20	3.00
407.8	20	3.00
406.6	20	3.00
405.4	20	3.25
404.1	20	3.25
402.8		

Continued next page

TABLE XXVII - Continued

Pressure (Micrometer Reading)	Number of Fringes	Change in Pressure Per 50 Fringes
402.8	20	3.25
401.5	20	3.00
400.3	20	3.50
401.7	20	3.00
402.9	20	3.00
404.1	20	3.25
405.4	20	3.25
406.7	20	3.00
407.9	12	3.75
408.8		
415.5	20	4.00
413.9	20	4.00
412.3		
411.3	20	3.25
410.0	20	3.00
408.8		
408.2	20	3.25
406.9	20	3.00
405.7	20	3.25
404.4	20	3.50
403.0	20	3.00
401.8	20	3.25
400.5	20	3.00
399.3	20	3.25
398.0		
396.5	20	3.75
396.2	20	3.00
395.0	20	3.00
393.8	20	3.25
392.5		
	Average	3.32

Calculated refractive index:

$n = 1.000951$

Molar volume at 25°C:

$V_m = 24,451$ cc./mole

Calculated molar refraction:

$MR = 15.48 \pm 0.56$ cc./mole

TABLE XXVIII

DATA FOR DETERMINATION OF THE MOLAR REFRACTION OF CHLORINE MONOFLUORIDE

Pressure (Micrometer Reading)	Number of Fringes	Change in Pressure Per 10 Fringes
414.9	10	1.5
413.4	10	1.3
412.1		
411.9	7	1.29
412.8		
415.0	10	1.3
413.7	9.5	1.36
412.4		
411.9	7	1.43
412.9		
	Average	1.363

Calculated refractive index:

$n = 1.000469$

Molar volume for 24°C:

$V_m = 24{,}369$ cc./mole

Calculated molar refraction:

$MR = 7.62 \pm 0.25$ cc./mole

TABLE XXIX

DATA FOR DETERMINATION OF THE MOLAR REFRACTION OF BROMINE TRIFLUORIDE

Pressure (Micrometer Reading)	Number of Fringes	Change in Pressure Per 20 Fringes
413.9	16	1.87
412.4	15	1.86
411.0	7	1.60
410.4		
415.4	15	1.73
414.0	15	1.86
412.6		
410.3	15	1.73
411.6	7	1.71
412.2		
412.2	15	1.60
411.0	14	1.86
412.3	14	1.71
411.1	9	1.55
411.8		
416.0	15	1.73
414.7	15	1.86
413.3	15	1.86
411.9	6	1.66
412.4		
	Average	1.745

Calculated refractive index:

$n = 1.000725$

Molar volume for 53°C:

$V_m = 26{,}749$ cc./mole

Calculated molar refraction:

$MR = 12.92 \pm 0.33$ cc./mole

TABLE XXX

DATA FOR DETERMINATION OF THE MOLAR REFRACTION OF CHLORINE TRIFLUORIDE

Pressure (Micrometer Reading)	Number of Fringes	Change in Pressure Per 20 Fringes
414.3	20	2.3
412.0	20	2.1
409.9	20	2.0
407.9	20	1.9
406.0	20	2.1
403.9	20	2.1
401.8		
414.2	20	2.3
411.9	20	2.1
409.8	20	2.0
407.8	20	2.1
405.7	20	2.0
403.7		
403.2	20	2.1
401.1		
414.4	20	2.1
412.1	20	2.0
410.1	40	3.9
406.2	40	3.8
402.4	40	3.9
398.5		
414.4	20	2.2
412.2		
414.3	20	2.1
412.2	20	1.8
410.4	20	1.7
408.7	20	1.8
406.9	20	1.9
405.0		

Continued next page

TABLE XXX - Continued

Pressure (Micrometer Reading)	Number of Fringes	Change in Pressure Per 20 Fringes
413.9	20	2.0
411.9	20	1.9
410.0	20	1.9
408.1		
406.7	20	1.9
404.8	20	1.9
402.9	20	1.8
401.1	20	1.8
399.3	20	2.0
397.4		
	Average	2.00

