1955

Ionization and dissociation equilibria in sulfur dioxide solution. Part 1: dissociation of ion pairs. Part II: equilibria of meta phenyl derivatives of trityl chloride. Part III: the apparent ionization of hexaphenylethane

BOSTON UNIVERSITY
GRADUATE SCHOOL

Dissertation

IONIZATION AND DISSOCIATION EQUILIBRIA IN SULFUR DIOXIDE SOLUTION

Part I. Dissociation of Ion Pairs.

Part II. Equilibria of Meta Phenyl Derivatives of Trityl Chloride.

Part III. The Apparent Ionization of Hexaphenylethane.

by

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(A.B., Boston University, 1950)

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1955

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To my wife

Selma

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PART I

Dissociation of Ion Pairs.

INTRODUCTION

All attempts to utilize conductivity data for ring substituted derivatives of triphenylchloromethane in sulfur dioxide solution for the direct estimation of the electronic influence of the ring substituents have, in the past, met with little quantitative success due to the complications arising from short range ionic interactions in solvents of low dielectric constant.

In a qualitative manner Lichtin and Bartlett (90) were able to demonstrate that ion pair association equilibria introduce only minor errors in the relative equilibrium constants for triphenylchloromethane and those ring substituted derivatives whose measured dissociation constants are less than 10^{-4}. On the basis of their assumptions, these workers were able to estimate qualitatively the electronic influence of several substituents. Since, however, many theoretically interesting substituents exert an effect resulting a dissociation constant greater than 10^{-4}, it was considered both interesting and valuable to examine possible methods of evaluating an ion pair correction term to be used with the experimental data for these compounds.

Therefore, the research described here was undertaken. Initially the dissociation constant of potassium chloride was determined by applying the Shedlovsky and least squares

treatment to the conductivity data for this salt over the dilution range between 2000 and 80,000 liters per mole. This value showed excellent agreement with the value calculated from Bjerrum's (16) equation employing the assumption that the distance of closest approach of the ions was exactly equal to the sum of ionic radii as determined from crystallographic data. This correlation was extended by measurements and calculations carried out on a series of alkali halides and tetramethylammonium bromide.

The significance of the apparent quantitative adherence to Bjerrum's theory of solutions of electrolytes in sulfur dioxide has been discussed in terms of the sphere-in-continuum model with a view toward a better understanding of the shortcomings of this model.

In part II of this dissertation the possibility of using the Bjerrum theory for the calculation of the experimentally inaccessible dissociation constants for triphenylcarbonium halide ion pairs has been explored and ion pair corrections have been applied to the experimental data for these compounds. Thus the investigations described in part I have produced results which have a direct bearing on the original problem of estimating substituent effects from conductivity data in sulfur dioxide solution.

Standard free energies, entropies and enthalpies have been calculated for the ion pair dissociation reaction of potassium chloride, bromide, iodide and of tetramethylammonium

bromide in sulfur dioxide solution. A theoretical expression relating ΔH^{o} of ion pair dissociation with ionic radii, dielectric constant, and temperature has been derived from the Bjerrum theory.

Franklin's (38) data for potassium iodide and bromide over a wide temperature range in sulfur dioxide solution have been treated by the Shedlovsky and least mean squares method to give ion pair dissociation constants which are in good agreement with those calculated for these compounds by the Bjerrum theory.

The conductivity of tetramethylammonium sulfate has been measured by the method of Lichtin and Glazer over the dilution range of 10^{2} to 10^{5} liters per mole in sulfur dioxide solution. A semi empirical treatment has been developed which serves to distinguish between 1-1 and 2-1 valence type electrolytes in sulfur dioxide solution.

RESULTS AND DISCUSSION

The conductivity data collected in this investigation are presented in figures 1-I to 1-IX as semilogarithmic plots of equivalent conductance versus dilution. At least two runs were performed on each compound and the precision of the data as estimated from the average percent deviation of the individual points from the best fitting smooth curve is plus or minus one percent or better for each compound in the range 10^2 to 10^5 liters per mole. Experimental equivalent conductance and dilution values used in the construction of the plots are summarized in tables 1-A to 1-J in Appendix 1-B.

Table 1-I summarizes the equilibrium results derived from the conductivity data. Experimental equilibrium constants, ($K_{exp.}$), for the process of the dissociation of ion pairs depicted by

$$(\dot{M}\tilde{X})^o \rightleftharpoons M^+ + X^-$$

and limiting equivalent conductance values (Λ_o) were evaluated by the extrapolation procedure described by Shedlovsky (117) and discussed by Fuoss and Shedlovsky (45).

Shedlovsky Extrapolation Method

The method involves the solution of the equation

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \frac{C\Lambda S(z) f_1^2}{K(\Lambda_o)^2} \qquad (1\text{-}1$$

in which the Shedlovsky function, S(z), is defined by the

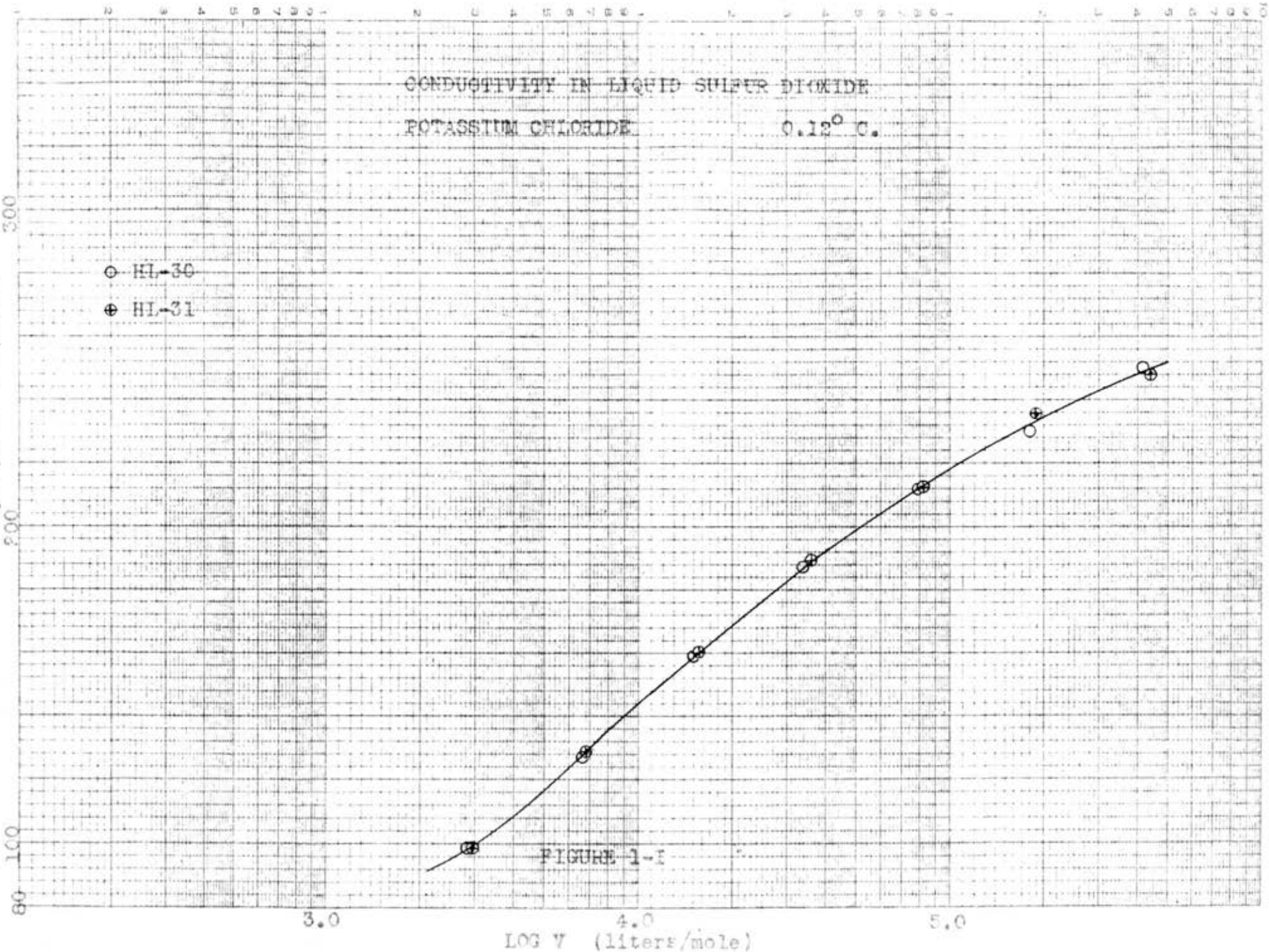

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
POTASSIUM CHLORIDE 0.12° C.
HI-30
HI-31
Λ (mhos cm.²/mole)
300
200
100
80
3.0
4.0
5.0
LOG V (liters/mole)

FIGURE 1-I

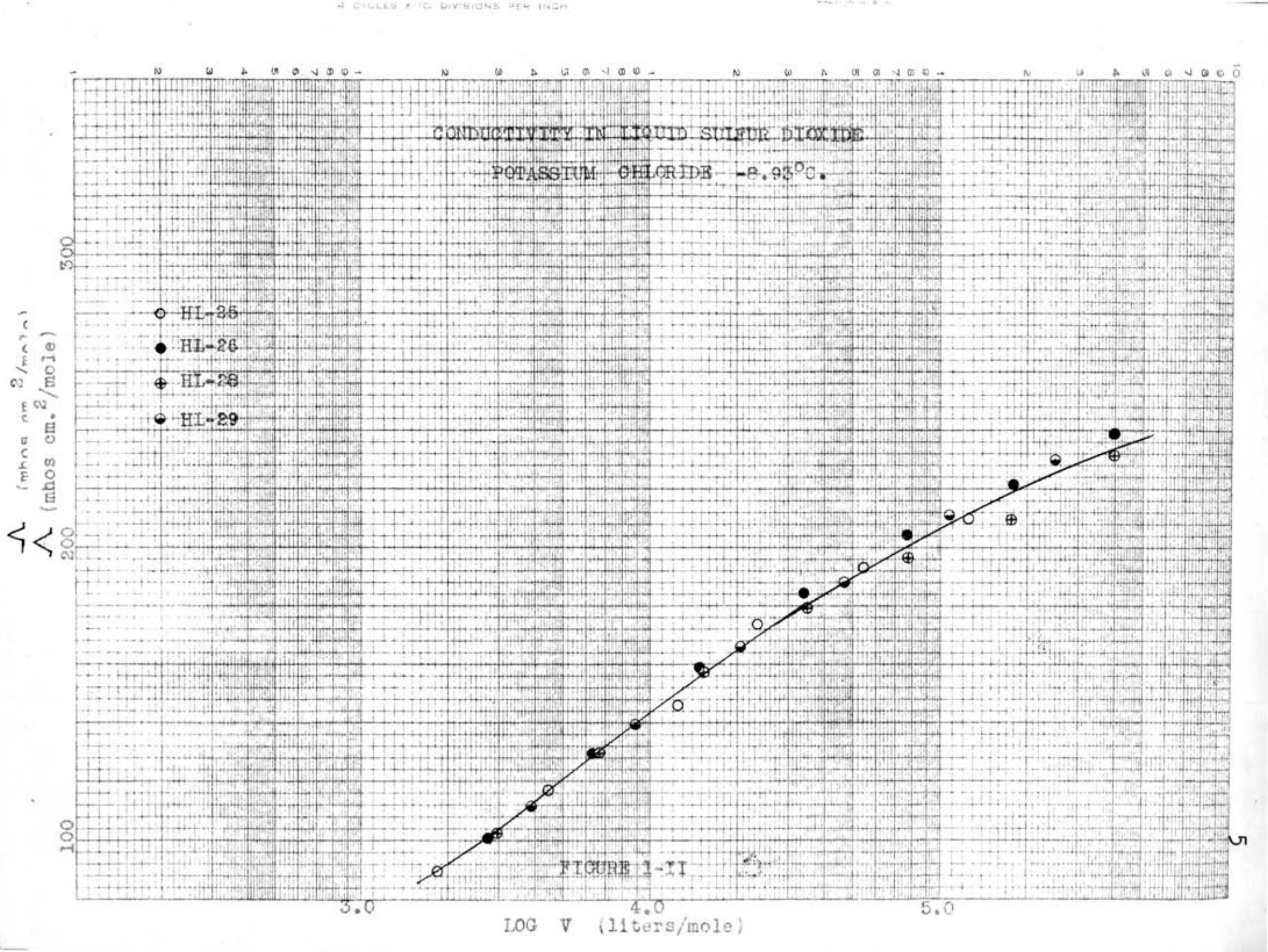

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
POTASSIUM CHLORIDE -8.93°C.
HL-25
HL-26
HL-28
HL-29
300
200
100
(mhos cm.²/mole)
3.0
4.0
5.0
LOG V (liters/mole)

FIGURE 1-XI

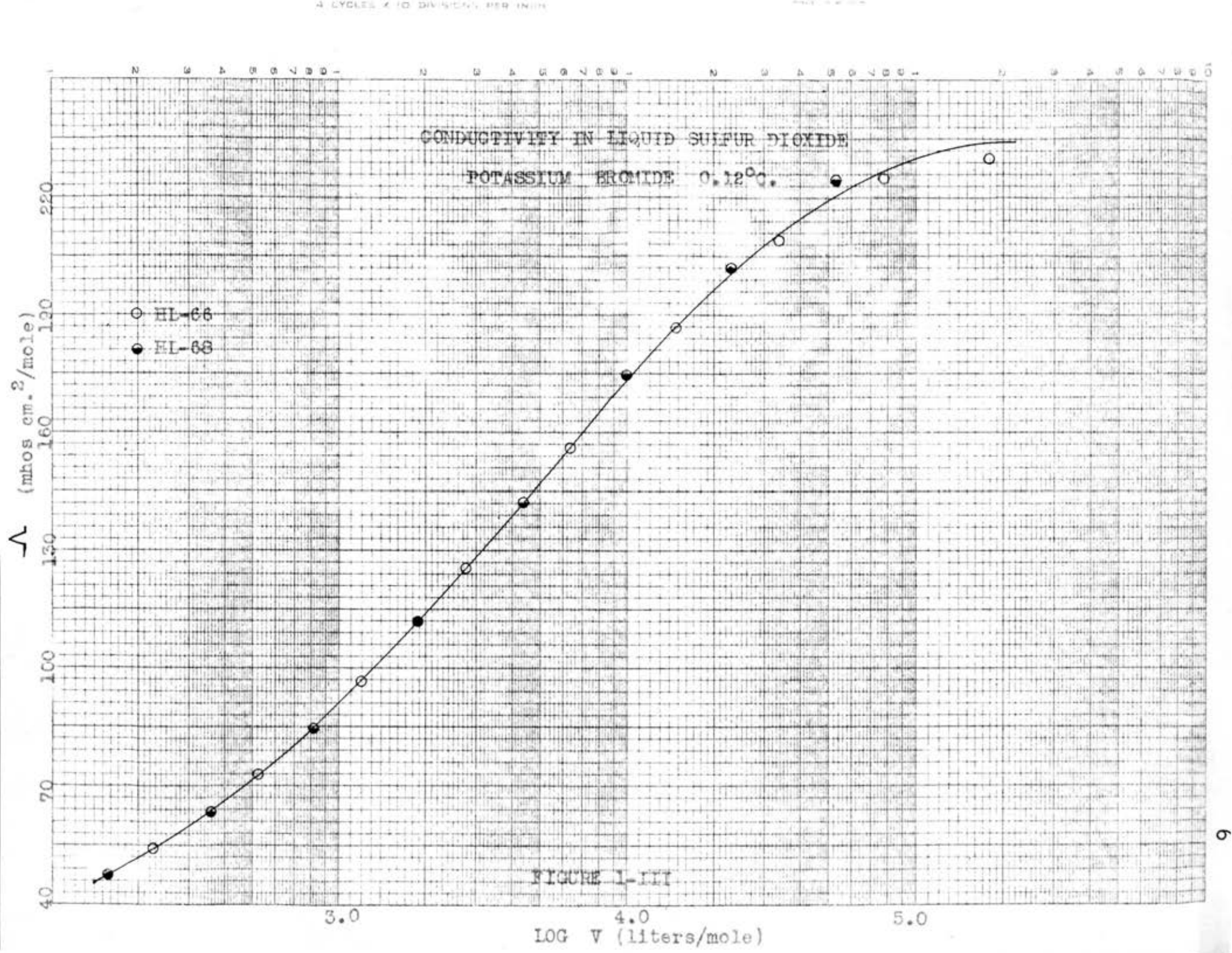

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
POTASSIUM BROMIDE 0.12°C.
HL-66
HL-68
Λ (mhos cm.²/mole)
40
70
100
130
160
120
220
3.0
4.0
5.0
LOG V (liters/mole)

FIGURE I-III

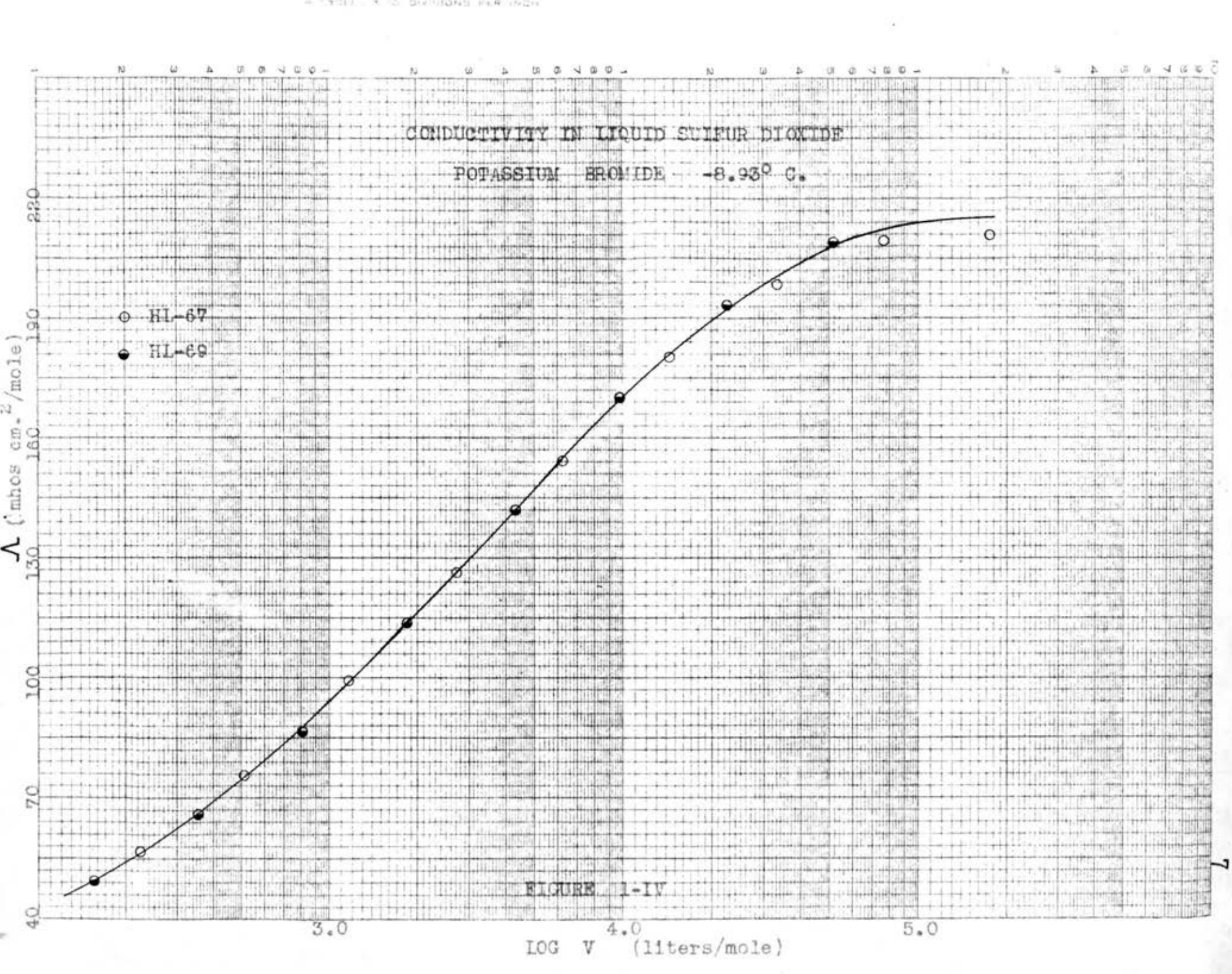

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
POTASSIUM BROMIDE -8.93° C.
HL-67
HL-69
Λ (mhos cm.²/mole)
40
70
100
130
160
190
220
3.0
4.0
5.0
LOG V (liters/mole)

FIGURE 1-IV

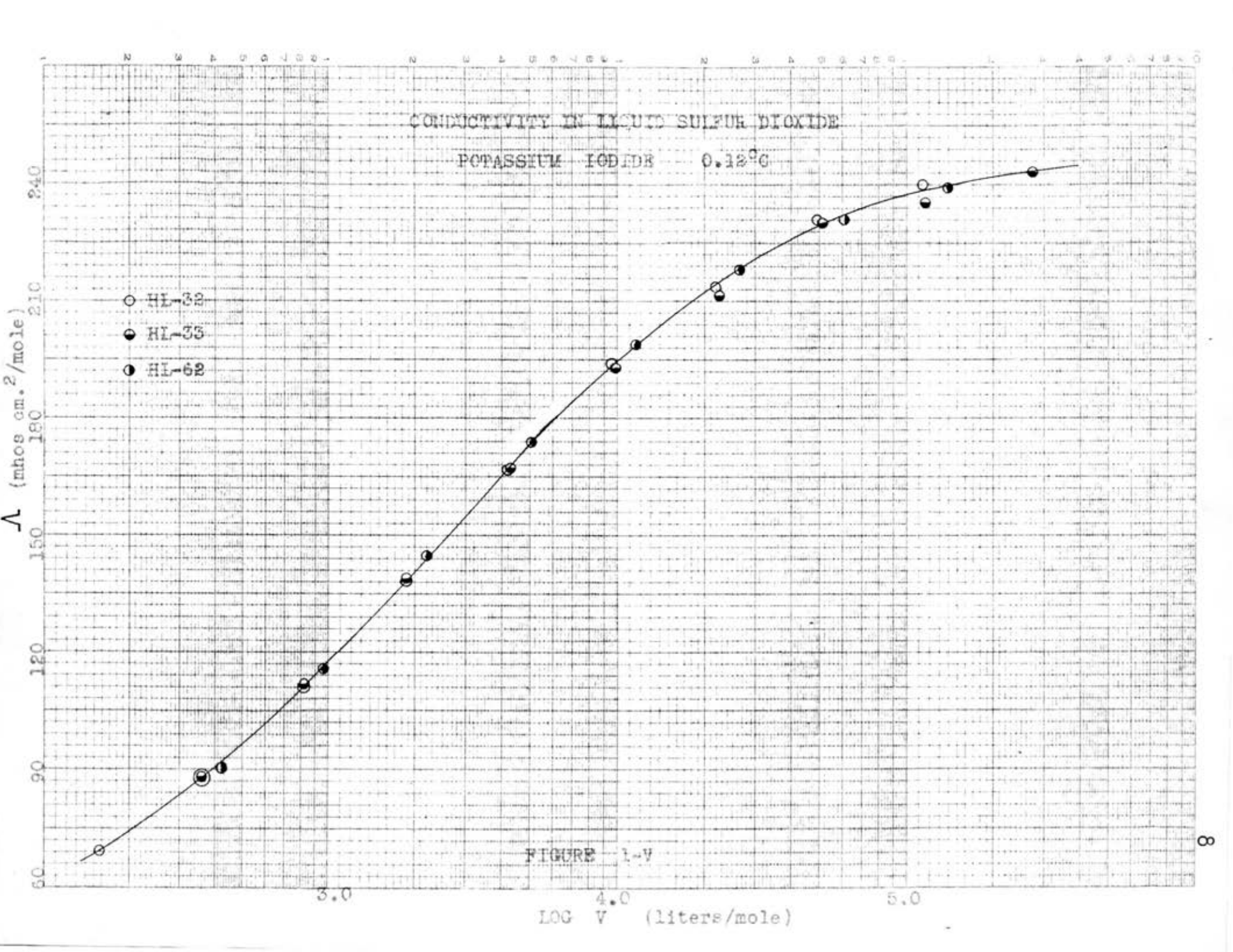

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
POTASSIUM IODIDE 0.12°C
HL-32
HL-33
HL-62
Λ (mhos cm.²/mole)
LOG V (liters/mole)
3.0
4.0
5.0
50
90
120
150
180
210
240

FIGURE 1-V

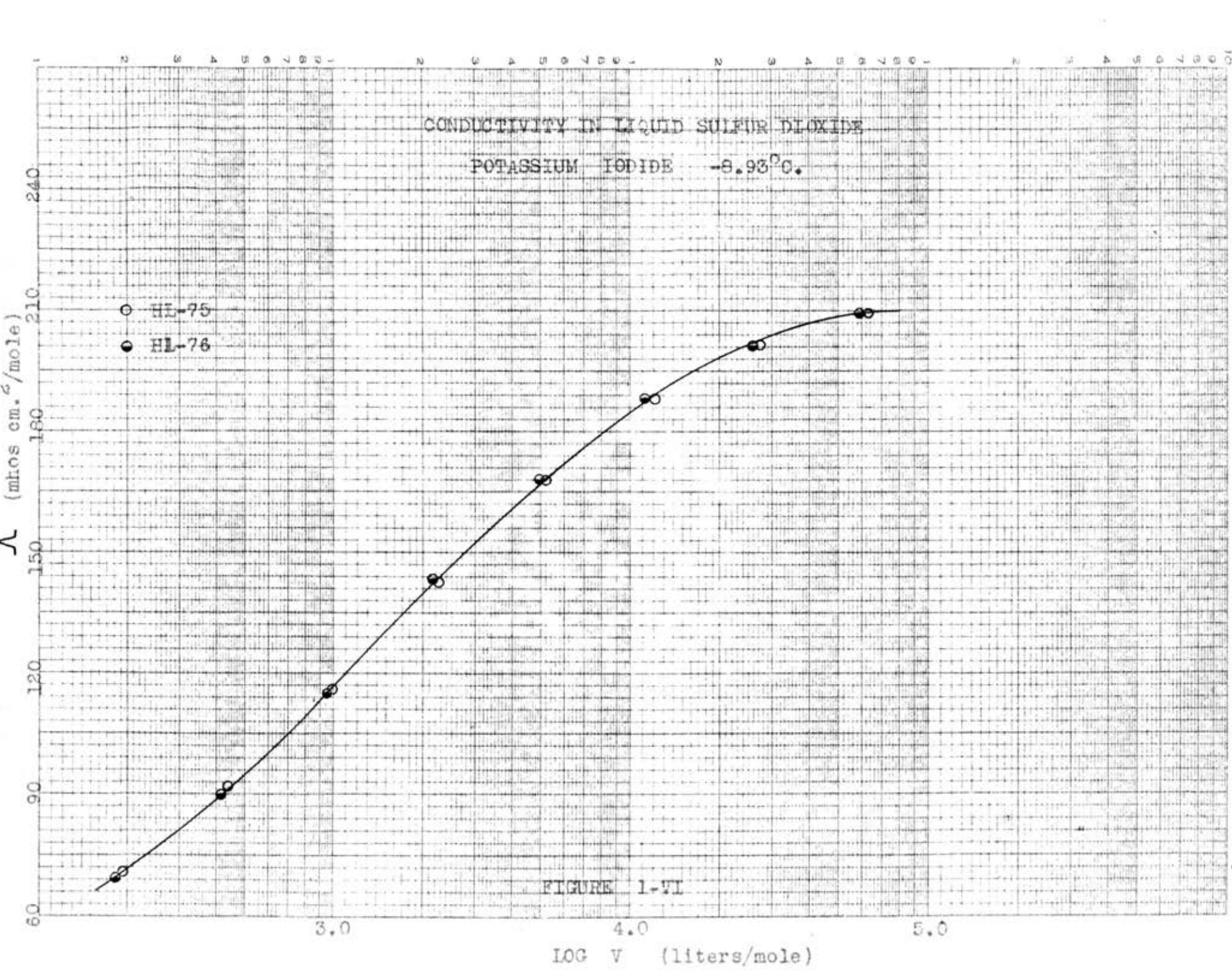

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
POTASSIUM IODIDE -8.93°C.
HL-75
HL-76
Λ (mhos cm.²/mole)
240
210
180
150
120
90
60
3.0
4.0
5.0
LOG V (liters/mole)

