

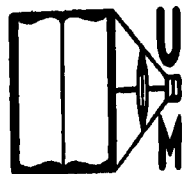
DOCTORAL DISSERTATION SERIES

TITLE APPARENT MOLAR REFRACTION
AND VOLUME OF SALTS IN
WATER, ETHER, AND ACETONE
SOLUTION

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APPARENT MOLAR REFRACTION AND VOLUME
OF SALTS IN WATER, ETHER, AND ACETONE SOLUTIONS

by
Oliver Johnson

A Dissertation Submitted in Partial Fulfillment
of the Requirements for the Degree of
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TABLE I

SYMBOLS USED IN "REFRACTOMETRIC INVESTIGATIONS"

- A. = equivalent weight M = molecular weight
- C_g = molal (weight) concentration = equivalents per 1000 grams solvent
- C_v = molar (volume) concentration = equivalents per 1000 cc solution
- p = concentration in grams solute per 100 grams solution
(% concentration)

$$C_v = \frac{10 p D}{A}$$

$$C_g = \frac{1000 p}{A (100-p)}$$

D = density of solution

D₀ = density of solvent

Δ = difference

▽ = error

ΔD = D - D₀

D = R_D - R_∞ = dispersion

Φ = Apparent molar volume of dissolved solute

$$\Phi = \frac{A}{D_0} - \frac{1000 \Delta D}{C_v D_0}$$

r = specific refraction of solution (refraction per gram)

r₀ = specific refraction of solvent

r_s = specific refraction of solute

rⁱ = specific refraction of impurity

n₀ = index of refraction of solvent

n = index of refraction of solution

*This investigation is a continuation of the series of "Refractometric Investigations" begun by Professor Fajans at the University of Munich (1924). The previous papers will be referred to by roman numerals. The references are arranged chronologically in part I of the Bibliography.

$$\psi = \frac{N^2 - 1}{N^2 + 2}$$

$$\psi_0 = \frac{N_0^2 - 1}{N_0^2 + 2}$$

α_e = electronic polarizability

N = Avogadro's constant

$$\Delta\psi = \psi - \psi_0$$

$$\pi = \text{function of } N \text{ and } C_v = \frac{1000 \Delta\psi}{C_v \psi_0}$$

ν = frequency of light

λ = wave length of light

R_{λ}^{25} = mol refraction for wave length λ at a temperature of 25° C.

$$R_{app} = \left(\frac{A}{D_0} - \frac{1000 AD}{C_v D_0} \right) \psi_0 + \left(\frac{1000 \Delta\psi}{C_v \psi_0} \right) \psi_0 = \psi_0 (\pi + \phi)$$

$$\nabla R (\text{error due to impurities}) = A_p (r' - r) 10^{-2}$$

$$\nabla R (\text{due to analysis error}) = A(\mu_0 - \mu_s) \frac{V_p}{p}$$

A. INTRODUCTION

The Lorentz-Lorenz expression for the molar refraction of a pure substance is given by the following formula, where n_λ is the refractive index for the wave length λ , D is the density and M the molecular weight:

$$R_\lambda = \frac{n_\lambda^2 - 1}{n_\lambda^2 + 2} \cdot \frac{M}{D} \quad (1)$$

Correspondingly, the refraction of a given weight, W , of solution is defined by equation (2) and the apparent refraction of a solute by equation (3), using the symbols given in Table I:

$$R_{\text{solution}} = \frac{n_{\text{solu}}^2 - 1}{n_{\text{solu}}^2 + 2} \cdot \frac{W}{D_{\text{solu}}} \quad (2)$$

$$R_{\text{APP}} = \left[(1000 + A \cdot C_g) n - 1000 n_0 \right] \cdot \frac{1}{C_g} \quad (3)$$

It is seen from equation (3) that the apparent molar refraction is obtained from the refraction of a solution by subtracting the refraction of the solvent considered as unchanged.

Molar refraction has the dimension of volume, but the physical interpretation given is that refraction is a measure of the electronic polarizability, strictly speaking only for infinite wavelength (R_∞), according to equation (4):

$$R_\infty = \frac{4}{3} \pi N \alpha_e \quad (4)$$

Analogously the apparent volume (Φ) is obtained by subtracting the volume of the solvent, considering it unchanged, from the total volume of solution. As shown by the formula in Table I it can be easily calculated from density and concentration data.

The variation of both apparent molar refraction and volume with concentration of the dissolved salt as well as their absolute values at infinite dilution are very useful for the understanding of chemical forces in solution.

The measurement of the index of refraction at several wavelengths gives a value for the molar dispersion. The molar dispersion is defined as the difference between the refraction measured with sodium light and the refraction for light of infinitely long wave length i. e. $D = R_D - R_\infty$. A recent systematic study of this property (See Bauer and Fajans, LV) has shown that the deviations from additivity parallel those found in the molar refraction, and that the molar dispersion is even more sensitive to changes in the chemical forces between particles than is the refraction.

The present investigation includes a refractometric study of aqueous solutions of silver fluoride and potassium cyanate, and of solutions of lithium perchlorate, lithium bromide and lithium iodide in ether, as well as of lithium perchlorate in acetone.

The investigation of silver fluoride is a continuation of the study of the behaviour of solutions of compounds of

non-rare gas cations of which only CdCl_2 (See Lündemann; XLII) and AgNO_3 (See Bauer; 1) had been studied before in the "Refractometric Investigations". A study of the properties of many in-organic compounds (See Fajans, 2,3) has shown that the greater polarizing power of non rare gas cations and their greater polarizability ~~as~~ compared to rare gas ions is very important for the behavior of compounds of these ions. The study of another salt could be expected to add to the understanding of the effects due to the mutual interaction of non rare gas cations with anions and water molecules. In the case of AgF it was of interest to verify the large change of apparent volume with concentration which is indicated by the measurements of A. Heydweiller (4) and to determine the concentration dependence of the apparent refraction which was not shown by his measurements. Furthermore, it could be expected that the loosening effect of F^- on Ag^+ (see Fajans, 5) would show up in the increase of apparent refraction with increasing concentration.

The determination of a value of the refraction of the cyanate ion (NCO^-) is of interest in completing data in the series of tri-atomic isoelectronic particles (N_2O , CO_2 , N_3^- etc.) containing 16 electrons.

The study of non-aqueous solutions was prompted by an interest in the unusually large solubility of LiClO_4 in ether which had been found by Willard and Smith (6). In this laboratory Miss Jean Chu (7) has been studying the

conductivity of LiClO_4 in ether and the conductivity and solubility of LiBr and LiI in ether. The present investigation of the apparent volumes, refractions and dispersions extends that study.

The conductivity measurements by Miss Chu (7) *have shown* that LiClO_4 is practically undissociated in ether i.e. the system consists of neutral molecules. In the "Refractometric Investigations", until now the emphasis has been placed on changes in refraction accompanying the formation of crystals from ions, changes upon dissolving electrolytes in water or changing their concentration. These investigations showed systematic deviations from additivity of the Lorentz-Lorenz refraction which are attributed to mutual interaction of ions and of ions and solvent. Mixtures of neutral molecules have been studied by many investigators, but only the more accurate determinations of Hubbard (8), M.L. Koenig-Gressmann (9) and Linton (10) show deviations from additivity with certainty, and these deviations are very small in the cases studied.

The system LiClO_4 - ether combines a very polarizable solvent ($R_D = 22.5$) with a solute having a large dipole moment; thus, relatively large deviations from additivity were to be expected if the effects observed in solutions of electrolytes are due to electric interactions.

There are very few previous measurements of refraction of salts in solvents other than water. Cheneveau (11) has reported the refraction of ZnCl_2 in ether and LeBlanc and

Rohland (12) have measured the refraction of KI and HgCl_2 in acetone. These data give approximate values for the apparent molar refraction but are not sufficiently accurate to show any change of refraction with increasing concentration. The concentration dependence of apparent refraction is shown, however, by the measurements of Schreiner (13) on HCl and LiCl in methanol and ethanol and of Pesce (14) on $\text{Ca}(\text{NO}_3)_2$ in methanol.

In order to compare the results obtained for LiClO_4 in ether with more similar cases, measurements were also made of LiClO_4 in acetone and of LiBr and LiI in ether.

B. EXPERIMENTAL

I. APPARATUS

The apparatus used in this laboratory for refraction measurements was set up by N. Bauer (1) and has been thoroughly described by him. A briefer discussion of the apparatus and its manipulation will be given here, but modifications necessary for the fluoride solutions and solutions in organic solvents will be described in detail.

(a). Pycnometer

Three 30cc. bicapillary pycnometers (see Fig. 1) were used in this investigation. The diameter of each capillary tube is approximately 0.6 mm which corresponds to 0.3 mg. water per mm. length. Graduated scales are attached to the back of each capillary arm, and by viewing the scale thru a telescope, the level of the liquid can be determined to within 0.05 mm. The capillary bores had been found to be very nearly uniform by measuring the length of a mercury thread in various parts of the capillary tube. From the weight of this mercury thread, the volume per mm. of capillary could be determined. The distance between the divisions on the scales had previously been calibrated by Bauer (1). With this information one can calculate the weight of water, which is the standard used, corresponding to any height of liquid in the capillaries.

Bauer had used the method of applying pressure to bring the level of liquid in the left capillary to a reference mark

and only taking readings on the level in the right capillary. In this investigation it was desired to be able to determine densities as rapidly as possible in view of working with organic solvents which evaporate easily. Thus both capillaries were calibrated, and when the proper amount of solution had been introduced, readings were quickly taken on the levels of liquid in both capillaries without using the often troublesome method of applying pressure to bring the level in one capillary to a reference mark. In this way the ground caps could be kept on during the measurement, thereby reducing evaporation of the solvent.

The temperature is kept at $25^{\circ} \pm 0.002^{\circ}$ during the density measurement by a precision thermostat.

(b). Refractometer

A Zeiss-Pulfrich Refractometer with a special graduated circle provided with accurate divisions was used for the measurement of refractive indices. With this instrument readings on spectral lines can be determined to within $\pm 0.05'$. Water from the precision thermostat is circulated around the prism and around the vessel containing the liquid being measured. Beckmann thermometers, placed in the path of the circulating water before and after it reaches the prism, indicate that the temperature is kept at $25^{\circ} \pm 0.05^{\circ}$ during a measurement. An air thermostat surrounding the refractometer is kept at $25^{\circ} \pm 0.3^{\circ}$.

Special precautions required in the measurements on AgF and ether solutions will be discussed later (Section II, c).

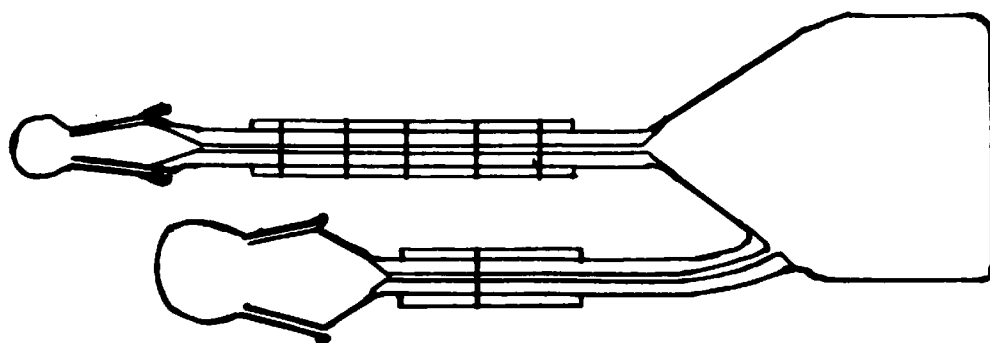


Fig. 1
Bicapillary pycnometer

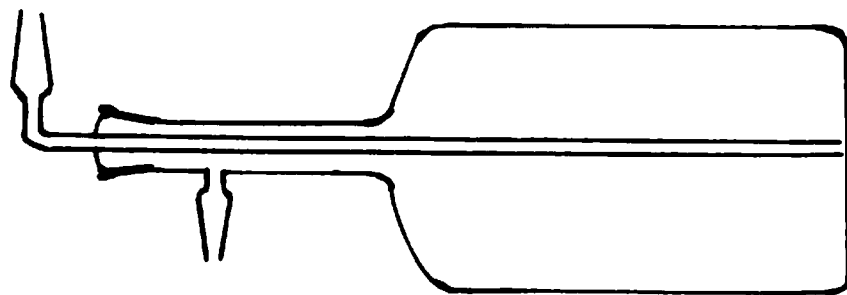


Fig. 2
Solution weighing bottle

The vessel which holds the liquid is attached to the prism with a ground joint, but to prevent leaking and to insure rigidity, a suitable cement is applied at this joint. Picein was used in the measurements of AgF and Orange Shellac (applied as a paste in alcohol) was found to be satisfactory for ether, acetone and their solutions.

(c). Light Source

During the investigation Bauer's original helium tube burned out; a new tube was designed after discussion with Mr. Kessler of the Physics Department. The new tube also operates on a 15,000 volt transformer supplying a current of 24 ma. In the construction, hollow nickel electrodes were outgased by heating in a vacuum, and the 30 cm. tube was filled with helium at a pressure of about 18 mm. The use of nickel electrodes and a higher pressure of helium than in the former tube are intended to prevent sputtering which was probably the cause of the failure of the previous tube. The work was done by Mr. Kessler. This tube gave a very intense helium spectrum in which seven lines are distinctly visible.

(d). Glassware and Miscellaneous Apparatus

The relatively large amount of stock solution was always kept in an Erlenmeyer flask having a siphon tube sealed into the cap. Both the cap and the outlet tube for forcing the liquid out of the storing flask had standard taper ground glass joints which could be sealed together by paraffin when not in actual use.

Dilutions were made by means of 100 ml. cylindrical flasks with a side arm and a ground glass stopper (See Fig. 2). These flasks were easily weighed on the analytical balance, and after weighing empty, with stock solution and after dilution to the desired concentration, a siphon tube was inserted. In this way solutions are easily transferred by applying pressure thru the outlet tube. All glass transferring tubes were used, a necessity in case of solutions in organic solvents which evaporate as well as absorb moisture when pipetted or poured directly from one flask to another.

Purified dried air (See N. Bauer, 1, page 54) was used for applying pressure in transferring the solutions, and for solutions in the organic solvents the air was passed through an auxiliary flask containing liquid of about the same concentration as the solution being transferred.

For the determination of concentrations by evaporation of the solution, a 40 cc. weighing bottle with a well fitting ground joint at the top was used.

II. SILVER FLUORIDE IN AQUEOUS SOLUTION

(a). PREPARATION OF SOLUTIONS.

A very pure sample of silver carbonate had been prepared by N. Bauer (1). Silver fluoride solutions were ^{obtained by} adding purified hydrofluoric acid to this silver carbonate in platinum vessels. Purification of HF. The following procedure similar to that described by Archibald (15), McAdam (16) and Moles (17) was used for the purification of

reagent hydrofluoric acid: About 2 grams of potassium carbonate and 0.5 gram KMnO_4 were added per 200 cc HF. The former removes traces of H_2SiF_6 , and the latter removes Cl^- and any organic matter present. The acid was distilled (110°) from these reagents in a platinum distilling apparatus, and then redistilled without further treatment. In both distillations initial and final portions of the distillate were rejected.

This reaction^{between Ag_2CO_3 and HF} was very vigorous in the initial stages, but the mixture finally had to be heated to complete the neutralization. This heating also served to remove excess carbon dioxide which is evolved in the reaction. The acidity was determined from time to time in the final stages of the reaction and the solution was filtered thru a sintered glass funnel when it became perceptibly alkaline.* It had been found previously that concentrated silver fluoride solutions are corrosive to glass (see also Guntz (18)); therefore the stock solution was diluted to approximately 5 molar before filtering and the filtrate collected in a paraffined flask. A specially purified high melting Kahlbaum paraffin was used to coat all the flasks used in this investigation.

The dilutions of the stock solution were made as described

* A final titration with 0.001 N HNO_3 was made according to a method described by Rosa and Vinal (1), see also Bauer, 1), in which the Ag^+ is precipitated with excess KCl before titration. The stock solution was shown to be alkaline presumably due to the presence of some carbonate which amounted to 0.005 ± 0.002 %.

in Section I, d using paraffined weighing bottles in every case.

(b) Analysis

In the evaporation method of analysis, a weighed amount of the stock solution was converted to AgNO_3 by a double evaporation with redistilled Nitric Acid in a platinum evaporating dish. The AgNO_3 was transferred carefully to a special evaporating vessel and purified dried air was passed over it. It was finally fused at 210°C .

A potentiometric titration with a silver electrode was also used to analyze the solution. DeHaen's "Guarantiert Reagent" KCl was used as a standard. A 0.2 molar solution of KCl was added from a "Soule" weight burette to a weighed amount of AgF solution in a paraffined titration beaker. Near the end point, 0.002 M KCl was added in small portions from a 10 ml burette. The procedure followed is described in detail by Lange and Schwartz (20). Table II gives the results of the two series of analyses.