Calculated refractive index:

$n = 1.0006326$

Molar volume at 26°C:

$V_m = 24{,}533$ cc./mole

Calculated molar refraction:

$MR = 10.34 \pm 0.50$ cc./mole

VII. DISCUSSION

The molar refraction of a compound may be considered to be the sum of the individual atomic refraction values for the atoms that form the compound. Since only the molar refraction values may be experimentally determined for a substance, there must be a standard or accepted value of some atomic refraction to which all the others will be referred. There seems to be no accepted standard, most authors merely choosing an initial value by a reasonable guess. This has resulted in some confusion and the data are usually not comparable with one another without some modification.

The procedure used here to choose the initial value is based on the assumption that ionic refractivities should be roughly proportional to the volumes of the ions. The radii of the spherical ions of several alkali halides are given by Pauling[155] and from these the respective volumes have been calculated. The molar refractions for several of the alkali halides at infinite dilution have been quite accurately determined from solution measurements. These have been divided into ionic refractions with the same ratio as the volumes of the ions. When this was done for several chloride salts a constant value for the ionic refraction of the chloride ion was found. This value provides the basis for the calculation of other ionic refractions.

The values for the ionic refractions at infinite dilution of all the ions determined by the author are listed in Table XXXI as calculated from

TABLE XXXI

IONIC REFRACTIONS

Ion	Ionic Refraction	Ion	Ionic Refraction
K^+	3.32	BF_4^-	6.45
Na^+	1.20	$SiF_6^=$	10.78
NH_4^+	4.60	$TiF_6^=$	20.04
H^+	-0.31	Cl^-	8.26
		HF_2^-	3.12

the data of Table XXXII. These empirical constants reproduce the observed molar refractions of the compounds with a mean deviation of ± 0.04 cc./mole. The molar refraction of the bifluoride ion has little significance since the very dilute solutions measured probably contained little of this ion.

Since covalent character tends to shorten bond lengths and decreases the effective size of a species, the ionic refractions should be the maxima observed or assigned for the given atom. The ionic refraction values for the bromide and iodide ions were taken from Fajans' set of values and that of fluoride had to be estimated since no ionic refraction value could be found for it.

Next, the covalent atomic refractions for the halogens were found. The atomic refractions of chlorine and bromine were calculated from the molar refractions of the halogen molecules while those of fluorine and iodine were the values assigned to them by Vogel[19] from his investigations

TABLE XXXII

MOLAR REFRACTIONS OF IONIC COMPOUNDS IN INFINITELY DILUTE SOLUTION

Compound	Molar Refraction
KCl	11.58 ± 0.10
NaCl	9.40 ± 0.20
NH_4BF_4	11.08 ± 0.21
HBF_4	6.14 ± 0.32
$NaBF_4$	7.63 ± 0.15
NH_4Cl	12.86 ± 0.16
NaF	2.47 ± 0.34
Na_2SiF_6	13.20 ± 0.22
K_2SiF_6	17.40 ± 0.70
K_2TiF_6	26.68 ± 2.5
KHF_2	6.44 ± 1.6
$K_4Fe(CN)_6$	69.06
$K_3Fe(CN)_6$	60.91

of numerous organic compounds. The ionic and covalent atomic refractions of the halogens used in this investigation have been assembled in Table XXXIII.

The atomic refraction should decrease if the atom loses electrons, i.e., changes to a higher oxidation state, but there seems to be no

TABLE XXXIII

COVALENT AND IONIC REFRACTIONS FOR THE HALOGEN ATOMS

Type of Bond	Fluorine	Chlorine	Bromine	Iodine
Ionic	1.80	8.26	11.59	18.16
Covalent	0.78	5.77	8.45	13.95

satisfactory way to determine the amount of decrease. A fixed value was chosen for the atomic refraction of fluorine and the differences between the refractivities of Cl^{I} and Cl^{III}, and of Br^{III} and Br^{V} estimated. Using these differences as a basis, an empirical set of atomic refractions for the halogen atoms in various oxidation states was obtained. These values are for use in pure covalent compounds and are shown in Table XXXIV.