FIGURE 1-VI

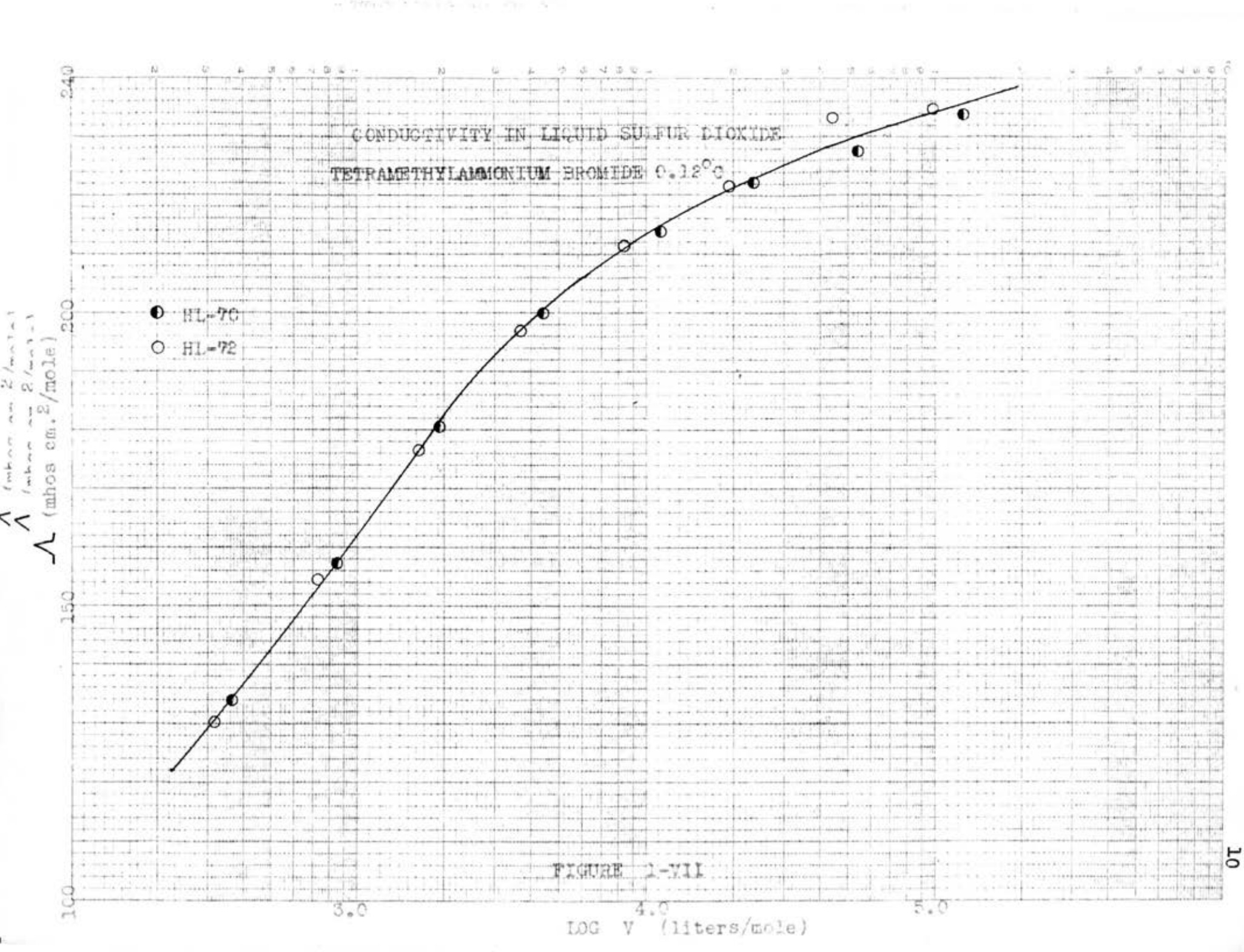

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
TETRAMETHYLAMMONIUM BROMIDE 0.12°C
HL-70
HL-72
Λ (mhos cm.²/mole)
240
200
150
100
3.0
4.0
5.0
LOG V (liters/mole)

FIGURE 2-VII

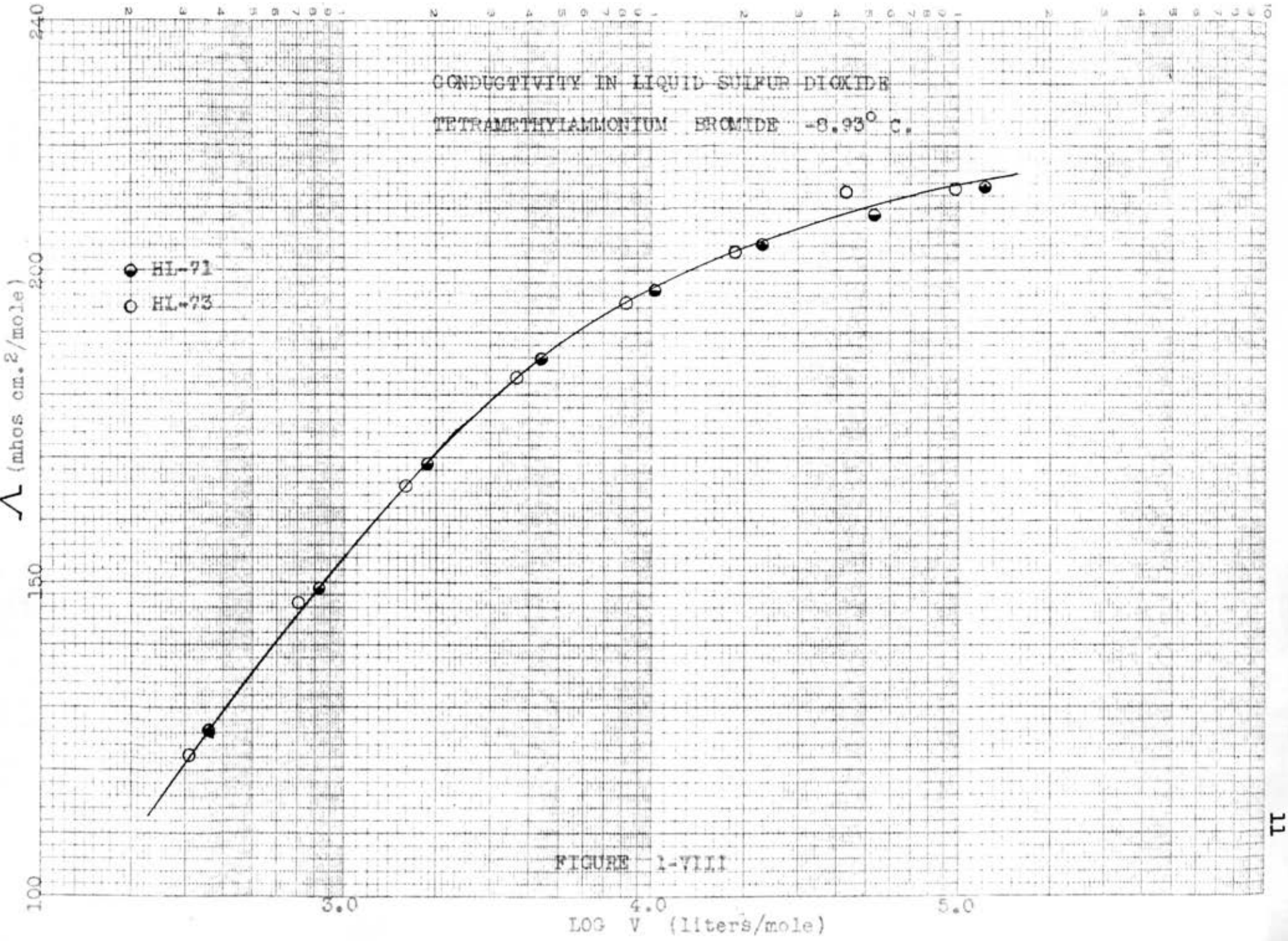


FIGURE 1-VIII

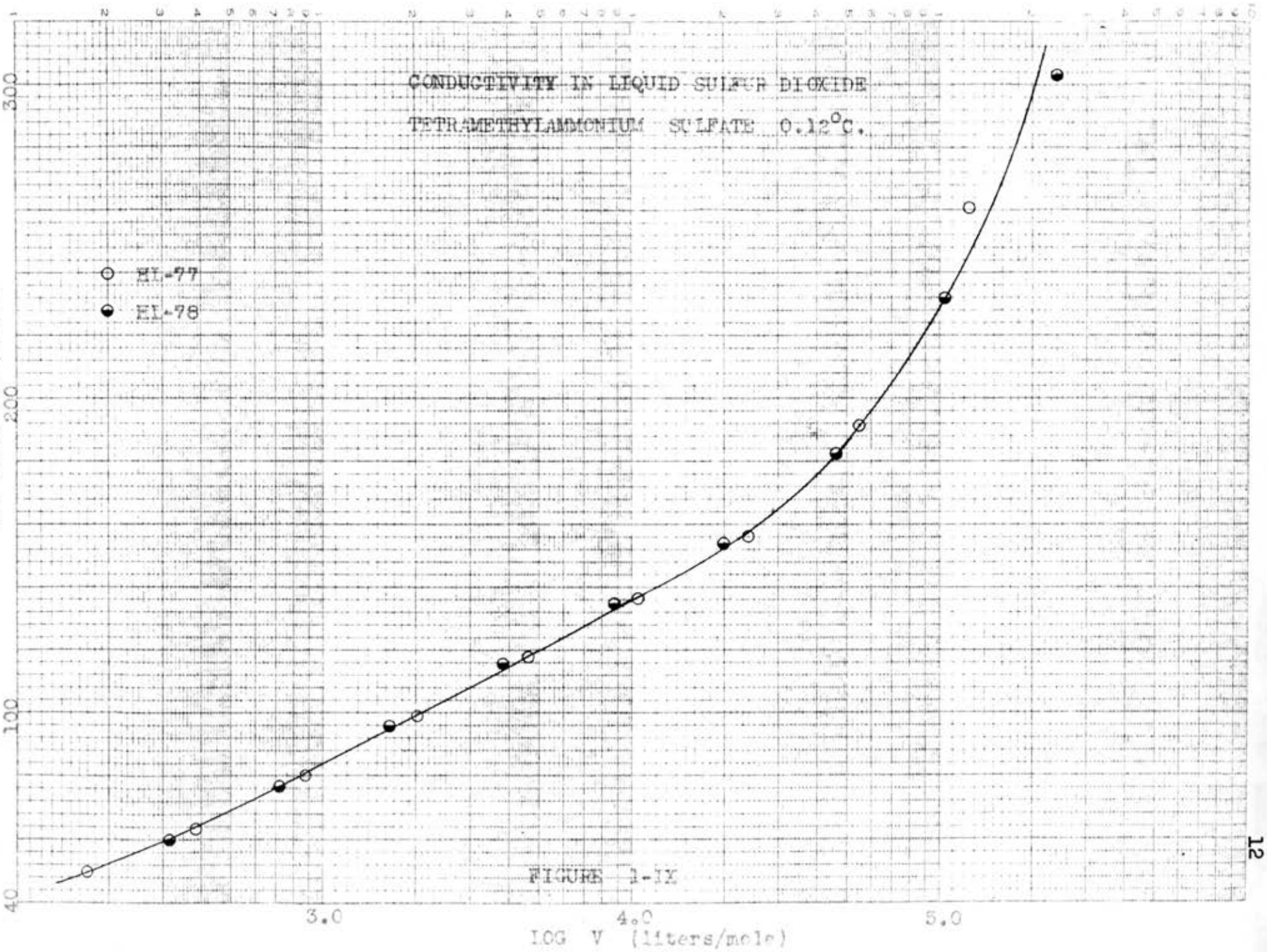

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
TETRAMETHYLAMMONIUM SULFATE 0.12°C.
EI-77
EI-78
Λ (mhos cm.²/mole)
300
200
100
40
3.0
4.0
5.0
LOG V (liters/mole)

FIGURE 1-IX

TABLE 1-I

.Summary of Equilibrium Data in Liquid Sulfur Dioxide.

Compound	Temp. (°C.)	Λ_o (mhos-cm.^{2}/mole)	$10^5 K_{exp.}$	ΔF^o (K-cal/mole)	$\Delta H^{o(a)}$ K-cal./mole	ΔS^o (cal/°-mole)
KCl	0.12	$243._4$	7.43_5	5.16	-5.92	-40.6
KCl	-8.93	$222._1$	10.7_8	4.80	-5.92	-40.6
KBr	0.12	$248._9$	14.3_1	4.81	-5.26	-37.0
KBr	-8.93	$228._0$	19.9_0	4.48	-5.26	-37.0
KI	0.12	$243._7$	30.1_0	4.40	-5.60	-36.7
KI	-8.93	220.8	42.7_7	4.08	-5.60	-36.7
$(CH_3)_4NBr$	0.12	$235._5$	118.4	3.66	-3.36	-25.7
$(CH_3)_4NBr$	-8.93	$215._0$	$146._2$	3.43	-3.36	-25.7

(a) Calculated by the integrated Van't Hoff equation assuming ΔH^o is temperature independent over the interval 0.12° to -8.93° C.

relationship(*)

$$S(z) = \left[\frac{z}{2} + \sqrt{1 + \left(\frac{z}{2}\right)^2}\right]^2 \qquad (1\text{-}2$$

where the variable z is defined as

$$z \qquad \frac{\alpha^* \Lambda_o + \beta}{(\Lambda_o)^{3/2}} \sqrt{c} \qquad (1\text{-}3$$

Values of the fuction S(z) were obtained directly from tables of S(z) as a function of z in the range $0.000 \leq z \leq 0.209$ which were computed by Daggett (27) from the expanded form of equation 1-2, namely

$$S(z) = 1 + z + z^2/2 + z^3/8 - z^5/128 + z^7/1024 \qquad (1\text{-}4$$

Although Daggett neglected terms higher than z^2 in evaluating S(z), it can be shown (118) that for the values of z considered this simplification introduces an error not greater than plus or minus one in the fourth decimal.

The variable z was calculated using equation 1-3, where

$$\alpha^* = \frac{1.9806 \times 10^6}{(DT)^{3/2}} \left(\frac{q^*}{1 + \sqrt{q^*}}\right) |Z_1 Z_2| \frac{1}{\nu} \left(\sum_i^P \nu_i Z_i^2\right)^{3/2} \qquad (1\text{-}5$$

(*) In order to avoid confusion, all symbols and conventions used in this dissertation were chosen to conform with those used by Harned and Owen (59). The reader is referred to appendix I-A for a complete description of all symbols.

In the above equation q* is defined by the relationship

$$q^* = \frac{|Z_1 Z_2|}{(|Z_1| + |Z_2|)} \frac{(\lambda_1^\circ + \lambda_2^\circ)}{(|Z_1|\lambda_1^\circ + |Z_2|\lambda_2^\circ)} \qquad (1\text{-}6$$

For the special case of symmetrical uni-univalent electrolytes where $Z_1 = Z_2 = 1$, equation 1-6 reduces to

$$q^* = 1/2 \qquad (1\text{-}7$$

and the other terms in equation 1-5 become

$$\left(\frac{q^*}{1 + \sqrt{q^*}}\right) = 0.2929 \qquad (1\text{-}8$$

and

$$\frac{1}{\nu}\left(\sum_1^P \nu_i Z_i^2\right)^{3/2} = \sqrt{2} \qquad (1\text{-}9$$

so that equation 1-5 becomes

$$\alpha^* = \frac{8.2023 \times 10^5}{(DT)^{3/2}} \qquad (1\text{-}10$$

The second Shedlovsky coefficient in equation 1-3 is defined

$$\beta^* = \frac{29.143\,(|Z_1| + |Z_2|)}{\eta\,(DT)^{\frac{1}{2}}}\, w' \qquad (1\text{-}11$$

in which

$$w' = (\nu |Z_1 Z_2|)^{\frac{1}{2}} \qquad (1\text{-}12$$

Equation 1-12 becomes $w' = \sqrt{2}$ for symmetrical 1-1 electrolytes so that 1-11 can be written

$$\beta^* = \frac{82.42}{\eta (DT)^{\frac{1}{2}}} \qquad (1\text{-}13$$

Numerical values for the important constants α^* and β^* have been calculated for 1-1 electrolytes is liquid sulfur dioxide at the several temperatures employed in this research. In table 1-II these values are tabulated along with the values calculated for the limiting slopes , $S_{f_\pm}$, of the Debye-Huckel limiting law (28,60) for the activity coefficient which were calculated from the equation

$$- \log f_\pm = S_{f_\pm} \sqrt{c\theta} \qquad (1\text{-}14$$

where

$$S_{f_\pm} = \frac{1.8243 \times 10^6}{(DT)^{3/2}} \; ; \text{ and } \quad \theta = \frac{\Lambda_{S(z)}}{\Lambda_o} \qquad (1\text{-}15$$

TABLE 1-II

Shedlovsky and Debye-Huckel Coefficients
(1-1 electrolytes in sulfur dioxide)

Temperature (°C.)	α^*	β^*	$S_{f_\pm}$
10.0	3.160	352.1	7.027
0.12	3.019	316.1	6.713
0.00	3.018	315.7	6.711
-8.93	2.901	288.7	6.452
-10.0	2.888	285.6	6.422
-17.0	2.804	267.0	6.235
-20.0	2.769	259.8	6.158
-33.5	2.625	231.6	5.839

The above data may be used for the construction of plots of α^*, β^*, and S_{f_t} as a function of temperature. These data give smooth curves of very gradual curvature which may be employed for the evaluation of the Shedlovsky and Debye-Huckel coefficients at any temperature in the range $\neq 10^\circ$ to -33.5°C.

Values of the variable z were calculated by equation 1-3 for various assumed values of Λ_o employing the coefficients given in table 1-II.

Physical Properties of Liquid Sulfur Dioxide

Dielectric Constant: Vierk's (125) data for the dielectric constant of liquid sulfur dioxide at various temperatures between -16.5°C. and -68.8°C. were treated by the method of least mean squares to obtain an analytical expression for the variation of the dielectric constant with temperature. The expression was of the form of the Abegg (1) equation

$$D = Ce^{-LT} \qquad (1\text{-}16$$

where C and L are constants and T is the absolute temperature.

The best fit was obtained when $C = 95.12$ and $L = 6.676 \times 10^{-3}$. All of the data in the reported range fit this equation with a mean deviation from the calculated curve of plus or minus 0.32%. Extension of this equation somewhat beyond its range of validity gave the values for D at $\neq 10^\circ$, 0.12°, and -8.93°C. of 14.37, 15.35, and 16.30 respectively. It should be

noted that the value obtained in this way for 0.12°C. is in fairly good agreement with the values of 15.08 reported by LeFevre and Ross (86) and 15.6 reported by I.C.T. (67) at 0°C. The latter values were not used in this work however, since it was desirable for internal consistency to use constants from one source for all computations. Further comparison with available data show good agreement at other temperatures; e.g., at 14.50°C. Coolidge (26) gives 13.75 while the value calculated by equation 1-16 is 13.95. At 22°C. Schlunt (113) found 12.35 as compared to 11.66 calculated. It should be pointed out however, that Schlunt's value is based on only one determination. Values obtained from equation 1-16 may be considered accurate to 2% or better on the basis of Maryott and Smith's (98) estimate of the accuracy of Vierk's data.

Viscosity: Viscosity data for liquid sulfur dioxide at the temperatures of the measurements were obtained from the data of Luchinskii (95). These data were treated by the method of least squares to give an expression

$$1000\,\eta = 4.03 - 0.0363\ T\ (^{\circ}C.) \qquad (1\text{-}17$$

for the variation of viscosity with temperature. The mean deviation of the individual experimental points from the best fitting line was $\pm 0.36\%$. Values calculated from equation 1-17 are in good agreement with the values given in I.C.T. (68); e.g., at 0°C. and -17°C., I.C.T gives 0.00394 and 0.00455 poise respectively while the calculated values are 0.00403 and 0.00455.

For reasons of internal consistency only viscosity values calculated from equation 1-17 were used in the computations.

The values of dielectric constant and viscosity of liquid sulfur dioxide used in this research are summarized below.

TABLE 1-III

Summary of Dielectric Constant and Viscosity Data[(a)]
(Liquid Sulfur Dioxide)

Temperature (°C.)	D	η (Millipoise)
10.00	14.37	3.67
0.12	15.35	4.02
0.00	15.36	4.03
-8.93	16.30	4.35
-10.00	16.42	4.39
-17.00	17.20	4.65
-20.00	17.55	4.76
-33.50	19.21	5.24

(a) The experimental data of Vierk and of Luchinskii, upon which the above values are based, are summarized in Appendix I-C.

Shedlovsky Calculations

Examination of equation 1-1 shows that a plot of $1/\Lambda S(z)$ versus $C\Lambda S(z)f_{\pm}^2$ should be a straight line with a slope of $1/K\Lambda_o^2$ and intercept of $1/\Lambda_o$. Since, however, the Shedlovsky variable z (equation 1-3) and also the activity coefficient (equation 1-14) are functions of Λ_o; the evaluation of Λ_o by the Shedlovsky method will require a series of approximations which may begin with a rough value of Λ_o obtained by extrapolation of Λ versus $\sqrt{C}$ plots, or by the application of Walden's (127) Rule. This preliminary value of Λ_o leads to approximate values of z and the degree of dissociation, θ. These values of θ are then used to estimate the activity coefficients by the Debye Huckel limiting law (equation 1-14).

A plot of $1/\Lambda S(z)$ versus $\Lambda CS(z)f_{\pm}^2$ constructed on the basis of the first approximation values of z and $f_{\pm}$ can be extrapolated to C=0 to afford a new value of Λ_o from which more accurate values of z and $f_{\pm}$ may be obtained and a new plot constructed. This process is repeated until a value of Λ_o is obtained which is identical with that used to evaluate θ and z, and K is derived from the slope found in this plot.

In the application of the Shedlovsky method to the data obtained in this research several factors influencing the final derived values had to be evaluated. In general all of the experimental data from the several runs on a particular compound were used in the calculations and the extrapolation

to infinite dilution was carried out by applying the method of least mean squares to the calculated variables $1/\Lambda S(z)$ and $C\Lambda S(z)f_{\pm}^2$. Mean deviations of the experimental points from the best fit straight line were calculated and it was found that in general the largest deviations occured in the regions corresponding to the most, and least concentrated solutions.

The sensitivity of the intercept to variation of the concentration range used in the calculations was explored. It was found that data above 80,000 liters per mole and below about 2000 liters per mole exhibited the greatest influence on the Λ_0 value obtained by extrapolation. Table 1-IV gives a summary of Λ_0 values obtained for tri-m-biphenylylchloromethane as a function of the concentration range employed in the calculation.

TABLE 1-IV

Variation of Λ_0 with Concentration Range Employed in the Shedlovsky Calculation for Tri-m-biphenylylchloromethane in Sulfur Dioxide Solution at -8.93°C.

Conc. Range (liters/mole)	Λ_0 (mhos-cm.^{2}/m.)	Conc. Range (liters/mole)	Λ_0 (mhos-cm.^{2}/m.)
500-80,000	167.8	2000-80,000	158.0
1600-80,000	162.2	5000-80,000	158.5

These data suggest that equation 1-1 is linear only over a limited concentration region.

Concentration Limits of Shedlovsky Equation

Theoretically the Shedlovsky equation should be most nearly valid at high dilutions merely as a result of the use

in its derivation of the Debye-Huckel limiting law for activity coefficients and the Onsager limiting law for conductance which are valid only in the more dilute regions. Experimentally, however, an upper dilution limit must be imposed in order to minimize errors due to uncertainties in the solvent correction inherent in measurements at high dilution. In this research the solvent conductance often amounted to more than 10% of the total conductance. An estimate, of the accuracy of the experimental value for solvent conductance leads to a value of ±10%. Thus the error due to solvent correction, when 10% of the total conductance is due to that of the solvent , can be greater than ±1% in most cases. For this reason it was decided to limit the dilution range so that in no case would the solvent conductance amount to more than 5-10% of the total conductance. Thus uncertainties due to this source would be of the order of 0.5-1.0% for the most dilute data employed in the calculations. An examination of the experimental conductance data (see tables 1-A to 1-J, in appendix I-B and figures 1-I to 1-IX) shows that this requirement is fulfilled by data in the dilution region of less than 80,000 liters per mole. This value then was chosen as the upper limit of dilution and only data below this limit were used in the calculations.

A high concentration limit of applicability of the Shedlovsky treatment for 1-1 electrolyte solutions in sulfur dioxide cannot be established without extensive and very precise experimental data. Since such data are not available

for sulfur dioxide solutions it will be necessary to resort to data in other solvents as well as to indirect and essentially intuitive reasoning which may be based qualitatively on the several approximations involved in the derivation of this equation.

First it can be argued that the limit selected should be as low as is compatible with experimental and statistical restrictions. In this respect it must be remembered that statistically it is desireable to include the largest possible number of experimental points in the calculations. If, then, we arbitrarily select five as being a reasonable number of points to retain from each run we find that, according to the experimental procedures employed in the measurements and the low concentration limit (1.25×10^{-5} moles per liter) imposed earlier for experimental reasons, the high concentration limit cannot be much smaller than 10^{-3} moles per liter.

Since the Shedlovsky equation is but an empirical extension of the Onsager limiting law for conductance we may explore the concentration limits of the latter in order to cast some light on the limits to be expected for the extended equation. In this respect it can be noted that Shedlovsky (117) concluded that the Onsager relationship is linear up to a concentration of 0.001 to 0.002 N. for 1-1 electrolytes in water. While it is true that the Shedlovsky equation represents the conductance data to concentrations greater than 10^{-3} N. for water solutions of 1-1 electrolytes it does not necessarily follow that this

will also be the case for solutions in solvents of low dielectric constant. Thus, for example, Fuoss (41) has concluded that his extension of the Onsager equation

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda_0} + \left[\frac{c\Lambda f_\pm^2/F(z)}{K\Lambda_0^2}\right] \qquad (1\text{-}18$$

will give a linear plot for 1-1 electrolytes up to a concentration not greater than 3×10^{-7} D. For liquid sulfur dioxide this corresponds to a concentration of 1.2×10^{-3} liters per mole at 0°C.

One further source of error in the Shedlovsky equation can be considered, namely, the errors introduced in the activity coefficients calculated by the approximate form of the Debye-Huckel limiting law. Fowler and Guggenheim (37) point out that, in water even at concentrations as low as 0.001 molar, errors in activity coefficients calculated by the limiting law are not negligible. Certainly if this approximation gives rise to appreciable errors at concentrations as low as 10^{-3} molar for aqueous solutions it must introduce more serious errors at this concentration in solvents of low dielectric constant where departures from the limiting law are known (54) to be greater.

In view of the above considerations and of the extraordinary sensitivity of the extrapolated results to conductance data from solutions more concentrated than 5×10^{-4} moles per liter it is possible to arrive at a reasonable high concentration limit. The value selected is 5×10^{-4} moles per liter or 2000 liters per mole dilution which, it should be pointed out, is

at best a first approximation. This value was chosen, however, since the experimental limitations, e.g. cell dimensions etc., were such as to make a more restricted dilution range impractical. In future work experiments should be designed to afford sufficient data over a much more restricted concentration range; e.g. 1×10^{-4} to 2×10^{-5} moles per liter.

The results summarized in table 1-I were obtained by applying the method of Shedlovsky to the experimental conductance data over the range of 2000 to 80000 liters per mole. The extrapolation was performed by the method of least squares to give values of the slope, "b"= $\frac{1}{K\Lambda_o^2}$ and the intercept, "a"= $\frac{1}{\Lambda o}$.

Deviations of the experimental points from the least square line were calculated in each case and mean deviations for the data of each compound were thus obtained. Values of the least square constants "a" and "b" and the mean deviations are summarized in table 1-V.

Table 1-VI presents the data of a typical Shedlovsky and least mean squares calculation and figure 1-X shows a plot of these data.

In addition to the data of this research, the data of Franklin (38) for potassium iodide and bromide at several temperatures have been treated by the above methods to obtain thermodynamic equilibrium constants and limiting conductance values. The results of these calculations are summarized in table 1-VII and the least square constants in table 1-VIII.

TABLE 1-V

Least Mean Square Parameters for Shedlovsky Plots.

(Alkali Halides in Sulfur Dioxide Solution.)

Compound	Temp. (°C.)	$10^3/\Lambda_o$ (intercept)	$10^2/K\Lambda_o^2$ (slope)	Mean dev. (+-%)
KCl	0.12	4.11	22.7	0.23
KCl	-8.93	4.50	18.8	1.03
KBr	0.12	4.02	11.3	0.62
KBr	-8.93	4.39	9.67	0.64
KI	0.12	4.10	5.59	0.57
KI	-8.93	4.53	4.80	0.71
$(CH_3)_4NBr$	0.12	4.25	1.52	0.24
$(CH_3)_4NBr$	-8.93	4.65	1.48	0.16

TABLE 1-VI

A Typical Shedlovsky Calculation.

Potassium Bromide[a] in Liquid Sulfur Dioxide at 0.12°C.

$10^4 C$	Λ [c]	$\sqrt{\Lambda C}$ x 10^2	$z = 0.2726/\sqrt{\Lambda C}$	$S(z)$ [b]	$C\theta$ x 10^6	$\sqrt{C\theta}$ x 10^3	$1 + \log f_\pm^2 = (1 - 13.43\sqrt{C\theta})$	$f_\pm^2$	$1/\Lambda S(z)$ ("Y") x 10^3	$C\Lambda S(z) f$ ("X") x 10^2
5.269	111.8	24.27	0.0662	1.0684	253.8	15.93	0.7862	0.6113	8.371	3.848
3.601	125.4	21.25	0.0579	1.0597	193.0	13.89	0.8136	0.6510	7.524	3.116
2.291	142.2	18.05	0.0492	1.0504	138.0	11.75	0.8423	0.6955	6.695	2.380
1.564	156.2	15.63	0.0426	1.0435	102.8	10.14	0.8639	0.7310	6.136	1.863
0.9960	174.4	13.18	0.0359	1.0366	72.58	8.519	0.8857	0.7686	5.533	1.383
0.6793	186.5	11.26	0.0307	1.0312	52.66	7.257	0.9026	0.7991	5.201	1.044
0.4331	202.1	9.356	0.0255	1.0258	36.20	6.017	0.9192	0.8303	4.823	0.746
0.2950	209.2	7.856	0.0214	1.0216	25.42	5.042	0.9323	0.8557	4.680	0.539
0.1880	224.3	6.494	0.0177	1.0178	17.30	4.159	0.9442	0.8794	4.380	0.377
0.1281	225.2	5.371	0.0146	1.0147	11.80	3.435	0.9539	0.8993	4.376	0.263

Least Mean Square Calculation:

$\Sigma"X" = 0.15559$ $\Sigma"Y" = 0.057719$ $\Sigma"X"^2 = 0.0037713$ $\Sigma"XY" = 0.0010503$ $n = 10$

$$na + b\Sigma"X" = \Sigma"Y"$$
$$a\Sigma"X" + b\Sigma"X"^2 = \Sigma"XY"$$

Solving for a and b gives:

$a = 0.004017$ $\Lambda_o = 248.9$

$b = 0.1128$ $K_{exp.} = 1.431 \times 10^{-4}$

(a) Data from runs HL-66, and 68.