TABLE II

ANALYSIS OF SILVER FLUORIDE STOCK SOLUTION

Trial Number	Electrotitration	Evaporation
1	49.473 %	49.457 %
2	49.486	49.464
3.	49.465	49.478
Mean	49.475 $\pm$ 0.008	49.466 $\pm$ 0.008
Concentration used	49.471 %	

The uncertainty in this concentration value as given in Table II is about 0.02 %. The agreement between the two methods is better than expected, but the analyses definitely shows that the short period of contact with glass in the filtration had no appreciable effect. By application of the formula for estimating the error in apparent refraction due to uncertainty in analyses (see Table I), one obtains

$$V_R = 0.004 \text{ cc.}$$

(c). Protection of Glass from Silver Fluoride Solutions

(1) Density Measurements. It was found that the change of the volume of the pycnometers due to the corrosive action of AgF solutions more concentrated than 2 Molar was large enough to make accuracy of 1 in 100,000 in density impossible. An attempt was made to silver the inside of the pycnometers, but it proved impossible to get an adhering film. Accordingly paraffin was applied to the insides of the pycnometers by rinsing them with a solution of paraffin in benzene, heating slightly to evaporate all benzene and to cause adherence of the paraffin, and then allowing them to stand in a vacuum desiccator for an hour. The weight of the paraffined pycnometer was reproducible to within a half milligram even after it had been calibrated with water. The process was repeated for each new density determination. The bores of the capillaries were also recalibrated with the weighed mercury thread (see Section I, a). After several tests, it was concluded that the variations

in the amount of paraffin in the capillary bore was so small that one calibration of the capillaries would suffice for the series of density measurements.

(a) Refractive Index Measurements. It was especially important to devise a means to protect the prism from the corrosive action of silver fluoride solutions. Various thin films of transparent substances were tried, but it was always uncertain whether they would adhere during the whole series of measurements; this was necessary since they cannot be reproduced. Finally a thin microscope cover glass, with a thin film of bromoform between it and the prism, was attached to the refractometer prism. (See Appendix).

(d) Discussion of Experimental Results for Aqueous Silver Fluoride Solutions.

(1) Analysis of the Accuracy of the results.

Kohner (IX) has given a formula for evaluating the errors in refraction for aqueous solutions from the known uncertainties in the determination of density and index of refraction.

In anticipation of the analagous discussion of errors for ether and acetone solutions, the derivation of the constants in this formula will be considered. From the formula for calculating R which was given in Table I, we obtain the following general equation for the error in R :

$$\nabla R = \frac{1000}{C_v} \left(\nabla(\Delta u) + \frac{\varphi_0}{D_0} \nabla(\Delta D) \right) \quad (5)$$

To evaluate the first part of the formula in terms of Δn , a Taylor expansion of Δu must be made (See Geffcken, XI). Neglecting the higher order terms, the resulting equation is

$$\nabla R = \frac{1000}{C_v} \left[\frac{6 n_0 \nabla(\Delta n)}{(n_0^2 + 2)^2} + \frac{\varphi_0}{D_0} \nabla(\Delta D) \right] \quad (6)$$

Substitution of the values $n_0 = 1.33$ and $D_0 = 0.997$ and $\varphi_0 = 0.2055$ in equation (6) give the following formula for water solutions, which is that given by Kohner:

$$\nabla R = \frac{100}{C_v} [5.6 \nabla(\Delta n) + 2.1 \nabla(\Delta D)] \quad (7)$$

For silver fluoride solutions the accuracy in the measurement of density and index of refraction is not as good as that obtained by Bauer for AgNO_3 for the reasons pointed out in the previous description. The errors for both n and d are ± 0.042 , and from equation (6) the resulting error in refraction is $0.015/C_v$. The scattering of the points (see Figure 5) between 1 and 3 molar indicates an uncertainty of 0.005 cc. which is to be expected from the above consideration.

The error in the apparent volume is proportional to the relative error in ΔD . For the most dilute solution (0.3M.), the error in $\bar{\phi}$ is 0.06 cc while for the 5.7 molar solution the

expected error is only 0.004 cc. The error due to impurity,* assuming it to be CO_3^{2-} , is only 0.005 cc so it is neglected.

One of the refraction values has been corrected due to a large deviation of one point from the π vs. $\sqrt{C}$ curve. A brief mention may be made of this method of testing refractometric data. It was shown by Geffcken (21), Masson (22) and Redlich (23) that when the apparent volume (Φ) or the π values (See Kruis, XXIX) are plotted against the square root of concentration, a straight line results for most electrolytes in water solutions. Since the former is only a function of concentration and density and the latter only a function of concentration and index of refraction, large accidental errors in a single measurement of either n or d can be corrected for when they fall off the curve. If a point falls off both curves it can only mean that there is a concentration error and the data for this concentration must be discarded.

* Since there is no method given in the literature for calculating errors in Φ due to impurities, a simple formula will be developed here.

v_0 = specific volume of water

V = volume of 100 grams of solution

P_1 and P_x = wt. % of salt and of impurity, respectively.

v_1 and v_x = apparent specific volumes of salt and impurity.

$$V = P_1 v_1 + P_x v_x + [100 - (P_1 + P_x)] v_0$$

$$\Phi = A v_1 = A \left[\frac{V - (100 - P_1) v_0 + P_x (v_0 - v_x)}{P_1} \right]$$

$$\Phi_{obs} = A \left[\frac{V - (100 - P_1) v_0}{P_1} \right]$$

$$\Phi_{obs} = A v_1 - A \frac{P_x}{P_1} (v_0 - v_x)$$

$$\frac{\Phi_{obs}}{V} = A \frac{P_x}{P_1} (v_0 - v_x)$$

(2). The Apparent Volume of Silver Fluoride in Aqueous Solution.

The apparent volume is a linear function of the square root of the concentration (see Fig. 3) in the region from 1 to 4 molar. The slope of this line in the linear region is $3.90 \text{ cc} \times (\text{mol/liter})^{-\frac{1}{2}}$.

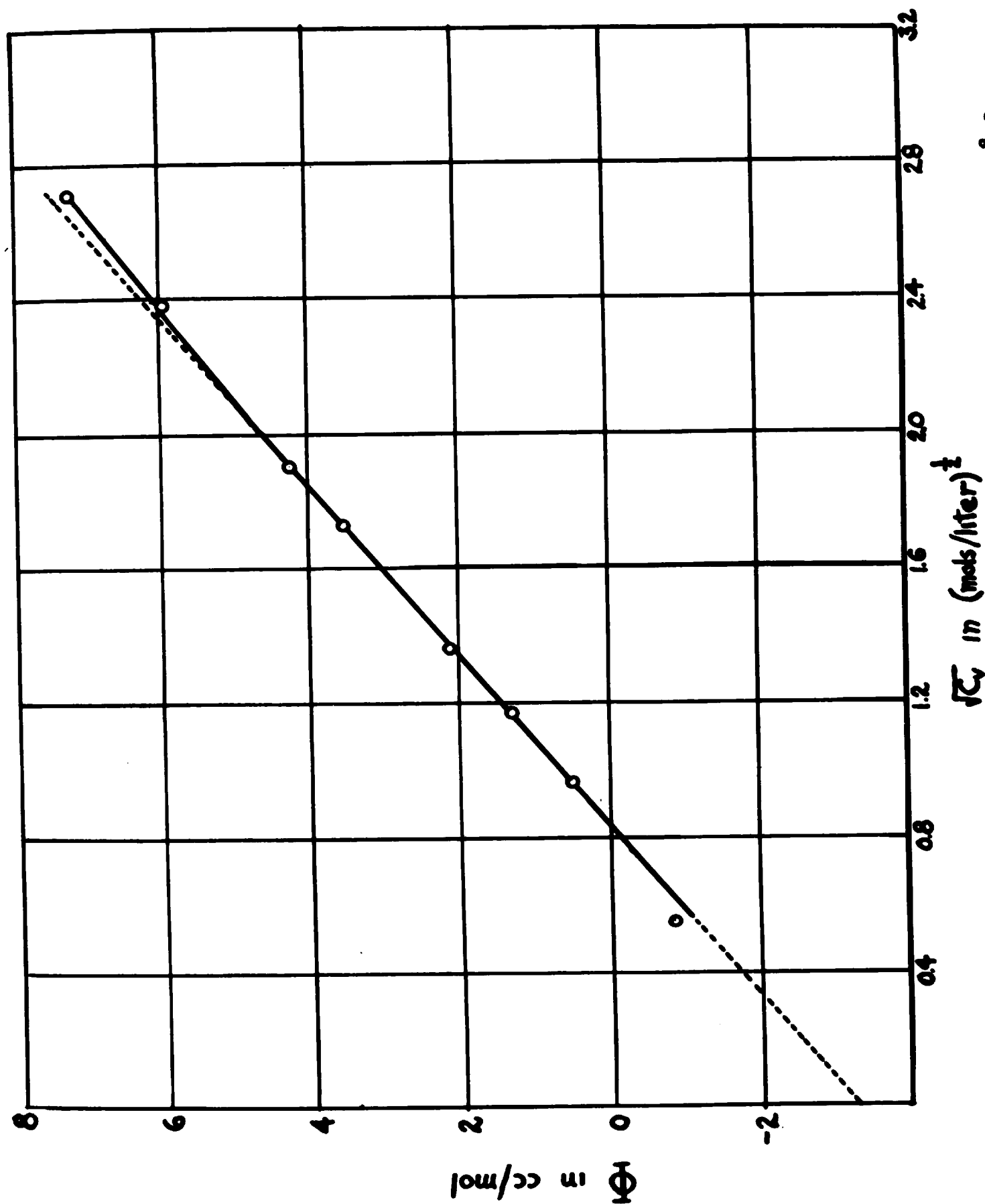


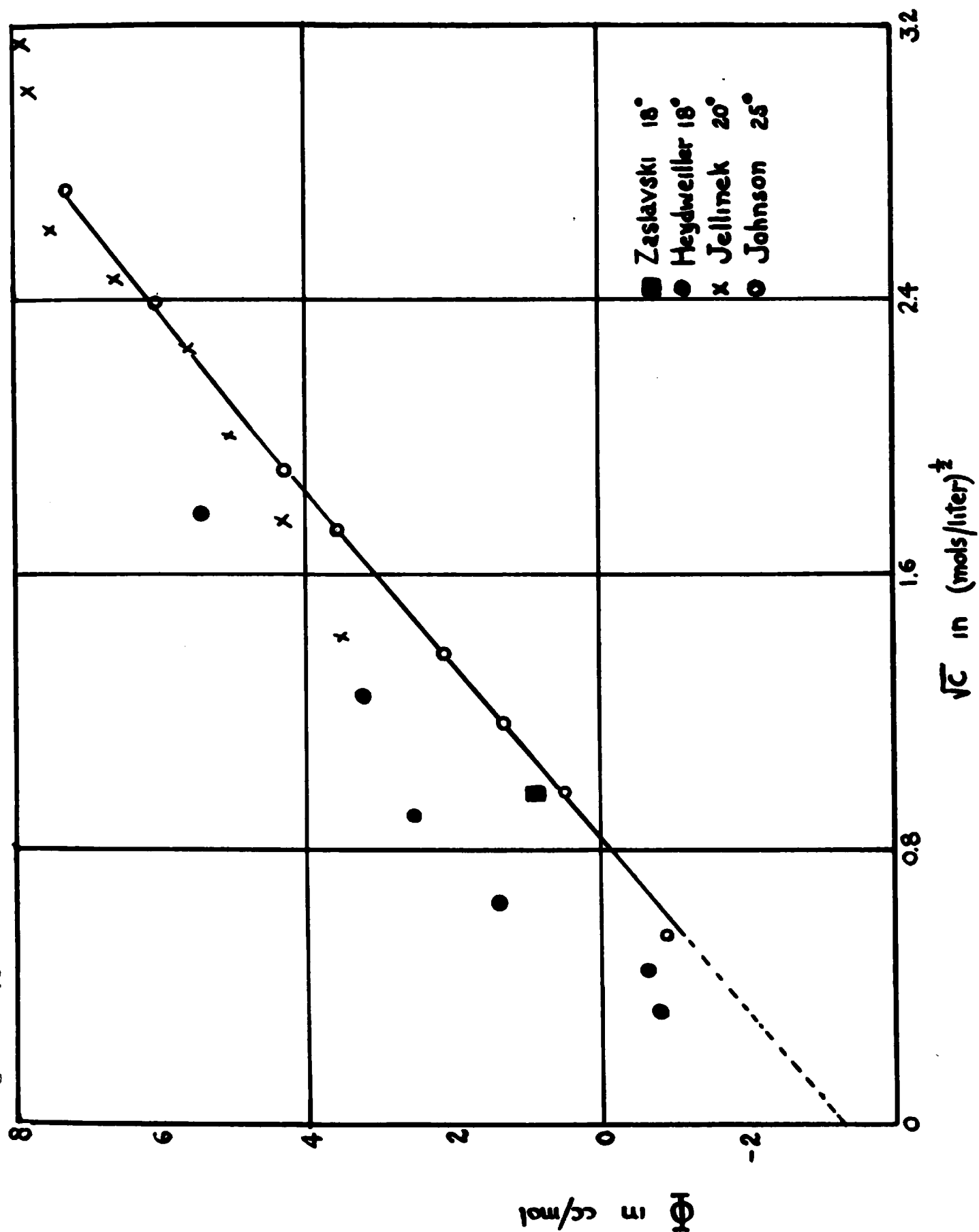
Fig. 3. Apparent molar volume of aqueous silver fluoride solutions at 25°C.

The apparent volume at infinite dilution (Φ_0) obtained by extrapolation of this straight line is -3.30 cc. The complete curve is s-shaped since the slope becomes smaller both above 4 molar and below 1 molar. The linear part can be represented by: $\Phi = -3.30 + 3.90 \sqrt{C_v}$. In general, the values of the apparent volume of salts for infinitely dilute aqueous solution are obtained by such an extrapolation of the linear Φ vs. $\sqrt{C_v}$ curves, using data in the concentration range above 1 molar. The Φ_0 value -3.30 cc was obtained in this way for AgF.

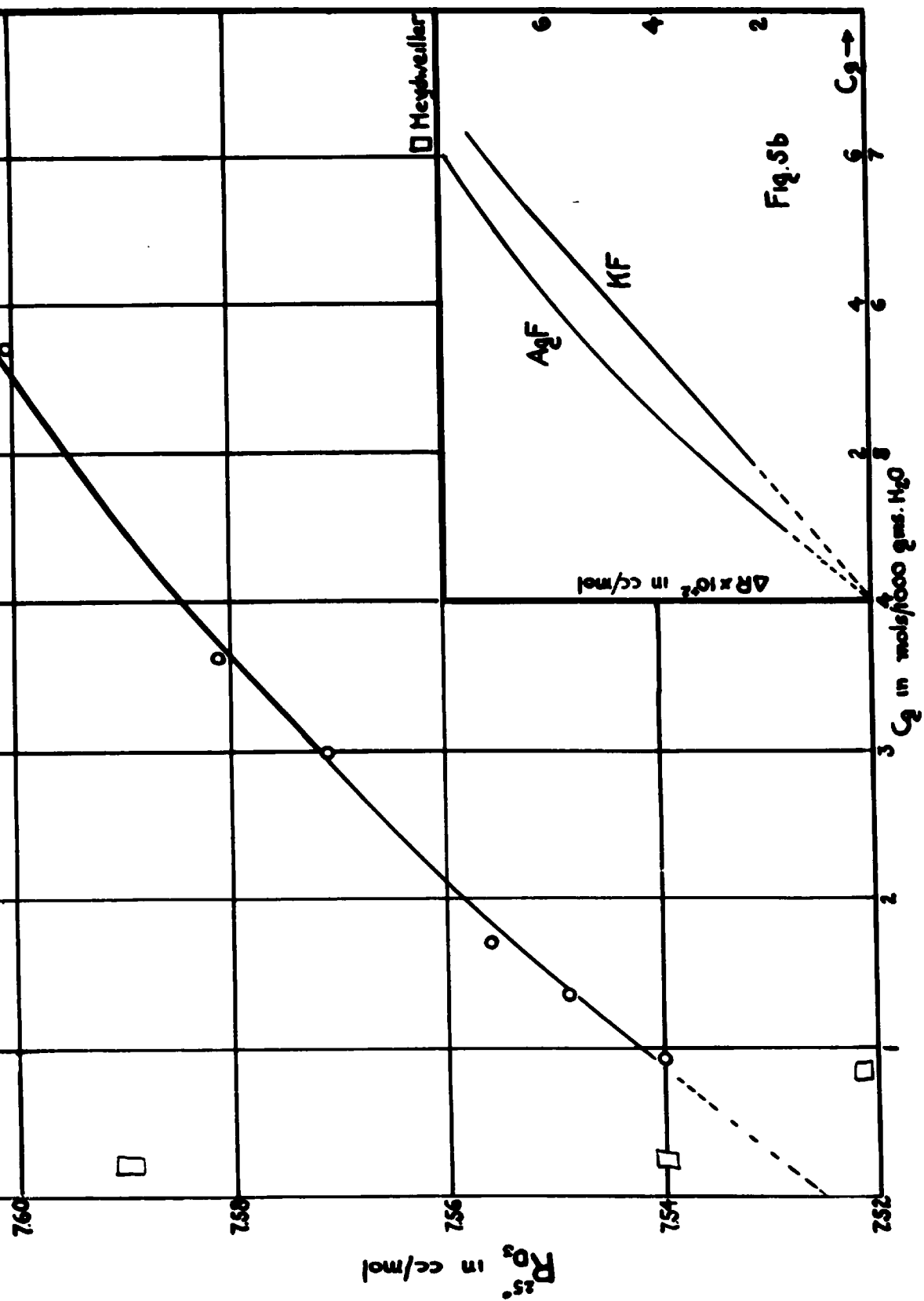
If such an extrapolation were exact, the Φ_0 value should be an additive property. However, even for the series of alkali halides, there are deviations from additivity of ± 0.2 cc, and there are larger deviations for hydroxides, nitrates and sulfates. The Φ_0 value of -3.50, calculated for AgF from $\Phi_{KF} + \Phi_{AgNO_3} - \Phi_{KNO_3}$, differs from the extrapolated value by 0.2 cc. which is beyond any experimental error. Such deviations in additivity are due to changes in slope of the Φ vs. $\sqrt{C_v}$ curve below 1 molar. This has been discussed in detail by Fajans and Johnson (24, 25).