Since the ionic radii are, in general, larger than the covalent radii of the elements it would be expected that increasing ionic character of bonds would tend to lengthen the internuclear distances. Atomic refractions, in turn, tend to increase with size hence the molecular refraction might be expected to increase with increasing ionic character. To test this hypothesis the molecular refraction of a simple molecule has been assumed to be larger than the value obtained by summing the covalent atomic refractivities by an amount proportional to the percent ionic character of the bonds. Thus

$$MR_{obs.} = MR_{cov.} + x\,[MR_{ionic} - MR_{cov.}] \qquad (56)$$

TABLE XXXIV

COVALENT ATOMIC REFRACTIONS FOR DIFFERENT OXIDATION STATES OF THE HALOGENS

Atom	Atomic Refraction
Cl^{I}	5.77
Cl^{III}	5.27
Br^{I}	8.45
Br^{III}	7.10
Br^{V}	6.45
I^{I}	13.95
I^{V}	8.60

where x is the fraction of ionic character. The values to be expected for pure ionic and pure covalent compounds were taken from Table XXXIII and the fraction ionic character was then calculated for each of the compounds in Table XXXVI from the observed molar refractions. For comparison, the estimates of the ionic character from electronegativity differences are also listed.[155]

For the fluorocarbon derivatives in Table XXXV, the atomic refractions of fluorine have been calculated by subtracting the atomic refractions values of the other atoms and bonds using the values given in Table II. The values obtained were all approximately 1.10 cc./mole which lies between the covalent refraction and the ionic refraction for fluorine and indicates about 36% ionic character (Table XXXVI).

TABLE XXXV

SUMMARY OF REFRACTIVE INDICES AND MOLAR REFRACTIONS FOR GASES

Compound	Refractive Index	Temperature °C	Molar Refraction
$CClF{=}CG_2$	1.0009622	20.0	15.77 ± 0.32
$(C_2F_5)_2O$	1.0014396	25.0	23.49 ± 0.48
n-C_3F_7H	1.001023	25.0	16.67 ± 0.33
$(C_2F_5)_3N$	1.002126	27.5	34.96 ± 0.64
ClF	1.000494	24.0	7.62 ± 0.25
ClF_3	1.0006326	26.0	10.34 ± 0.50
BrF_3	1.000725	53.0	12.92 ± 0.33
BrF_3	1.000951	25.0	15.48 ± 0.56
IF_5	1.001156	29.0	19.17 ± 0.27

TABLE XXXVI

IONIC CHARACTER OF VARIOUS COMPOUNDS

Substance	Calculated Ionic Character From the Refractivities	Ionic Character From Electronegativity Differences
CCl_4	8%	6%
CHF_3	35% *	42%
CF_4	39%	42%
$C_6H_{11}F$	36% *	42%
C_3H_7Cl	5% *	6%
ClF	30%	22%
ClF_3	49%	47%
BrF_3	55%	51%
BrF_5	61%	65%
IF_5	72%	73%
HF	61%	59%
HCl	16%	18%
HBr	14%	11%
HI	23%	4%
SiF_4	64%	70%
$SiCl_4$	59%	30%
$SiBr_4$	16%	22%

* Ionic contribution from carbon-hydrogen bonds ignored.

VIII. SUMMARY

An interferometer of the Rayleigh type, which is adaptable for measurements of the refractive indices of both solutions and gases, has been constructed. An extensive review of the literature concerning the instrument, its theory, and applications is included along with a discussion of refractive indices and molar refractions. A discussion of methods of solving various experimental problems encountered in building and using the instrument has been included.

The use of the interferometer for solution measurements has been discussed in detail including the method of calibration and the problem of the zero-order fringe loss or gain.