(b) Daggett's Table, reference 27.

(c) Λ_o assumed to be 248 for this calculation.

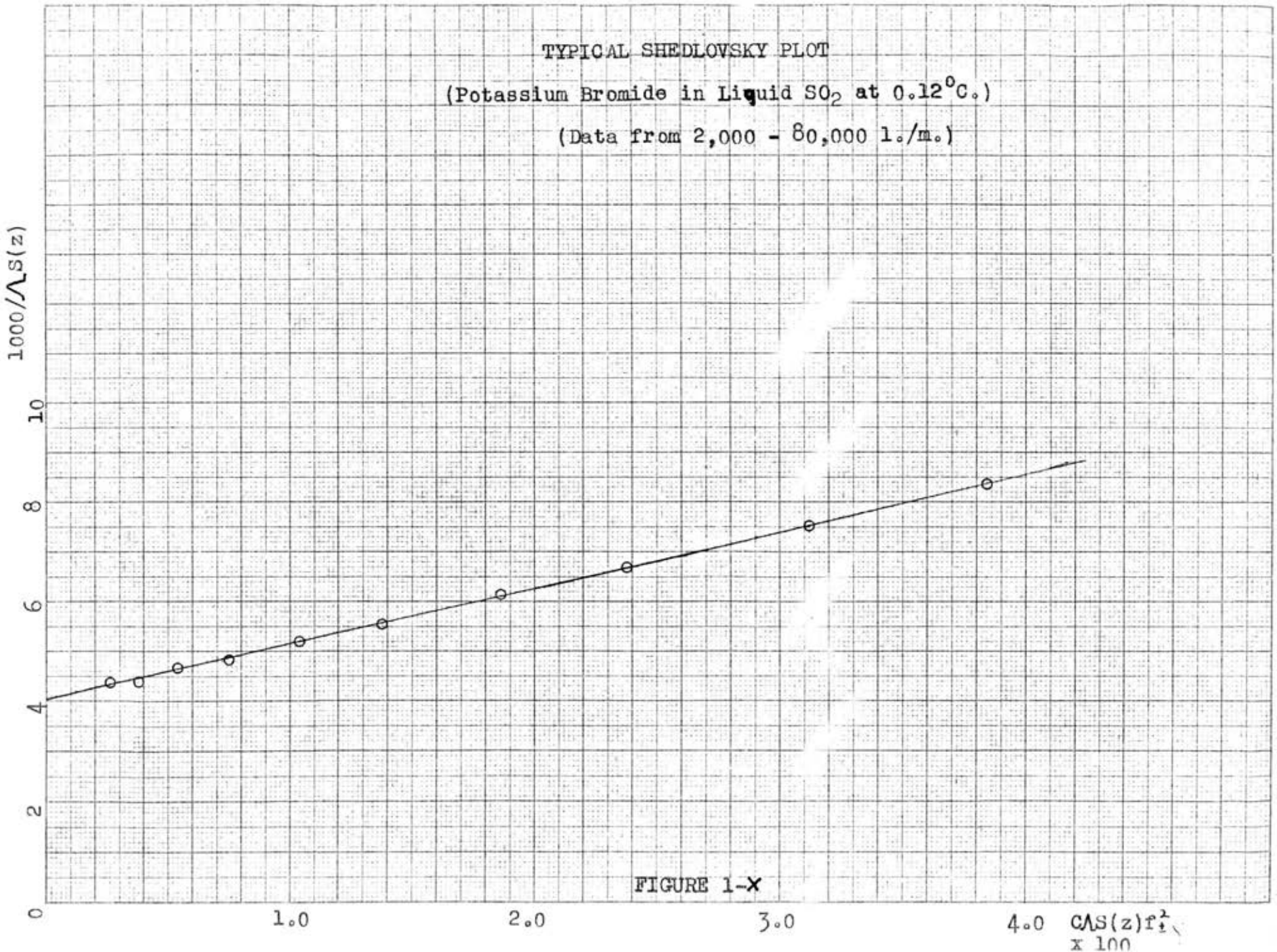


FIGURE 1-X

TABLE 1-VII

Summary of Equilibrium Results Based on the Conductance Data of Franklin (38).

Compound	Temp. (°C.)	Λ_o (mhos-cm.^{2}/m.)	K x 10^5	ΔF^o (K-cal./m.)	ΔH^o (K-cal./m.
KBr	10.0	309.1	7.42	5.35	-----
"	0.0	267.4	12.4	4.98	-4.91[a]
"	-10.0	237.1	18.5	4.49	-8.50[b]
"	-20.0	206.6	28.8	4.10	-5.86[c]
"	-33.5	190.0	34.5	3.79	-1.53[d]
KI	10.0	272.3	21.0	4.76	-----
"	0.0	247.3	29.3	4.41	-5.10[a]
"	-10.0	228.5	37.8	4.12	-3.66[b]
"	-20.0	204.4	49.0	3.83	-3.41[c]
"	-33.5	179.2	65.7	3.49	-2.51[d]

ΔH^o values were calculated bt the integrated Van't Hoff equation over the interval (a) 10.0° to 0.0°C. (b) 0.0° to -10.0°C. (c) -10.0° to -20.0°C. (d) -20.0° to -33.5°C.)

TABLE 1-VIII

Least Mean Square Parameters for Shedlovsky Plots.

(Data of Franklin (38) in Liquid Sulfur Dioxide.)

Compound	Temp. (°C.)	$10^3/\Lambda_o$ (intercept)	$10^2/K\Lambda_o$ (slope)	Mean dev. d (±%)
KBr[a]	10.0	3.235	14.10	0.21
"	0.0	3.740	11.31	0.29
"	-10.0	4.217	9.60	0.16
"	-20.0	4.841	8.12	0.21
"	-33.5	5.264	8.03	0.15
KI[b]	10.0	3.672	6.41	0.60
"	0.0	4.043	5.58	0.40
"	-10.0	4.376	5.06	0.23
"	-20.0	4.891	4.89	0.76
"	-33.5	5.581	4.74	0.40

(a) Six experimental points in the region 1000 to 4800 l./m. were used in the Shedlovsky calculation for this compound.

(b) Nine experimental points in the region 1000 to 12,000 l./m. were used in the Shedlovsky calculation for this compound.

Precision and Reliability of The Data.

The precision of the conductance data of this research as estimated either from the mean deviations of the experimental points from the best fitting smooth curve or from the mean deviations of the Shedlovsky plots is better than plus or minus one percent over the entire dilution range for each compound. Comparison of the data for potassium iodide and bromide at 0.12°C. with Franklin's 0°C. data for these compounds permits an estimate of the accuracy of the internal dilution technique. Franklin estimated his data to be precise to ±0.1% and accurate to about 0.5% with greater accuracy at high dilutions. Figure (1-XI) shows a plot of Franklin's data and of the data of this research for potassium iodide at 0°C. Excellent agreement exists between the data obtained by the two different methods over the entire dilution range in which comparison is possible.

A comparison of the derived equilibrium constants and limiting conductance values calculated from the data of this research (table 1-I) and from Franklin's data (table 1-VII) shows good agreement at 0°C. only for potassium iodide. In the case of potassium bromide rather poor agreement exists. Direct comparison of experimental data for this compound fails to account for the poor agreement of the extrapolated values. This discrepancy can, however, be explained on the basis of the limitations of the extrapolation procedure discussed earlier.

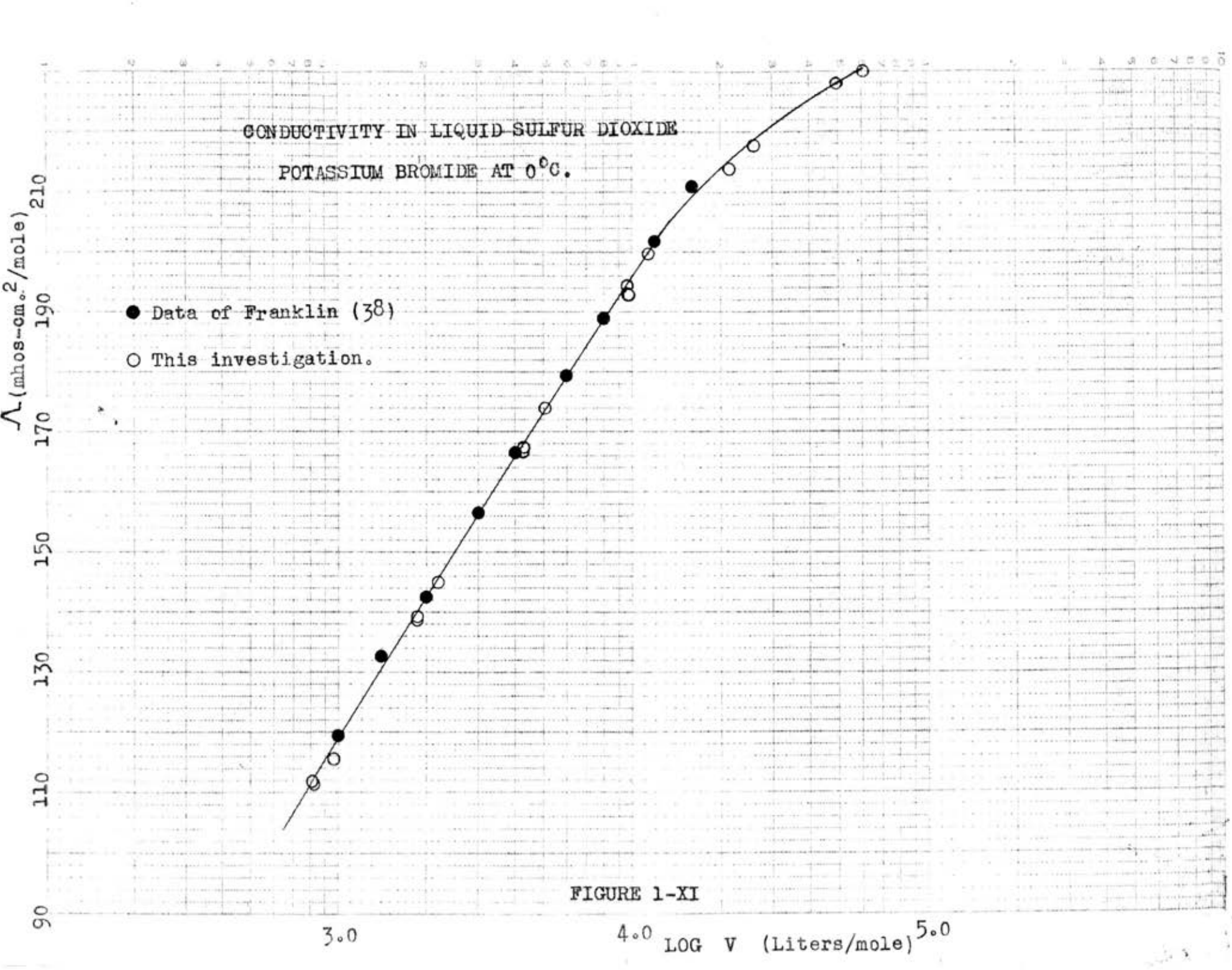

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
POTASSIUM BROMIDE AT 0°C.
● Data of Franklin (38)
○ This investigation.
Λ (mhos-cm.²/mole)
210
190
170
150
130
110
90
3.0
4.0
5.0
LOG V (Liters/mole)

FIGURE 1-XI

In this respect it should be noted that Franklin's data for potassium bromide extend only to a dilution of 4800 liters per mole and in order to have a sufficient number of points to define the Shedlovsky curve it was necessary to include in the calculation all of the data in the range 1000-4800 liters per mole. An estimate of the validity of the Shedlovsky treatment applied to data in this dilution range is reflected by the poor agreement of the derived constants with those obtained in the region of 2000-80,000 liters per mole. It is quite probable that all of Franklin's data for this compound lie out of the region of linearity of the extrapolation procedure and these observations may be considered as lending support to the dilution limits selected in this dissertation.

The derived equilibrium quantities $K_{exp.}$ and Λ_o suffer limitations which are inherent in the extrapolation procedure and are distinct from errors arising from applicability limits or from experimental uncertainties. Thus for strong electrolytes, $K > 10^{-3}$, the Shedlovsky curve will have a slope of very small absolute magnitude. Small uncertainties in the value for the slope of such compounds will result in large percentage errors in the equilibrium constant. On the other hand, for such cases, the intercept and hence the Λ_o values will be more reliable than is the case for the weaker electrolytes, $K < 10^{-3}$, where the slope is larger and more reliable while the intercept becomes less reliable. It should be pointed out that the reliability of the Λ_o value will in general not depend on its absolute value but only on the slope of the extrapolated

curve and hence for very weak electrolytes, $K < 10^{-7}$, large uncertainties are introduced in the extrapolated limiting conductance values. In conclusion then, the method will give reliable equilibrium constants for those systems where the constant falls in the range between 10^{-3} and 10^{-7}.

Thermodynamic Properties

Standard free energies ΔF^0 for ion pair dissociation were calculated from the experimental equilibrium constants by the equation

$$\Delta F^0 = -RT \ln K_{exp.} \qquad (1\text{-}19$$

Standard enthalpies were calculated by using the integrated form of the Van't Hoff equation

$$\Delta H^0 = \frac{R \ln (K_1/K_2)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \qquad (1\text{-}20$$

which, over the temperature range employed, Viz., 0.1° to -8.9°C., becomes

$$\Delta H^0 = -3.672 \times 10^4 \, \Delta \log K_{exp.} \qquad (1\text{-}21$$

Equation 1-21 involves the assumption that ΔH^0 is independent of temperature over the temperature interval involved. This assumption is not strictly true for solutions of electrolytes (88) and the error involved in this assumption has been evaluated in part II. The thermodynamic quantities are

summarized in table 1-I. Similar results obtained from Franklin's data are summarized in table 1-VII.

Reference to the ΔH° values calculated by equation 1-20 for potassium iodide in the range 0.12° to -8.93°C. from this research and in the 0° to -10°C. range from Franklin's data clearly illustrates the extreme sensitivity of ΔH° values calculated by this equation to small errors in equilibrium constants. It can be seen that while the equilibrium constants differ by only three percent at 0°C., and by about ten percent at -8.9° as compared to -10°C., the ΔH° values calculated from the two sets of data differ by more than fifty percent. This observation lends further support to the contention advanced in part II that ΔH° values calculated by the Van't Hoff equation from equilibrium data in liquid sulfur dioxide must be considered of doubtful significance and that conclusions based on small differences in these values are completely unreliable.

A more exact calculation of ΔH° for ion pair dissociation will be discussed below.

Apparent standard entropies, ΔS°, calculated by equation 1-22 are tabulated in table 1-I

$$\Delta F^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (1\text{-}22$$

Very little significance can be assigned to these ΔS° values

since the apparent ΔH° values employed in 1-22 do not correspond to the actual ΔH° values at the experimental temperatures.

Ionic Association.

The theory of ionic association of Bjerrum (16) and the theory of the formation of triple ions and quadrupoles of Fuoss and Kraus (44) predict the existence of short range interactions between ions which give rise to ion pairs and higher ionic aggregates in solutions of electrolytes in solvents of low dielectric constant. In sulfur dioxide solution, the theory of Fuoss and Kraus (63) restricts short range interactions to ion pairs except in very concentrated solutions.

Bjerrum Theory

In a solution of a binary electrolyte in a solvent of low dielectric constant free ions will be in equilibrium with associated ion pairs as follows:

$$(\dot{M}\tilde{A})^{\circ} \underset{}{\overset{K_a}{\rightleftharpoons}} M^{+} + A^{-}$$

The Bjerrum ion pair is defined as two oppositely charged ions held at a distance r, by Coulombic forces only. Non polar quantum bonds between ions as well as ion solvent interactions are not considered as constituting ion pairs.

Assuming the simple model of rigid, spherical, non polar-

izable-ions in a solvent of fixed and uniform dielectric constant, Bjerrum (16) derived an expression relating the reciprocal of the ion pair dissociation constant with temperature, dielectric constant and the distance of closest approach of the ions. The Bjerrum* equation can be written

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|Z_1 Z_2|\epsilon^2}{DkT}\right)^3 Q(b) \qquad (1\text{-}23$$

where the function Q (b) is

$$Q(b) = \int_2^b e^y y^{-4} dy = \frac{1}{6}\left\{e^2 - Ei(2) + Ei(b) - \frac{e^b}{b}\left(1 + \frac{1}{b} + \frac{2}{b^2}\right)\right\} \qquad (1\text{-}24$$

and Ei (x) is the exponential integral

$$Ei(x) = \int_{\infty}^{-x} e^{-t} t^{-1} dt \qquad (1\text{-}25$$

The variable b is defined by

$$b = \frac{|Z_1 Z_2|\epsilon^2}{aDkT} \qquad (1\text{-}26$$

Another deduction of equation 1-23 has been made by Fuoss and Kraus (43) employing the more general phase integral.

Ion pair dissociation constants may be calculated from equation 1-23 provided that reliable values of $\overset{o}{a}$, the distance parameter, are known. Unfortunately, in most solvents the effective radii of the ions are influenced by general solvation or by specific ion-solvent interactions (109). Thus even for simple ions, for which a rigid sphere approximation should not

(*) For a complete derivation of the Bjerrum equation see reference 61.

be bad, a direct corelation between the $\mathring{a}$ parameter and known crystallographic ionic radii cannot be expected.

Calculations of this type for 1-1 electrolyte solutions in sulfur dioxide demonstrate a remarkably quantitative adherence to the Bjerrum theory. The results indicate that a direct comparison of the distance parameter with known crystallographic ionic radii is possible in this solvent. This, it is believed constitutes the first example of completely quantitative adherence to the Bjerrum theory.

Ion-Pair Dissociation Constants

Table 1-IX summarizes ion pair equilibrium data calculated by the Bjerrum theory for a series of alkali halides in liquid sulfur dioxide employing the assumption that the distance of closest approach is exactly equal to the sum of crystallographic radii of the ions involved. A slight variation of this procedure was used for the calculations involving symmetrical tetraalkylammonium halides. Since crystallographic radii are not available for these ions, they were estimated from Fisher-Hirschfelder-Taylor models as being equal to the distance from the central nitrogen atom to the extreme end of an alkyl chain. When the alkyl group is larger than methyl this procedure becomes uncertain since the actual ionic radius may have any value between that corresponding to the completely puckered or coiled configuration and that corresponding to the maximum extension of the alkyl chain. Two dissociation constants,

TABLE 1-IX

Calculated Ion Pair Dissociation Constants and Free Energies.

Compound	Temp. (°C.)	$10^5 K_{calcd.}$	$\Delta F^\circ_{calcd.}$ (K-cal./mole)
KCl	0.12	10.1	5.00
"	-8.93	13.4	4.70
KBr	10.0	10.3	5.14
"	0.12	14.3	4.80
"	0.00	14.4	4.79
"	-8.93	18.9	4.52
"	-10.0	19.5	4.49
"	-20.0	25.6	4.14
"	-33.5	35.0	3.80
KI	10.0	16.8	4.87
"	0.12	22.2	4.57
"	0.00	22.3	4.56
"	-8.93	28.3	4.30
"	-10.0	29.0	4.25
"	-20.0	37.0	3.94
"	-33.5	50.0	3.61
$(CH_3)_4NBr$	0.12	119.0	3.66
"	-8.93	141.0	3.46
$(n\text{-}C_4H_9)_4NI$	0.12	281 (a)	3.20
"	-0.12	385 (b)	3.02

(a) Based on compressed configuration of the butyl group.
(b) Based on extended configuration of butyl group.

TABLE 1-X

Ionic Radii Employed in the Bjerrum Calculations.

Ion	Radius (Å)
K^+ (a)	1.331
Cl^- (a)	1.806
Br^- (a)	1.951
I^- (a)	2.168
ClO_4^- (b)	2.36
$(CH_3)_4N^+$ (c)	3.30
$(n\text{-}C_4H_9)_4N^+$ (c,d)	6.00
$(n\text{-}C_4H_9)_4N^+$ (c,e)	7.80

(a) Reference 105

(b) Reference 136

(c) Estimated from Fisher-Hirschfelder-Taylor models.

(d) Based on compressed configuration of butyl group.

(e) Based on extended configuration of butyl group.

corresponding to the two extreme values for the radius of the cation, were calculated for tetrabutylammonium iodide and by comparison with the measured equilibrium constant some insight into the actual conformation of the cation may be gained. Table 1-X summarizes the ionic radii employed in these calculations. Values for the alkali metal cations and halide ions were obtained from the values listed by Pauling (105). Radii for ions for which such data are not available were estimated from molecular models.

The model assumed in these calculations is essentially identical with the simple model on which the Bjerrum theory is based. The ions are considered to be rigid nonpolarizable spheres in a medium of fixed macroscopic dielectric constant. One additional simplifying assumption is introduced namely that the solvation shells of the ions are considered to be completely penetrated by the gegen ions in the associated ion pair. Thus the influence of solvation on the distance of closest approach is eliminated and $\overset{o}{a}$ may be estimated as being equal to the sum of ionic radii as exhibited by the ions in the crystalline state.

Details of Bjerrum Calculations

In order to facilitate the calculation of ion pair dissociation constants equation 1-23 can be reduced to

$$K^{-1} = C_K Q(b) \qquad (1\text{-}27$$

where

$$b = \frac{C_b}{\overset{o}{a}} \qquad (1\text{-}28$$

The constant coefficients C_k and C_b are dependent only on the temperature and the dielectric constant of the solvent. Values of these coefficients have been calculated for 1-1 electrolyte solutions in liquid sulfur dioxide at several temperatures and are summarized in table 1-XI. Physical constants employed in these calculations have been described earlier.

TABLE 1-XI

Bjerrum Coefficients for 1-1 Electrolytes in Sulfur Dioxide.

Temperature (°C.)	C_b x 10^7	C_k x 10^{-2}
10.00	4.105	5.237
0.12	3.982	4.780
0.00	3.981	4.776
-8.93	3.878	4.414
-10.00	3.866	4.372
-17.00	3.791	4.124
-20.00	3.760	4.022
-33.50	3.628	3.615

Values of the function Q(b) were obtained directly from a large scale plot of Q(b) versus (b). Q(b) values used in the construction of this plot were calculated from equation 1-24 employing W.P.A. Tables (134) of the integral exponential function. Table 1-XII summarizes the values of Q(b) at various values of b and figure 1-XII shows a plot of these data.

TABLE 1-XII

Values of theFunction Q(b).

b	Q(b)
2.50	0.18791
3.00	0.32564
4.00	0.54961
5.00*	0.77120
6.00	1.04078
7.00	1.41824
8.00	1.99454
9.00	2.95052
10.00	4.62532
11.00	7.65992
12.00	13.4038
13.00	24.6824

(*) Bjerrum's (16) calculated values of Q(b) contains an error for this value of b.

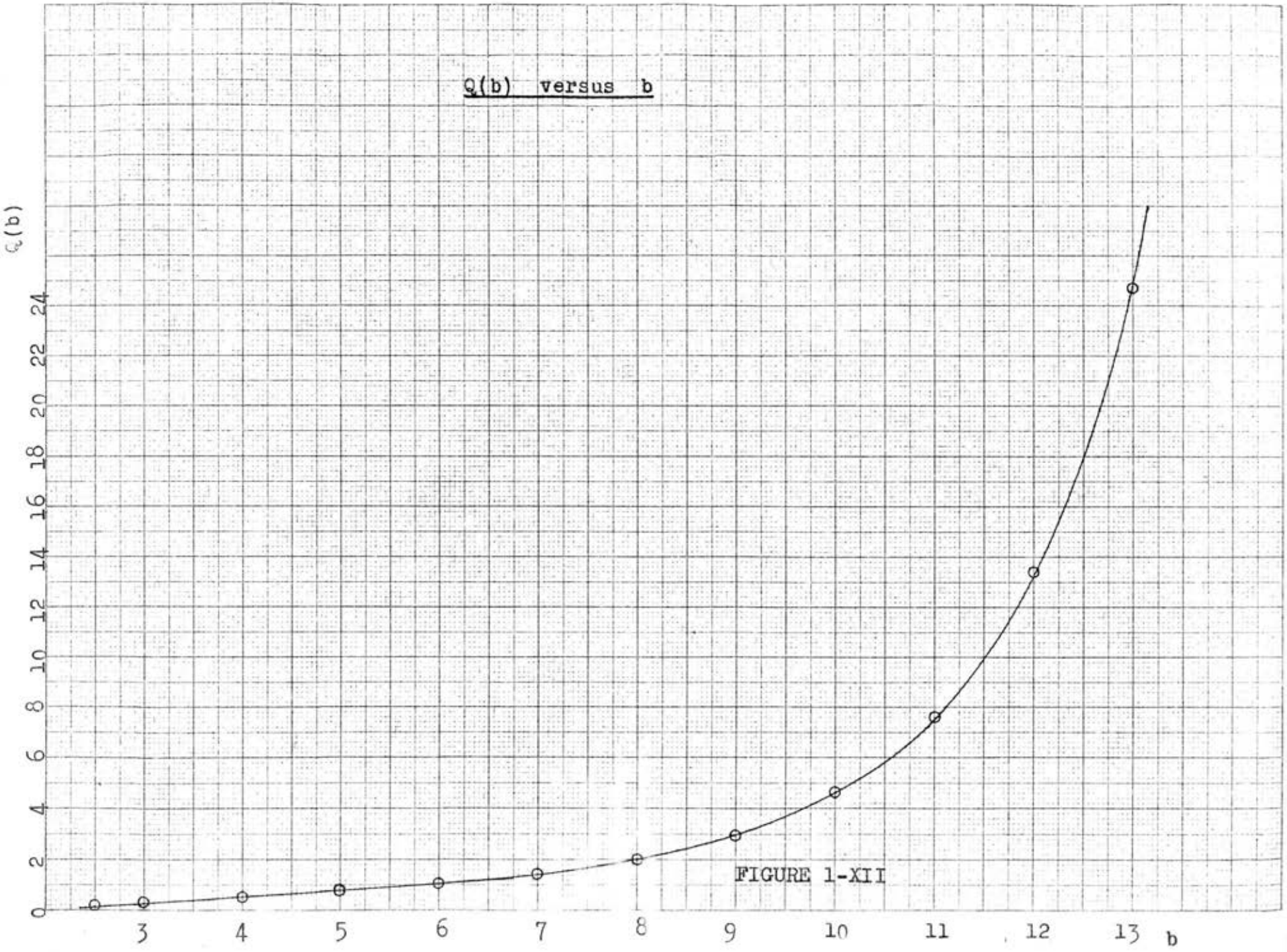


FIGURE 1-XII

Table 1-XIII summarizes the Bjerrum calculations for the compounds considered in this investigation.

TABLE 1-XIII

Summary of Bjerrum Calculations.

Compound	Temp. (°C.)	a (Å)	b	Q(b)	K x 10^5
KCl	0.12	3.14	12.69	20.75	10.1
KCl	-8.93	3.14	12.36	16.85	13.4
KBr	10.00	3.28	12.51	18.45	10.3
KBr	0.12	3.28	12.14	14.62	14.3
KBr	0.00	3.28	12.13	14.55	14.4
KBr	-8.93	3.28	11.82	11.97	18.9
KBr	-10.0	3.28	11.78	11.75	19.5
KBr	-20.0	3.28	11.46	9.78	25.6
KBr	-33.5	3.28	11.06	7.90	35.0
KI	10.00	3.50	11.73	11.40	16.8
KI	0.12	3.50	11.38	9.40	22.2
KI	0.00	3.50	11.38	9.40	22.3
KI	-8.93	3.50	11.08	8.00	28.3
KI	-10.0	3.50	11.05	7.88	29.0
KI	-20.0	3.50	10.75	6.75	37.0
KI	-33.5	3.50	10.37	5.53	50.0
$(CH_3)_4NBr$	0.12	5.25	7.58	1.75	119
$(CH_3)_4NBr$	-8.93	5.25	7.39	1.61	141
$(n\text{-}C_4H_9)_4NI$	0.12	8.17	4.88	0.745	281[a]
$(n\text{-}C_4H_9)_4NI$	0.12	9.97	3.98	0.545	385[b]

(a) Based on compressed configuration of butyl group.

(b) Based on extended configuration of butyl group.

Comparison of Experimental and Calculated Equilibrium Constants.