In this investigation of AgF, the points at the two lowest concentrations already show a deviation from linearity, and a very rough extrapolation of these points gives a Φ_0 value of -2.2 cc. This clearly illustrated that without accurate measurements in the region below 1 molar, no "true" Φ_0 value can be given.

Fig. 4. Apparent molar volume of aqueous silver fluoride solutions at 18, 20, 25°.



In Fig. 4 are plotted some other data on the apparent volumes of silver fluoride at different temperatures. The data of Heydweiller at 18° C give about the same slope as that found in this investigation but the absolute value of the apparent volume is about 1 cc larger. That determined by Zaslovskii (26) at 1 N is near the curve, and those determined by Jellinek and Jahn-Held (27) at 20° for high concentrations also fall near the curve.

Fig. 5a. Apparent molar refraction of aqueous silver fluoride solutions at 25°C (D₂)

(3). The Apparent Refraction of Silver Fluoride in Aqueous Solution.

The slope of the apparent refraction vs. concentration curve (see Fig. 5) is $0.017 \text{ cc} \times (\text{mol}/1000 \text{ g H}_2\text{O})^{-1}$ up to 4 molar. Above 4 M the curve becomes less steep. The value obtained for the apparent refraction at infinite dilution by extrapolation of this curve is $7.52_5 \pm 0.01 \text{ cc}$. This value may be checked by comparing the difference between AgF and KF ($7.52_5 - 4.86 = 2.66_5$) with that for AgNO_3 and KNO_3 ($15.95 - 13.25 = 2.70$). In the case of AgNO_3^* , the refraction at infinite dilution was obtained by extrapolating the linear part of the R vs C_g curve (see Bauer, 1) above 1 molar since this corresponds to the concentration range for which the other 3 salts were measured.

The data of Heydweiller (4) are also plotted in Fig. 4 to show the greater accuracy realized in this investigation. His data give no information about the concentration dependence of the refraction, but the average value of the refraction does not differ very greatly from that given above.

* There is a distinct indication for a maximum in the apparent refraction of AgNO_3 at 1 molar and the refraction decreases again toward more dilute solutions. Such changes in apparent refraction in dilute solution have been observed for other salts also (see Geffcken and Kruis, XXIX and Brodskii, 28). The extrapolation of the data in the dilute region gives a R_0 value which is 0.06 cc . smaller than that obtained by the linear extrapolation mentioned above and with it the difference $\text{AgNO}_3 - \text{KNO}_3$ would be 2.64 cc .

TABLE III

Density, Refractive Index, Apparent Molar
Volume, and Refraction of Aqueous Solutions
of Silver Fluoride at 25° C. at various
concentrations

P	C _v	$\sqrt{C_v}$	Cg	D ₄ ²⁵	N _{D3} ²⁵
0	0	0	0	0.99707	1.32264
3.7728	0.30826	0.555	0.30901	1.03635	—
10.5814	0.93026	0.964	0.93266	1.11464	1.34503
14.7739	1.36131	1.166	1.36625	1.16801	1.35041
19.13895	1.85538	1.362	1.86546	1.22854	1.35636
27.7439	2.99243	1.730	3.02622	1.36612	1.36959
31.81296	3.62140	1.903	3.67713	1.44123	1.37660
42.8583	5.71686	2.392	5.91138	1.68821	1.39906
49.4710	7.33097	2.707	7.71644	1.87433	1.41503

π	ϕ	R
(39.45)	(-3.30)	(7.525)
—	-0.864	—
36.190	0.502	7.540
35.426	1.310	7.549
34.627	2.143	7.556
33.280	3.563	7.571
32.647	4.245	7.581
31.001	6.002	7.604
29.830	7.237	7.617

III. APPARENT REFRACTION AND VOLUME OF POTASSIUM

CYANATE IN AQUEOUS SOLUTION

Reagent Potassium cyanate (General Chemical Co.) was used in preparing the solutions. The purity of a weighed amount of the dried salt was checked by the method described by Lewis and Brighton (29). According to these authors, AgOCN can be quantitatively precipitated by an excess of AgNO₃. This procedure was followed and after filtration and washing with 1 N Ca(NO₃)₂, the excess AgNO₃ in the filtrate was titrated with KBr using phensofranine as an adsorption indicator. Preliminary experiments with 0.5 gram samples of KOCN, ^{showed that} the correction for the AgOCN dissolved by the wash solution amounted to 0.4 %. The results of three analyses are as follows: % CNO⁻ calculated 52.02; % CNO⁻ found 51.97, 51.86, 51.80; Mean 51.88 %. This was considered to indicate a purity satisfactory for this purpose.

Each solution for measurement was prepared by adding distilled water to a weighed amount of the dried salt. In this particular case this is a more accurate way of determining the concentration than the usual dilution by weight of a stock solution because of the appreciable hydrolysis of cyanate and continuous loss of NH₃ according to the equation:



Table IV
APPARENT VOLUME AND REFRACTION OF POTASSIUM
CYANATE IN AQUEOUS SOLUTIONS AT 25° C

α_v	D_4^{25}	$n_{D_3}^{25}$	Φ^{25}	$R_{D_3}^{25}$	
1.68 ₀	1.07164	1.34642	36.8	12.1 ₇	
3.91 ₆	1.16531*	1.36241*	38.2 ₅	12.0 ₉	Mean = 12.13

* Values have been corrected for hydrolysis (see text)

For this same reason, the measurements had to be completed quickly, and were finished about 6 hours after making up the solutions. To establish the rate of change of n and D , the measurements were repeated after about 4 hours. No change was observed for the refractive index of the 1.68 molar solution, but for the 3.92 molar solution, the first measurements gave the values $n = 1.36330$ (5 hr. after preparing the solution) and $D = 1.16730$ (6 hr.); the second measurements gave $n = 1.36442$ (11 hr.) and $D = 1.16865$ (10 hr.). The values given in Table IV for n and D of the 3.8 molar solution are obtained by extrapolation to zero time from this observed rate of change. The observed increase in n and D with time are large, but the corresponding decrease in apparent molar refraction over a 6 hour period amounted to 0.04 cc according to the data given above.

In ordinary cases of hydrolyses where K_h is known, a

a correction can be applied as was done by Kohner (IX) for AlCl_3 ; the correction was only 0.002 cc in this case.

The mean of the apparent refraction for these two measurements is 12.13 cc. The total errors due both to impurities and errors in n and D will be less than 0.1 cc. Upon subtracting the value $R = 2.26$ for the potassium ion (XLIII), the value $R = 9.87 \pm 0.1$ cc is obtained for the cyanate ion.

The values obtained for the apparent volume have the same magnitude and show the same gradation as reported by J. Traube (30) of 35.4 at 1.1 molar and 38.2 at 4.1 molar at 18°C . The molar volume of the solid potassium cyanate is 39.4 cc/mol.

IV. Solutions of Lithium Perchlorate in Ether.

(a). Preparation of LiClO_4 .

There was available a pure sample of lithium perchlorate prepared by Wm. Spurgeon (31). This was used in the first series of measurements on LiClO_4 in ether. The following method was used to prepare LiClO_4 for the second series of measurements in ether as well as for the acetone solutions. Lithium carbonate (Baker's C.P.) was washed with hot distilled water about ten times, and perchloric acid (Baker's Vacuum distilled) was added until the solution was neutral to methyl red. The solution was filtered, concentrated on the hot plate, cooled, and the white needle shaped crystals were

filtered. This product was recrystallized twice from re-distilled water and dried at 130° C. The salt, a trihydrate, fuses upon heating and must be stirred during the final stages of drying to facilitate grinding. It is redried after grinding it to a powdered form.

(b). Purification of Ethyl Ether.

Anhydrous Ethyl Ether (Mallinckrodt Chemical Works, Anal. Reagent) was refluxed over sodium ribbon for at least four hours and then distilled in an all-glass distilling apparatus; first and last portions of ether were rejected. The constants of the ether prepared in this way are: $d_4^{25} = 0.70776$ and $n_{25}^D = 1.34944$. The density of ether from different distillations varied only 1 unit in the fifth decimal which is within the errors of the determination. Because of the great expansibility of ether, the temperature control must be very good. The variations in the index of refraction ^{were} up to 3 units in the fifth decimal; this is due to the fact that the index decreases by 0.043 per 0.01° increase in temperature. This temperature coefficient of n is about 20 times as great as that for water.

TABLE V

Wave lengths and Frequencies of the lines of the Helium
Spectrum and the Refractive Index of the Refractometer
Prism at various wave lengths

Spectral Line	Abbr.	λ in Å	ν^2 in $\text{sec}^{-2} \times 10^{28}$	$(N^{25})^2_{\text{prism}}$
weak red	w.r	7065.1	18.0055	2.602343
red	r	6678.15	20.1530	2.609006
yellow (D_3)	y (D_3)	5875.6	26.0342	2.627556
green	gr	5015.68	35.7267	2.658984
blue-green	bl. gr.	4921.93	37.1006	2.663679
blue	bl.	4713.14 ₃	40.4604	2.675223
violet	v	4471.48	44.9520	2.691118

The value 0.70776 obtained for the density of ethyl ether agrees very well with that of $D_4^{25} = 0.70778$ reported by Timmermans (See Annual Tables (32)). Taylor (33) give the density as 0.70768. There have been no value of the refractive index at 25° C, previously reported.

The molar refraction and volume calculated from the observed density and refractive index are given in Table VI. For the molar dispersion, $1/R$ values are plotted against $\sqrt{\nu^2}$ in Fig. 6 and the $\underline{D}$ value is also included in Table VI.

Table VI

Constants of the Solvents Water, Ethyl Ether
and Acetone at 25° C

	<u>Ether</u>	<u>Acetone</u>	<u>Water</u>
d_4^{25}	0.70776	0.78482	0.99707
$N_{D_3}^{25}$	1.34944	1.35603	1.33264
Molar Volume	104.730	74.003	18.070
$R_{D_3}^{25}$	22.502	16.170	3.74
$\underline{D}$	0.507	0.384	0.0824

(c). Preparation of Solutions.

The flasks used for storing the stock solution as well as the flasks for making the dilutions were suitable for ether solutions and only small modifications in technique were necessary. The chief difficulty involved in working with ether solutions is the change in concentration due to evaporation

of the solvent. The greatest loss of weight during weighing a 100 cc flask with a ground glass stopper was about 0.1 mg. per min. A correction could be applied to find the weight of stock solution originally added as well as to find the weight after the dilution with pure ether. When not being used for a measurement, the solutions in all flasks were sealed by applying Kahlbaum paraffin to the joints (ordinary paraffin was softened by the ether vapor). One source of error which cannot be corrected for is the change of concentration of the stock solution. However the vapor pressure of concentrated solutions of LiClO_4 is quite low and in the transfer of liquids, pure dry air was passed over an auxiliary ether solution to minimize the effect of ~~evaporation~~ of ether. ^{The} analyses of the stock solution made at the beginning of the measurements and after the dilutions were made are identical within the experimental errors of the determination. The method of using an auxiliary flask containing the solvent vapor was used in transferring the solution to pycnometers and refractometer as well.

(d). Analysis of Solutions.

A portion of the solution was weighed in a small glass stoppered bottle and the solution evaporated in the same bottle over a water bath. After the ether had completely evaporated, the solid LiClO_4 was heated for several hours at 130°C . In one trial there was a slight dark residue. A small amount of HClO_4 was added to it and upon evaporation a white solid was

formed which gave no test for chloride. The concentrations results were as follows:

Series 1 30.749 %; 30.762 % Mean 30.755₆ %

Series 2 52.93₆ %; 53.09₆ % Mean 53.016 %

(e). Refractive Index Measurements

The vessel which rests on the refractometer prism and contains the liquid being measured has a cover with a ground glass fitting. This proved to be the cause of considerable change of refraction due to evaporation of the solution while in the refractometer vessel. Accordingly after the liquid was introduced, apiezone wax was pressed around the top of the ground joint, and with this precaution the evaporation was negligible during the time required for a measurement. The slight changes still present made the results for dispersions of dilute solutions of LiClO_4 in ether less accurate than usual.

(f). Discussion of Experimental Results for LiClO_4 in ether.

(1). Analysis of the accuracy of the measurements.

The experimental points on the Refraction vs. molality curve as shown in Fig. 8 deviate from the smooth curve up to 0.02 cc. This is a large deviation compared to the accuracy attainable in water solutions. However with ether solutions the error in the density determination is ± 0.042 as compared with an error of only ± 0.055 with aqueous solutions, and the error in the determination of refractive index is also 0.042 as compared with 0.041 in water solutions.

Using the general formula (6) for estimating the resulting uncertainty in apparent refraction, and substituting the value $n_o = 1.35$, $\rho_o = 0.215$ and $D_o = 0.708$ for ether, the following formula is obtained for ether solutions:

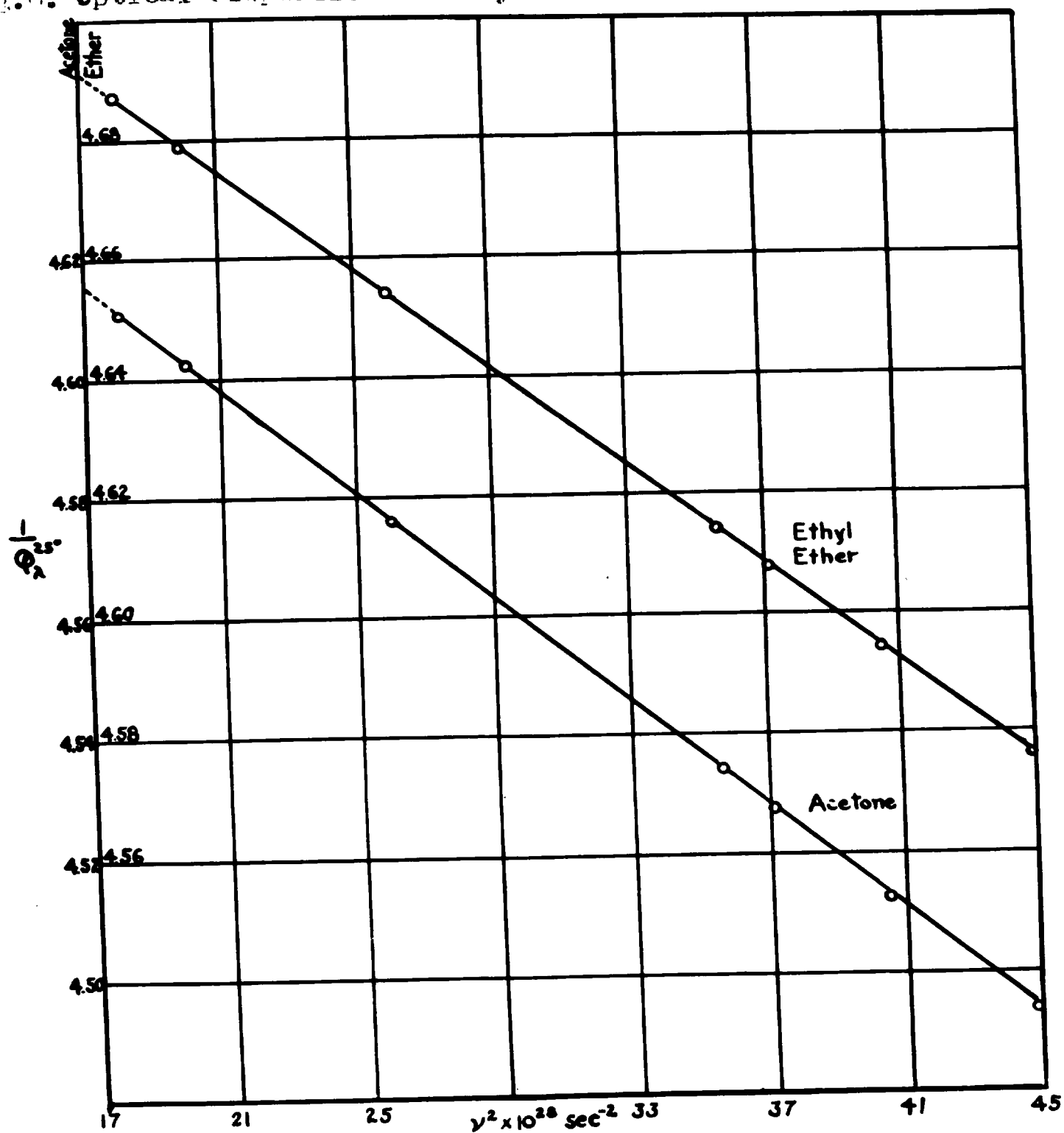
$$\nabla R = \frac{100}{C_v} (5.6 \nabla (\Delta n) + 3.0 \nabla (\Delta d)) \quad (8)$$

For the estimated uncertainties in density and refractive index measurements, this leads to the result that $\nabla R = 0.017/C_v$. This is in addition to any concentration error due to evaporation. Thus the deviation of 0.02 cc. in the refraction curve is within the expected errors. There is an error in the absolute value of the refraction which arises from any impurities in the salt used and any error in the analysis of the stock solution. However, few substances can dissolve in ether as impurities, ^{and} the fact that the two series of measurements fall on a smooth curve makes it unlikely that the absolute value is off by more than 0.02 cc. An error of 0.05 % in the analysis will lead to an error of 0.015 cc in R.

(2). The refraction versus Concentration curve for LiClO_4 in ether.