A vacuum system was designed for handling both unreactive gases and the corrosive halogen fluorides. It consisted of copper tubing, copper-plated brass gas cells, and brass Sylphon valves wherever the halogen fluorides were in contact with the system. The remainder of the vacuum system was of conventional construction for handling ordinary gases and materials for calibration of the instrument. A special pressure gage was made for measuring pressures of the gaseous halogen fluorides. It consisted of a Bourdon tube, the movement of which was measured by a micrometer. An electronic device was designed to indicate contact between the micrometer screw and the Bourdon tube.

The molar refractions of potassium chloride, sodium chloride, ammonium fluoborate, fluoboric acid, sodium fluoborate, ammonium fluoborate, sodium fluoride, sodium silicofluoride, potassium silicofluoride, potassium fluotitanate, potassium bifluoride, potassium ferrocyanide, and potassium ferricyanide were determined at infinite dilution from the measured refractive indices and densities of dilute aqueous solutions of each. A set of ionic refractions has been calculated from these molar refraction values which reproduces the observed molar refractions with a mean deviation of ±0.04 cc./mole. The ionic refractions were assigned to the atoms in the ratio of the volume of the free spheres calculated from the ionic radii.

The refractive indices of nitrogen, chlorotrifluoroethylene, perfluoroethyl ether, 1,1,1,2,2,3,3-heptafluoropropane, perfluorotriethyl amine, chlorine monofluoride, chlorine trifluoride, bromine trifluoride, bromine pentafluoride, and iodine pentafluoride were determined and the respective molar refractions were calculated. An empirical procedure was devised to estimate degree of ionic character in simple molecules. The value of the ionic character determined in this manner was compared with the percent ionic character as determined by the electronegativity differences for the atoms involved.

LITERATURE CITED

1. W. Bielenberg, Z. angew. Chem., 42, 972 (1929).
2. A. V. Grosse and R. C. Wackher, Ind. Eng. Chem., Anal. Ed., 11, 614 (1939).
3. A. L. Ward and W. H. Fulweiler, ibid., 6, 396 (1934).
4. A. L. Ward and S. S. Kurtz, Jr., ibid., 10, 559 (1938).
5. Riviere, Compt. rend., 131, 671 (1900).
6. J. Timmermans, J. chim. phys., 29, 529 (1932).
7. J. Timmermans, ibid., 31, 85 (1934).
8. L. W. Telton, J. Research Natl. Bur. Standards, 14, 393 (1935).
9. C. Cheneveau, Ann. Chim. Phys., 12, 145, 289 (1907).
10. K. Lichtenecker, Physik. Z., 27, 115 (1926).
11. G. DeLattre, J. chim. phys., 24, 289 (1927).
12. D. A. G. Bruggeman, Physik. Z., 37, 906 (1936).
13. A. Weissberger, "Physical Methods of Organic Chemistry" Interscience Publishers, Inc., New York, Vol. I, 1935.
14. E. Gehrcke, "Anwendung der Interferzen," 120 1906.
15. C. Candler, "Modern Interferometers", Hilger and Watts, Ltd., Great Britain, 1951.
16. Delambre, Mem. de l'Inst., Paris, 7, 1 (1806).
17. J. B. Biot and D. F. Arago, ibid., 7, 301 (1806).
18. Hankshee, "Physico-Mechanical Experiments", 1709.
19. J. R. Partington, "An Advanced Treatise on Physical Chemistry", Longmans, Green and Co., Inc., New York, Vol. IV, 1953.