A direct and quantitative verification of the Bjerrum theory of ion pair formation lies in a comparison of the experimental equilibrium constants determined in this research with those values calculated for ion pair dissociation by this theory. Table 1-XIV summarizes the experimental and theoretical equilibrium constants and apparent errors calculated in terms of the departure of the calculated values from the experimental. In the last column several values of the difference between the true sum of ionic radii, Σr_{ij} , and the distance parameter $\overset{o}{a}$ calculated from experimental equilibrium constants are tabulated.

Several interesting deductions can be drawn from this comparison. First, the agreement between calculated and experimental ion pair dissociation constants, while not excellent, is certainly good within the combined experimental and calculational errors involved. The apparent errors in equilibrium constants are, however, misleading and a more complete analysis of the method is required in order to arrive at a true evaluation of the adherence to the theory of sulfur dioxide sulfur solutions.

Several features of the relative errors are at once apparent and can be explained on the basis of the method. The calculated equilibrium constants are significantly larger than the corresponding experimental values for potassium chloride

at 0°C. and for potassium bromide at +10°C. This would seem to imply that the sum of ionic radii is larger than the actual distance of closest approach of these ions. Theoretically, of course, this is a completely untenable situation for the ions can certainly not penetrate beyond their ionic radii because of the infinite potential barrier arising from electrostatic repulsion. In the case of potassium chloride at 0.12°C. and potassium bromide at +10°C., the distance of closest approach seems to be 0.18Å and 0.13Å smaller than their respective ionic radii sum. For potassium chloride at -8.9° the discrepancy is of the order of 0.04Å or an error of about 1% in the value calculated by the Bjerrum theory. This is well within experimental error and therefore need not be considered further.

The Influence of Dielectric Constant

A possible explanation of the apparent discrepancy for potassium chloride at 0.12°C. and bromide at +10°C. lies in the uncertainty of the dielectric constant of liquid sulfur dioxide at these temperatures. The values of dielectric constant used in all of the calculations were obtained by extrapolation of Vierk's (125) data as has been described earlier. Since Vierk's data extend from -63°C. up to -16.5°C. the 0.12° and +10°C. values are the result of an extrapolation which extends beyond the range of validity of the empirical equation representing the dielectric constant as a function

TABLE 1-XIV

Comparison of Experimental and Calculated Ion Pair Dissociation Constants.

Compound	Temp. (°C.)	10^5K (exp.)	10^5K (calc.)	ΔK[a] (±%)	å (Angstroms) (obs.)	å (theory)
KCl	0.12	7.44	10.1	≠35	2.96	3.14
KCl	-8.93	10.8	13.4	≠25	3.10	3.14
KBr	10.0	7.42	10.3	≠39	3.15	3.28
KBr	0.12	14.3	14.3	0	3.28	3.28
KBr	0.00	12.4	14.4	≠16	3.24	3.28
KBr	-8.93	19.9	18.9	-5	3.31	3.28
KBr	-10.0	18.5	19.5	≠5	3.26	3.28
KBr	-20.0	28.9	25.6	-11	3.34	3.28
KBr	-33.5	34.5	35.0	≠1	3.26	3.28
KI	10.0	21.0	16.8	-20	3.63	3.50
KI	0.12	30.1	22.2	-26	3.58	3.50
KI	0.00	29.3	22.3	-24	3.67	3.50
KI	-8.93	42.8	28.3	-31	3.78	3.50
KI	-10.0	37.8	29.0	-23	3.66	3.50
KI	-20.0	49.0	37.0	-24	3.66	3.50
KI	-33.5	65.7	50.0	-24	3.56	3.50
$(CH_3)_4NBr$	0.12	118	119	0	----	5.25
$(CH_3)_4NBr$	-8.93	146	141	-3	----	5.25
$(n\text{-}C_4H_9)_4NI$	0.1	382[d]	281[b]	----	----	8.17
$(n\text{-}C_4H_9)_4NI$	0.1	382[d]	385[c]	----	----	9.97

(a) $K_{calc.} - K_{exp.}/K_{exp.}$
(b) Compressed configuration. (c) Extended configuration.
(d) Data of Alster (3).

of temperature which was derived from these data. By this procedure values of 15.36 and 14.37 are obtained for the dielectric constant at 0.12° and +10°C. respectively. Experimental values are not available for comparison at +10°C., however, at 0°C. Maryott and Smith (98) have selected Le Fevre and Ross's (86) value of 15.08 as being the most reliable value for the dielectric constant at this temperature. For most purposes the agreement between the extrapolated value of 15.36 and the experimental best value of 15.08 can be considered quite satisfactory. Thus, for example, since the dielectric constant enters the Shedlovsky equation only to the 3/2 power the maximum error in the experimental constant at 0.12°C. is only about 5% on the basis of the apparent error in the dielectric constant.

The Bjerrum equation on the other hand contains the dielectric constant to the 4th power and therefore the calculated equilibrium constant is very sensitive to errors in the dielectric constant.

Ion pair dissociation constants for potassium chloride at 0.12°C. have been calculated for several possible values of the dielectric constant. Table 1-XV summarizes these data.

TABLE 1-XV

Variation of the Dissociation Constant of Potassium Chloride with Dielectric Constant.

($0.12^{\circ}C.$, $\mathring{a} = 3.14$ Å.)

Dielectric Constant	$K \times 10^{5}$ (*)
14.90	7.26
15.00	7.90
15.10	8.36
15.20	8.90
15.30	9.49
15.36	10.1

(*) $K_{obs.} = 7.44 \times 10^{-5}$ for this compound.

The above data clearly demonstrate the sensitivity of the calculated dissociation constant of potassium chloride at $0.12^{\circ}C.$ to variations in the dielectric constant value used in the calculations. Indeed, if we had used the more reliable value of Le Fevre and Ross the large discrepancy between the experimental and calculated dissociation constant would be greatly reduced (to about 12%) and good agreement could be claimed.

The observed sensitivity of the Bjerrum equation to the dielectric constant is more complex than is at once apparent. The dielectric constant, shown as a term of the first power in equation 1-26, actually enters the Bjerrum

equation as a complicated exponential term in the integral Q(b). Figure 1-XII shows Q(b) as an exponential function of (b). From this figure and from equation 1-26 it is obvious that the dielectric constant becomes increasingly important at large values of the variable b. By definition, the variable b is inversely proportional to $\mathring{a}$ and, therefore, one can conclude that sensitivity of the calculation to errors in the dielectric constant will decrease rather rapidly with increasing values of the distance parameter. Thus, while a small error in the dielectric constant will have a marked effect on the calculation for potassium chloride at 0°C. (b=12.7, Q(b)=21) it will not be as important for potassium bromide (b=12.1, Q(b)=14.6) or salts with larger ions at this temperature. On the other hand at $\neq 10^{\circ}$C., where the dielectric constant is lower than at 0°, the values of b for potassium bromide again becomes sufficiently large (b=12.5) to put us in the region of steepest slope in the Q(b) vs. b plot. Since at $\neq 10^{\circ}$C. $K_{calc.} > K_{exp.}$ the dielectric constant used at this temperature appears to be somewhat too high. The dielectric constant for liquid sulfur dioxide at $\neq 10^{\circ}$C. calculated by the Bjerrum theory from the experimental equilibrium constant and the sum of ionic radii of potassium bromide is found to be 14.0 compared to the value of 14.4 obtained by extrapolation of Vierk's data. It should be interesting to measure the dielectric constant at this temperature in order to provide another experimental test of the Bjerrum theory.

Thermodynamics of Ion Pair Formation

It has been shown that the ion pair dissociation constants for 1-1 electrolytes in liquid sulfur dioxide are dependent only on the temperature, dielectric constant, and the distance of closest approach. The latter property can be approximated by the sum of ionic radii obtained from crystallographic data or by direct measurements made on molecular models of the compounds. It should therefore be possible to calculate the thermodynamic quantities ΔF^{o}, ΔH^{o}, and ΔS^{o} directly from equation 1-23. In principle this can be done as follows.

The reciprocal of the ion pair dissociation constant is given by the Bjerrum theory as

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|Z_1 Z_2|\epsilon^2}{DkT}\right)^3 Q(b) \qquad 1\text{-}23$$

The standard enthalpy according to the Van't Hoff equation, is

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H^{o}}{RT^2} \qquad (1\text{-}20\text{-}a$$

Thus if we take the natural logarithm of equation 1-23, namely,

$$-\ln K = \ln C - 3\ln D - 3\ln T \neq \ln Q(b). \qquad (1\text{-}28$$

(where C is a product of fundamental constants) and differentiate with respect to temperature, we obtain

$$\frac{\partial \ln K}{\partial T} = \frac{3}{D}\left(\frac{\partial D}{\partial T}\right) \neq \frac{3}{T} - \frac{1}{Q(b)}\left(\frac{\partial Q(b)}{\partial T}\right) \qquad (1\text{-}29$$

and we find that the standard enthalpy can be expressed in terms of the Bjerrum theory by

$$\Delta H^{o} = RT^{2}\left[\frac{3}{D}\left(\frac{\partial D}{\partial T}\right) + \frac{3}{T} - \frac{1}{Q(b)}\left(\frac{\partial Q(b)}{\partial T}\right)\right]. \qquad (1\text{-}30$$

In order to evaluate ΔH^{o} from equation 1-30 it is necessary to expand the terms enclosed by brackets and collect the expanded terms in a manner which will be convenient for numerical computation.

The term $\frac{3}{D}\left(\frac{\partial D}{\partial T}\right)$ can be easily expanded if we recall the expression derived for the dielectric constant of liquid sulfur dioxide as a function of temperature, namely

$$D = C\, e^{-LT} \quad . \qquad (1\text{-}16$$

Differentiating 1-16 with respect to temperature gives

$$\frac{\partial D}{\partial T} = -LC\, e^{-LT} = -LD \qquad (1\text{-}31$$

Substituting the results of 1-31 into 1-30 gives

$$\Delta H^{o} = RT^{2}\left[-3L + \frac{3}{T} - \frac{1}{Q(b)}\left(\frac{\partial Q(b)}{\partial T}\right)\right]. \qquad (1\text{-}32$$

Now, $Q(b)$ is defined as

$$Q(b) = \frac{1}{6}\left\{e^{2} - Ei(2) + Ei(b) - \frac{e^{b}}{b}\left(1 + \frac{1}{b} + \frac{2}{b^{2}}\right)\right\}. \qquad (1\text{-}24$$

Differentiating 1-24 with respect to temperature gives,

$$6\left(\frac{\partial Q(b)}{\partial T}\right) = \frac{\partial Ei(b)}{\partial T} - \frac{\partial\left(\frac{e^{b}}{b}\right)}{\partial T} - \frac{\partial\left(\frac{e^{b}}{b^{2}}\right)}{\partial T} - \frac{\partial\left(\frac{2e^{b}}{b^{3}}\right)}{\partial T}. \qquad (1\text{-}33$$

The exponential integral, $Ei(b)$, can be approximated by the asymptotic expansion (42)

$$Ei(b) = \frac{e^{b}}{b}\left(1 + \frac{1}{b} + \frac{1\cdot 2}{b^{2}} + \frac{1\cdot 2\cdot 3}{b^{3}} + \cdots\right) \qquad (1\text{-}34$$

If we neglect (*) terms of order higher than b^3 and differentiate 1-34 with respect to temperature we obtain

$$\frac{\partial[Ei(b)]}{\partial T} = \frac{\partial\left(\frac{e^b}{b}\right)}{\partial T} + \frac{\partial\left(\frac{e^b}{b^2}\right)}{\partial T} + \frac{\partial\left(\frac{2e^b}{b^3}\right)}{\partial T} + \frac{\partial\left(\frac{6e^b}{b^4}\right)}{\partial T} . \qquad (1\text{-}35$$

By combining 1-35 and 1-33 we effect the cancellation of several terms and obtain the result,

$$\frac{\partial Q(b)}{\partial T} = \frac{\partial\left(\frac{e^b}{b^4}\right)}{\partial T} . \qquad (1\text{-}36$$

Since b can be defined as

$$b = \frac{|Z_1 Z_2|\epsilon^3}{8\pi DkT} = \frac{|Z_1 Z_2|\epsilon^2}{a_o C e^{-LT} kT} , \qquad (1\text{-}37$$

the temperature derivative of b can be shown to be

$$\frac{\partial b}{\partial T} = \frac{-b(1-LT)}{T} . \qquad (1\text{-}38$$

Substituting 1-38 into 1-36 and expanding, we obtain the expansion of the third term in equation 1-30, namely,

$$\frac{\partial Q(b)}{\partial T} = \frac{e^b(1-LT)(4-b)}{Tb^4} \qquad (1\text{-}36\text{-a}$$

This result can now be substituted into equation 1-32 to give the analytical expression for ΔH^o of ion pair dissoci-

(*) This approximation introduces an error of about 0.5 K-cal./m. in the final result.

ation, namely,

$$\Delta H^{o} = RT^{2}\left[-3L \neq \frac{3}{T} - \frac{e^{b}(1-LT)(4-b)}{Q(b)b^{4}T}\right] \qquad (1\text{-}39$$

Equation 1-39 can be somewhat simplified for computational purposes to give

$$\Delta H^{o} = 3RT(1-LT) - \frac{RTe^{b}(1-LT)(4-b)}{Q(b)b^{4}} \qquad (1\text{-}40$$

Equation 1-40 is the theoretical expression for ΔH^{o} of ion pair dissociation. Since this equation is based entirely on the Bjerrum theory it is subject to the limitations and approximations involved in the sphere-in-continuum model of electrolyte solutions and should be expected to yield agreement with experiment only in those systems which can accurately be described by this model. One further restriction is implied in equation 1-40 , namely, that the dielectric constant of the medium must be described by equation 1-16 over the temperature range involved. In case the dielectric is not described by this relationship a more complicated expression for ΔH^{o} can be derived.

Several interesting features of equation 1-40 can be noted. First we note that, as expected, ΔH^{o} is not independent of temperature.

More interesting is the dependence of ΔH^{o} on the dielectric constant. Although the dielectric constant does not enter the equation explicitly, it is implicit in the

constant L, the slope of the logarithm of the dielectric constant as a function of temperature. The importance of this solvent parameter in controlling the heat of dissociation of ion pairs is easily seen in equation 1-40. For example, we find here, that for all values of $b > 2.5$, ΔH^0 goes to zero when $L = 1/T$, becomes exothermic when $L > 1/T$, and endothermic when $L < 1/T$. In liquid sulfur dioxide $L = 1/T$ at approximately $150^\circ K$. (according to equation 1-16). This temperature is well below the freezing point of the solvent and therefore for all solutions in the liquid phase $L > 1/T$ and ΔH^0 is exothermic. Further consideration of the solvent parameter L at this time would be unprofitable since lack of necessary experimental data in other solvents leaves such considerations squarely in the realm of speculation.

By far the most interesting feature of equation 1-40 is the dependence of ΔH^0 on the distance of closest approach. Again since the expression is not explicit in the $\mathring{a}$ parameter we must consider a function of $\mathring{a}$, namely, b. Equation 1-40 shows that(*) when $b = 4$ the ΔH^0 of dissociation is independent of the distance of closest approach(**). When $b > 4$, ΔH^0 is negative and when $b \ll 4$, ΔH^0 becomes less negative. In liquid sulfur dioxide $b = 4$ when the distance of closest approach is of the order of $10\mathring{A}$.

(*) In this discussion it should be noted that for the system under consideration the term (1-LT) is a negative quantity.

(**) This is a direct result of neglecting terms of higher order in equation 1-34.

Equation 1-40 can be used to calculate ΔH^{o} for ion pair dissociation as a function of the distance of closest approach or as a function of temperature. Since most of the data of this research do not extend over a wide temperature range it is more pertinent to consider the variation of ΔH^{o} with the distance of closest approach at several temperatures. The values calculated from equation 1-40 can be compared to the experimental values as a quantitative test of the applicability of Bjerrum's equation to solutions of electrolytes in liquid sulfur dioxide.

Calculation of Bjerrum ΔH^{o}

In order to facilitate the calculation of ΔH^{o} by equation 1-40 for various electrolytes in liquid sulfur dioxide solution it was decided to evaluate ΔH^{o} at several round values of the distance parameter $\mathring{a}$ and prepare plots of ΔH^{o} as a function of $\mathring{a}$. In this way ΔH^{o} can be evaluated for any compound if the distance of closest approach is known.

The results of these calculations are presented in figures 1-XIII and 1-XIV as plots of ΔH^{o} versus $\mathring{a}$ at 0.12^{o}C. and -8.93^{o}C. respectively. Table 1-XVI summarizes the data used in the construction of these plots.

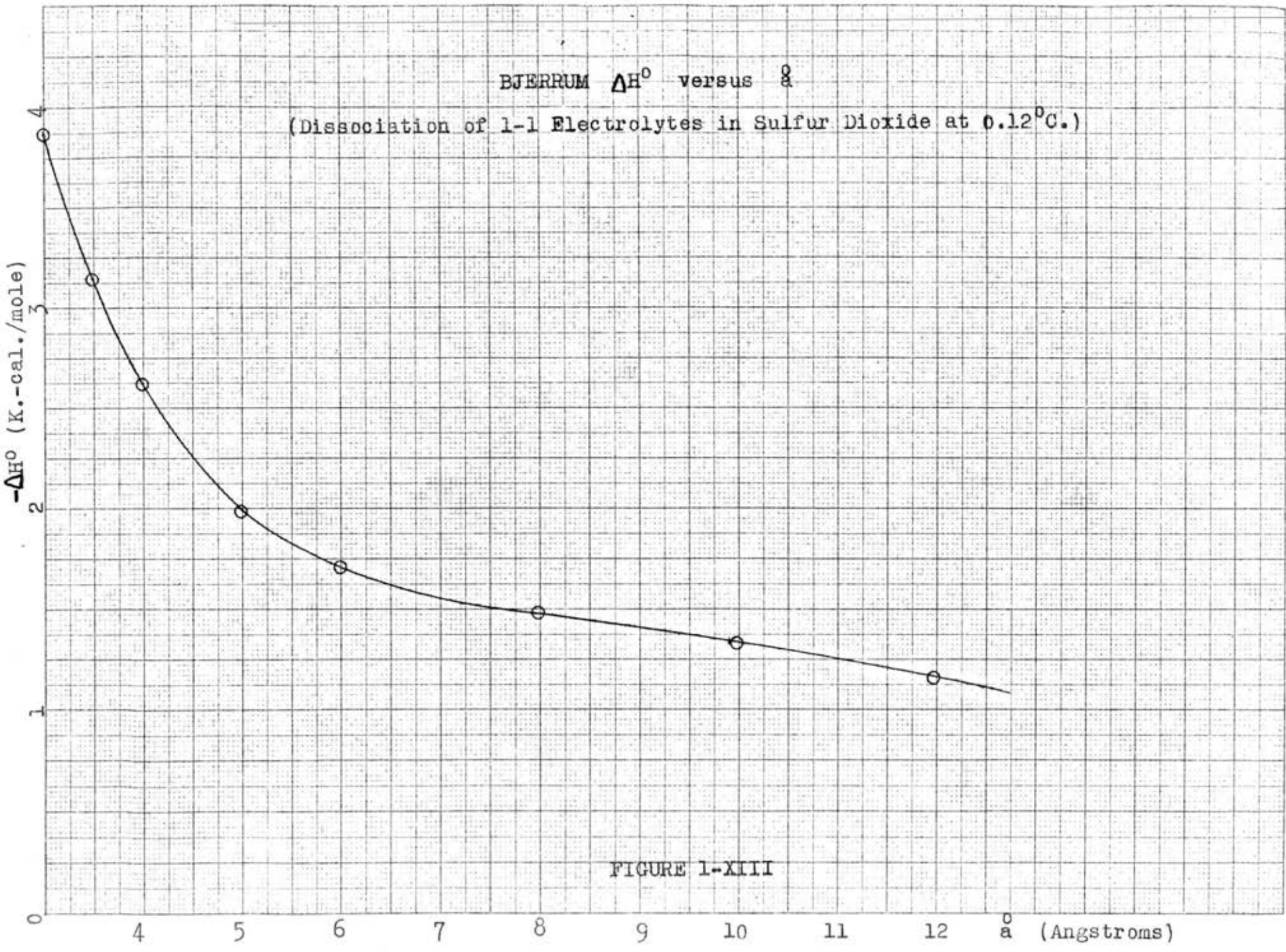


FIGURE 1-XIII

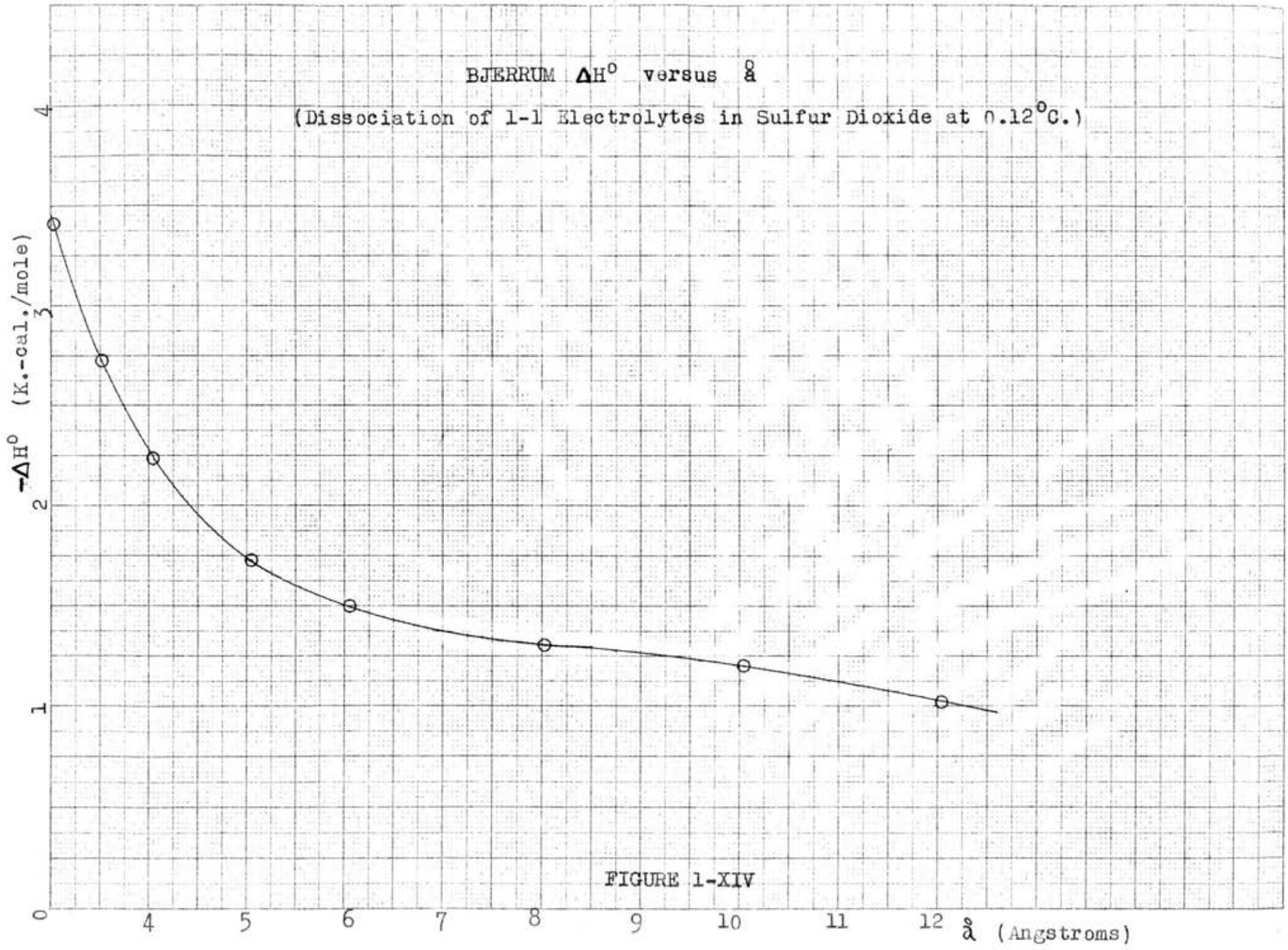

BJERRUM ΔH° versus å
(Dissociation of 1-1 Electrolytes in Sulfur Dioxide at 0.12°C.)
-ΔH° (K.-cal./mole)
0
1
2
3
4
4
5
6
7
8
9
10
11
12
å (Angstroms)

FIGURE 1-XIV

TABLE 1-XVI

Bjerrum ΔH^{o} for Ion Pair Dissociation in Liquid Sulfur Dioxide.

$\overset{o}{a}$ (Å.)	ΔH^{o} calculated by eq. 1-40. 0.12°C(K-cal./ mole)	-8.93°C.
3.0	-3.85	-3.42
3.5	-3.14	-2.73
4.0	-2.60	-2.24
5.0	-1.99	-1.74
6.0	-1.71	-1.51
8.0	-1.48	-1.31
10.0	-1.34	-1.18
12.0	-1.17	-1.01

In order to test equation 1-40 we must have accurate experimental ΔH^{o} values. For the most part, the data of this research do not afford ΔH^{o} values of sufficient accuracy. This results from the fact that ΔH^{o} values calculated from two temperature data by the integrated Van't Hoff equation are extremely sensitive to small experimental errors in the individual equilibrium constants employed since these enter the calculation as two large numbers used for the calculation of a small difference. It is possible, however, to evaluate accurate ΔH^{o} values from the multi temperature data of Franklin (38) for potassium iodide by fitting an analytic expression to these data over the entire temperature range.

ΔH^o for Potassium Iodide

An empirical equation was fitted to the equilibrium constants derived from Franklin's data for potassium iodide at several temperatures. The equation is of the form

$$-R \ln K = A e^{B/T} \quad (^oK.) \qquad (1\text{-}41$$

where A = 34.60 and B = -206.4. Equation 1-41 expresses the data over the range -33.5°C. to +10.0°C. with a mean deviation of K of the order of $\pm$ 5 %.

Equation 1-41 was solved to give an analytical expression for ΔH^o as a function of temperature, namely,

$$\Delta H^o = 7.141 e^{-206.4/T} \quad (^oK.) \qquad (1\text{-}42$$

Table 1-XVII summarizes the ΔH^o values at various temperatures calculated from equation 1-42 for potassium iodide and comparable values calculated directly from the experimental K values by the integrated Van't Hoff equation.

TABLE 1-XVII

ΔH^o for Potassium Iodide in Liquid Sulfur Dioxide. (Data of Franklin (38)).

Temperature	ΔH^o (K-cal./mole)	
(°C.)	Equation 1-42	Van't Hoff equation
10.0	-3.44	---- [a]
0.0	-3.35	-5.10 [b]
-10.0	-3.26	-3.66 [c]
-20.0	-3.16	-3.41 [d]
-33.5	-3.02	-2.51

(a) 10.0° to 0.0°C. (b) 0.0° to -10.0°C. (c) -10.0° to -20.0°C. (d) -20.0° to -33.5°C.

Table 1-XVII shows fairly good agreement between ΔH^0 calculated from equation 1-42 and from the integrated Van't Hoff equation at all temperatures except for the range between 10°C. and 0°C., where a considerable difference is found. The difference found here must be attributed to the extreme sensitivity of the Van't Hoff calculation to small deviations in the experimental equilibrium constants and should serve as an indication of the caution which must be used whenever this method is employed for calculating ΔH^0 values. Similar calculations have not been performed for Franklin's potassium bromide data as these data do not extend over a sufficiently wide dilution range to afford reliable equilibrium constants.

Comparison of Bjerrum ΔH^0 with Experimental Data

According to equation 1-40 ΔH^0 for potassium iodide at 0°C. should be equal to -3.15 K cal./mole. This result is in excellent agreement with the 0° value of -3.35 K-cal./mole obtained from Franklin's data. Similar good agreement is also found at -10°C. where Franklin's data gives -3.26 K-cal./m. while the Bjerrum value at -8.93°C. is -2.75 K-cal./mole.

A direct comparison between Bjerrum ΔH^0 values and those calculated from the experimental data by the integrated Van't Hoff equation demonstrates qualitative agreement as shown by the data summarized in table 1-XVIII. These data do not serve as a valid test of the Bjerrum equation for the experimental values are not reliable. "Order of magnitude" agreement exists,

however, and this must be accepted until more accurate experimental values become available.

TABLE 1-XVIII

Comparison of Experimental and Bjerrum ΔH^{o} Values
(Ion Pair Dissociation in Liquid Sulfur Dioxide.)
0.12°C.

Compound	Bjerrum ΔH^{o} (K-cal./mole)	Experimental ΔH^{o} (K-cal./mole)
KCl	-3.65	-5.92
KBr	-3.40	-5.26
KI	-3.15	-5.60 (-3.35)[a]
$(CH_3)_4NBr$	-1.90	-3.36
$(C_4H_9)_4NI$	-1.45[c]	(-1.0)[b],
$(C_4H_9)_4NI$	-1.35[d]	(-1.0)[b],

(a) Calculated from Franklin's data.

(b) Estimated from the data of Alster(3).

(c) Compressed butyl group.

(d) Extended butyl group.

THEORETICAL DISCUSSION

The experimental data and calculations presented in this dissertation clearly demonstrate that the theory of ion pair association of Bjerrum is an accurate representation of the behavior of 1-1 electrolytes in liquid sulfur dioxide solution. The distance of closest approach $\overset{o}{a}$ of the ions in an ion pair can be calculated from experimental equilibrium constants by the Bjerrum equation. Values obtained from the data on pure ionic compounds in liquid sulfur dioxide solution are in excellent agreement with the sum of known ionic crystal radii for these compounds. Conversely, ion pair dissociation constants calculated from crystal radii agree closely with the experimental values obtained in this research. In two cases, where crystallographic radii were not available, values estimated directly from measurements of Fisher-Hirschfelder-Taylor models gave the desired agreement with experiment.