The apparent refraction of LiClO_4 in ether shows the largest change with increasing concentration of all the substances measured up to now. The initial slope is 0.21 cc/mol (1000g)⁻¹ but the curve gradually becomes less steep above 3 molal and the final slope at 10 molal is 0.04. The next highest positive refraction slope is that for iodic acid which is 0.11. The largest negative slope was found for HI and is -0.06. The slope of the same curve for LiClO_4 in water is 0.008 (XI).

Fig. 6. Optical dispersion of ethyl ether and acetone at 25° C.



The R vs. C_g curve in the lowest concentration region can be extrapolated to obtain the value of the apparent molar refraction at infinite dilution (See Fig. 8). Including all the errors discussed above as well as the uncertainty in extrapolation the value of the refraction of LiClO_4 in an infinitely dilute ether solution is 11.40 ± 0.05 cc. The great difference between this value and that for the sum of the ions in aqueous solution (12.90 cc) will be discussed in the theoretical section.

(3). Apparent Molar Volume of LiClO_4 in ether as a function of Concentration.

Fig. 7 shows that when the apparent volume is plotted against either the weight concentration (C_g) or the volume concentration (C_v), a nearly linear curve is obtained (See discussion in C, IV, b). However, the extrapolation of the two curves to infinite dilution by drawing a straight line thru the last points gives $\bar{V}$ values differing by 0.2 cc; accordingly the average value of 14.2_0 cc. is taken as the apparent volume at infinite dilution. The slope of the $\bar{V}$ vs. C_v curve is $2.75 \text{ cc} \times (\text{mol/liter})^{-1}$ up to 4 molar; that of the $\bar{V}$ vs. C_g curve is initially 1.98 and changes to $1.73 \text{ cc} \times (\text{mol/1000 gram ether})^{-1}$ in the range of 4 to 10 molal. The apparent volume calculated for a saturated solution from the data of Willard and Smith (6) is also plotted.

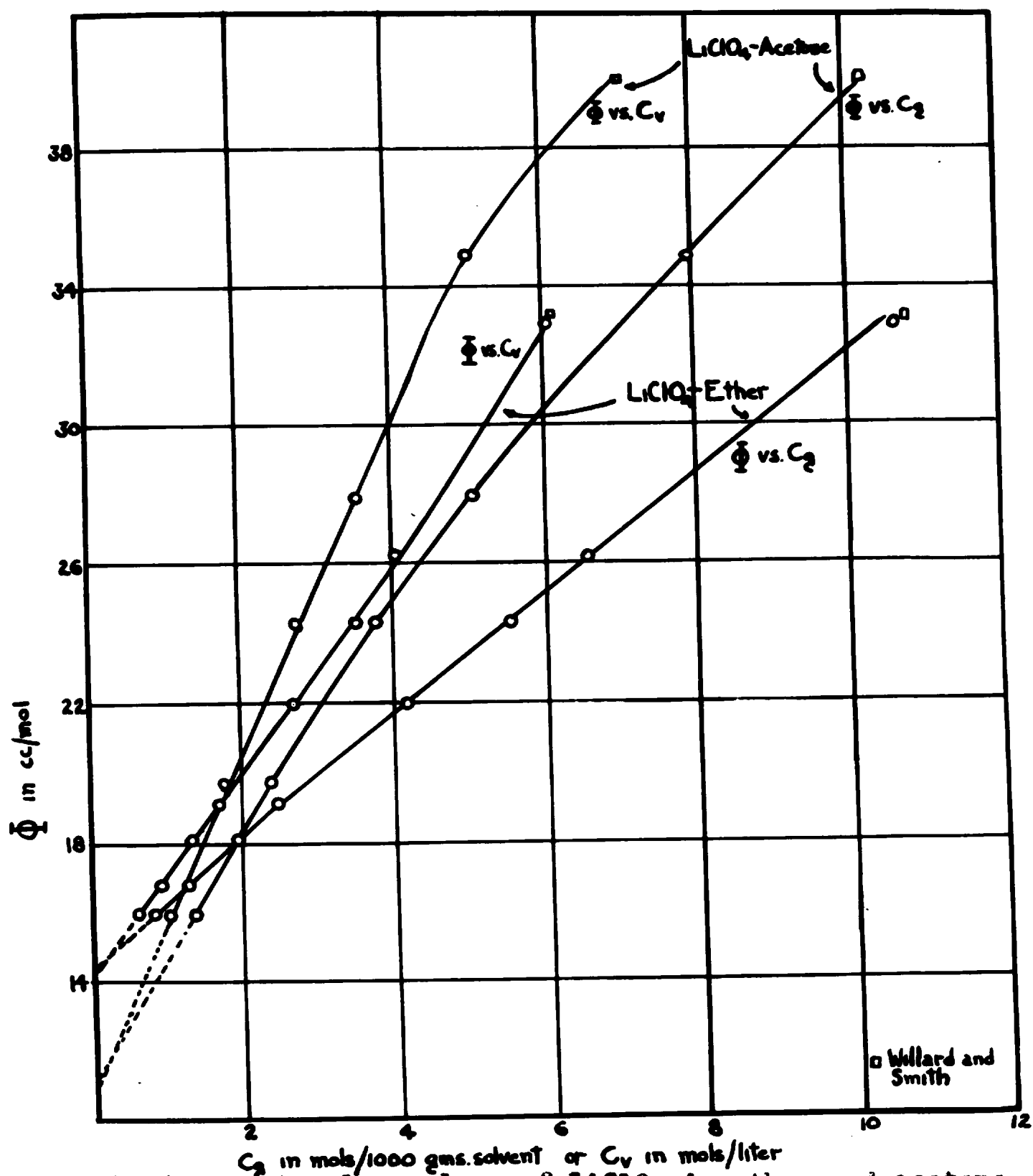


Fig. 7. Apparent molar volume of LiClO_4 in ether and acetone solutions at 25°C .

TABLE VII

Density, Refractive Index (D_3), Apparent
Molar Volume and Refraction of LiClO_4 in
Ether Solutions at 25.00°C .
for various concentrations

Series 1 P	C_v	C_g	d_4^{25}	$n_{D_3}^{25}$	π
0	0	0	0.70776	1.34944	(38.70)
8.5012	0.612	0.8732	0.76595	1.35846	37.92
12.0581	0.8983	1.2887	0.79265	1.36255	37.50
17.0906	1.3381	1.9374	0.83301	1.36872	36.95
20.8629	1.6970	2.4778	0.86661	1.37352	36.35
30.7556	2.7750	4.1746	0.95999	1.38691	34.42
Series 2					
36.9406	3.5608	5.5059	1.02559	1.39507	32.56
41.0232	4.1383	6.5376	1.07330	1.40100	31.59
53.0160	6.0196	10.6054	1.20807	1.40940	25.19

Series 1 Φ	$R_{D_3}^{25}$
(14.20)	(11.40)
15.95	11.576
16.81	11.669
18.07	11.821
19.05	11.901
21.90	12.100

Series 2	
24.22	12.202
26.20	12.273
32.90	12.481

TABLE VIII

Indices of Refraction and Reciprocals of the
Molar Refraction for ether solutions of
 LiClO_4 for various wave lengths of the Helium
Spectrum at 25°C

Spectral Line	$\frac{1.697 \text{ M}}{(N_D^{25})^2} \frac{1000}{R}$		$\frac{4.138 \text{ M}}{(N_D^{25})^2} \frac{1000}{R}$		$\frac{5.10 \text{ M}}{(N_D^{25})^2} \frac{1000}{R}$	
w.r	----	--	1.950843	82.028	1.969685	81.327
r	1.880375	84.947	1.952960	81.954	1.971711	81.268
y(D_3)	1.886196	84.774	1.958837	81.726	1.977723	81.031
gr	1.895688	84.381	1.968642	81.393	1.987961	80.574
bl.gr	1.897130	84.225	1.970020	81.340	1.989399	80.502
bl	1.900607	84.069	1.973594	81.208	1.999312	80.341
v	1.905170	83.801	1.978331	81.004	1.997365	80.135
R_D	11.90		12.23 _b		12.34 _i	
R_e	11.76		12.097		11.181	
$\underline{D}$	0.14		0.13 _g		0.160	

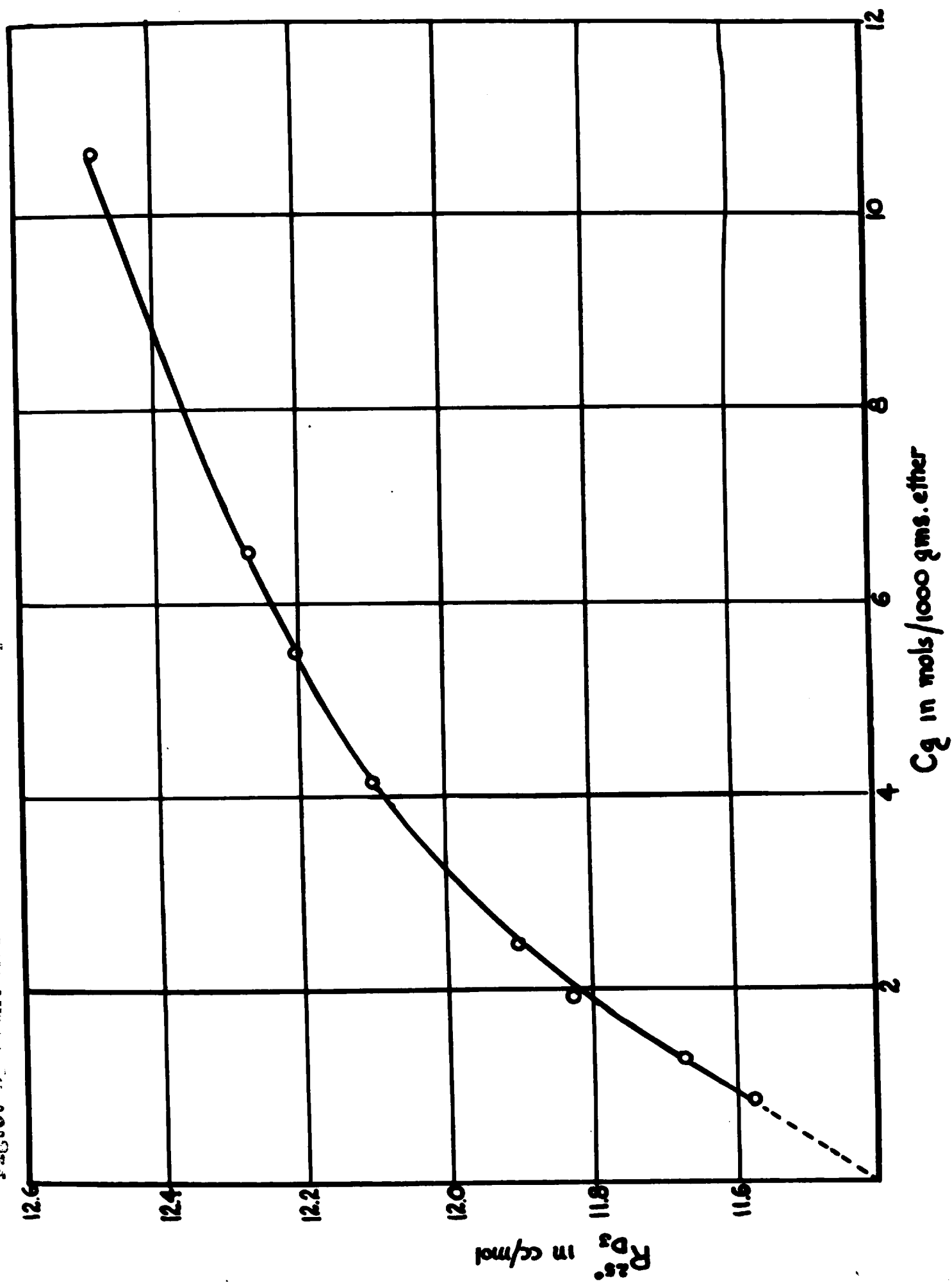
(4). The apparent molar dispersion of LiClO_4 in ether.

The reciprocal plotting method of Wulff (XXV) is used to obtain the molar dispersion which is taken as the difference between the refraction measured at the wave length of sodium light and that for infinite wave length. This method is based on dispersion theory and involves the plotting of reciprocal refraction against the square of the frequency. Unless there is an absorption band near the visible region, a straight line results and the extrapolation to zero frequency gives the value of $1/R$ for infinite wave length.

Because of the extreme sensitivity of the index of refraction of ether solutions to small temperature changes as well as a slight amount of evaporation, the dispersion values obtained for lithium perchlorate in ether are not as accurate as desired. However measurements were made on several solutions, those at high concentrations giving the more reliable results, and in this way an average dispersion value is obtained which can be compared to the dispersion determined for aqueous solution and for crystals.

The data for the molar dispersion is given in Table VIII and the $1/R$ values are plotted against ν^2 in Fig. 9. The value $\underline{D} = R_D - R_{\infty} = 0.14$ is taken as the most probable value at infinite dilution; the dispersion increases to 0.16 at 5.1 molar.

FIG. 3. Apparent molar refraction of LiClO_4 in eth. at 25°C . (no-ry line)



V. LITHIUM PERCHLORATE IN ACETONE

(a). Purification of Acetone

The starting product was reagent Acetone (General Chemical Co.). The drying of acetone is rather difficult because of its reaction with drying agents. J. Timmermanns (34) used phosphorus pentoxide as the final drying agent in his careful work. He reports the density value, $D_4^{25} = 0.78492$.

Since the treatment with P_2O_5 leads to some polymerization, an elaborate fractionating system was used by Timmermanns. Accordingly other less efficient drying agents were tried. Using anhydrous K_2CO_3 , the lowest density obtained, 0.78554, was 0.036 higher, the corresponding refractive index, $n_D^{25} = 1.35622$. Hartley and Hughes (35) have shown that the presence of small amounts of moisture increases the density and the measurements of M.L. Gressmann-Koenig (9) show that moisture also increases the refractive index in spite of the fact that pure water has a smaller index (1.33). Anhydrous copper sulfate was tried next as a drying agent and the values $D = 0.78482$ and $n = 1.35603$ which were obtained were unchanged after a second treatment with the drying agent and a subsequent distillation. Accordingly, this method of drying was used for the acetone in this investigation.

It is believed that the acetone prepared in this way is sufficiently pure, first of all because of the difference of only 0.031 from Timmermanns density value, and secondly because the conductivity was found by Miss Chu (7) to be very low in concentrated solutions of $LiClO_4$ (see Sect. C, IV, a).

TABLE IX

Optical Dispersion of Ethyl Ether and Acetone at 25° C

Spectral Line	Ethyl Ether ^{<i>ye</i>}			Acetone	
	Trial 1	2	3	1	2
w. r.	4.68724	4.68864	4.68760	4.61038	4.614802
r	4.67871	4.67913	4.67876	4.60209	4.60214
y (D ₃)	4.65434	4.65438	4.65413	4.57657	4.57657
gr	4.61444	4.61456	4.61444	4.53504	4.53492
bl. gr.	4.60909	4.60947	4.60900	4.52848	4.52906
bl	4.59478	4.59551	4.59478	4.51313	4.51393
v	4.57552	4.57665	4.57665	4.49312	4.49413

Since only the difference in densities and refractive indices between solution and solvent enters in the calculation of apparent refraction and volume (See Table I), any error due to impurities will be minimized because the same acetone is used in the solutions as that used to determine the physical constants given above.

Using the values $D_4^{25} = 0.78482$ and $n_{D_3}^{25} = 1.35603$, one obtains 74.003 cc as the molar volume of acetone at 25° C. and 16.17₀ for the molar refraction for the helium-D₃ line.

Two measurements were made of the molar dispersion of acetone. The $1/\nu$ values are plotted against ν^2 in Fig. 6. The numerical values are tabulated in Table IX. The mean of these two measurements give $\underline{D} = R_D - R_\infty = 0.384$ cc.

(b). Experimental details and accuracy of the measurements.

The same precautions were used in the handling of acetone solutions as already described for ether solutions. Since the vapor pressure is much lower for acetone solutions, there was less error due to evaporation of the solvent and a greater accuracy was attained. In making the dilutions of the stock solutions of LiClO_4 in acetone, there was observed a large heat of dilution. Because of this, the weighings could not be made until the solution had cooled to room temperature.

The formula developed for estimating the errors in apparent refraction has the following constants for acetone

solutions (cf. Sect. II, d; IV, f).

$$\nabla R = \frac{100}{c_v} (5.5(\Delta n) + 2.6 \nabla(\Delta d)) = 0.008/c_v$$

The errors in both density and index of refraction for these solutions are ± 0.041 . The resulting error in refraction is $0.008/c_v$. That the deviations from a smooth curve is less than 0.005 cc. for points above 2 molar shows that the expected accuracy has been realized.