20. Dulong, Ann. chim., 31, 154 (1826).

21. E. Ketteler, Ann. Phys., 124, 390 (1865).

22. Lord Rayleigh, Proc. Roy. Soc. (London), A59, 201 (1896).

23. Lord Rayleigh, Sci. Papers, 4, 218 (1896).

24. F. Haber and F. Lowe, Z. angew. Chem., 23, 1393 (1910).

25. J. Edwards, Bull. Bur. Stand., 14, 474 (1917).

26. J. Edwards, J. Am. Chem. Soc., 39, 2382 (1917).

27. L. Adams, J. Am. Chem. Soc., 37, 1811 (1915).

28. G. K. Bell, J. Am. Pharm. Assoc., 29, 126 (1940).

29. F. A. Patty, J. Ind. Hyg. Toxicol., 21, 469 (1939).

30. R. Stamm and J. Whalen, ibid., 29, 203 (1947).

31. J. Edwards, J. Am. Chem. Soc., 39, 2382 (1917).

32. O. Wolff, Chem.-Ztg., 39, 197 (1915).

33. J. Edwards, Tech. Paper (Bur. Std.), 131, 1 (1920).

34. W. Geffcken, Z. Electrochem., 37, 233 (1931).

35. J. M. Hansen, Z. Instrumentk., 50, 460 (1932).

36. W. E. Williams, Proc. Phys. Soc. London, 44, 45 (1933).

37. P. Wulff, Z. Krist., 77, 61 (1931).

38. A. Kruis, Z. physik. Chem., B34, 1, 13, 82 (1936).

39. A. Kruis and W. Geffcken, ibid., B34, 51, 70 (1936).

40. W. Geffcken and A. Kruis, ibid., B23, 175 (1933).

41. W. Geffcken, Z. Elektrochem., 37, 233 (1931).

42. A. Kruis and W. Geffcken, Z. physik. Chem., A166, 16 (1933).

43. L. Adams, J. Wash. Acad. Sci., 5, 256.

44. R. Gans and Bose, Z. Instrumentk., 36, 137 (1918).

45. W. Barth, Z. wiss. Phot., 24, 145 (1926).

46. J. G. Malik, J. L. Speirs and M. T. Rogers, J. Chem. Educ., 30, 437 (1953).

47. O. Mohr, Z. angew. Chem., 25, Aufsatz 1313 (1914).

48. E. Cohen and H. Bruins, Proc. Acad. Sci. Amsterdam, 24, 114 (1921); C. A., 16, 1533 (1922).

49. R. L. VanKlemperer, Chem.-Ztg., 35, 557 (1911).

50. R. Marc. Kolloid Z., 14, 181 (1914); C. A., 8, 3651 (1914).

51. L. Adler and H. Luers, Chem. Zentr., 1, 1276 (1916).

52. H. Kappen, Landw. Vers. Stat., 83, 385 (1914).

53. H. Nothdurft and J. Hopp, Arch. ges. Physiol., 242, 97 (1939); C. A., 33, 9344 (1939).

54. J. Ziegler, Magyar Orvoie Arch., 34, 224 (1933); C. A., 27, 4607 (1933).

55. F. Seibert and W. Harpster, Tech. Paper, 185, (1918); C. A., 12, 1626 (1918).

56. P. Ya. Nedviga, Zavodskaya Lab., 9, 598 (1940); C. A., 34, 7147 (1940).

57. J. May, Zeiss. Nachr. 2, #8, 280 (1939); C. A., 33, 8059 (1939).

58. M. Hahn and R. Heim, Berl. klin. Wachschr., 50, 197 (1913); C. A., 7, 2049 (1913).

59. M. Opladen, Z. Physik, 42, 160 (1927); C. A., 21, 2217 (1927).

60. R. Heim, Z. klin. Med., 78, 501 (1914); C. A., 8, 3684 (1914).

61. P. Hirsch, Z. physiol. Chem., 91, 440 (1914); C. A., 8, 3570 (1914).

62. R. Marc and K. Sack, Kolloidchem. Beihefte, 5, 375 (1914); C. A., 8, 3651 (1914).

63. J. Howell, Phys. Rev., 6, 81 (1915).

64. R. Lucion, Bull. soc. chim. Belg., 27, 343 (1913); C. A., 9, 2329 (1915).