An equation for ΔH^{o} derived solely from the Bjerrum theory gave values which were in good agreement within the uncertainties inherent in the experimental values of this property.

On the basis of the above observations it is possible to conclude that the Bjerrum treatment is quantitatively exact for electrolytes in liquid sulfur dioxide solution. This, is in all probability the first demonstration of quantitative adherence to Bjerrum's theory.

Fuoss and Kraus (42) have previously demonstrated qualitative agreement between equilibrium data for tetraisoamylammonium nitrate in water-dioxane mixtures and the Bjerrum ion pair dissociation theory. These workers demonstrated that the $\overset{o}{a}$ parameter remained reasonably constant ($\pm$ 11%) over a wide range of dielectric constant. The $\overset{o}{a}$ parameter could not, however, be identified directly with known ionic radii for their system although it was of the order of ionic dimensions. They concluded, that since the molar water concentration was always greater than that of the solute, the ions were always hydrated and therefore their effective diameter remained constant.

While this work constituted the first test of the Bjerrum theory, it was not possible to check the equation by independent determination of $\overset{o}{a}$ and thus this quantity has never been clearly defined in terms of actual ionic dimensions or structure.

In the derivation of the Bjerrum equation, $\overset{o}{a}$ is interpreted as the distance between centers of uniformly charged spheres in contact. Ions however are in general neither spherical nor uniformly charged and the problem of solvation in respect to its effect on the distance of closest approach remains as yet unsolved. Qualitatively, however, we would expect this over-simplified physical picture to be most nearly approached in systems composed of large spherically symmetric ions in solvents of low polarizability.

The distance parameter $\mathring{a}$ is in general a rather loosely defined physical property of electrolytes in solution. A rigorous definition of $\mathring{a}$ in terms of a physically reasonable model is of paramount importance for the advancement of electrolyte theory. Therefore a detailed discussion of this parameter is desirable.

The Effect of Temperature on the $\mathring{a}$ Parameter

The results of numerous investigations indicate beyond question that the distance of closest approach remains constant over wide temperature ranges. An excellent example is provided by the data of Bien et. al. (14) for tetrabutylammonium nitrate in anisole. Table 1-XIX constructed from their data, demonstrates that in this system $\mathring{a}$ remains constant over a temperature range of 125°C.

TABLE 1-XIX[(a)]

Bjerrum $\mathring{a}$ for Tetrabutylammonium Nitrate in Anisole.

Temperature (°C.)	K x 10^{11}	Λ_o (mhos-cm.^{2}/mole)	$\mathring{a}$ x 10^8 (cm.)
-33	2.08	14.22	4.88
0	5.42	31.8	4.95
25	9.20	49.5	4.96
61.3	16.3	82.1	4.91
80.2	20.6	102.1	4.89
95.1	23.2	118.9	4.85

(a) Data of Bien et. al. (14).

These data clearly establish that $\mathring{a}$ for a given compound is constant over a wide temperature range. Further demonstration of this fact is provided by the results of this investigation summarized in tables 1-XX and 1-XXI.

TABLE 1-XX

Bjerrum $\mathring{a}$ for Potassium Bromide in Liquid Sulfur Dioxide.

Temperature (°C.)	K x 10^5	Λ_o (mhos-cm.^{2}/mole)	$\mathring{a}$ x 10^8 (a) (cm.)
10.0	7.42	309	3.15 (b)
0.12 (c)	14.3	249	3.28
0.0	12.4	267	3.24
-8.93 (c)	19.9	228	3.31
-10.0	18.5	237	3.26
-20.0	28.5	207	3.34
-33.5	34.5	190	3.27

(a) The sum of crystal radii for KBr is 3.28 x 10^{-8} cm.

(b) Some uncertainty in the value for the dielectric constant exists at this temperature.

(c) Results from the present investigation.

TABLE 1-XXI

Bjerrum $\mathring{a}$ for Potassium Iodide in Liquid Sulfur Dioxide.

Temperature (°C.)	K x 10^5	Λ_o (mhos-cm.^{2}/mole)	$\mathring{a}$ x 10^{8} [a] (cm.)
10.0	21.0	272	3.64
0.12 [b]	30.1	244	3.58
0.0	29.3	247	3.67
-8.93 [b]	42.8	221	3.77
-10.0	37.8	228	3.66
-20.0	49.0	204	3.66
-33.5	65.7	179	3.56

(a) The sum of crystal radii for KI is 3.50×10^{-8} cm.

(b) This investigation.

The more recent data also demonstrate that $\mathring{a}$ is very nearly equal to the sum of ionic radii obtained from crystal studies.

Effect of Solvation on $\mathring{a}$ Parameter

Although several examples of the influence of solvent on the $\mathring{a}$ parameter are available in the literature it is unnecessary to consider these since a detailed examination of the effect of solvation on ion pair dissociation equilibria has recently been undertaken by Fuoss and co-workers. Fuoss is currently studying the effect of solvent mixtures on the

behavior of electrolytes. Table 1-XXII constructed from the data of several papers in the recent series by Fuoss demonstrates the sharp variations in the value of $\mathring{a}$ with change in solvent composition.

TABLE 1-XXII

Bjerrum $\mathring{a}$ for Tetrabutylammonium Bromide in Various Solvent Systems.

Solvent	$K_{exp.}$	$\mathring{a} \times 10^8$ (cm.)	Reference
Methanol	0.038	4.46	109
77% " + Nitrobenzene	0.14	7.89	"
8.4% " + "	0.12	6.58	"
Nitrobenzene	0.022	2.28	"
Methanol	0.055	4.70	102
96.1% " + Nitromethane	0.16	7.08	102
99% " + Benzene	0.31	8.22	102
Methanol	0.069	5.28	110
Ethanol	0.010	3.54	111

Sadek and Fuoss (112) have interpreted these data in terms of solvation and specific ion solvent interactions and have concluded that the Bjerrum sphere-continuum model is not quantitatively satisfactory.

Treatment of Sadek and Fuoss

A tentative solution to the problem of variation of the $\overset{o}{a}$ parameter with solvent composition has recently been advanced by Sadek and Fuoss (112). In this treatment it is assumed that an anion and cation approach through a dielectric continuum up to a point where one layer of solvent molecules is between the ions. For the process of formation of the solvated ion pair they write the static equilibrium

$$S + A^{+} + B^{-} \rightleftharpoons \left[\overset{+}{A}S\overset{-}{B}\right]^{o} \qquad 1\text{-}43$$

where S represents one or more solvent molecules depending upon the polar nature of the solvent. The solvent concentration should not appear in the mass action expression which in terms of activities is

$$aA^{+} \cdot aB^{-} = K_D \, a\left[\overset{+}{A}S\overset{-}{B}\right]^{o} \qquad 1\text{-}44$$

Here K_D represents the formal dissociation constant which can be expressed in terms of a sphere-in-continuum model by the Bjerrum equation.

The assumption is then made that in certain cases (for example, in nitrobenzene-carbon tetrachloride mixtures) the solvent molecule is expelled by the process

$$\left[\overset{+}{A}S\overset{-}{B}\right]^{\circ} \rightleftharpoons \left[\overset{+}{A}\overset{-}{B}\right]^{\circ} + S \qquad 1\text{-}45$$

for which the mass action expression is

$$a\left[\overset{+}{A}\overset{-}{B}\right]^{\circ} \cdot aS = k\, a\left[\overset{+}{A}S\overset{-}{B}\right]^{\circ} \qquad 1\text{-}46$$

The symbol S means local concentration of polar solvent near the ion pair and is assumed to be constant, independent of the bulk composition of the solvent mixture.

For abbreviation they set

$$k/aS = k_s \qquad 1\text{-}47$$

Denoting $aA^{+} = aB^{-}$ by $c\gamma$ and using the stoichiometric relationship

$$a\left[\overset{+}{A}\overset{-}{B}\right]^{\circ} + a\left[\overset{+}{A}S\overset{-}{B}\right]^{\circ} = c(1-\gamma) \qquad 1\text{-}48$$

Equations 1-44 and 1-48 may be combined to give

$$c\gamma^2/1-\gamma = K_D/(1 + k_s) \qquad 1\text{-}49$$

Since $c\gamma^2/1-\gamma$ is the constant obtained by extrapolation of conductance data it therefore follows that

$$K_{exp.} = K_D/(1 + k_s) \qquad 1\text{-}50$$

The above expression may be restated as follows: formation of a solvated ion pair is assumed to be described by the sphere-in-continuum model, where the distance $\overset{o}{a}$ represents center-to-center distance between ions which trap a solvent molecule between them. Then the solvent molecule is expelled by a discrete process described by the solvation constant k_S.

Conductance data for tetrabutylammonium bromide in nitrobenzene-carbon-tetrachloride mixtures were correlated by the above expression by Fuoss. Essentially what was found was that the equilibrium constants from conductance data were directly proportional to constants calculated from Bjerrum's equation assuming a constant value of $\overset{o}{a}$ for all solvent mixtures involved. The data fit the following expression

$$K_{exp.} = \frac{K\,(D_1;\ 4.25)}{2.63} \qquad 1\text{-}51$$

where $K_{exp.}$ is the experimental value and $K(D_1; 4.25)$ is the Bjerrum value calculated at dielectric constant D_1 and $\overset{o}{a}$ equal to $4.25\overset{o}{A}$.

Critique of Sadek and Fuoss Model

It is a relatively simple matter to demonstrate that the hypothesis of Fuoss is not a useful representation of a real physical system, and that in all probability the observed

agreement found by these workers in the nitrobenzene-carbon tetrachloride system is merely a consequence of introducing another empirical constant into the equations.

Consider the expression

$$K_{exp.} = K_D/(1 + k_s) \qquad 1\text{-}50$$

where k_S represents the process of ejection of a solvent molecule from a solvated ion pair. This latter process may be depicted by the equation

$$\left[\overset{+}{A}S\overset{-}{B}\right]^0 \rightleftharpoons \left[\overset{+}{A}\overset{-}{B}\right]^0 + S$$

where $\left[\overset{+}{A}S\overset{-}{B}\right]^0$ represents an ion pair in which the distance of closest approach includes a contribution from solvent molecules interposed between the ions.

In liquid sulfur dioxide we have demonstrated that $K_{exp.} = K_D$ over a wide range of $\overset{o}{a}$ values. The $\overset{o}{a}$ values were found to be exactly equal to the sum of the crystallographic ionic radii and hence the ion pairs must in fact not be solvated in the Sadek-Fuoss sense. Thus the Sadek-Fuoss treatment would require that k_S be very large while in fact in order to satisfy the experimental observation that $K_{exp} = K_D$, its value must be extremely small if not indeed equal to zero. Thus the new model fails to account for the observed behavior in sulfur dioxide solution.

Fuoss's recent work (102,109,110,111,112) on electrolyte-

solvent interactions is subject to one very fundamental criticism, namely, that the system chosen for these studies lacks the maximum possible simplicity. Tetrabutylammonium bromide is certainly not an ideal choice regardless of how excellent the experimental procedures may be. For example, the ionic radius of the tetrabutylammonium cation is a rather nebulous quantity whose value depends on the conformation of the long butyl chain. Furthermore, the large size of this cation results in large values for the measured equilibrium constant and therefore rather unreliable values as a consequence of the inability of the extrapolation procedures to give accurate results for strong electrolytes. Evidence of this can be found in the equilibrium constant values for tetrabutylammonium bromide in pure methanol shown in table 1-XXII. It can be seen that the value reported by Fuoss in three successive papers vary over a factor of two. The accurate value may possibly be different from either of these values by another factor of two or even more.

Perhaps potassium bromide would have been a much better choice for these investigations.

Bjerrum's Model

The sphere-in-continuum model employed by Bjerrum prescribes no limitations to the å parameter other than that it be the distance separating the centers of two uniformly charged spheres. Factors contributing to the size of these

spheres are not considered in the treatment. It is merely stated that in a solvent of fixed macroscopic dielectric constant an electrolyte will have an ion pair dissociation constant whose value will depend upon the value of the $\mathring{a}$ parameter. Since, in general, the $\mathring{a}$ parameter has been found to be dependent upon both the nature of the solute and that of the solvent, no quantitative physical significance has been assigned to it. The possibility that the macroscopic dielectric constant does not adequately describe the medium between two ions in close proximity has been suggested (43). This does not seem to be the only solution in view of the pronounced variation of the $\mathring{a}$ parameter in several solvents of essentially the same dielectric constant (2)(81). In much of the work in which the $\mathring{a}$ parameter exhibits anomalous behavior the ions considered were highly unsymmetrical and hence probably not spherical even to a first approximation. Obviously in such cases a model based on spherical ions need not be expected to be exact.

It is now possible in view of the results obtained in these investigations to ascribe an exact physical meaning to the $\mathring{a}$ parameter and to consider in some detail variations in $\mathring{a}$ in terms of ion solvent interactions.

Limiting Values of $\mathring{a}$

In the formation of ion pairs, the ions are considered to approach to a certain equilibrium position such that the

distance separating the centers of charge is equal to a parameter $\overset{o}{a}$. While the exact value of $\overset{o}{a}$ cannot be predicted a priori for any given system of electrolyte in a solvent it is very instructive to consider possible extreme values of this parameter.

In ionic crystals of the alkali halides we know that $\overset{o}{a}$ is equal to the sum of ionic radii. It should be reasonable then to assign this as the minimum value $\overset{o}{a}$ can have in solution. This means that when there is no solvent interposed between the ions in a solution, $\overset{o}{a}$, is equal to the sum of crystal radii of the ions. This has been found to be the case in liquid sulfur dioxide solutions of alkali halides. We may therefore tentatively assign a value to $\overset{o}{a}$ in the lower limit which is equal to the sum of ionic radii.

An exact maximum value for $\overset{o}{a}$ cannot be assigned as easily. However, it is not unreasonable to consider that increases in $\overset{o}{a}$ values over the minimum value are the result of interposition of solvent molecules between the ions. Whether one or more molecules are involved cannot be determined. For the sake of simplicity however we can consider the case of one molecule of solvent interposed between the ions. The quantitative nature of the effect will not suffer from this simplification. The process can be depicted as follows:

$$\left[\overset{+}{A}S\overset{-}{B}\right]^{\circ} \rightleftharpoons \left[\overset{+}{A}\overset{-}{B}\right]^{\circ} \neq \quad S$$

and the distance parameter $\mathring{a}$ will be equal to the sum of crystal radii plus an increment of distance related to the dimension of the solvent molecule.

The question which must now be answered is, what exactly is the dimension of a solvent molecule? The answer of course is simply that we do not know, however, it should be possible to deduce several qualitative requirements which must be fulfilled by a model.

First, regardless of the exact value for the increase in $\mathring{a}$ due to the size of the solvent molecule, the model must require that this increment be of constant value for each solvent. This results in a restriction that the ion pair either has or does not have solvent interposed between the ions depending only upon the polar nature of the solvent. In other words, in certain media no solvent molecules are interposed between the ions and the $\mathring{a}$ value is at its minimum, while in more polar solvents one or several molecules of solvent are interposed between the ions and the $\mathring{a}$ parameter is larger by an amount which is a characteristic constant for a particular solvent.

Experimentally it is found that the $\mathring{a}$ parameter is a constant in a given solvent. Moreover in a solvent mixture of water and dioxane the $\mathring{a}$ parameter remains constant over a wide range of the dielectric constant. This has been interpreted as being due to the fact that the molar concentration of water in this system was always great enough to effect

complete solvation of all ions and ion pairs present in the solution.

Contrary to this behavior expected on the basis of the present model, Fuoss has found solvent systems in which the $\overset{o}{a}$ value continuously changed with the composition of the solvent pair. Several undesirable features of these investigations not withstanding, it remains clear that the yes-no assumption of the model is a gross oversimplification.

Model for Ion Pairs

Any detailed model of Bjerrum ion pairs must correlate the following facts and restrictions:

1) The lower limit of the $\overset{o}{a}$ parameter must be equal to the sum of crystal radii of the ions.

2) The $\overset{o}{a}$ parameter must be independent of temperature to a good first approximation.

3) The distance of closest approach must contain an increment (this may of course by zero) which is a constant for a given solvent and whose value will differ with the nature of the solvent.

4) In solvent mixtures the $\overset{o}{a}$ parameter may change continuously with change in composition of the mixture.

It is beyond the scope of this dissertion to provide such a model.

Future Work

It has been shown that, contrary to observations in other solvents, in liquid sulfur dioxide the Bjerrum theory quantitatively represents the ionic association behavior of 1-1 electrolytes. This result is surprising in view of the over-simplified model assumed in this theory. Future work on this problem should be directed toward two goals, namely, (1) extension of the scope of exact agreement by means of measurements on simple 1-1 electrolytes, and (2) establishment of structural limits beyond which agreement with Bjerrum's theory cannot be expected. In this respect a series of measurements on n-alkyltrimethylammonium halides where the alkyl group ranges from hexyl to hexadecyl would be of interest.

Investigations intended to illucidate the particular properties of liquid sulfur dioxide which make this solvent ideal as far as the Bjerrum theory is concerned cannot be suggested at this time.

EXPERIMENTAL SECTION

Preparation of Compounds

Potassium chloride: The potassium chloride used in this research was Baker's C.P. grade and was recrystallized from conductivity water. This sample was part of the same material previously used by Glazer (46) for the cell constant determination.

The pure sample was pulverized in a Coor's "Mullite" mortar and was oven dried for four hours at 120°C. before use.

Potassium iodide: Baker's C.P. grade potassium iodide (granular, Lot #10650) was twice recrystallized from conductivity water. The crystals were washed on a sintered glass funnel with Baker's C.P. diethyl ether and were air dried. After being pulverized in a Coor's "Mullite" mortar the sample was oven dried for three hours at 115°C. The compound was pure white and was stored in a desiccator over indicating Drierite. The sample, designated as lot KI-I, was used in runs HL-32, 33, 34, 35, and 36.

Sample KI-2: Merck reagent grade potassium iodide (Lot 52141A) was dissolved in hot (preboiled) conductivity water and the resulting solution was rapidly filtered through a sintered glass funnel. An atmosphere of nitrogen was maintained by carrying out all operations under a large

inverted funnel through which flowed a rapid stream of nitrogen. On slow cooling the filtered solution produced white needles of potassium iodide. The mother liquor was colorless and at no time during the purification was there any evidence of free iodine in the solution. The crystals were filtered on a sintered glass funnel and washed with cold conductivity water, a small amount of C.P. acetone, and finally with C.P. petroleum ether. This sample was oven dried for three hours at 120°C. and cooled in a desiccator over calcium chloride before use. Sample KI-2 was employed in runs HL-37, 38, 62, 75, and 76.

Potassium bromide: Merck and Co. reagent grade potassium bromide was twice recrystallized from conductivity water, washed with 95% ethanol and with Baker's C.P. diethyl ether. Following preliminary drying at 115°C., for one hour, the crystals were pulverized in a Coor's "Mullite" mortar and finally dried in a vacuum oven for four hours at 130°C.

Tetramethylammonium bromide: Eastman Kodak Co. White Label tetramethylammonium bromide was twice recrystallized from 95% ethanol. The crystals were washed with ethanol and petroleum ether and oven dried at 110°C. for two hours. Before use the purified product was pulverized and dried in a vacuum oven for four hours at 125°C.

Preparation of Tetramethylammonium sulfate

Experiment I. Preparation of silver sulfate.

A solution of 174.3 gms. (1.0 mole) of Baker's C.P.

potassium sulfate in 250 ml. of distilled water was added slowly to a stirred solution of 340 gms. (2.0 moles) of Baker's C.P. silver nitrate in 100 ml. of distilled water. The solutions were mixed under darkroom conditions and the resulting precipitate of silver sulfate was allowed to stand in a closed flask for twenty four hours before isolation. The product was filtered on a sintered glass funnel and washed with ice cold distilled water until the washings gave a negative test for silver ion. After washing with absolute ethanol and C.P. diethyl ether the product was dried in a vacuum desiccator over phosphorus pentoxide.

Experiment II. Tetramethylammonium sulfate.

Solid silver sulfate, 61.0 gms. (0.25 mole) was added to a solution of 77.0 gms. (0.50 mole) Eastman Kodak Co. White Label tetramethylammonium bromide in 100 ml. of distilled water contained in a glass stoppered flask. The reaction flask was protected from light with aluminum foil. The reaction was carried out by vigorously shaking the charged flask for twenty four hours on a Burrell wrist action shaking machine set for maximum speed. After the shaking period, the silver bromide precipitate was removed and a fresh charge of silver sulfate (10 gms.) was added. After ten hours of shaking no evidence of further reaction was observed when another fresh charge of silver sulfate was added.

The reaction mixture was chilled in an ice bath and filtered rapidly through a sintered glass funnel. The

solution was concentrated to about 25 ml. by evaporating on a steam bath. Twenty five ml. of 95% ethanol was added and the solution was filtered to remove a small amount of silver sulfate which had precipitated during the evaporation. The filtered solution was evaporated to dryness on a steam bath and the product was dissolved in 95% ethanol and filtered. Acetone was added to the hot ethanolic solution until a faint cloudiness appeared. Addition of a few drops of ethanol gave a clear solution, which, when allowed to cool slowly gave the desired product in the form of long prismatic needles. The product was recrystallized three times from an acetone-ethanol mixture, filtered, and washed with C.P. acetone. The pure product was pulverized and dried in a vacuum desiccator over phosphorus pentoxide for two weeks. The final product was extremely hygroscopic and utmost care was exercised to prevent exposure of the product to moisture during handling operations. Gravimetric analysis for sulfate indicated 99.53 and 99.36% of the theoretical amount.

Materials

Acetone and petroleum ether: The solvents for washing the conductivity cell were always Baker's C.P. grade solvents from freshly opened bottles which were thereafter very carefully protected from contamination.

Liquid sulfur dioxide: The solvent used in all of the conductivity measurements was "Refrigeration" grade sulfur

dioxide supplied as a liquid in pressurized tanks by the Virginia Smelting Co. under the trade name of "Extra-Dry ES-O-TOO". This material was further dried in the gas phase by passage through two columns, (50 x 2.5 cm.) of Baker's C.P. anhydrous magnesium perchlorate (Anhydrone) containing a one inch band of indicating Drierite. In some of the runs the condensed dried sulfur dioxide was outgassed by pumping at -78°C. The specific conductivity of the solvent, determined separately after each run, varied between 0.6×10^{-8} and 3.0×10^{-7} mhos cm^{-1}.

Conductivity Measurements

Apparatus and procedures:

Conductivity cell: The conductivity cell used throughout this research was the same one used by Lichtin and Glazer (91) and by Lichtin, Weston and White (93) and is adequately described elsewhere (46). The calibration data for this cell are as follows:

Cell constant = 0.2226

Electrode bulb volume = 42.985 ml. at the 1.20 ml. mark

Dilution bulb volume = 18.730 ml.

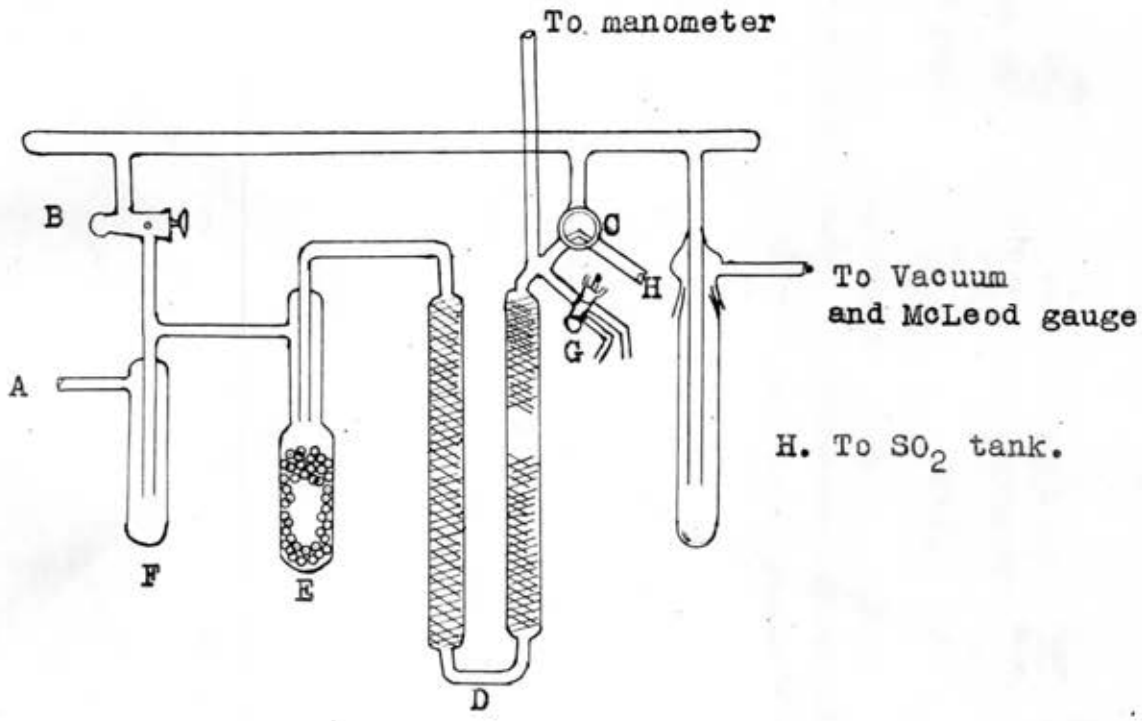
Preparation of Conductivity Cell: Before each run the cell was rinsed at least six times with acetone and four times with petroleum ether. Residual solvent was then removed by

alternately pumping on a water aspirator and flushing with dried air. The cell was then sealed to the vacuum line and thoroughly dried by pumping (10^{-3} to 10^{-5} mm. pressure) for at least twelve hours while being baked out with a battery of infra-red lamps. The uncalibrated portions of the cell were further dried by heating with a brush flame while under high vacuum. At the end of the drying period the cell was slowly filled with dry air and opened to receive the sample. The sample was introduced directly into the cell by means of a small cylindrical weighing bottle which could be inserted into the receiving arm of the cell. The receiving arm was then sealed and the cell and sample were evacuated (10^{-3} to 10^{-5} mm. pressure) for periods varying between four and twelve hours. All samples weights were determined by difference to an accuracy of 0.01 mg. on a semi-micro balance which was periodically calibrated against Wm. Ainsworth Co. Class S weights calibrated against National Bureau of Standards weights. The samples were protected against moisture by storing in vacuum desiccators over indicating Drierite. Transfer of a sample from the desiccator to the special weighing bottle was always carried out under an atmosphere of dry nitrogen by working directly under a large inverted funnel connected to a tank of dry (oil pumped) nitrogen. Whenever possible sample handling was restricted to relatively dry days in order to avoid possible contamination by atmospheric moisture.

Vacuum line: The vacuum line used for filling the cell with, and purification of, liquid sulfur dioxide is shown schematically in figure 1-XV.

The conductivity cell was sealed to the line at A, and after adding the sample was evacuated to a pressure of about 10^{-5} mm. Stopcocks B and C were then used to isolate the cell and drying train from the manifold while the sulfur dioxide inlet tube was being evacuated up to the packing gland of the sulfur dioxide storage tank. Stopcock C was then turned to connect the sulfur dioxide tank to the drying train. Sulfur dioxide gas was slowly bled into the line through a Hoke "Bellows type" needle valve. After passing through the drying towers, D, the gas was condensed in trap E which was immersed in a dry-ice trichloroethylene bath at -78°C. The gas flow rate was adjusted so that about one hour was required to collect about 60 ml. of liquid sulfur dioxide.

When the required amount of liquid was collected in trap E, the electrode bulb of the cell was immersed in a large Dewar flask containing kerosene maintained at -35°C. by adding dry ice when required. Trap F was immersed in an ice-water slush and the sulfur dioxide was distilled into the cell by warming trap E with an infra-red lamp. Trap E was filled with 1/8 inch glass helices to prevent bumping and mechanical carry over of the liquid during the distillation. When the cell was filled with the required volume of liquid sulfur dioxide, trap E was cooled to -40°C. and the cell



Vacuum Line for Preparation of Conductivity Runs.

FIGURE 1-XV

was sealed off at A. Excess sulfur dioxide was removed from the line with a water aspirator through stopcock G and the external drying columns.

Thermostat: The thermostat used throughout this work has been described elsewhere (46). Temperature was regulated by means of a three contact Red Top* thermoregulator connected through a selector switch to an electronic relay** which controlled the heating cycle. The thermoregulator was preset so that the temperature could be changed by means of the selector switch. For all runs reported the temperature was $0.12^{\circ} \pm 0.02^{\circ}$C. and $-8.93^{\circ} \pm 0.03^{\circ}$C.

Conductivity Bridge: The conductivity bridge employed in this work has been described elsewhere (46) with the exception that resistances beyond the bridge capacity were measured with the aid of both a 20,000 and 40,000 ohm shunt, either of which could be introduced into the bridge circuit by means of a toggle switch thus reducing possible errors due to faulty connections.