Concentration determinations by evaporation of the solvents gave the following results for the stock solution:

45.749 %; 45.755 % Mean = 45.752 %

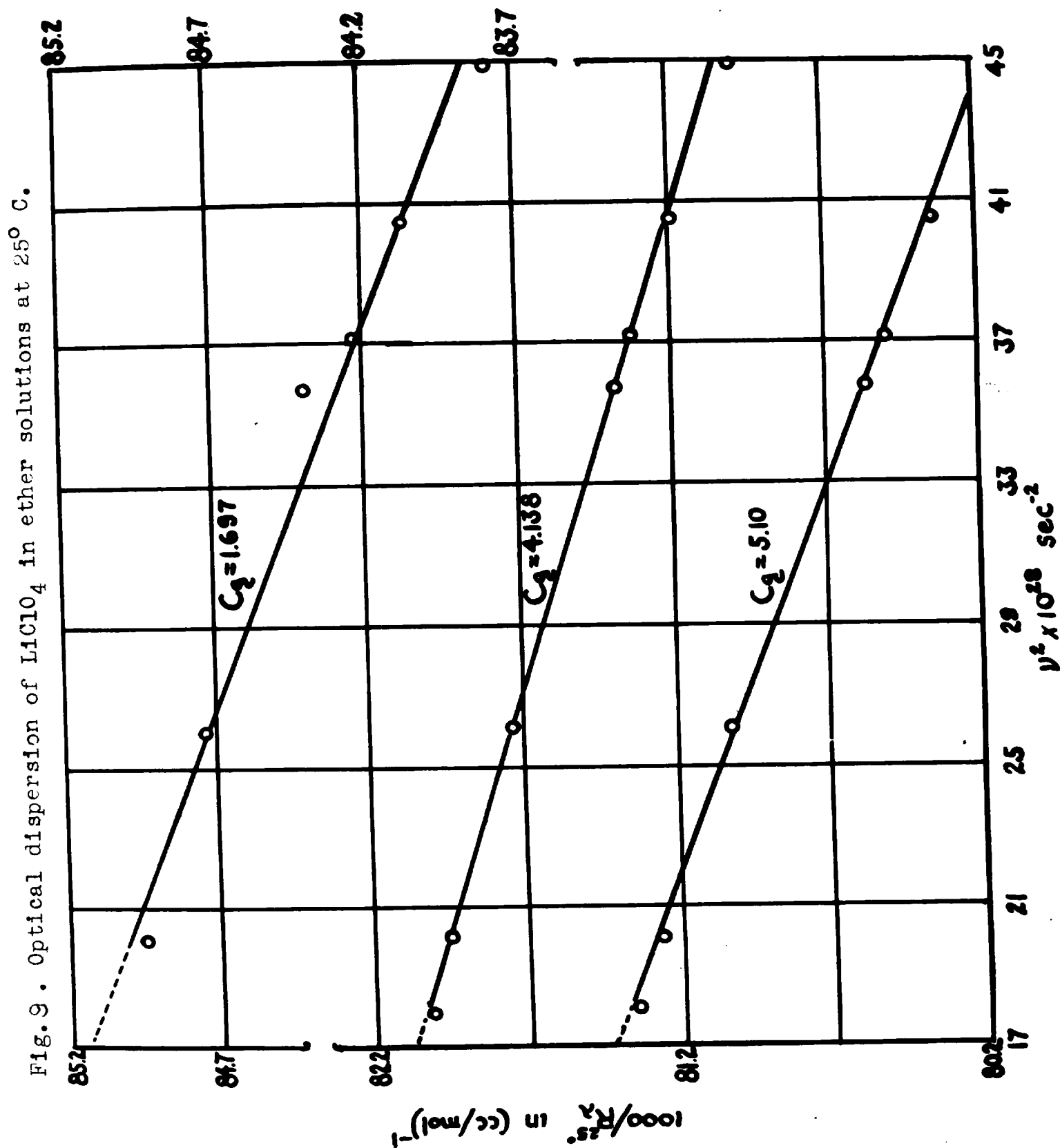
(c). The dependence of Apparent molar Volume on Concentration for acetone solutions.

Just as for LiClO_4 in ether, the apparent volume in acetone is plotted against both C_v and C_g . The former plot is linear between 1 and 5 molar and has a slope of 4.65 cc x (mol/liter) $^{-1}$. The Φ vs. C_g curve has an initial slope of 3.63 but is curved in the range between 2 and 10 molal. An average Φ_0 value of 11.00 cc. is obtained from the extrapolations of the two curves. The Φ value calculated from Willard and Smith's (6) data for a saturated solution falls on a smooth curve extending beyond the points obtained in this investigation.

(d). The Apparent Refraction versus Concentration curve.

The apparent refraction curve (Fig. 10) exhibits a minimum at about 3.8 molar. The absolute value of the apparent refraction is between that in ether and in water but the extrapolation of the curve to infinite dilution gives a value only slightly lower than that in water. The extrapolation of the

curve is rather uncertain but the best value at infinite dilution appears to be 12.88 ± 0.01 cc/mol.



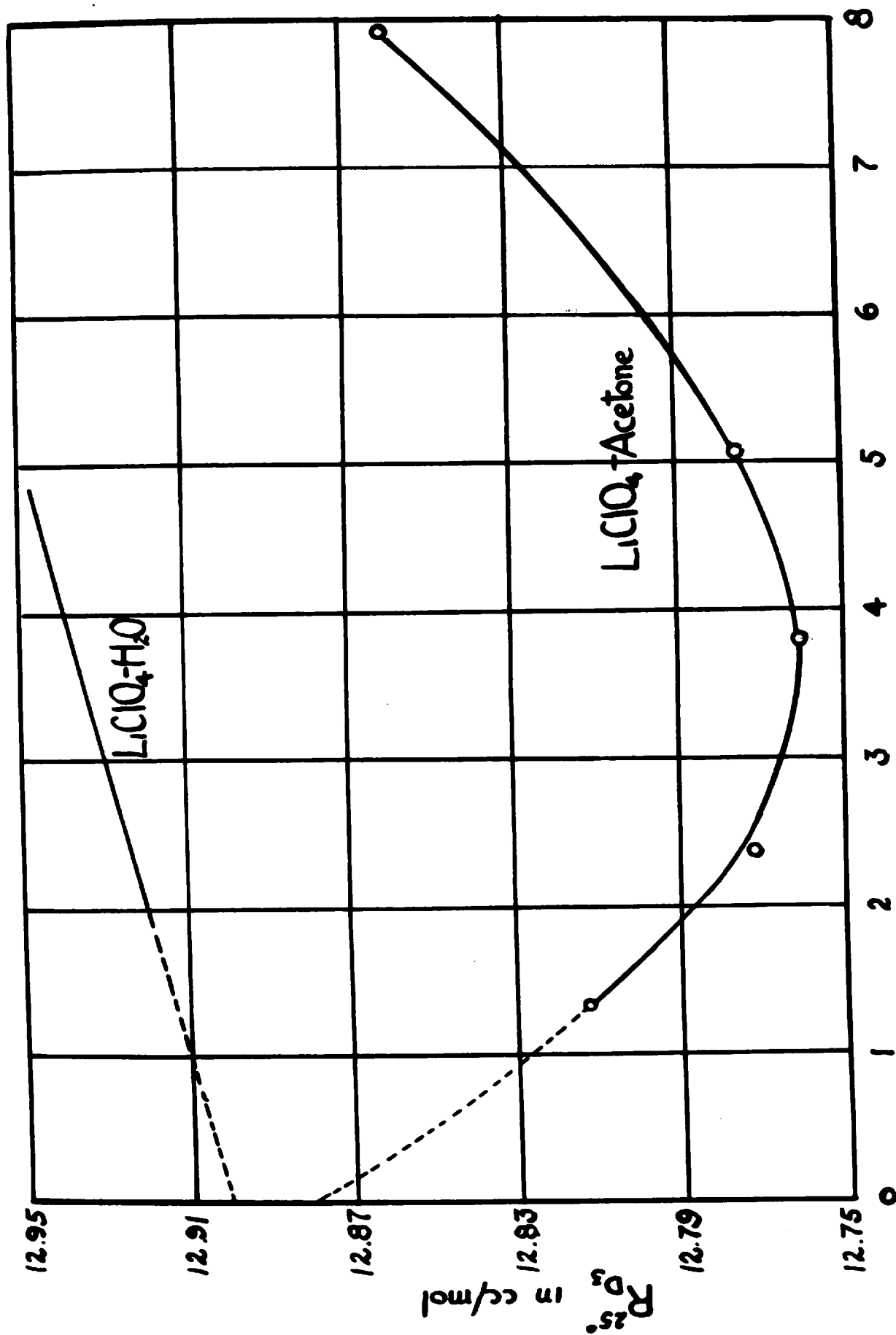


Fig.10. Apparent molar refraction of LiClO_4 in acetone and water solutions at 25°C .
 C_g in mols/1000 gms. solvent

(e). The Apparent Molar Dispersion of LiClO_4 in Acetone.

The linear relationship between $1/R$ and V^2 (see Sect. D (5)) seems to be fulfilled for LiClO_4 in acetone (See Fig. 11). However, there is a distinct tendency for a positive deviation from linearity in the region of lower frequency i.e. toward the infra-red. This was observed for liquid water in the infra-red region (1). In the present case the accuracy of the dispersion measurements is not as great but the deviation of the last two points is well beyond the experimental error. Therefore the extrapolation to infinite wave length (zero frequency) was made by neglecting the points which deviate from a straight line.

The dispersion values D at various concentrations obtained from the extrapolation to $\lambda = \infty$ of the $1/R$ vs. V^2 curves (Fig. 11) are tabulated in Table X. The gradation of values shows that there is a minimum in the apparent dispersion at about 3 molal just as was observed for the refraction. The extrapolation of the curve through the points at 1.37 and 2.38 molal give the value 0.19 ± 0.05 cc for the apparent molar dispersion at infinite dilution. The value observed in aqueous solution is 0.19_0 cc.

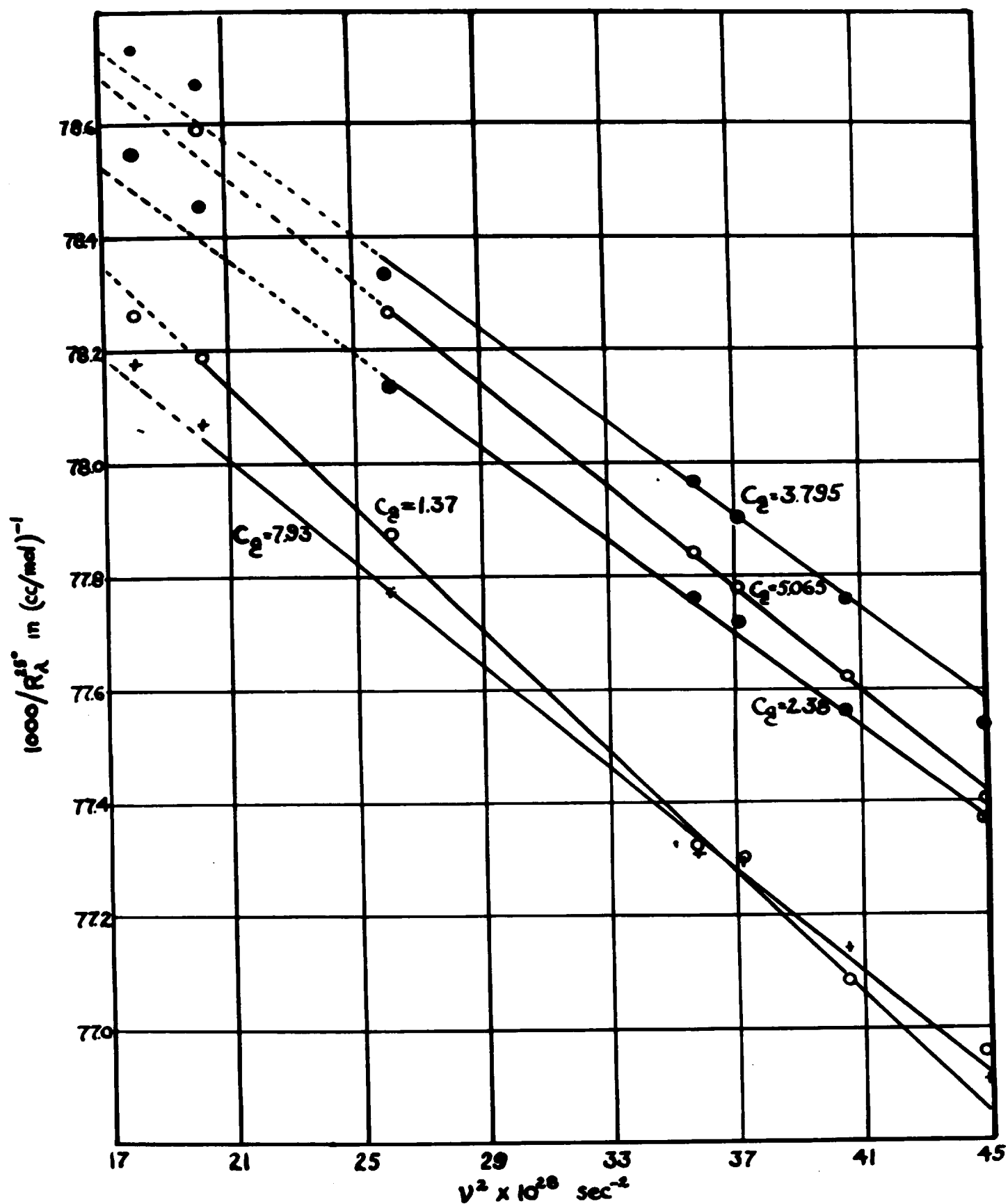


Fig. 11. Optical dispersion of solutions of LiClO_4 in acetone at 25°C .

TABLE X

Density, Refractive Index, Apparent Molar Volume and Refraction for acetone solutions of LiClO_4 at 25°C for various concentrations

P	C_v	C_g	D_4^{25}	n_D^{25}
<u>-0-</u>	<u>0</u>	<u>0</u>	0.78482	1.35603
12.7317	1.0585	1.3712	0.88420	1.37413
20.2106	1.8028	2.3807	0.948172	1.38402
28.7629	2.7787	3.7949	1.02753	1.39415
35.0163	3.5790	5.0645	1.08713	1.40002
45.7522	5.1160	7.9268	1.18933	1.40563
	π	Φ^{25}	R_D^{25}	
	(46.75)	(11.00)	(12.88)	
	42.69	15.93	12.812	
	38.705	19.72	12.772	
	34.115	24.26	12.760	
	30.515	27.93	12.775	
	24.03	34.81	12.860	

TABLE XI

Indices of Refraction and Reciprocals of the Molar
Refraction of acetone solutions of LiClO_4 for various
wave lengths of the Helium Spectrum at 25°C .

		<u>Cg</u>				
		<u>1.37</u>	<u>2.38</u>	<u>3.795</u>	<u>5.065</u>	<u>7.93</u>
Spectral Line	$(N^{25})^2$	1.880061	1.906919	1.934767	1.951101	1.967022
w.r	$\frac{1000}{R}$	78.260	78.740	77.852	78.734	78.180
r	$(N^{25})^2$	1.882050	1.909121	1.937057	1.953361	1.969270
	$\frac{1000}{R}$	78.192	78.555	78.672	78.599	78.070
y(D_3)	$(N^{25})^2$	1.888498	1.915546	1.943675	1.960059	1.975826
	$\frac{1000}{R}$	77.876	78.131	78.339	78.266	77.773
gr	$(N^{25})^2$	1.898761	1.926166	1.954281	1.970796	1.986557
	$\frac{1000}{R}$	77.322	77.767	77.961	77.845	77.316
bl gr	$(N^{25})^2$	1.900362	1.927806	1.955974	1.972489	1.987629
	$\frac{1000}{R}$	77.304	77.724	77.900	77.785	77.399
gr	$(N^{25})^2$	1.904315	1.931797	1.959961	1.976077	1.992095
	$\frac{1000}{R}$	77.089	77.561	77.767	77.622	77.143
v	$(N^{25})^2$	1.909359	1.937006	1.965323	1.981394	1.997436
	$\frac{1000}{R}$	76.965	77.369	77.537	77.405	76.923
R_{D_3}		12.812	12.772	12.760	12.775	12.860
R_{∞}		12.623	12.589	12.595	12.596	12.671
<u>D</u>		0.189	0.183	0.167	0.179	0.189

VI. APPARENT REFRACTION AND VOLUME OF LITHIUM BROMIDE
AND LITHIUM IODIDE IN ETHER

(a). Preparation of Lithium Bromide and Lithium Iodide.

Lithium Bromide was prepared by Miss Chu by recrystallizing lithium bromide (Eimer and Amend, N.F.) three times from water. It was necessary to grind small portions (after a preliminary drying) because of the extreme deliquescence of anhydrous LiBr . Just as in the case of lithium perchlorate the hydrate melts and unless stirred in the final stages of drying, it becomes a hard cake which is very difficult to break up. After grinding, the powdered solid was dried at 280° . An analysis of this preparation by Miss Chu gave the following results:
% Br^- calculated, 92.02 %; % Br^- found, 92.06, 91.94;
Mean 92.00 %. Qualitative tests had shown no ~~LiBr~~ I^- to be present.

After several attempts by Miss Chu to prepare anhydrous lithium iodide by evacuating the hydrate with and without heating, the direct reaction between lithium and iodine in ether as described by Ziegler (36) was used as a means of preparation. Metallic Lithium was cut into thin slices, washed with pure dry ether and placed in a solubility tube which had a reflux condenser and drying tube attached. Slightly less than the equivalent amount of reagent iodine (Resublimed, General Chemical Co.) was added, and finally pure ether was added thru a sidearm in the 250 cc solubility tube. The whole tube was

cooled in ice because the reaction is very vigorous under ordinary conditions. The tube was heated to 60°C when the initial reaction had subsided, and the reaction was complete after about 7 hours.

One solution was prepared in the manner described above. For the others, lithium iodide was prepared in a similar way, but by using an excess of lithium and iodine to produce an amount of lithium iodide much greater than that soluble in ether. This solid was used in preparing the saturated solutions.

(b). Analysis.