65. F. Lowe, Colbeig. Guardian, 144, 833 (1932); C. A., 26, 3411 (1932).

66. H. Bartels, Umschau, 40, 583 (1935); C. A., 30, 7735 (1935).

67. H. Nagaoka, Proc. Tokyo Math. Phys. Soc., 9, 49 (1917); C. A., 11, 901 (1917).

68. A. A. Michelson and Benoit, Trav. Bur. Int. Pds. Mes., 11, 3, 85 (1895).

69. H. Fromberz and W. Menschick, Z. physik. Chem., Abt. B2, 399 (1929); C. A., 23, 3377 (1929).

70. G. Merritt, Bur. Stds. Sci. Papers, (485), 19, 375 (1924).

71. P. Hirsch and F. Lowe, Fermentforschung, 3, 311 (1922); C. A., 16, 266 (1922).

72. W. Bachmann, Z. Immunitats, 35, 462 (1923); C. A., 17, 1668 (1923).

73. W. Bachmann, ibid., 40, 325 (1925); C. A., 19, 114 (1925).

74. W. Bachmann, ibid., 33, 551 (1922); C. A., 17, 2607 (1923).

75. L. Van Doren and L. H. Parker and P. Lotz, J. Am. Chem. Soc., 43, 2497 (1921).

76. J. Edwards, ibid., 39, 2382 (1917).

77. J. Manley, Proc. Phys. Soc. London, 40, 57 (1928); C. A., 23, 2074 (1929).

78. A. Ignatiew, Ann. Physik, 43, 1117 (1914).

79. W. Kinder, Zeiss Nachr., 2, No. 7, 223 (1938); C. A., 33, 4468 (1939).

80. L. Szigo, Gazz. chim. ital., 60, 212 (1930); C. A., 24, 4209 (1930).

81. Wollschitt, Bothe, Ruska and Schenck, Arch. exptl. Path. Pharmakol., 177, 625 (1935); C. A., 29, 4037 (1935).

82. K. Schaum and W. Barth, Z. wiss. Phot., 24, 166 (1926); C. A., 21, 2413 (1927).

83. I. Newton, "Optiks", book II, 1931.

84. P. LaPlace, Mecanique Celeste, 4, 237 (1805).

85. P. LaPlace, Oeuvres, 4, 237 (1805).

86. J. Jamin, Ann. Chim., 52, 163 (1858).

87. J. B. Biot and D. F. Arago, Ann. Phys., 25, 345 (1807).

88. J. B. Biot and D. F. Arago, ibid., 26, 36 (1808).

89. D. F. Arago and Petit, Ann. Chim., 1, 5 (1816).

90. Dulong, ibid., 31, 154 (1826).

91. Bertholet, ibid., 48, 342 (1856)

92. Beer, "Einleitung in die hohere Optik", Brunwick, 1853.

93. Gladstone and Dale, Phil. Trans., 148, 887 (1858).

94. Gladstone and Dale, ibid., 153, 317 (1863).

95. Gladstone and Dale, Phil. Mag., 17, 222 (1859).

96. Dufet, Bull. Soc. Min., 8, 406 (1885).

97. Sutherland, Phil. Mag., 27, 141 (1889).

98. Gladstone and Dale, Phil. Trans., 153, 317 (1863).

99. Landolt, Ann. Phys., 123, 595 (1864).

100. Landolt, ibid., Ber., 15, 1031 (1882).

101. Ruhlmann, Ann. Phys. 132, 177 (1867).

102. Wullner, ibid., 133, 1 (1868).

103. Quincke, ibid., 19, 401 (1883).

104. Zehnder, ibid., 34, 91 (1888).

105. J. F. Eykman, "Recherches refractometriques", Natuurkund. Verhandel. Hollandsche Mij Wetenachappen Haarlem, 1919.

106. F. Eisenlohr, Ber., 54, 2857 (1921).

107. Gibson and Kincaid, J. Am. Chem. Soc., 60, 511 (1938).

108. Mathews, J. Franklin Inst., 177, 673 (1914).

109. von Lang, Ann. Phys., 153, 448 (1874).