The A.C. bridge was calibrated at 2000 C.P.S. against 10,000 and 100,000 ohm secondary standard fixed wire wound resistors*** guaranteed to $\pm$ 0.05% of their rated values. The precision of the bridge is estimated from the reproducibility

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* Red Top Multijunction thermoregulator. H.B. Instrument Co.
**Emil Greiner Co., catalogue number G24873.
*** International Resistance Co. "Precision Resistors"

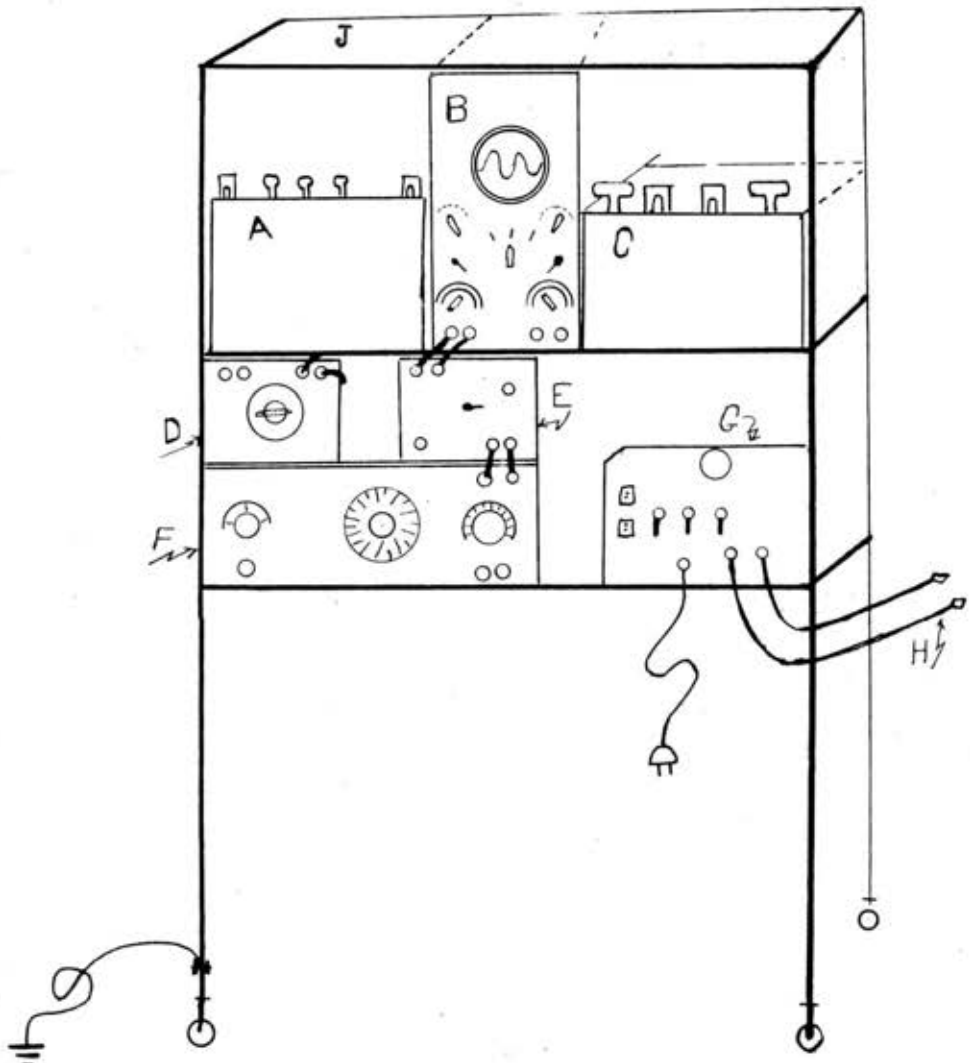
of measurements of fixed resistances, as better than ±0.01% in the range 0-10,000 ohms and ± 0.02% in the range 10,000-100,000 ohms.

Resistance values were not independent of variations in frequency even when measuring a fixed, inductively wound, resistor. Thus for example the measured resistance of a 10,000 ohm wire wound resistor varied between 9800 and 10,150 ohms when the frequency was changed from 200 to 20,000 C.P.S. This behavior has recently also been reported (32) for a bridge of similar construction. These workers were able to eliminate the frequency dependence by using only low loss cable throughout the connecting circuits. Unfortunately, all measurements reported here were completed long before this publication appeared. However, since all measurements in this work were carried out at the frequency of calibration (2000C.P.S.) the accuracy is not impaired by the failure to eliminate frequency dependence and the accuracy of the resistance values can not be less than ±0.05% resulting from the uncertainty in the value of the resistances used for calibration of the bridge.

Due to the space requirements of the laboratory it was found convenient to assemble the bridge on a portable instrument rack as shown in figure 1-XVI.

Measurements

The measurements were carried out by the method of Lichtin



Conductivity Bridge Assembly

FIGURE 1-XVI

A. Shakleton Ratio Box.
B. Oscilloscope.
C. Decade resistance boxes.
D. Variable capacitance.
E. Amplifier.
F. Oscillator.
G. Control panel.
H. Leads to conductivity cell.
J. Safety glass top.

and Bartlett (90) and since this procedure has been adequately described elsewhere (46) the details involved do not warrant repetition here.

Individual Conductivity Runs

A brief summary of each conductance run, the data of which are summarized in tables 1-A to 1-J in the Appendix I-B, is presented below. The runs are described by compound and in the order in which they were performed. The description of the runs therefore parallels the arrangement of the data in tables 1-A to 1-J. All runs reported here were carried out at 0.12± 0.02°C. or -8.93± 0.03°C. unless otherwise specified.

Potassium Chloride: Due to the limited solubility of this salt in liquid sulfur dioxide, the general procedure described above required the following modification. Since the largest sample which could be dissolved was of the order of 1 mg., a micro balance was required for the weighings. A Wm. Ainsworth Co. Micro balance was used for this purpose. An alternate technique employed was that of introducing the sample as an aliquot of a dilute standard aqueous solution and then carefully evaporating to dryness. A standard solution of potassium chloride in conductivity water was prepared containing 0.5373 mg. of the salt in 1.000 ml. of solution. The solution

was carefully introduced into the cell from a self-filling micro buret graduated directly in 0.01 ml. divisions. Approximately 2.0 ml. aliquots of solution (hence about 1 mg. of KCl) were used for each run. The solvent was slowly and carefully removed by pumping with a water aspirator. When all visible water was removed the cell was baked out with an infra-red heating lamp while pumping was continued. The cell was then sealed to the vacuum line and baked out for four to six hours under high vacuum followed by pumping overnight at room temperature. The run was then carried out as usual.

A total of six reproducible runs were carried out on potassium chloride at two temperatures. Runs HL-30 and 31 at 0.12°C. were carried out by the aliquot method. The results of HL-28 and HL-29 at -8.93°C. employing this technique were in good agreement with the results obtained in runs HL-25 and 26 in which the samples were weighed directly on the micro balance. Potassium chloride gave a colorless solution in all cases.

Potassium bromide: Measurements on this compound were facilitated by employing two thermostats. In this way runs could be carried out at two temperatures on the same sample preparation. The possibility of using several thermostats in this manner is suggested for future measurements at several temperatures. The runs are set up in the usual manner and the cell is placed in the low temperature thermostat for equilibration and measurement. After the equilibrium

measurement is obtained the cell is removed and the solvent volume recorded. To facilitate equilibration at the higher temperature the cell may be immersed in an ice slush and the solution mixed several times. The cell is then placed in the other thermostat and equilibrium measurements obtained. The solution volume must be determined at each temperature since the concentration units employed in this work are expressed in terms of moles of solute per liter of sulfur dioxide solution.

Two runs were performed on potassium bromide at each temperature. Run HL 66 and 68 at 0.12°C. and HL 67 and 69 at -8.93°C. In each case the solvent was outgassed by pumping at -78°C. for two hours. Solutions of potassium bromide in liquid sulfur dioxide were colorless.

Potassium Iodide: Runs on this compound were first performed at 0.12°C. The results obtained in runs HL-32 and HL-33 were in excellent agreement with each other and with the 0°C. data of Franklin (Appendix I-B table I-K). After each run the cell was thoroughly cleaned. Sample KI-1 was used in HL 32 and 33.

Several runs were then carried out at -8.93°C. in which very poor reproducibility was experienced. Runs HL 34, 35 and 36 (table I-L) used in constructing the plot shown below (Figure 1-XVII) are representative of the poor quality of the data obtained at -8.93°C. A possible explanation of

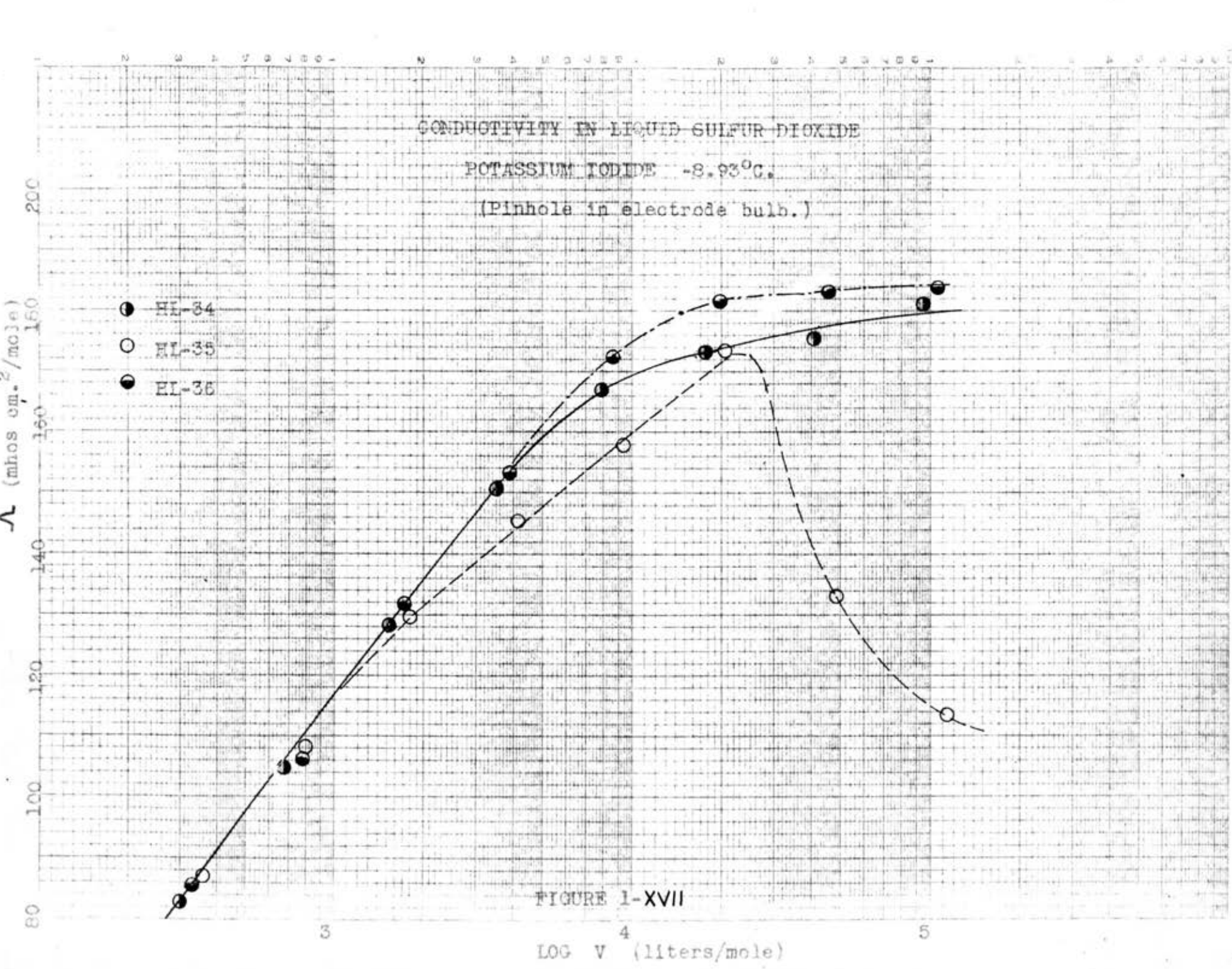


FIGURE 1-XVII

these results may lie in the fact that in these runs the residues in the distillation bulb of the cell were not removed completely. This may have been a source of molecular iodine which could have slowly distilled into the electrode compartment during the course of the run. The presence of iodine in the potassium iodide solution would react to form potassium triodide and the resulting decreased mobility of the anion could account for the decrease in the observed conductivity as illustrated in figure 1-XVII. It should be pointed out that resistance drifts were noted at the high dilution measurements on these runs.

A new sample of potassium iodide (KI-2) was prepared and several more runs were performed at -8.93°C. These runs, HI-36, 37, 38 (data not reported) failed to resolve the difficulty even though the cell was exhaustively cleaned before each run.

Work on this compound was discontinued temporarily in favor of measurements on tri-m-biphenylylchloromethane which were required for the research described in Part II. The first two runs on this aryl chloride failed to give reproducible conductance values. In an effort to determine the source of the difficulty, the cell was checked carefully for leaks. A small leak was discovered in a De Khotinsky cement seal around a ring seal in the electrode bulb. The leak was repaired and reproducible results were again obtainable.

It seems probable therefore that the difficulties experienced in the potassium iodide runs could be attributed to a leak in the cell. It should be pointed out that the De Khotinsky cement used to seal the pinhole in the cell was subject to slow deterioration in kerosene. Failure of this seal during a run often caused trouble. Several grades of De Khotinsky cement were evaluated for resistance to kerosene and low temperatures. Best results were obtained with the medium grade cement, however, care had to be exercised to prevent softening the cement during the baking out of the cell. In all subsequent runs the De Khotinsky seal was tested with a Tessla coil both before and after the run.

Three more runs were performed on potassium iodide in the leak free cell. Run HL-62 at 0.12°C. gave results which were in excellent agreement with runs HL-32 and 33 at this temperature. Good reproducibility was obtained in two runs at -8.93°C. (runs HL-75 and 76).

The calculations on potassium iodide thus are based on three runs at 0.12°C. (HL-32,33 and 62) and two runs (HL-75, 76) at -8.93°C. In runs HL-62, 75 and 76 the solvent was outgassed between 1 to 2 hours at -78°C. before being introduced into the cell. Solutions of potassium iodide in liquid sulfur dioxide were greenish yellow.

Tetramethylammonium bromide: Two runs were carried out at each temperature by employing two thermostats. In each case the

solvent was outgassed by pumping at -78°C. Runs HL-70 and 72 at 0.12°C. and runs HL-71 and 73 at -8.93°C. were in good agreement up to about 25,000 liters per mole. The data for the last point (50,000 liters per mole) deviated considerably. A dilution error following the 25,000 liter per mole point is suspected in the second run (HL-72 and 73) at each temperature. Therefore the 50,000 liter per mole data were not included in the calculations.

Tetramethylammonium bromide forms colorless solutions in liquid sulfur dioxide.

Tetramethylammonium sulfate: The data reported for this compound represent the only high dilution measurements available on an unsymmetrical electrolyte in liquid sulfur dioxide solution.

Tetramethylammonium sulfate is readily soluble in sulfur dioxide and forms solutions which are essentially colorless with an extremely faint yellow hue in the more concentrated region. The resistance of the concentrated solutions is very low, of the order of several hundred ohms, and therefore in order to minimize polarization effects the measurements were carried out with a 1000 ohm resistance in series with the cell.

Since this work was of an exploratory nature, measurements were carried out at one temperature only. Runs HL-77 and 78 at 0.12°C. were in good agreement with each other over the entire dilution range. In both runs the solvent was outgassed

by pumping at -78° C. for at least one hour.

Recovery of Compounds

Recovery was attempted only in the case of potassium iodide. The solution from run HL-32 was poured into a clean beaker. A brown residue remained after evaporation of the solvent. Pumping for eight days at less than 10^{-3} mm. failed to remove the color. Heating for several hours with an infra-red lamp while pumping also failed to decolorize the residue.

The residue formed a colorless solution in distilled water which had a slight odor of sulfur dioxide. Evaporation to dryness gave white crystals of potassium iodide.

Residues from all other runs on inorganic salts were colorless solids and were not subjected to further tests. It should be pointed out that in general the quantity of material recovered from a conductance run was too small (10-30 mg.) for extensive testing.

Experimental Difficulties

Other than the problems arising from a pinhole in the conductance cell this work was not accompanied by any major experimental difficulties.

PART II.

Equilibria of Meta-Phenyl Derivatives of Trityl Chloride.

INTRODUCTION

The equivalent conductance of the mono-, di-, and tri-m-phenyl derivatives of triphenylchloromethane have been measured in liquid sulfur dioxide solutions at 0.12° C. and -8.93°C. over a wide range of concentration. Similar data for triphenylchloromethane and its mono-p-phenyl derivative have been obtained at -8.93°C.

Thermodynamic equilibrium constants were calculated from these data by applying Shedlovsky's extrapolation procedure and the method of least squares over the dilution range from 2,000 to 80,000 liters per mole. Standard free energies, "enthalpies" and "entropies" were calculated from the equilibrium constants. These have been correlated with the electronic effects of the phenyl group on the stabilization of the triphenylcarbonium ions.

The influence of variations in structure and size of the carbonium ions has been treated by the theory of ionic association. In this way ionization and ion pair dissociation constants have been calculated for a series of ring substituted triphenylchloromethanes in sulfur dioxide solutions and correlations with group effects have been proposed.

The ionization constant of m-phenylbenzoic acid has been measured in 50% aqueous butyl cellosolve at 25°C. by a potentiometric titration employing a glass electrode. From these data the Hammett sigma value for m-phenyl has been calculated.

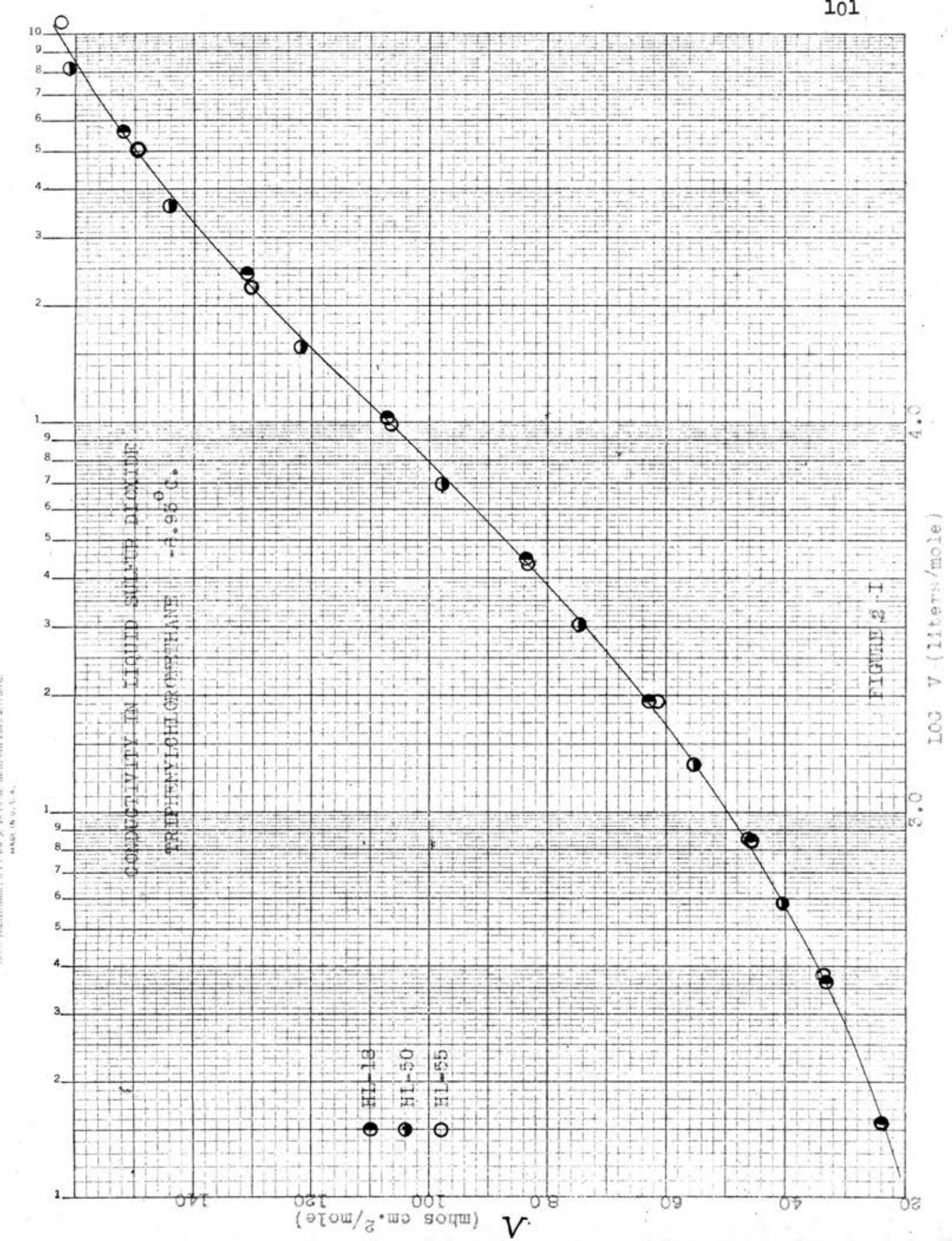
RESULTS AND DISCUSSION

The conductivity data collected in this research are presented graphically in figures 2-I to 2-VIII as semilogarithmic plots of equivalent conductance versus dilution. At least three runs were carried out for each compound and the precision of the data as estimated from the average percent deviation of the individual points from the best fitting smooth curve is plus or minus 1 % or better for each compound in the region of 10^2 to 10^5 liters per mole. Experimental equivalent conductance and dilution values used in the construction of the plots are summarized in tables 2-A to 2-N in the appendix.

Table 2-I summarizes the equilibrium values derived from the conductivity data. Experimental equilibrium constants ($K_{exp.}$) for the process:

$$R_3C\text{-}Cl \overset{K_1}{\rightleftharpoons} [R_3C^+)(Cl^-]^\circ \overset{K_2}{\rightleftharpoons} R_3C^+ + Cl^-$$

and limiting equivalent conductance (Λ_o) values were evaluated by the extrapolation procedure described by Shedlovsky(117) and discussed by Fuoss and Shedlovsky (45). The extrapolation was performed by the method of least squares to give values of the slope, $1/K\Lambda_o^2$, and of the intercept, $1/\Lambda_o$. Deviations of the experimental points from the least square line were computed in each case and mean deviations for the data of each compound were thus obtained. Values of the least square slopes and intercepts and the percent mean deviations are summarized in table 2-II.


CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
TRIPHENYLCHLOROMETHANE -1.96°C.
FIGURE 2
HL-18
HL-50
HL-55
(mhos cm.²/mole)
Λ
10³ V (liters/mole)

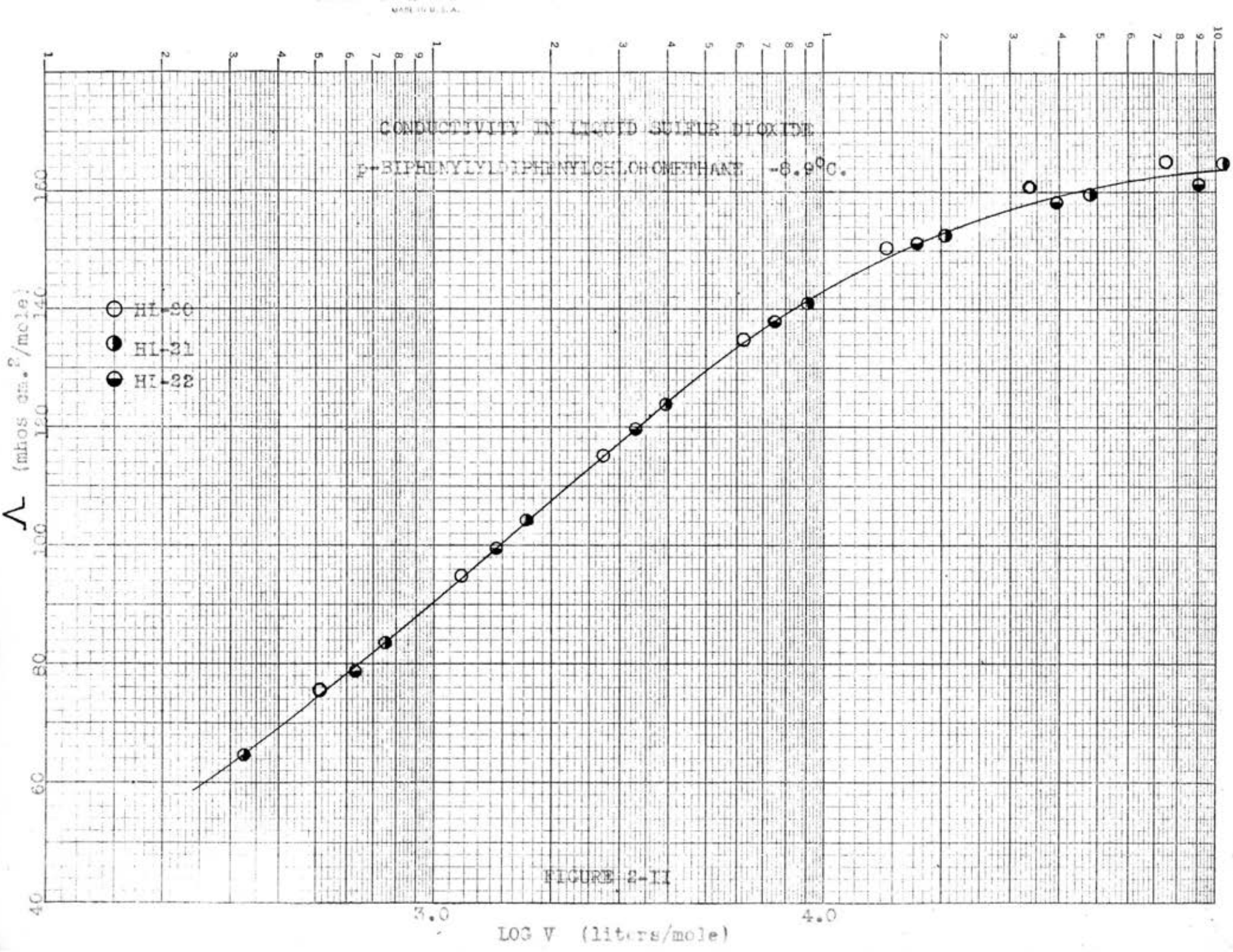
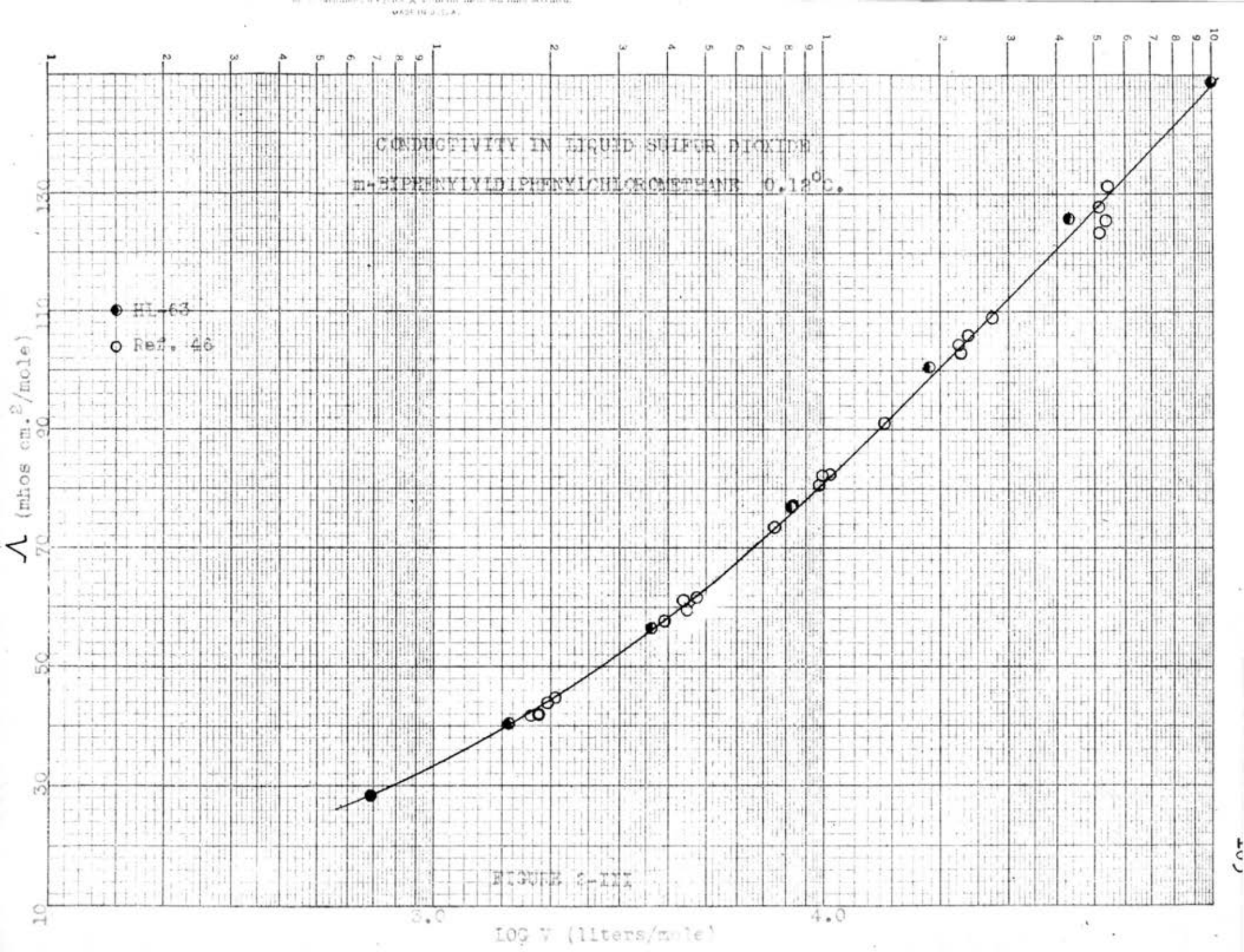