Both the evaporation method and an analysis by titration with standard silver nitrate were used to determine the concentrations of lithium bromide and lithium iodide solutions in ether. The uncertainty in the analysis ($\pm 0.1\%$) account for part of the scattering of the points of the apparent volume ($\pm 0.2\text{ cc}$) and refraction curves ($\pm 0.05\text{ cc}$). The general method for determining the concentration is to make up a concentrated stock solution analyze it accurately, and make accurate weight dilutions. In the case of LiBr and LiI solutions the errors due to evaporation would be quite large since the vapor pressure of ether in these solutions is much larger than that for LiClO_4 solutions. However, the following additional factors made such a technique impossible. When ether was added to an ethereal lithium bromide solution, it

caused precipitation of the LiBr . This phenomenon was probably due to traces of moisture in the ether since addition of a drop of water to the solution caused the same effect. Ether solution of lithium iodide proved to be very sensitive to light and perhaps air. Upon standing any length of time the color of iodine in the solution appeared. Therefore for both LiBr and LiI the solution of the concentration desired was made up from the solid and measured as quickly as possible. Later it was found that keeping metallic lithium in contact with the solution would inhibit the decomposition.

The titration mentioned above was made using eosin as an adsorption indicator. Weighed amounts of the ether solution were added from a Soule weight burette. It was found that the use of Meloche-stopcock grease (insoluble in ether) on the cap and on the stopcock prevented evaporation during weighing and was not dissolved by the solution.

(c). Discussion of Experimental Results for LiBr and LiI in Ether.

Since each concentration for which the density and the index of refraction were determined involved a separate analysis, the errors in the apparent refraction of LiBr and LiI are large. No accurate value can be given for the refraction at infinite dilution for this reason. The measurements for LiBr are in the concentration range below 1 molar where errors are expected to be especially large even for aqueous solutions. Thus only an average value $R = 11.39$ can be given.

The refraction values for LiI show a distinct increase from 1 molar to 3.5 molar which is well beyond the experimental errors. The approximate value $R = 16.2$ can be given for the refraction in an infinitely dilute solution.

The apparent volume curves show considerable scattering of the points for the same reason. Lithium Bromide has an apparent volume which increases rapidly with increasing concentration (See Fig. 12); the Φ value is 10.0 cc. The best straight line through the three values determined for LiI in ether has a slope of $2.0 \text{ cc} \times (\text{mol/liter})^{-1}$ and the Φ value is 8.0 cc.

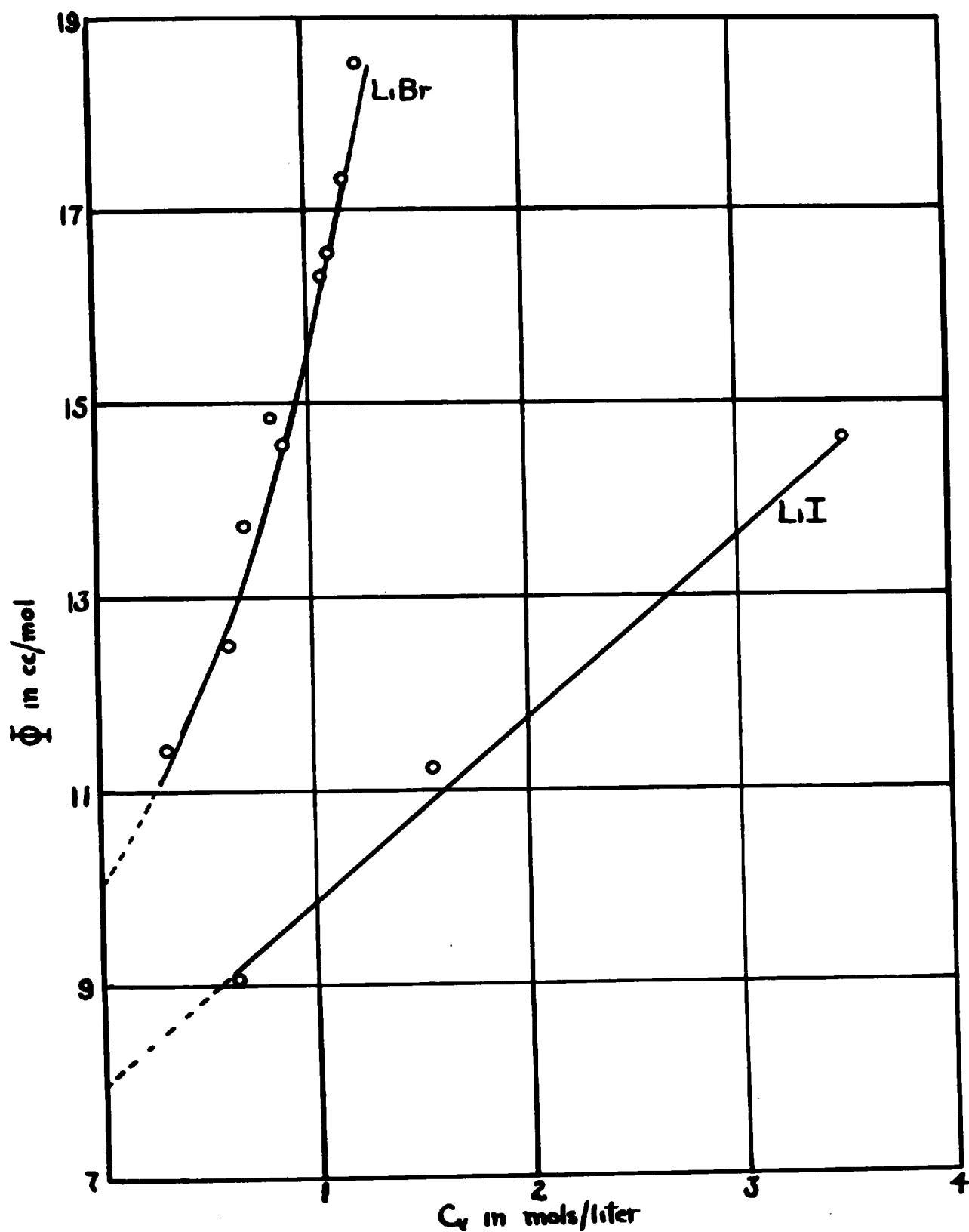


Fig. 12. Apparent molar volume of LiBr and LiI in ether at 25° C.

TABLE XII

Density, Refractive Index, Concentration, Apparent
Molar Volume and Apparent Molar Refraction of ether
solutions of LiBr and LiI at 25° C.

LiBr C_v	D_4^{25}	$N_{D_3}^{25}$	Φ	π	$R_{D_3}^{25}$	Mean R_{D_3} =
0	0.70776	1.34944	(10.0)	----	----	
0.298	0.73126	1.35444	11.45	43.25	(11.75)	
0.609	0.75526	1.35789	12.50	39.73	11.22	
0.675	0.76002	---	13.93	----	----	
0.826	0.77090	---	14.79	----	----	
0.908	0.77697	---	14.33	----	----	
1.10	0.79134	1.36520	16.55	36.79	11.46	
1.048	0.78668	---	16.29	----	----	
1.177	0.79570	1.36582	17.30	35.72	11.39	
1.22	0.79704	---	18.6	----	----	
LiI						
0.652	0.79085	1.36634	9.08	66.38	16.21	
1.56	0.90410	1.38897	11.30	64.54	16.29	
3.469	1.13635	---	14.56	----	----	
3.489	1.14213	1.43899	14.23	64.22	16.93	

C. THEORETICAL

I. DISCUSSION OF REFRACTOMETRIC EFFECTS

In the "Refractometric Investigations" which have been carried out by Fajans and his collaborators since 1924, extensive experimental data on refraction, volume and dispersion of crystals, vapors and solutions have been collected (See e.g. XXX and XLIII). It has been shown on the basis of this experimental material together with a few simple theoretical considerations that, when gaseous ions combine to form molecules or crystals or act on neutral molecules, the Lorentz-Lorenz molar refraction can show large deviations from additivity. The individual effects to which these deviations are due are the following:

(1). A cation tightens the electronic shell of an adjacent anion or neutral molecule, i.e., decreases their molar refraction and size.

(2) An anion loosens the electronic shell of a neighboring cation or neutral molecule, i.e., increases their refraction and size.

(3). Solvent dipoles lower the refraction of anions and increase the refraction of cations. These effects in general will be smaller than (1) and (2).

(4). Interaction between neutral molecules may lead to either a decrease or increase in refraction.

The first two effects have been thoroughly discussed in "Refractometric Investigations" (see e.g. Fajans, I, VII,

XXX and Kruis, XLVII). The magnitude of these effects depends on the intensity of the electric field of the acting charges and on the deformability of the other particle. Effect (2) has been demonstrated in a direct manner recently (see Fajans, 5) also by the consideration of lattice distances in crystals.

The evidence for the tightening effect (3) of solvent dipoles on anions is based (see Fajans, Hölemann and Shibata (XXI)) on data concerning the temperature dependence of the apparent refraction and volume of some salts in infinitely dilute aqueous solution. The results for the sodium salts are plotted in Fig. 13. The temperature coefficient of the apparent volume has been discussed by Gibson (37), and by Fajans and Johnson (24). It was shown that the effect of the breaking of the tetrahedral structure of water (see Bernal and Fowler, 38) gave a positive component and the effect of the attractive forces between ions and water gave a negative component to this temperature coefficient. The positive influence of the "breaking effect" increases from Cl^- to ClO_4^- since it was shown (24) to become greater as the difference between the volume of the ion and that of the water molecule increases. The negative influence of the effect of the forces becomes weaker with decreasing field of the anion i.e. from Cl^- to ClO_4^- . Thus as both effects act in the same direction, the observed gradation (Fig. 13) for the apparent volumes is qualitatively explained.

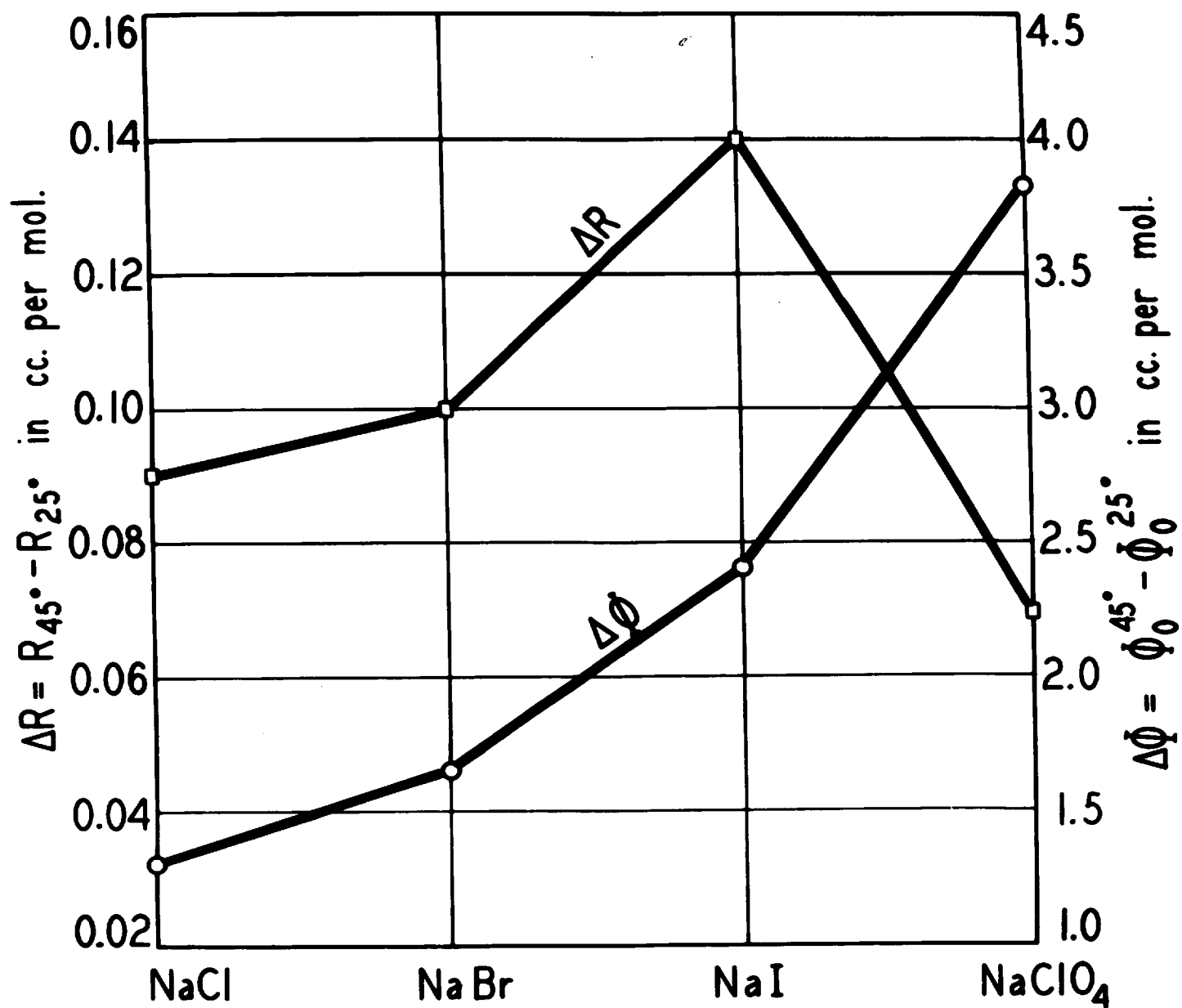


Fig. 13. Temperature coefficient for the apparent molar refraction and volume of NaCl, NaBr, NaI and NaClO₄

The $\Delta R/\Delta T$ values show the gradation $\text{ClO}_4^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ which indicates that the deciding factor is not the size but in all probability the polarizability which is smallest for ClO_4^- and largest for I^- . Since the increase in apparent refraction must be obviously due to a weakening of a negative effect in the interaction of ions and solvent as the temperature increases i.e. ion-water distance increases, these data offer evidence for a tightening effect of water dipoles on anions.

The ion-solvent interactions discussed above are to be expected for all solvents. However, in the case of water solutions, there will be an additional effect due to the breaking of the loose tetrahedral structure of water by the ions. That this factor may have an appreciable effect not only on volume but also on refraction has been pointed out by Kruis (LI). The molar refraction of all liquids investigated increases with increasing temperature (XXI), but Kruis' plot of the data for liquid water shows that the refraction decreases from 3.735 cc at 0° to 3.728 at 50° C. Just as for many other anomalous properties of water, the explanation lies in the fact that the increase in temperature breaks the tetrahedral structure of water, and the closer packing leads to a lower refraction.

In his discussion of the minimum in the apparent volume vs. concentration curve for methyl alcohol- H_2O mixtures at

about 10 mol percent methyl alcohol, Gibson (39) attributes it to the effect of the alcohol on the water structure. The data of Koenig (9) and Linton (10) shows the same kind of a minimum for acetone and ethyl alcohol in water solutions for the apparent volume and the apparent refraction as well. In these latter cases, it is very likely that the change of the structure of water is responsible for the refraction minima as well as that for the apparent volume.

Effect (4), the interaction between neutral molecules may cause the small deviations from additivity in the apparent molar refraction found for binary mixtures of organic liquids (8,9,10). These deviations are of the order of magnitude of one part per thousand in molar refraction. Such an interaction has also been made responsible for the increase in the apparent refraction of nitric acid found by Löhdemann (XLII) and of perchloric acid (XII,XIII) in concentrated solutions.

A distinct interaction between neutral molecules is also shown by the decrease in the refraction of acetic acid vapor as the temperature is increased (see Goldschmidt and Hölemann, XLV). The decrease takes place as the acetic acid dimers dissociate with increasing temperature and amounts to 0.2 cc per mol of the dimer. Fajans (40) considers the increased refraction of the dimer to be the result of a diminished tightening effect on the oxygen octet of the OH group because of the shift of the proton in hydrogen bond formation.

Some examples of interactions of neutral molecules in

aqueous solution are the following: Spacu and Popper (41) have shown that the apparent refraction of mannite in water increases with increasing concentration. Decreases in the apparent refraction of some amino acids were observed by Hedestrand (42) and of urea by Pesce (43) in water (See also Brodskii, 28). The case of amino acids is more complicated due to the "zwitter-ions" nature of these molecules.

In the following discussion of the results, the molar dispersion will also be included. The same effects are responsible for changes in dispersion as in the case of the molar refraction, but the former is relatively more sensitive to forces between particles than the molar refraction (see Bauer and Fajans, LV).

These general points of view concerning refractometric effects will now be used in considering the observed refractions and dispersions for the substances investigated. It is obvious that since so many effects enter, it is not always possible to decide which of them is of decisive influence.

II. ELECTRIC INTERACTION IN AQUEOUS SOLUTIONS OF SILVER FLUORIDE

(a). Properties of the Silver ion and the Fluoride ion.

Many of the properties of silver compounds differ greatly from those of alkali compounds. Fajans (44) concludes from a consideration of lattice distances, lattice energies, crystal structure, solubilities, formations of complexes in solution, color, that the factor responsible for these differences is

the greater polarizing power as well as the greater polarizability of the Ag^+ , which has an outer 18 electron shell, as compared with that of the alkali ions of noble gas character.

In crystals where the anion is not easily deformed and does not strongly deform the cation e.g. in AgClO_4 , the silver ion and sodium ion appear to be of equal size. Bauer's (1) data on solutions of AgNO_3 and the present data on AgF show that the ϕ value of silver ion is about 0.5 cc. larger than that of Na^+ . Bauer attributed this larger size of Ag^+ in aqueous solution to a specific hydration of Ag^+ in which it probably attaches only 2 water molecules but those very strongly. Analogous to the behavior of H_3O^+ and $(\text{Li}\cdot\text{H}_2\text{O})^+$, the field of Ag^+ is effectively screened and thus the ~~water~~ electrostriction of the more distant water molecules is less for Ag^+ than for Na^+ . The higher equivalent conductance of Ag^+ (61.9 at 25°) as compared to Na^+ (50.1) also indicates a screening of its field, but the value for K^+ (73.5) gives evidence that the Ag^+ exerts stronger forces on water than K^+ . The gradation of the relative viscosities at 1 molar, AgNO_3 (1.05), KNO_3 (0.97) is further evidence that the electrostriction of Ag^+ is larger than for K^+ .