110. M. E. Mascart, Compt. rend., 78, 617, 679 (1874).

111. H. Kohner, Z. physik. Chem., 131, 427 (1928).

112. W. Geffcken, Z. Elektrochem., 37, 233 (1931).

113. W. Geffcken, C. Backmann and A. Kruis, Z. physik. Chem., B20, 398 (1933).

114. W. Geffcken and A. Kruis, ibid., B23, 175 (1933).

115. W. Geffcken and A. Kruis, ibid., B45, 411 (1939).

116. A. Kruis and W. Geffcken, ibid., A166, 16 (1933).

117. A. Kruis, ibid., B34, 1, 13, 82 (1936).

118. A. Kruis and W. Geffcken, ibid., B34, 51, 70 (1936).

119. P. A. Guye, Compt. rend., 110, 141 (1890).

120. P. A. Guye, ibid., 119, 852 (1894).

121. P. A. Guye, J. de Phys., 9, 312 (1890).

122. P. A. Guye, Ann. Chim., 21, 206, 211 (1890).

123. P. A. Guye, Z. phys. Chem., 6, 372 (1890).

124. P. A. Guye, Arch. sci. phys. et nat., 23, 197, 204 (1890).

125. P. A. Guye, ibid., 31, 38 (1894).

126. P. A. Guye, Ann. Chim., 27, 352 (1892).

127. S. W. Wan, J. Phys. Chem., 45, 903 (1941).

128. R. Livingston, ibid., 46, 341 (1942).

129. R. Livingston, ibid., J. Phys. Chem., U.S.S.R., 11, 325 (1938).

130. Traube, Ann. Phys., 5, 548 (1901).

131. P. Walden, Z. phys. Chem., 65, 129 (1909).

132. P. Walden, ibid., 66, 385, 424 (1909).

133. P. Walden, ibid., 70, 569, 598 (1910).

134. W. Herz, Z. anorg. Chem., 123, 132 (1922).

135. L. Lorenz, ibid., 94, 290 (1916).

136. L. Lorenz and W. Herz. ibid., 142, 80 (1925).

137. W. Herz, ibid., 153, 269 (1926).

138. W. Herz, ibid., Z. phys. Chem., 98, 175 (1921).

139. W. Herz, ibid., 101, 54 (1922).

140. S. S. Joshi and G. D. Tuli, J. Chem. Soc., 837 (1951).

141. H. A. Lorentz, Ann. Phys., 9, 641 (1880).

142. W. Ostwald, "Grundriss der allgemeinen Chemie," 3rd Ed., Engelmann, Leipzig, 1899.

143. K. Fajans, Z. physik. Chem., B24, 133 (1934).

144. K. Fajans, ibid., J. Chem. Phys., 10, 759 (1942).

145. K. Fajans and T. Berlin, Phys. Rev., 63, 309 (1943).

146. K. Fajans, J. Am. Chem. Soc., 64, 3023 (1942).

147. A. J. Vogel, J. Chem. Soc. 636 (1943).

148. A. J. Vogel, ibid., 644, 654 (1948).

149. A. L. von Steiger, Ber., 54, 1381 (1921).

150. K. Fajans and G. Joos, Z. Phys., 23, 1 (1924).

151. K. Fajans and C. A. Knoor, Chem.-Ztg., 48, 403 (1924).

152. K. Fajans and C. A. Knoor, Ber., 59, 249 (1926).

153. K. G. Denbigh, Trans. Faraday Soc., 36, 936 (1940).

154. E. L. Warrick, J. Am. Chem. Soc., 68, 2455 (1946).

155. L. Pauling, "Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1948.

156. W. E. Williams, "Applications of Interferometry", Methuen and Co., Ltd., London, 1941.

157. F. A. Jenkins and H. E. White, "Fundamentals of Optics", McGraw-Hill Book Co., Inc., New York, 1950.

158. G. R. Robertson, Ind. Eng. Chem., <u>11</u>, 464 (1939).

159. J. Jamin, Compt. rend., <u>42</u>, 482 (1856).

160. F. Haber and F. Lowe, Z. angew. Chem., <u>23</u>, 1393 (1910).

161. Landolt-Bornstein, "Physikalisch-Chemische Tabellen", Berlin, 1905.

162. International Critical Tables of Numerical Data, Physics, Chemistry and Technology, McGraw-Hill Book Co., Inc., New York, VII, 1930.

163. I. F. Halverstadt and W. D. Kumler, J. Am. Chem. Soc., <u>64</u>, 2988 (1942).

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