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
p-BIPHENYLYLDIPHENYLCHLOROMETHANE -8.9°C.
HI-30
HI-31
HI-32
Λ (mhos cm.²/mole)
LOG V (liters/mole)
3.0
4.0
40
60
80
100
120
140
160

FIGURE 2-II


CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
m-BIPHENYLYLDIPHENYLCHLOROMETHANE 0.12°C.
HL-63
Ref. 46
Λ (mhos cm.²/mole)
LOG V (liters/mole)
3.0
4.0
10
30
50
70
90
110
130

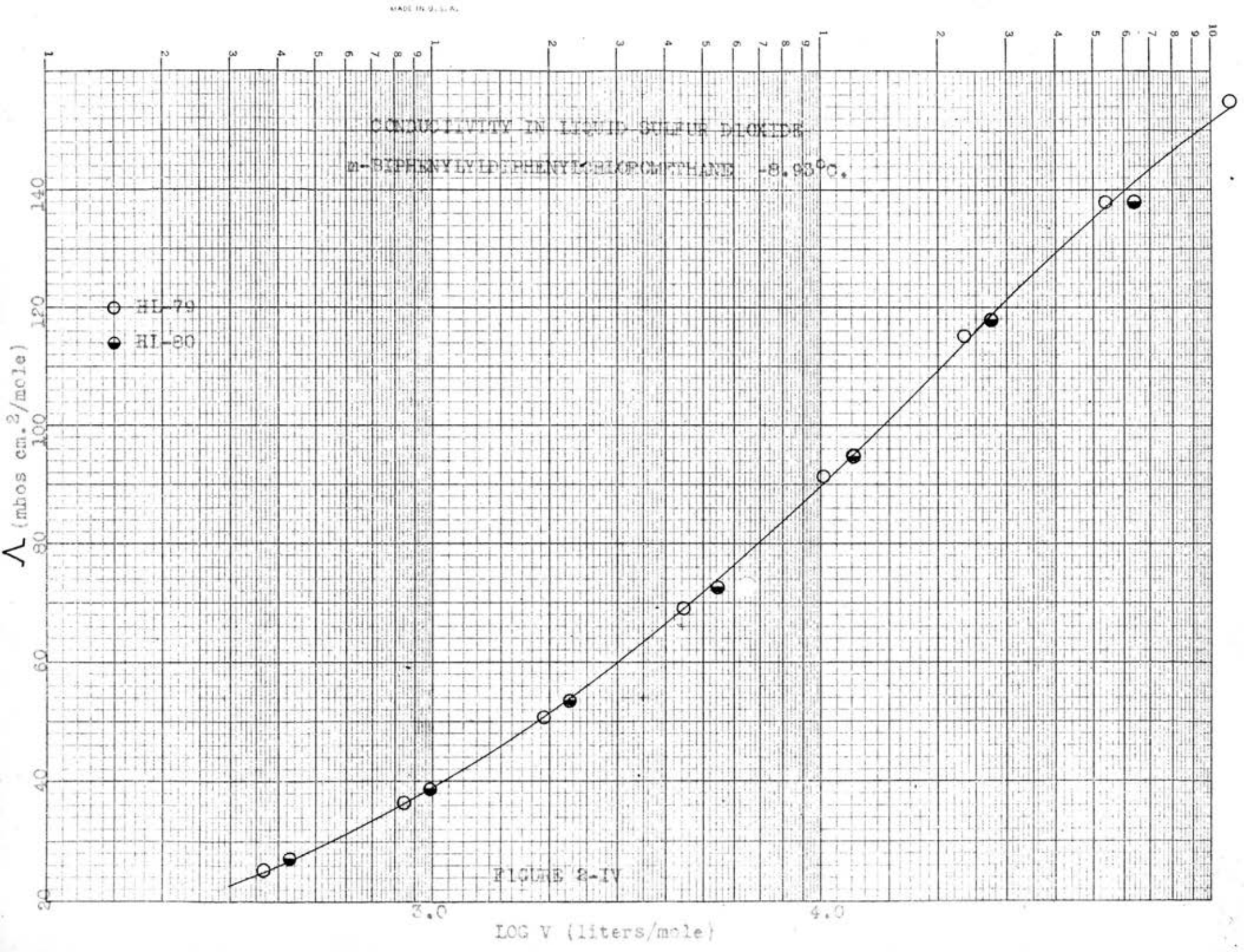

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
4-BIPHENYLYLDIPHENYLCHLOROMETHANE -8.93°C.
HL-79
HL-80
Λ (mhos cm.²/mole)
LOG V (liters/mole)
3.0
4.0

FIGURE 2-IV

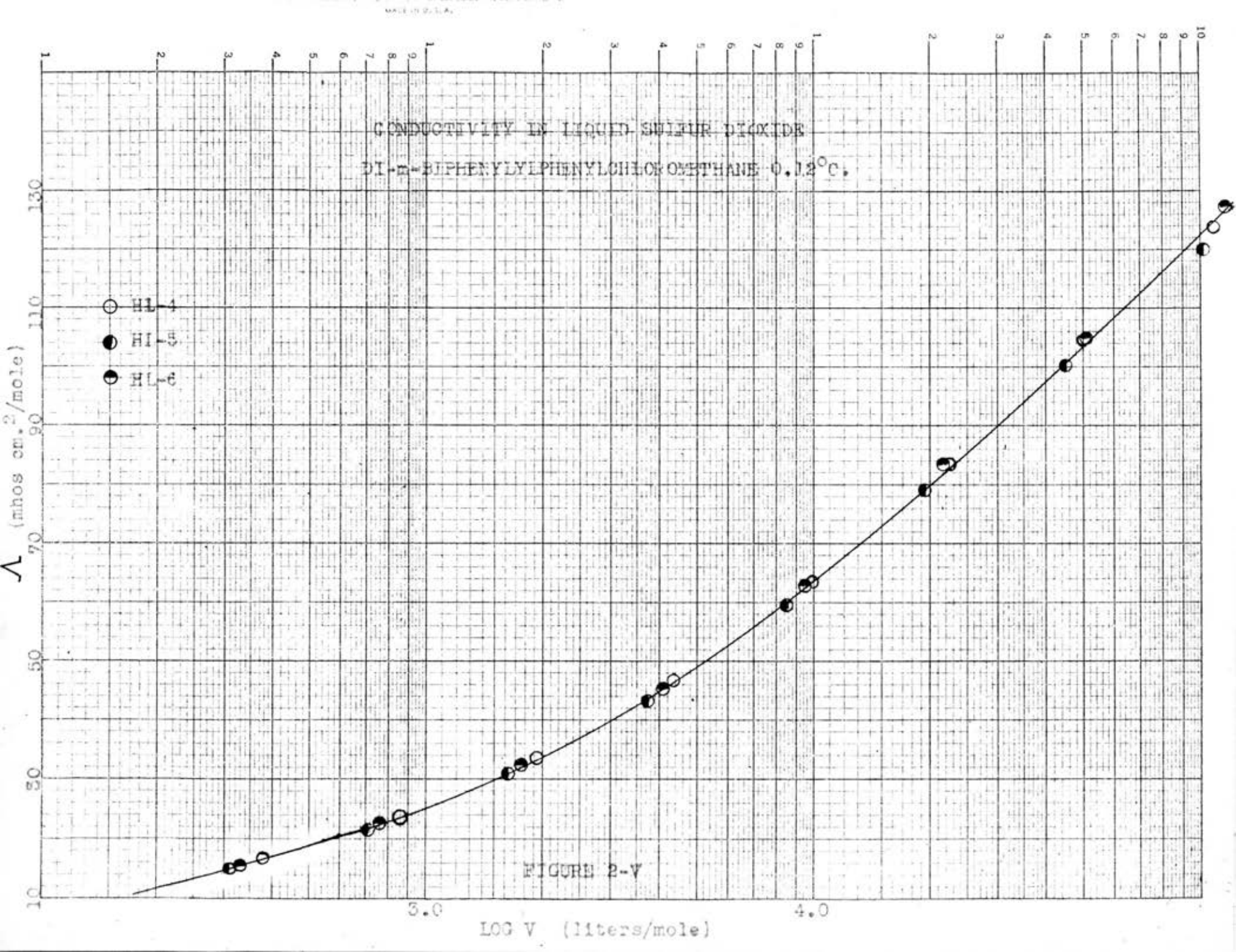
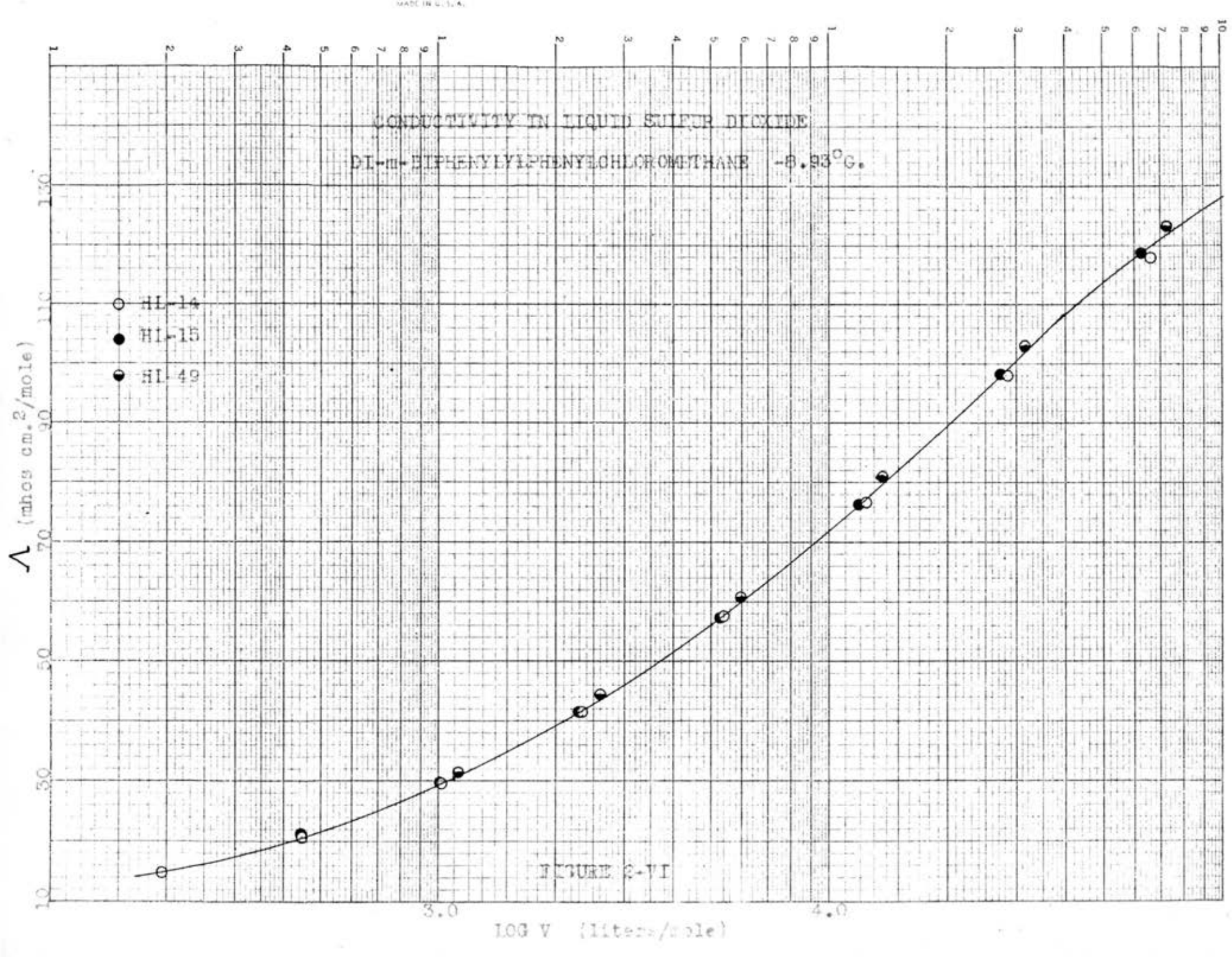

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
DI-m-BIPHENYLYLPHENYLCHLOROMETHANE 0.12°C.
HL-4
HL-5
HL-6
Λ (mhos cm.²/mole)
LOG V (liters/mole)
3.0
4.0
10
30
50
70
90
110
130

FIGURE 2-V


CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
DL-m-BIPHENYLYLPHENYLCHLOROMETHANE -8.93°C.
HL-14
HL-15
HL-49
Λ (mhos cm.²/mole)
LOG V (liters/mole)
3.0
4.0
FIGURE 8-VI
106

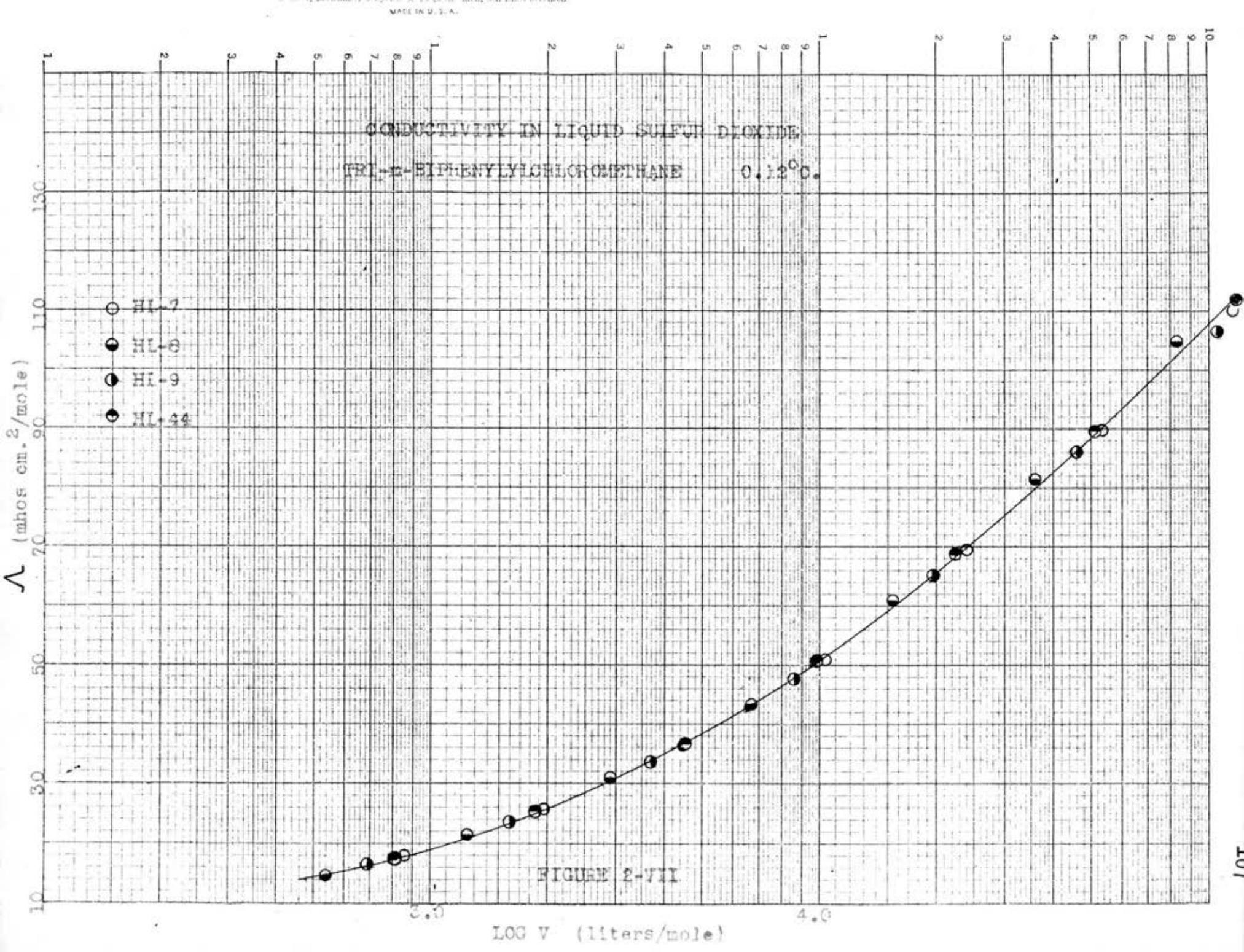

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
TRI-P-BIPHENYLYLCHLOROMETHANE 0.12°C.
HL-7
HL-8
HI-9
HL-44
Λ (mhos cm.²/mole)
LOG V (liters/mole)
3.0
4.0

FIGURE 2-VII

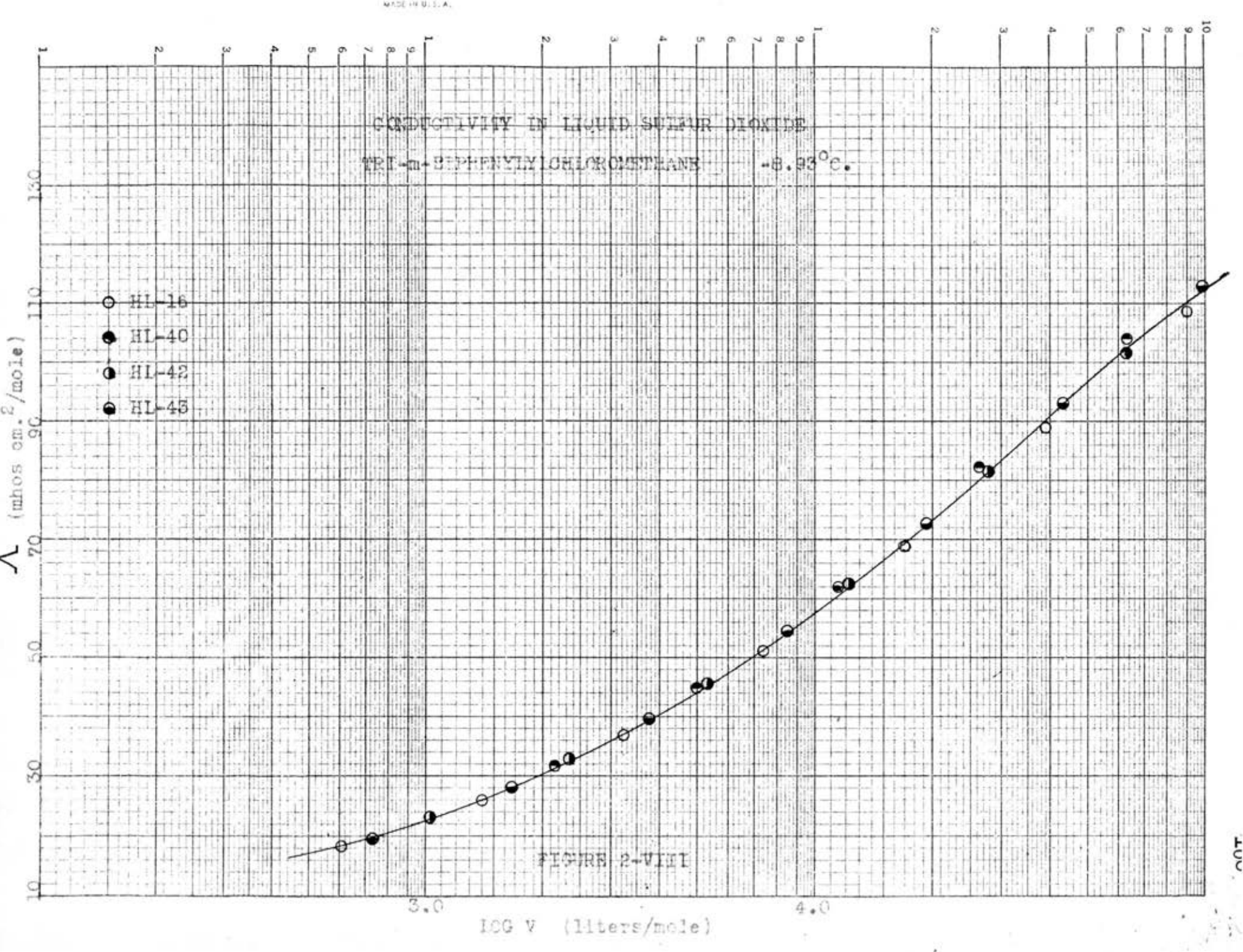
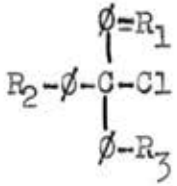

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
TRI-m-BIPHENYLYLCHLOROMETHANE -8.93°C.
HL-16
HL-40
HL-42
HL-43
Λ (mhos cm.²/mole)
ICG V (liters/mole)
FIGURE 2-VIII

TABLE 2-I

Summary of Equilibrium Data in Liquid Sulfur Dioxide.

Compound



R_1	R_2	R_3	$10^5 K_{exp.}$ 0.12°	$10^5 K_{exp.}$ -8.93°	ΔF° (K-cal/mole) 0.12°	ΔF° (K-cal/mole) -8.93°	$\Delta H^{\circ(a)}$ (K-cal/mole) 0.12° to -8.93°	ΔS° (cal./deg.m.) 0.12°	ΔS° (cal./deg.m.) -8.93°	Λ_o (mhos-cm.^{2}/m.) 0.12°	Λ_o (mhos-cm.^{2}/m.) -8.93°
H	H	H	4.14_8	6.69_3	5.48	5.05	-7.53	-48.0	-48.0	$206._5$	$187._9$
H	H	m-Ø	3.07_4	4.63_2	5.64	5.24	-6.54	-44.6	-44.6	$183._7$	$177._4$
H	m-Ø	m-Ø	2.21_7	3.10_1	5.82	5.44	-5.80	-42.6	-42.6	$162._7$	$161._8$
m-Ø	m-Ø	m-Ø	1.36_1	1.93_6	6.09	5.70	-5.62	-42.9	-42.9	$158._6$	$156._6$
H	H	p-Ø	24.1_1	42.4_4	4.52	4.08	-9.02	-49.5	-49.6	$189._2$	$171._6$

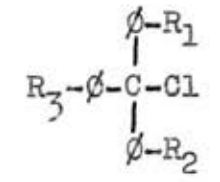
(a) Calculated for the temperature range 0.12° to -8.93°C. ΔH° is assumed to be constant over this interval.

TABLE 2-II

Least Mean Square Parameters for Shedlovsky Extrapolations.

(Triarylchloromethanes in Sulfur Dioxide Solution)

Compound



R_1	R_2	R_3	Temp. (°C.)	$10^3/\Lambda_o$ (intercept)	$1/K\Lambda_o^2$ (slope)	Mean dev. (± %)
H	H	H	-8.93	5.32_1	0.423	1.24
H	H	m-ø	0.12	5.44_4	0.964	1.30
H	H	m-ø	-8.93	5.63_6	0.686	1.22
H	m-ø	m-ø	0.12	6.14_5	1.70_4	0.77
H	m-ø	m-ø	-8.93	6.18_1	1.19_7	1.14
m-ø	m-ø	m-ø	0.12	6.30_6	2.92_2	1.08
m-ø	m-ø	m-ø	-8.93	6.38_9	2.10_9	1.40
H	H	p-ø	-9.93	5.82_6	0.080	0.55

Table 2-III presents the data of a typical Shedlovsky and least mean square calculation and figure 2-IX shows a plot of these data.

TABLE 2-III

A Typical Shedlovsky Calculation.

Tri-m-biphenylylchloromethane[(a)] in Liquid Sulfur Dioxide at 0.12°C.

10^4C.	Λ	$\sqrt{C\Lambda}$ x/0²	z=0.3993 $\sqrt{C\Lambda}$	S(z)[b]	Cθ x 10^6	$\sqrt{C\theta}$ x10^3	$1/\log f_\pm^2 = (1-13.43\sqrt{C\theta})$	$f_\pm^2$	"Y" $1/\Lambda S$ x10^2	"X" $C\Lambda S(z)f_\pm^2$ x10^3
3.446	30.79	10.30	0.0411	1.0419	69.95	8.363	0.8877	0.7721	3.118	8.532
2.698	33.88	9.561	0.0382	1.0389	60.10	7.752	0.8959	0.7868	2.841	7.471
2.339	36.38	9.224	0.0368	1.0375	55.87	7.475	0.8996	0.7936	2.650	7.006
2.233	26.73	9.056	0.0362	1.0369	53.83	7.337	0.9015	0.7970	2.626	6.778
1.492	43.70	8.075	0.0322	1.0327	42.61	6.528	0.9123	0.8172	2.216	5.502
1.165	47.68	7.453	0.0298	1.0302	36.22	6.018	0.9192	0.8302	2.036	4.751
1.021	50.61	7.188	0.0287	1.0291	33.65	5.801	0.9221	0.8358	1.920	4.444
0.9775	50.85	7.050	0.0282	1.0286	32.36	5.688	0.9236	0.8387	1.912	4.288
0.6439	61.00	6.267	0.0250	1.0253	25.49	5.049	0.9322	0.8554	1.599	3.445
0.5030	65.20	5.727	0.0229	1.0232	21.24	4.605	0.9382	0.8673	1.499	2.911
0.4456	68.67	5.532	0.0221	1.0223	19.80	4.450	0.9402	0.8714	1.424	2.726
0.4275	69.44	5.449	0.0218	1.0220	19.20	4.382	0.9412	0.8733	1.409	2.649
0.2784	81.86	4.774	0.0191	1.0193	14.70	3.834	0.9485	0.8882	1.198	2.063
0.2172	86.09	4.324	0.0173	1.0174	12.04	3.470	0.9534	0.8983	1.142	1.708
0.1944	89.80	4.178	0.0167	1.0168	11.23	3.351	0.9550	0.9016	1.095	1.600
0.1872	89.48	4.093	0.0163	1.0164	10.77	3.282	0.9559	0.9035	1.100	1.538

Least Square calculation:

Σ"X" = 0.067412 Σ"Y" = 0.29785 Σ"X"^{2} = 0.00036150 Σ"XY" = 0.0014814 n = 16

$$na + b\Sigma\text{"X"} = \Sigma\text{"Y"}$$
$$a\Sigma\text{"X"} + b\Sigma\text{"X"}^2 = \Sigma\text{"XY"}$$

Solving for a and b gives:

a = 0.006306 Λ_o = 158.6

b = 2.922 $K_{exp} = 1.361 \times 10^{-5}$

(a) Data from runs HL-7, 8, 9, 44.

(b) Daggett's Table, reference 27.

(c) Λ_o assumed to be 158 for this calculation.