It is evident that the fluoride ion exerts very strong forces on the surrounding water molecules. It was pointed out (38,34) that although the free gaseous fluoride ion is larger than the sodium ion, in aqueous solution the fluoride ion appears to be slightly smaller, obviously due to a greater

electrostriction of the water. Strong interaction with water is also indicated by the fact that fluorides produce the greatest increase in viscosity of all monovalent ions in aqueous solution (see Bingham, 45).

From the discussion (see sect. C, I) concerning the effects of the ions on the tetrahedral structure of water, one can expect the strong electrostriction of F^- to give a negative component to the apparent refraction of the aqueous fluoride ion. However, from a consideration of the gradation of the refractions of gaseous ions and the observed apparent refractions in aqueous solution, it was concluded (XXX) that the refraction of the aqueous F^- is 0.16 cc. larger than the gaseous ion. This positive refractometric hydration effect is considered to be the result of the loosening effect of this small anion on the adjacent water molecules. The polarization of the cation by the fluoride ion should also give a positive refractometric effect. The positive slope of $0.012 \text{ cc} \times (\text{moles}/1000 \text{ grams } H_2O)^{-1}$ found by Geffcken (XI) for the R vs. C_g curve for potassium fluoride in aqueous solutions was attributed mainly to this effect when ions associate.

(b). The Concentration Dependence of the Apparent Refraction and Volume.

The specific properties of the two ions, Ag^+ and F^- , can now be used in considering the changes in R and ϕ for AgF solutions as the concentration is increased. The analogous

data on KF offer a convenient comparison which can be expected to show how the nonrare gas Ag^+ differs from the rare gas K^+ in its effects on volume and refraction in aqueous solutions.

The factors which influence the slopes of apparent volume and refraction vs. concentration curves for KF and AgF are as follows: (1). Removal of the effects of ions on water as concentration increases. (2). Interaction between ions in formation of ion-pairs.

Effect (1) is the result of the screening of the electric fields of the ions due to the approach of the counter ion or to the formation of ion-pairs, as well as of the smaller relative amount of water per ion in the concentrated solution.

The change in apparent refraction^{at 25°C} removal of these effects of ions on water will be influenced not only by sign and magnitude of the effect, but also by the degree of screening and association of ions which increases as the concentration increases. Considering that a smaller osmotic coefficient (g) indicates a larger degree of screening and association of ions in solution, the lower g value for AgF (0.59) as compared with KF (0.71) means that there is more association or screening of the fields of the ions in AgF solutions than for KF.

Since the refractometric hydration effect of the Ag^+ was shown to be at least as great as that of the sodium ion (-0.27 cc/mol; see Bauer (1)) and that of the K^+ is certainly

smaller (XXX), the increase in R for the same degree of association must be greater for AgF than for KF , and since the association is also stronger for AgF , the dR/dC_g value can be expected to be more positive for AgF solutions than for KF .

However, the removal of the positive refractometric effect of F^- on water will cause a greater decrease in apparent refraction for AgF than for KF since there is more association in the former.

For factor (2), the loosening effect of F^- on the cation, which was considered to cause the increase of apparent refraction of KF with increasing concentration, will be still more important for the more polarizable Ag^+ ($R = 4.9$). Thus, the presence of a stronger individual effect and the greater degree of association for AgF indicate a higher slope of R vs. C_g for AgF as compared to KF .

For the observed change of apparent refraction with concentration all the factors except the more extensive removal of the loosening effect of F^- on water for AgF give greater positive components for AgF solutions than for KF . The measurements show that the initial slope of the R vs. C_g curve for AgF (0.017) is substantially larger than for KF (0.012). However, the AgF curve is not linear (see Fig. 5a) and the slopes become equal at about 4.0 molal, the slope for the KF curve which is linear up to 6 molal being higher above this concentration (See Fig. 5b). Since the removal

of the loosening effect of F^- on H_2O gives the only negative component which is greater for AgF , even without precise knowledge of the magnitude of the various effects, the reversal of the gradation of slopes indicates the predominance of this effect at high concentrations where more association occurs. This can be considered as a new support for the existence of a loosening effect of small anions on water molecules.

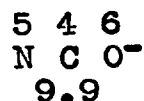
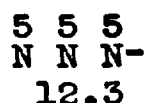
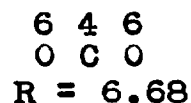
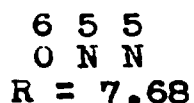
In the case of the apparent volume, the removal of the effects of ions on the water will result in a greater increase in ϕ for AgF than KF since the Ag has the larger electrostriction. The more extensive screening and association in the case of AgF will remove the electrostrictive effect for AgF to a greater extent than for KF . In addition the loosening action of F^- on Ag^+ can also be expected (see Fajans, 46) to result in an increase in the apparent volume.

All the factors mentioned above indicate greater positive components to the apparent volume for AgF than KF as the concentration is increased. The considerably higher slope ($K = 3.35$) is thus obviously due to the greater electrostrictive effect of Ag^+ , the loosening effect on Ag^+ by F^- and to the formation of more neutral ion-pairs in AgF solutions at high concentrations.

III. THE REFRACTION OF THE CYANATE ION

The cyanate ion belongs to the series of linear triatomic particles with 16 electrons. One of the possible ways of comparing their properties is to consider these particles as

composed of 3 charged cores with 16 electrons in common to them (see Fajans and Berlin, 47). Four of the series are tabulated below with core charges and molar refraction indicated:



Comparing the refraction of NCO^- with CO_2 and N_3^- with N_2O , it is seen that an increase of the charge on the cores results in a smaller molar refraction i. e., stronger binding of electrons. The refraction values for N_3^- and NCO^- are in aqueous solution. That the change from 6 to 5 in the charge of an outer core is more effective than the simultaneous change from 4 to 5 in the center core is shown by the increase in refraction from NCO^- to N_3^- , both in aqueous solution, and from CO_2 to N_2O , both gaseous.

IV. ELECTRICAL INTERACTIONS OF LiBr , LiI and LiClO_4 Molecules with Ether

(a). Properties of Lithium salts.

The lithium ion in aqueous solution has a larger apparent volume than the sodium ion; in analogy to the corresponding behavior of H^+ Gronwall and LaMer (49 see also 24) take this as evidence that $(\text{Li} \cdot \text{H}_2\text{O})^+$ is formed, and because of the screening of the field of the ion in the complex, it exerts a smaller electrostrictive effect on the water than does Na^+ .

There is a clear indication that LiClO_4 forms a molecular crystal lattice. The compressibilities of perchlorate crystals, as communicated to Prof. Fajans by Prof. P. W. Bridgeman of Harvard University, show LiClO_4 to be more compressible than NaClO_4 whereas the opposite gradation would be expected from the consideration that Li^+ exerts greater forces if both salts formed a coordination lattice. The low melting point (236°C.) of LiClO_4 is also in agreement with the assumption of a molecular lattice. Also the relatively low heats of sublimation and melting points (37) of LiBr and LiI indicate that these salts also deviate from a coordination lattice.

The lithium salts listed in the previous paragraph are the only alkali salts which are appreciably soluble in a solvent of such low dielectric constant as ether. This is a further indication for a molecular lattice of these salts. As expected LiBr , LiI and LiClO_4 in ether (Dielectric Constant = 4.35) are only very slightly ionized. Miss Chu (7) has obtained the following results for the electrical conductivity of these solutions: For LiClO_4 in ether $\Lambda = 1.6 \times 10^{-3} \text{ ohm}^{-1} \text{ cm.}^2$ for a 0.6 molar solution; For LiBr and LiI , $\Lambda = \text{ca. } 10^{-3}$ for 1 molar solutions.

The properties mentioned above can be considered the result of the strong forces exerted by the small lithium ion and the consequent strong interaction with adjacent particle. How this interaction affects the properties of the ether solutions of LiBr , LiI and LiClO_4 can now be discussed.

(b). LiClO_4 in Ethyl Ether

Willard and Smith (6) discovered the unusually large solubility of LiClO_4 in ether which is 0.792 moles LiClO_4 per mole of ether at 25°C . Since LiClO_4 is present in ~~ether~~ in ether solutions as molecules and not ions (paragraph a), the high solubility must be due to a strong interaction between the LiClO_4 molecule and the ether molecules. The large heating effect observed when LiClO_4 dissolves in ether, as well as the heating produced upon diluting a solution, are direct indications of such an interaction. The consideration of the dipole moment of LiClO_4 in dioxane gives a more detailed picture of the interaction. Ferguson and Malone (49) report a dipole moment of 7.8 Debyes for LiClO_4 in dioxane. This very large dipole moment is obviously the result of the following two factors (see Fajans and Spurgeon (40)): First, the field of the lithium ion is not strongly screened by the ClO_4^- which is not easily deformed. Secondly, this unscreened lithium ion can strongly polarize the ether molecule ($R = 22.5$) to which it is attached.

The strong action of LiClO_4 on ether shows up in the large decrease of the apparent molar volume in ether as compared either to the volume of the solid or to ϕ_s in H_2O . (See Table XIII). Since LiClO_4 is a fairly rigid molecule, the whole diminution effect must be the compression of ether by the field of the dipole. The compressibility of ether is large ($K = 200 \times 10^{-6} \text{ cc/atm.}$).

The following table shows that the apparent volume of LiClO_4 in ether solutions is much less than in other solvents, even in a saturated solution. The apparent volumes are calculated from data of Willard and Smith (6).

TABLE XIII

Apparent Volume of LiClO_4 in Various Solvents at

Infinite Dilution and in Saturated Solution

<u>Solvent</u>	<u>$\Phi_{\text{sat'd}}$</u>	<u>Φ_c</u>	<u>Solvent</u>	<u>$\Phi_{\text{sat'd}}$</u>
ether	32.9 cc	14.2	methyl alcohol	44.8 cc
acetone	40.0	11.0	ethyl alcohol	44.9
water	45.7	43.4	n-propyl alcohol	46.2
V_{solid}	43.8		iso-butyl alcohol	40.0

As mentioned previously, the apparent volume versus concentration curve is linear with the first power of the concentration just as for other cases of non-coulombic interaction e.g. non-electrolytes in water and mixtures of organic liquids. Redlich and Klinger (50) have discussed this linear relation of Φ vs. C in contrast to the Φ vs. $\sqrt{C}$ linear relation for electrolytes in aqueous solution.

The apparent refraction at infinite dilution for LiClO_4 in water is 12.9 cc. while that in ether is only 11.4 cc; the corresponding values for the molar dispersion are 0.191 and 0.14₀ cc. The large diminution of both refraction and dispersion from the values in aqueous solution are obviously the result of a strong tightening effect of LiClO_4 molecules on

adjacent ether molecules.

Such a large refractometric effect becomes quite reasonable when one considers that there is a decrease of molar refraction of ether when the vapor is condensed ($R_{\text{vapor}} - R_{\text{liq}} = 22.76 - 22.47 = 0.29$ for $\lambda = 5461 \text{ \AA}$; see Stuart and Volkmann, 51 and Holemann, XLVI). The corresponding decrease in R for water is only 0.04 cc. It is evident from the consideration of the apparent volume of LiClO_4 in ether that LiClO_4 compresses the ether strongly. Thus, if the condensation produces a diminution in R of 0.29 cc, a further and stronger compression would be expected to produce still further decrease in R . In addition to this effect there is the direct interaction of LiClO_4 with adjacent ether molecules which can lead to a considerable decrease in R due to the unscreened field of the Li^+ ($\mu_{\text{LiClO}_4} = 7.8$; $\mu_{\text{ether}} = 1.17$ debyes).

Accordingly, the large diminution of apparent refraction and dispersion compared to the values in aqueous solution must be the result of both the tightening effect of LiClO_4 on adjacent ether molecules and interaction between more remote ether molecules which are compressed by the LiClO_4 .

The large increase in apparent refraction and dispersion (see Fig. 9) as concentration increases is due to the removal of the above effects as the amount of ether per mole of LiClO_4 becomes less.

The data of Cheneveau (11) on zinc chloride in ether is in agreement with these results. At 16°C he found the value

of 17.7 for the refraction of a 20% aqueous solution and only 16.8 cc for the salt in 17% ether solution. The change of about 1 cc. is of the same order of magnitude as that observed for LiClO_4 in the present investigation.

It is of interest to compare the relative changes of refraction and dispersion, since it was shown (LV) from a theoretical consideration that dispersion changes should be about twice as great as the changes in molar refraction. The diminution of refraction upon going from aqueous solution to ether solution is 1.50 cc (12%) and the analogous decrease in dispersion is 0.05₁ cc (26%). The observed relative decrease in molar dispersion is very nearly twice that of the molar refraction.

A further indication of a strong interaction between LiClO_4 and ethyl ether is shown by the change of the infrared absorption spectrum (in the region 2-12 μ) of the ether by dissolved LiClO_4 . From the results kindly communicated by Professor Barker and Mr. Gates of the Physics Department, it suffices here to mention the following: A 1.3 molar solution shows a decrease in the intensity and a widening of the strong absorption band at 8.9 μ , and a new band is observed at 11 μ . With increasing concentration there is a shift of this band to longer wavelengths.

(c). LiBr and LiI in ether.

The data on conductivity mentioned in paragraph (a) of this section shows that LiBr and LiI , like LiClO_4 , are present

in ether solutions as molecules.

Table XIV shows the apparent volumes of crystals, aqueous ions and the molecules in ether for LiBr, LiI and LiClO₄. The difference between the volume in water and ether is distinctly smaller for LiBr (14cc) than for LiI (27 cc) and LiClO₄ (29.4 cc).

One striking feature of these data is that the apparent volume of LiI is smaller than that of LiBr; in aqueous solution the iodide appears to be over 11 cc. larger. Two factors can be responsible for this: (1). A strong compression of the iodide ion by the Li⁺ and by the surrounding ether molecules. (2). A stronger compression of ether by LiI than by LiBr.

TABLE XIV

Refractions and Volumes of Lithium Salts in
Crystals, in Water and in Ethyl Ether

<u>Refractions</u>	LiBr	LiI	LiClO ₄
R (gaseous ions)	12.76	19.3	13.3
R in H ₂ O	12.34	18.90	12.90
R in Ether	11.39	16.31	11.40
R crystals	10.56	15.98	---
<u>Volumes</u>			
V crystal	25.08	32.75	43.8
In H ₂ O	24.07	35.60	43.44
In ether	10.0	8.0	14.0

Since LiI and LiBr are present in ether as molecules, a considerable decrease in refraction from that of the sum of the gaseous ions (see Table XIV) or from the ions in water is expected as a result of the tightening effect of the Li^+ on the halide ion. The decrease in apparent volume from water to ether shows that there is compression of ether which as in the case of LiClO_4 should lead to an additional lowering of refraction in ether solutions.

It is of interest to note that the crystal refraction of both LiBr and LiI is lower than that of molecules in ether. The extent of lowering of refraction will depend on the distance of the approach of the Li^+ and the halide ion, and this will obviously be influenced by the surroundings which are different in the two cases.

V. CHEMICAL FORCES IN SOLUTIONS OF LITHIUM PERCHLORATE IN ACETONE

The heat evolved in dissolving lithium perchlorate in acetone is great enough to cause vigorous boiling of the solution. The solubility is 0.745 moles LiClO_4 per mole of acetone which is only slightly lower than that in ethyl ether. Conductivity measurements by Miss Chu (7) show that in dilute solutions of acetone, LiClO_4 is highly ionized. The equivalent conductance approaches $140 \text{ ohm}^{-1} \text{ cm}^2$ for infinite dilution, but the conductivity falls very rapidly with increasing concentration, becoming 34.03 at 1.06 molar and 0.824 at 5.12 molar. Therefore, in considering the properties of the

solution, interaction of both ions and molecules with the acetone molecules must be considered.

Table XIII shows that ϕ in acetone is still a little lower than in ether in spite of the smaller compressibility of acetone ($K = 82 \times 10^{-6}$ cc/atm. at 0° C). This indicates clearly the much greater electrostrictive effect of ions as compared to molecules; for concentrations above 2 molal (See Fig. 7) the ϕ value in acetone is larger. The large difference between the ϕ values in water and acetone demonstrates the effect of the greater compressibility of acetone solvent as compared to water ($K = 49 \times 10^{-6}$) since at infinite dilution, LiClO_4 is present as the Li^+ and ClO_4^- in acetone as well as in water.

Other examples of the differences between the apparent volume of a salt in the state of ions and molecules are given in Table XV. In Table XVI are shown the apparent volumes of several salts in alcohols, glycol and liquid ammonia. These latter examples are further illustration of the dependence of apparent volume on the compressibility and structure of the solvent. The Alcohols are more compressible than water and glycol is less compressible. The table will not be discussed further but it gives characteristic examples of the dependence of ϕ on the solvent.

The large change in apparent volume with concentration (See Fig. 7) for LiClO_4 in acetone is clearly due to the strong compression of the acetone by Li^+ and ClO_4^- in dilute solution

TABLE XV

Substance	$\phi_{\text{mol}} - \phi_{\text{ions}}$	$R_{\text{mol}} - R_{\text{ions}}$	R_{anion}
H_3CCOOH (XLII)	11.37 cc	-0.85 cc	14.4 cc
HCOOH	8.0	-0.81	9.88
$\frac{1}{2}\text{HgCl}_2$ (XI)	16.4	-0.40	9.06
$\frac{1}{2}\text{HgBr}_2$	12.7	-0.42	12.87

TABLE XVI
Apparent Volumes of Salts in Various Solvents
at Infinite Dilution

Salt	ϕ_{water}	ϕ_{methanol}	$\phi_{\text{glycol (b)}}$	V_{solid}
LiCl	17.06	-3.8 (d)	(ethanol) -4.4	20.62
NaCl	16.28	-3.3		27.02
KCl	26.36	5.2		37.49
LiBr	24.07	6.9	21.71	25.07
NaBr	23.45		27.29	32.13
NaI	35.02	11.8 (c)	38.37	40.92
KI	45.23	21.9	47.16	53.17
KCNS	48.0	28.2		
NH_4NO_3	47.5	32.6		46.41
$\frac{1}{2}\text{Ca}(\text{NO}_3)_2$	22.4	14.4	$\phi_{\text{liq. NH}_3^a} (-35^\circ\text{C})$	
NaCl	16.28		-6.0	27.02
NaNO_3	27.40		3.0	37.87
NH_4Cl	36.00		0.2	35.03
NH_4Br	43.0		6.0	40.32
NH_4NO_3	47.5		1.0	46.41

References:

- a. See Akhomov (52)
b. Gibson (53)

- c. Stark (54)
d. Vosburgh (55)

and the removal of this effect as the ions associate.

The concentration dependence of the apparent refraction and dispersion are complicated in this case due to the fact that the ions as well as molecules of LiClO_4 both interact with the acetone. The apparent refraction (See Fig. 10) as extrapolated to infinite dilution is 12.88 cc which is only slightly lower than that in water (12.90 cc), decreases to a minimum of 12.76 at 3 molal and increases again at higher concentrations to 12.76 at 7.9 molal.

The increase in refraction above 3 molar corresponds to the effect observed in ether since at this concentration the salt in acetone is less than about $\frac{1}{2}\%$ dissociated and the observed effect is one between LiClO_4 dipoles and the acetone. Since acetone is less deformable than ether, the increase in refraction and dispersion upon removal of acetone (i.e. increasing the concentration) is much less than that observed in ether solutions.

Some kind of a loosening effect of ions on acetone or vice versa which is removed as the ions associate can explain the initial decrease of the refraction of LiClO_4 in acetone (see Fig. 7). However, until there is more knowledge about the nature of the groups in the acetone molecule, or until data for this salt in other ketones is available for comparison, no detailed explanation can be given.

In an infinitely dilute solution of LiClO_4 in acetone there are present only Li^+ and ClO_4^- and acetone molecules.

From the consideration of apparent volume it is certain that the ions compress the acetone very strongly. An appreciable decrease in refraction when compared with that in water would be expected as a result of this, since condensation of acetone vapor produces a decrease of 0.15 cc. (see Lowery (53)) in refraction. However, the apparent refraction⁵ extrapolated to infinite dilution* are nearly equal in acetone and water (see Fig. 7). This also indicates that the ions have some loosening effect on the acetone or vice versa which balances the decrease in refraction expected as a result of the strong electrostriction. This is analogous to the positive refractometric hydration effect for the fluoride ion in aqueous solution; as was pointed out in Sect. II, a, in spite of the strong electrostriction, the loosening effect of F^- on the water molecules produced an increase in refraction.

An indication that the effect is due to some property of the acetone molecule is given by data of LeBlanc and Rohland (12) for KI and $HgCl_2$ in acetone. The apparent refraction for each is about 0.3 cc. larger than that for aqueous solutions.

VI. REFRACTOMETRIC STUDIES OF SOLUTIONS IN ALCOHOLS

Table XVII gives some data showing changes in apparent refraction in different solvents. The measurements of E. Schreiner (13) on HCl and $LiCl$ in alcohols and of B. Pesce

*Since $LiClO_4$ is only about 20% ionized at the lowest conc. for which R was measured, the extrapolation of the R vs. Cg curve to infinite dilution can involve a large error. A reversal of the slope of the R vs. Cg curve has been observed for some salts in water (see Sect. 8.1.3)

(14) on $\text{Ca}(\text{NO}_3)_2$ both show the concentration dependence as well as the absolute value at infinite dilution which is given in the table (see Fig. 14).

TABLE XVII

APPARENT MOLAR REFRACTION OF SUBSTANCES IN WATER,
METHANOL AND ETHANOL FOR INFINITE DILUTION

Solvent	HCl (13)	LiCl (13)	$\frac{1}{2}\text{Ca}(\text{NO}_3)_2$ (14)
H_2O	8.52 cc	8.73	11.36
Methanol	8.30	8.55	11.20
Ethanol	8.10	8.38	

Since the ions all lower the refraction of the solvent and since the deformability of the solvent increases in the order water, methanol, ethanol, the lower apparent refraction at infinite dilution of the salt in the latter is clearly due to the negative refractometric effect on the solvent.

HCl and LiCl show a decrease in refraction with increasing concentration which is even larger than that observed in aqueous solutions. The decrease in all cases is due to the large tightening effect of the Li^+ on Cl^- upon association, and a greater degree of association in the alcohols accounts for the greater negative slopes.

The results on calcium nitrate are interesting because just the opposite slope is observed for the R vs. C curve (see Fig. 14) in methanol than in water. In aqueous solutions the slope is $-0.005 \text{ cc} \times (\text{mol}/1000 \text{ grams})$ and in methanol, $0.002 \text{ cc} \times (\text{mol}/1000 \text{ grams methanol})$. The previous discussion showed

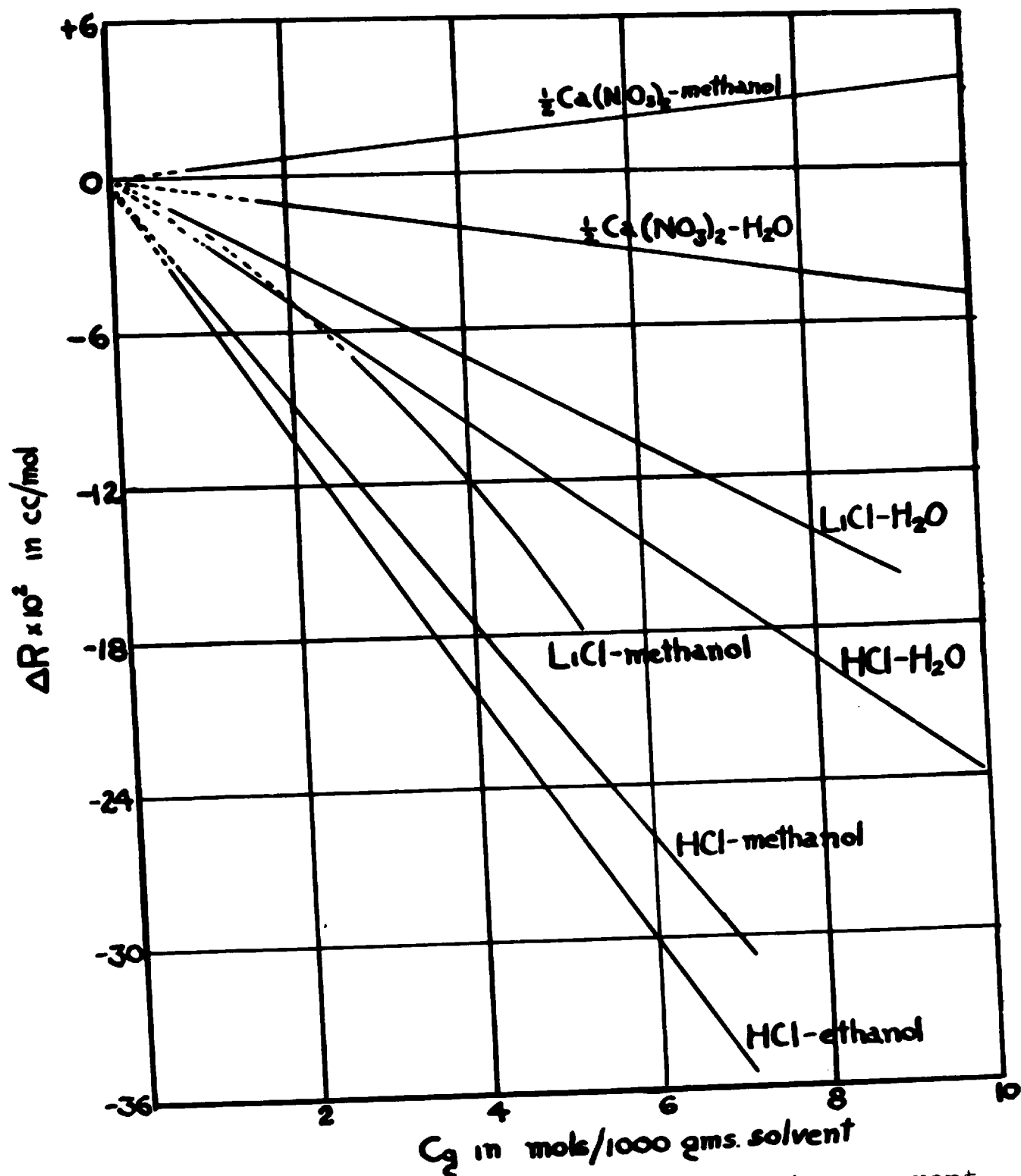


Fig. 14. Concentration dependence of the apparent molar refraction of substances in aqueous and alcoholic solutions

that when ions are dehydrated and association occurs upon concentrating a solution, an increase in refraction occurs if the anion is less polarizable than the solvent and a decrease occurs when the anion is the more polarizable. In water ($R = 3.7$ cc) a decrease is observed since the calcium ion lowers the refraction of the nitrate ($R_{\text{oxygen}} = 4$ cc) more than it did the water. However in methanol ($R = 8.23$) the refractometric effect on the solvent is greatest, and an increase in refraction is observed.

This type of study may be a method of deriving estimates of the refraction of groups in the organic molecules.

D. APPENDIX to B, II, c, 2

Some of the details of the protection of the prism from the corrosive action of AgF solutions by use of a microscope cover glass with a liquid between it and the prism will be discussed here.

If one assumes that the microscope cover glass has very nearly plane parallel surfaces, the relation between the indices of refraction can be calculated.

Let n_g = index of refraction of the glass

n_1 = " " " " of the liquid being measured

n_2 = " " " " of the liquid between the cover glass and the refractometer prism

θ_1 and θ_g = angle of incidence and refraction at the first surface

θ_g and θ_2 = angle of incidence and refraction at the second surface

Using Snell's Law, one obtains:

$$n_1 \sin \theta_1 = n_g \sin \theta_g = n_2 \sin \theta_2 \quad (a)$$

As a condition for refraction of the light at the cover glass: $\sin \theta_2 < 1$

From equation (a)

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

$$\frac{n_1}{n_2} = \sin \theta_2 < 1 \quad \text{since } \theta_1 = 90^\circ$$

$$\therefore n_1 < n_2$$

This shows that to obtain refraction i.e. to prevent total reflection at either interface, the liquid between the prism and the cover glass must have a greater index of refraction

than the liquid being measured. Bromoform ($n = 1.58$) has a higher n value than any solution of silver fluoride and thus fulfills this requirement.

There will be a change in the observed refractive index of a solution due to the presence of the microscope cover-glass only if the surfaces of the cover glass are not plane parallel. To determine whether this is so, water and a KCl solution ($N_1 = 1.35609$) were measured before and after the cover glass was put on the prism. An increase in refractive index of 0.0320 was observed for water and an increase of 0.0318 for the KCl solution. Accordingly, an average correction of 0.0319 was applied to all silver fluoride solutions measured. To check the validity of this average correction, a more exact treatment will be made.

The equation* connecting the true refractive index (n_1) and the refractive index observed with the cover glass ($n_{\text{obs.}}$) is

$$n_1 - n_{\text{obs.}} = \tan \alpha (N_g^2 - n_{\text{obs.}}^2)^{\frac{1}{2}} \quad (a)$$

where α is the angle made by the two faces of the cover glass and n_g is its refractive index. The derivation will not be given here. By substituting the above data on water ($N = 1.33264$) and the KCl solution in equation (a), the values $n_g = 1.52$ and $\alpha = 0.7'$ are obtained. The correction for any

*I thank Mr. Theodore Berlón for developing the mathematical expressions (a) and (b) and for valuable discussion concerning this optical system for protecting the prism from AgF solutions.

refractive index can now be calculated. For $n = 1.41$, that of the most concentrated AgF solution measured, the calculated correction is 0.0317 . This is still within the errors of the correction of 0.0319 which was applied.

Another important consideration in choosing a liquid to place between the cover glass and the prism is the intensity of the light. It can be shown that in order to obtain the maximum light intensity, the following equation must hold:

$$(n_2^2 - n_1^2) = (n_p^2 - n_1^2)^{\frac{1}{2}} (n_g^2 - n_1^2)^{\frac{1}{2}} \quad (b)$$

In the range of indices measured, the value of n_2 for the liquid between the prism calculated from equation (b) to give the maximum intensity is $n_2 = 1.61$. Bromoform ($n = 1.59$) appears to have an index near enough to this value to give good intensity. However, the light intensity was diminished considerably by the cover glass with bromoform between it and the prism, and only the very intense yellow line could be measured. The reason for the cutting down of intensity may be due to imperfections in the cover glass, absorption by bromoform or to lack of parallelness of surfaces (the equation (b) is based on this assumption.)

E. SUMMARY

I. EXPERIMENTAL

(a) Apparatus used in this laboratory for the precise measurement of densities, indices of refraction and concentrations of solutions has been described briefly. Modifications necessary in the handling of solutions in organic solvents were pointed out.

(b) The apparent molar refraction and volume (ϕ) have been determined for silver fluoride in aqueous solution from 0.4 to 7.8 molal. The apparent molar refraction extrapolated to infinite dilution was found to be 7.52₅ cc for the helium D₃ line at 25° C. The apparent volume in the range between 1 and 4 molar, can be represented by the equation:

$$\phi = -3.30 + 3.90 \sqrt{C_v}.$$

(c) The refraction of the cyanate ion has been determined from measurements on potassium cyanate for which the apparent molar refraction is 12.12 cc. This gave the result $R_{D_3}^{25^\circ} = 9.86$ for the cyanate ion in aqueous solution.

(d) The apparent molar refraction, volume, and dispersion of solutions of LiClO₄ in ether, have been determined in the concentration range between 0.87 and 10.6 molal. The apparent volume can be represented by the equation: $\phi = 14.2 + 1.73 C_g$. The apparent molar refraction was shown to increase rapidly with increasing concentration. At infinite dilution $R_{D_3}^{25} = 11.40$ cc and at 10.16 molal it is 12.5 cc. Measurements of refractive indices at 7 wave lengths gave the value of 0.14 cc for the molar dispersion ($\underline{D} = R_D - R_\infty$) at infinite dilution.

(c) The apparent molar refraction, volume and dispersion of solutions of LiClO_4 in acetone have been investigated from concentrations of 1.37 to 7.927 molal. The ϕ vs. C_v curve from 1.37 to 7.927 molal can be represented by the equation: $\phi = 11.0 + 4.65 C_v$. Both the apparent molar refraction and dispersion were shown to have a minimum at 3 molal. At infinite dilution $R_{D_3}^{25} = 12.88$ cc and $\underline{D} = 0.19$ cc.

(d) The apparent molar refraction and volume have been determined in ether solutions of LiBr from concentrations of 0.60 to 1.2 molar and for LiI from 0.65 to 3.49. For LiBr , $\phi = 10.0$ cc, and $R_{D_3}^{25} = 11.39$ cc (average value between 0.6 and 1.2 molar). For LiI , $\phi = 8.0 + 2.0 C_g$; the approximate value of 16.2 cc is given for the apparent refraction at infinite dilution, and it increases to 16.9 at 3.49 molar.

II. THEORETICAL

(1) The various refractometric effects are discussed and the evidence for a tightening effect on anions by water molecules is presented.

(2) The concentration dependence of apparent refraction and volume of AgF in aqueous solution is considered in terms of effects of ions on the water and the loosening of Ag^+ by F^- . The comparison of the R vs. C_g curves for KF and AgF gave additional support for the existence of a loosening effect of F^- on water.

(3) A model of the triatomic cyanate ion consisting of 3 charged cores and 16 electrons in common to them is used

to show the effect of core charges on the molar refraction.

(4) The fact that the absolute values of apparent refraction volume and dispersion of LiClO_4 in ether are much smaller than for aqueous solutions was shown to be the result of a strong interaction between LiClO_4 molecules and the ether as well as interactions between the ether molecules which are brought closer together by LiClO_4 . The strong field of Li^+ , unscreened by the rigid ClO_4^- , was considered to be the main cause of this interaction. The great increase of value of these properties with increasing concentration is due to the decreasing amount of ether per mole of LiClO_4 .

(5) The very small apparent volume of LiClO_4 in acetone was shown to be due to the effect of the ions on the solvent. The increase in refraction above 3 molal was shown to be analogous to that in ether, but the initial decrease in refraction and the high absolute value of the refraction and dispersion could only be explained on the assumption of some loosening effect in the interaction between the ions and the acetone molecule.

(6) The fact that the apparent volume of LiI in ether is smaller than that for LiBr was considered to be either the result of a strong compression of iodide by Li^+ and the surrounding ether molecules or to a stronger interaction with ether in the case of LiI . The apparent refraction was shown to be influenced strongly by the tightening effect of Li^+ on the halide ion as well as by solvent interactions.

(7) Data from the literature were presented to show some relatively strong refractometric effects for solutions of other salts in alcohols.

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