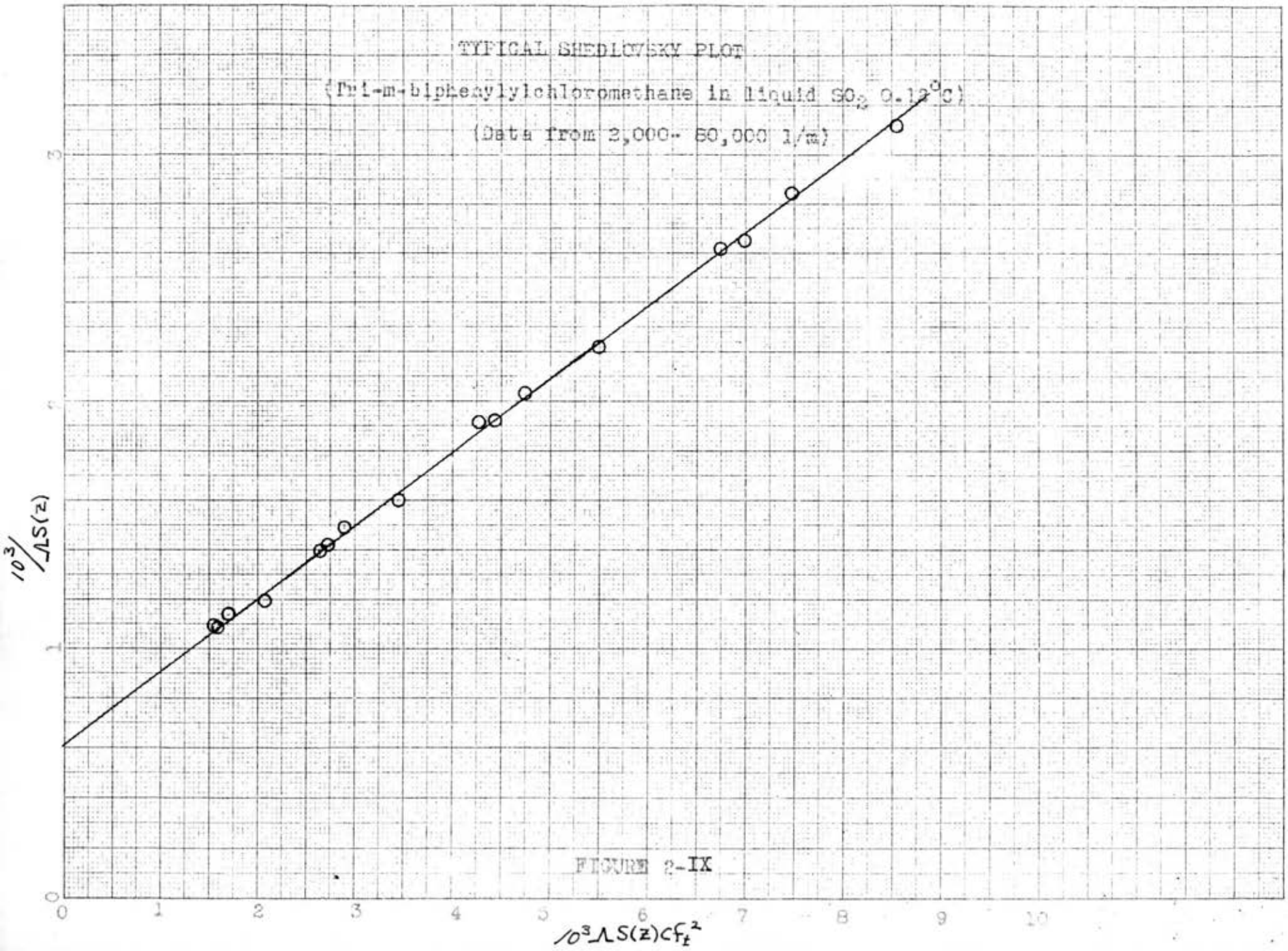

TYPICAL SHEDLOWSKY PLOT
(Tri-m-biphenylylchloromethane in liquid SO_2 0.12°C)
(Data from 2,000- 80,000 1/m)
$10^3/\Lambda S(z)$
$10^3 \Lambda S(z) c f_t^2$
0
1
2
3
4
5
6
7
8
9
10

FIGURE 2-IX

Thermodynamic Properties

Standard free energies ΔF° were calculated from the experimental equilibrium constants by the equation.

$$\Delta F^{\circ} = -RT \ln K_{exp.} \qquad (2\text{-}1$$

Apparent standard heats and entropies of dissociation were calculated from the data at two temperatures by using the integrated form of the Vant Hoff equation,

$$\Delta H^{\circ} = \frac{R \ln(K_1/K_2)}{1/T_2 - 1/T_1} \qquad (2\text{-}2$$

which, over the temperature range employed, viz., 0.12°C to -8.93°C., becomes

$$\Delta H^{\circ} = -3.672 \times 10^4 \log(K_2/K_1) \qquad (2\text{-}3$$

Equation 2-3 involves the assumption that ΔH° is constant over the temperature interval employed. Since this assumption is only approximate for solutions of electrolytes (88) it was necessary to evaluate the error introduced by this assumtion. Data for triphenylchloromethane at three temperatures were examined in order to evaluate the error. The -17°C. data of Lichtin and Bartlett (90) and the 0°C. data of Lichtin and Glazer (91) were recalculated by the Shedlovsky method involving the limitations described in Part I and employing the most recent values of the fundamental physical constants in order to make these results consistent with the -8.93°C. data of this research.

In order to evaluate ΔH° for triphenylchloromethane more accurately an equation

$$-R\ln K_{exp.} = -185.2 \pm 1.178 \times 10^{5} T^{-1} - 1.686 \times 10^{7} T^{-2} \quad (2\text{-}4$$

was fitted to data for this compound at three temperatures. The mean deviation of the experimental points from equation 2-4 is +- 0.35%. Figure 2-X depicts the temperature variation of the equilibrium constant for triphenylchloromethane.

Differentiation of the right member of equation 2-4 with respect to temperature^{-1} gave an equation

$$\Delta H^{\circ} = 1.178 \times 10^{5} - 3.372 \times 10^{7} T^{-1} \quad (2\text{-}5$$

for ΔH° as a function of temperature. Values of ΔH° at the temperatures of the measurements calculated from equation 2-5 are presented in table 2-IV.

TABLE 2-IV

Thermodynamic Properties for Trityl Chloride in SO_2. (Equation 2-5)

Temperature (°C)	ΔH° (K-Cal/m.)	ΔF° (K-Cal/m.)	ΔS° (e.u.)
0.1	-5.60	5.48	-40.6
-8.93	-9.80	5.05	-54.3
-17	-13.8	4.56	-71.1

The above data clearly demonstrate that ΔH° for triphenylchloromethane is not constant with respect to temperature even over the short temperature interval involved. It should be safe to conclude, moreover, that this

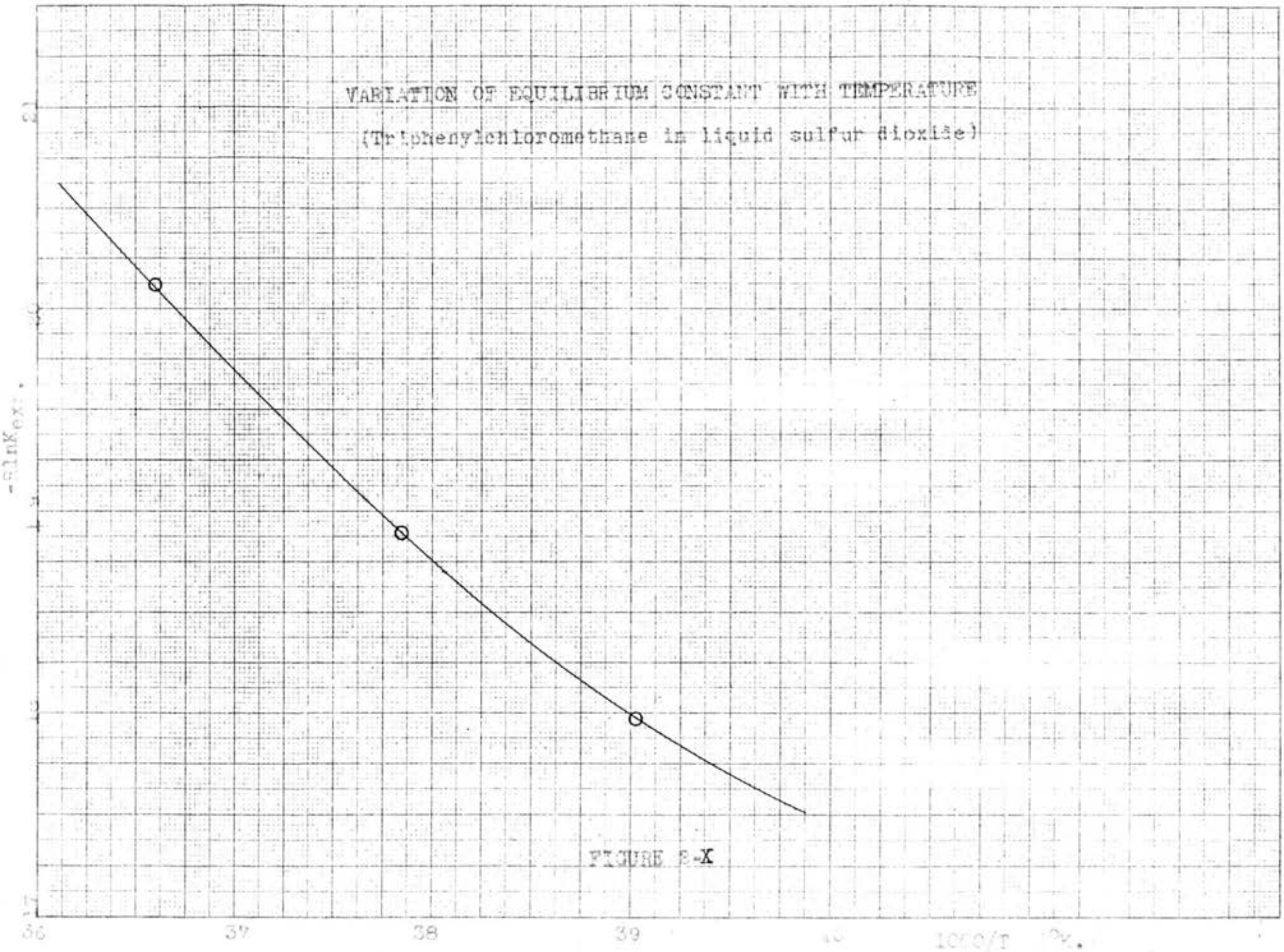

VARIATION OF EQUILIBRIUM CONSTANT WITH TEMPERATURE
(Triphenylchloromethane in liquid sulfur dioxide)
-2.3nK
36
37
38
39
1000/T °K.

FIGURE 8-X

is also the case for the other compounds studied. One may demonstrate, however, that the relative error introduced by the assumption employed in using equation 2-2 is probably not large when the resultant ΔH° values are compared over the same temperature range for a series of similar compounds. It must be remembered however that the ΔH° values obtained in this manner do not correspond to those for either of the temperatures used in equation 2-2 but rather to some intermediate temperature.

Over a sufficiently small temperature range the ΔH° from equation 2-2 can be shown to correspond very nearly to the correct ΔH° for the temperature which is at the mid-point of the temperature range. In order to demonstrate this fact it is necessary to compare ΔH° from equation 2-2 with those calculated from equation 2-5 at the temperature corresponding to the mid-point of the temperature interval used in equation 2-2. The former values are considered as apparent ΔH° while the latter can be considered as the correct ΔH° at the particular temperature involved. Table 2-V shows the results of a comparison of the apparent ΔH° values over several temperature ranges with the correct ΔH° at the mid-points of the corresponding intervals. These data indicate that equation 2-2 gives values which are in good agreement with those calculated at the mid-range temperature by the more exact relationship (equation 2-5).

TABLE 2-V

Comparison of ΔH° for triphenylchloromethane calculated by equations 2-2 and 2-5 as an estimate of the relative errors to be expected in a comparison of apparent ΔH° values.

Temperature Range used in eqation 2-2(°C.)	Mid-range Temperature (°C.)	Apparent[a] ΔH° (K-Cal./m.)	Correct[b] ΔH° (K-Cal./m.)	Relative Error (%)
0° to -8.9°C.	-4.40	-7.63	-7.6	0
0° to -17°C.	-8.45	-9.4	-9.5	1.1
-8.9° to -17°C.	-12.9	-11.2	-11.8	5.0

(a) Equation 2-2.
(b) Equation 2-5.

It may thus be concluded that serious errors are not introduced when apparent ΔH°s are compared over the narrow temperature range employed in this work. This conclusion must, however, be used with caution when deductions are to be based on small absolute differences in apparent ΔH° values.

Apparent standard entropies of dissociation were calculated by equation 2-6 from the data and are tabulated in table 2-I.

$$\Delta F^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (2\text{-}6$$

Very little significance can be assigned to the resulting entropy values since the ΔH° values used do not correspond to the experimental temperatures employed in equation 2-6. The apparent constancy of ΔS° with temperature for a given compound is a fortuitous consequence of the assumption involved in equation 2-2. That ΔS° is not temperature independent for

the systems under consideration can be readily shown from the data for triphenylchloromethane at three temperatures. The ΔS^{o} values summarized in table 2-IV were calculated from the ΔF^{o} values of table 2-I and the ΔH^{o} values from equation 2-5. These values are clearly not independent of temperature.

Precision and Reliability of the Data

The precision of the experimental conductance data as estimated by the mean deviation of individual points from the best fitting smooth curve for a given compound is plus or minus 1% or better over the entire concentration range (see figures 2-I to 2-VIII). Further support for this value can be obtained from the mean deviations of the calculated points from the least mean square straight lines of the Shedlovsky plots. The latter values of course assume perfect linearity of the Shedlovsky equation over the concentration range employed in the calculations. This assumption has been discussed earlier and allowing for the uncertainties involved the precision estimated from the Shedlovky plots is in excellent agreement with that estimated directly from the experimental data.

Direct evaluation of the accuracy of the experimental data is not possible. However an estimate may be obtained from a comparison of potassium iodide results obtained by the method employed in this research with Franklin's (38) data for this compound. Franklin estimates that his conductance

data are accurate to ≤ 0.5% over the entire concentration range. The comparison is presented in Part I of this dissertation. On the basis of the agreement found between Franklin's results and the more recent measurements it can be concluded that the conductance data obtained in this investigation are certainly accurate to better than ±_ 2%.

A detailed analysis of the errors involved in the determination of dissociation constants by the extrapolation method has been presented by Kilpatrick (77). On the basis of his study it can be concluded that a 2% error in experimental conductance data will result in an error of the same magnitude in the extrapolated equilibrium constant except in the case of very strong electrolytes where such an error may be associated with almost total uncertainty in the K value.

Hammett's Sigma Value for m-Phenyl

The apparent dissociation constants of benzoic acid and its m-phenyl substituted derivative in 50% aqueous butyl cellosolve at 25°C. with an ionic strength of 0.05 were obtained from potentiometric titration curves as shown in figures 2-XI and 2-XII. The end points were determined accurately from differential plots of the slope, $\Delta pH/\Delta ml.$, of the titration curves as a function of the volume of base used. Figure 2-XIII shows a typical plot for the end point of the neutralization of m-phenylbenzoic acid.

Dissociation constants as defined by equation 2-7

$$K_A = \frac{(H^+)(Ac^-)}{(HAc)} \qquad (2\text{-}7$$

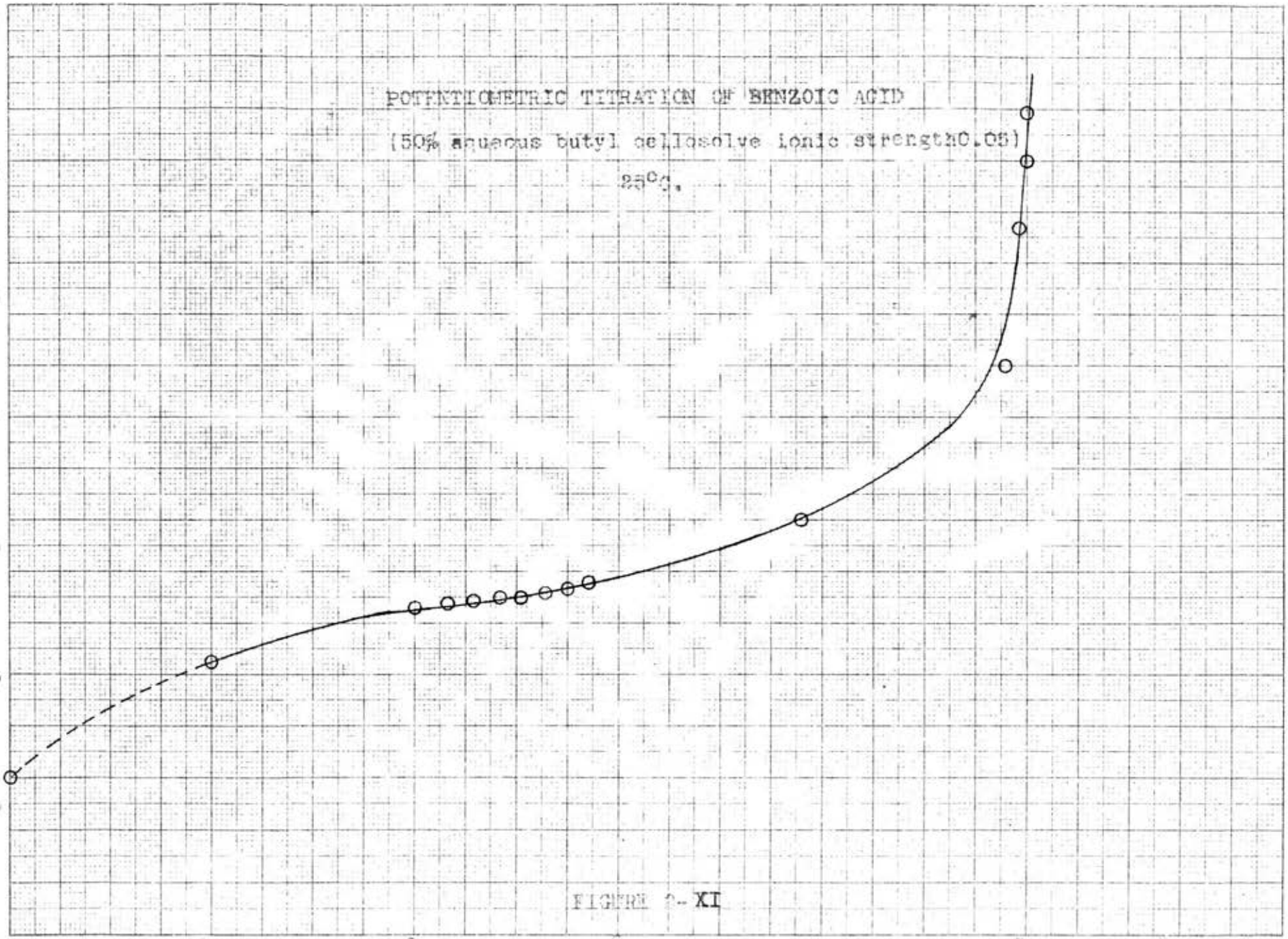

POTENTIOMETRIC TITRATION OF BENZOIC ACID
(50% aqueous butyl cellosolve ionic strength 0.05)
25°C.
pH
VOLUME OF BASE (ml. NaOH)

FIGURE 2- XI

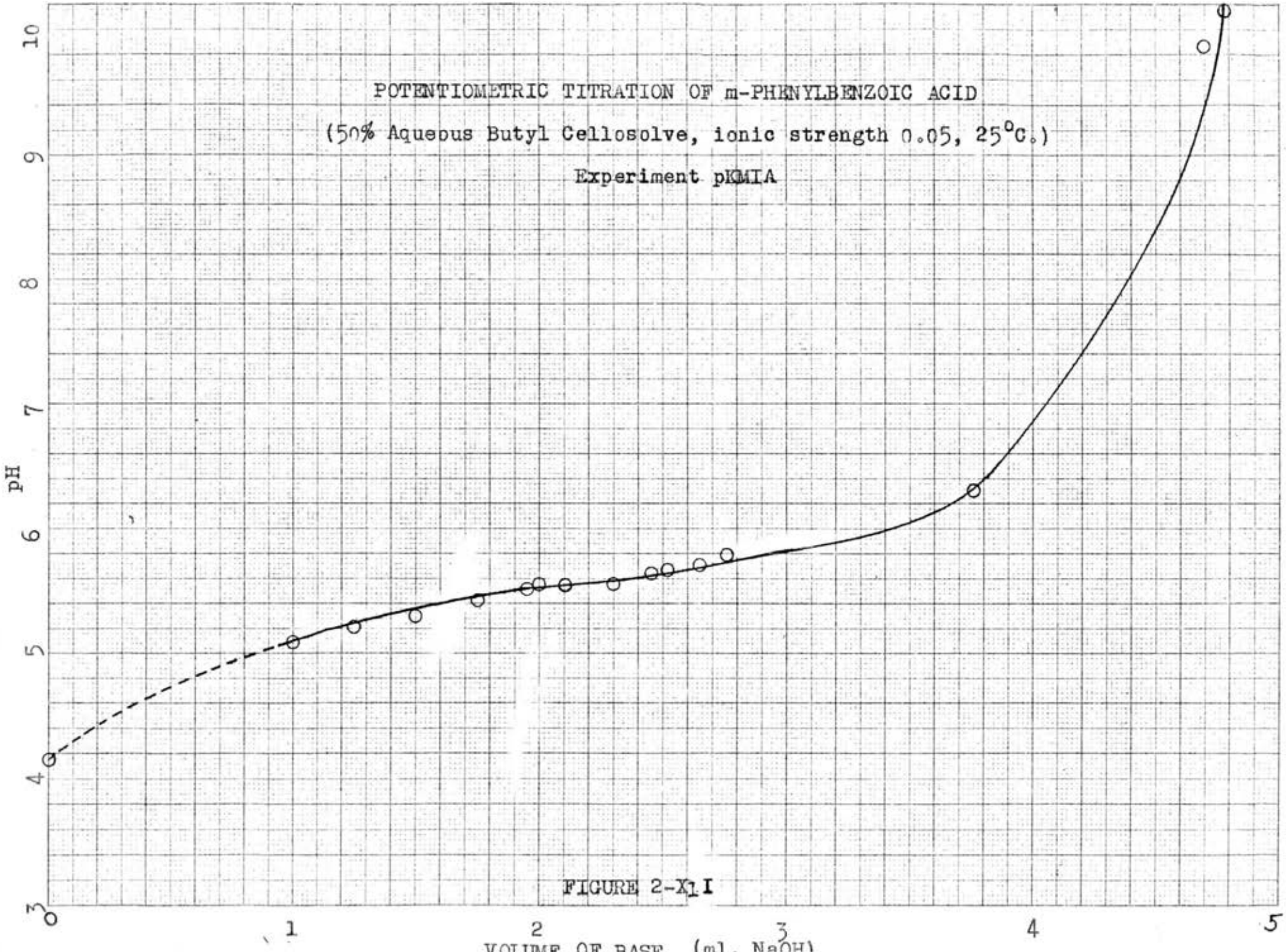

POTENTIOMETRIC TITRATION OF m-PHENYLBENZOIC ACID
(50% Aqueous Butyl Cellosolve, ionic strength 0.05, 25°C.)
Experiment pKMIA
pH
VOLUME OF BASE (ml.) NaOH)
10
9
8
7
6
5
4
3
0
1
2
3
4
5

FIGURE 2-XII

FIGURE 2-XIII

were calculated directly by the buffer formula 2-8, assuming the activity of the anion to be equal to the concentration of the salt.

$$[H^+] = K_A \frac{[\text{Acid}]}{[\text{Salt}]} \qquad (2\text{-}8$$

At the half neutralization point equation 2-8 becomes

$$[H^+] = K_A \qquad (2\text{-}9$$

and by taking the negative logarithm of both sides of 2-9 we obtain the relationship.

$$pH = pK_A \qquad (2\text{-}10$$

The pH values at half neutralization were obtained directly from the titration curves. Table 2-VI summarizes the apparent dissociation constants for the two acids studied.

TABLE 2-VI

Apparent Ionization Constants
(50% aqueous butyl cellosolve, 25°C., ionic strength 0.05.)

Acid	pK_A	Number of Determinations
Benzoic [a]	5.66 ±0.024	5
m-Phenylbenzoic	5.58 ±0.018	4

(a) Berliner and Blommers (12) found $pK_A = 5.65 \pm 0.01$ for this compound.

The value for the sigma constant of the meta-phenyl group was calculated from the Hammett (57) equation

$$\log K - \log K_0 = \rho\sigma \qquad (2\text{-}11$$

where K is the dissociation constant of m-phenylbenzoic acid and K_0 that for benzoic acid. Sigma is a constant whose value depends only upon the nature of the ring substituent, and rho is defined as a reaction parameter whose value is determined by the nature of the reaction, temperature, and the influence of the medium.

Rho for the conditions employed in this investigation has been established as $+ 1.32$ by Berliner and Blommers (12). When this value is substituted into equation 2-11 together with the data summarized in table 2-VI the resulting σ value is found to be $+ 0.06 \pm 0.03$. This value differs appreciably from that previously reported (58). It has been pointed out (91) that the values of $+0.218$ was calculated on the basis of admittedly unreliable kinetic data (23). The new value offered here is far more reliable and shows a small but definite electron attracting influence for the meta-phenyl group.

SIGNIFICANCE OF THE DATA

Pertinent Equilibria.

The conductivity data obtained for solutions of weak electrolytes in sulfur dioxide solution can best be interpreted by consideration of the following equilibria

$$R_3C\text{-}Cl \underset{}{\overset{K_1}{\rightleftharpoons}} [R_3C^+Cl^-]^\circ \overset{K_2}{\rightleftharpoons} R_3C^+ + Cl^- \qquad (2\text{-}20$$

where K_1 is the ionization constant of the weak electrolyte and K_2 is a constant describing the effects of interionic association.

In order to study the effect of substituents on the stability of stable carbonium ions it is required that the relative ease of ionization of the carbon chlorine covalent bond be known. This necessitates evaluation of K_1 in the above expression. Unfortunately conductance measurements fail to provide a measure of the concentration of ion pairs, since these are nonconducting in nature, and therefore the measured equilibrium constant represents the combined processes shown in equation 2-20. The mass-action expression describing the measured equilibrium constant can be shown to be

$$K_{exp.} = \frac{[R^+][Cl^-]}{[RCl] + [R^+Cl^-]^\circ} = \frac{[R^+][Cl^-]}{[RCl][1+K_1]} = \frac{K_1K_2}{1+K_1} \qquad (2\text{-}21$$

and

$$K_1 = \frac{K_{exp.}}{K_2 - K_{exp.}} \qquad (2\text{-}22$$

For the two steps shown in equation 2-20, K_1 should be increased by any factors which stabilize the carbonium ion relative to the covalent molecule. The value of K_1 for a substituted trityl chloride compared to K_1 for triphenylchloromethane should therefore be a measure of the effect of the substituent on the stabilization of the triphenylcarbonium ion. For the other step, K_2, the ion pair dissociation constant should, according to the theory of Bjerrum (16), be influenced by structual changes only through their effects upon the distance of closest approach of the ions.

Lichtin and Bartlett (90) have presented evidence in support of the assumption that K_2 values vary but little within a series of compounds where the cations are meta-, and para-alkyl or aryl substitution derivatives of triphenylcarbonium ions. This assumption will be shown to be valid to a first approximation even though the model on which it is based has no physical significance in solution theory and is indeed an incorrect model for an ion in solution.

These workers have suggested that the value of K_2 is in the range of 10^{-2} to 10^{-3} for all substituted triphenylchloromethanes considered. On the basis of their conclusions it can be shown from equation 2-22 that when K_{exp} falls appreciably below 10^{-4} a direct and approximately constant proportionality appears between K_1 and K_{exp}.

A test of these assumptions lies in $K_{exp.}$ values for the series consisting of triphenylchloromethane and its mono-, di-, and tri-m-phenyl substituted derivatives (where the substituent appears on different rings). The meta phenyl group has a small electron attracting influence (91) with a Hammett sigma value of $+ 0.06 \pm 0.03$ determined in this research. Thus $K_{exp.}$ values in the above series should fall in the desired range of proportionality between K_1 and K_{exp}. Since the m-phenyl group does not participate directly in resonance distribution of charges and since the triphenylmethyl group is highly symmetrical, the introduction of each phenyl group should change K_1 and hence $K_{exp.}$ by the same factor. Any deviation in $K_{exp.}$ from such regularity may be ascribed to a change in the value of K_2 and should be quite small.

Table 2-VII summarizes the factors by which $K_{exp.}$ changes on successive introduction of m-phenyl groups.

TABLE 2-VII

The Relative Effects of m-Phenyl Substituents on the Ionization of Triphenylchloromethane.

n (Number of m-Phenyl Substituents)	K_n/K_{n-1} 0.12°C.	K_n/K_{n-1} -8.93°C.
1	0.741	0.690
2	0.721	0.689
3	0.614	0.610

It is apparent that at both 0.12° and -8.93°C. the introduction of the first and second m-phenyl group decreases $K_{exp.}$ slightly less than does the third. The effects of the first and second are the same, however, within the experimental precision of the measurements. These facts are in accord with the initial assumptions. In the first case the decrease in K_1 due to the introduction of the first m-phenyl group is partially compensated by an apparent increase in K_2 over its value for the unsubstituted compound. This is in accord with the established increase in dissociation constant of ion pairs with increase in the distance of closest approach.

The same mechanism must be operative for the introduction of the second m-phenyl group. Here again the expected decrease in K_1 is partially compensated by an increase in K_2 resulting from the increased size of the cation. Consideration of Fisher-Hirschfelder-Taylor models supports the fact that a m-phenyl group added to m-biphenylyldiphenylcarbonium ion does in fact increase the size of this ion by about the same amount as that when the group is added to the triphenylcarbonium ion. It can also be shown that the introduction of a third m-phenyl group to the disubstituted ion has a much smaller effect on the size of that ion. Thus one would predict that any increase in K_2 resulting from the addition of the third m-phenyl group would be small and therefore would not compensate as much for the expected decrease in K_1.

Thus it follows that the decrease in $K_{exp.}$ on the introduction of the third m-phenyl group should most closely reflect the expected decrease in K_1 due to the electronic influence of the m-phenyl group on the stabilization of the carbonium ion. The decrease in $K_{exp.}$ due to the third m-phenyl group should be greater than those for the first two groups where changes in K_2 are operative. These conclusions are amply supported by the observed relative effects of the groups shown above, and moreover, any detailed model of the carbonium ion must be in accord with these limitations on $K_{exp.}$

The Influence of Ionic Association

Both the theory of ionic association of Bjerrum(16) and the theory of multiple ionic aggregates of Fuoss and Kraus (44) predict the existence of short range interactions between ions which give rise to stable ion pairs, triplets, and higher aggregates in solutions of electrolytes in solvents of low dielectric constant. According to the Bjerrum theory aggregation is restricted to ion pairs in liquid sulfur dioxide (63). Since these interactions result from Coulombic forces only, it follows that the degree of ion pairing will depend only upon charge type, dielectric constant of the medium, temperature, and the distance of separation of the ions. The exact meaning of the latter property of the ions is often times obscure. The derivation requires that the ions be rigid spheres separated by a distance $\mathring{a}$ which may or may not be the sum of ionic radii. That $\mathring{a}$ is often influenced by solvation is known. In some instances evidence

has been produced which can be interpreted as indicating that the solvation shells are not inpenetrable (112). Notable in this respect is the work of Taube (124) who found that the tightly bound molecules in the solvation shell undergo rapid exchange with the bulk solvent. Evidence has been presented in Part I to show that solutions of electrolytes in liquid sulfur dioxide fall into an extreme example of the penetration theory. In fact it was shown that the solvation shell is completely penetrated and $\mathring{a}$ values are, to a good approximation, exactly equal to sum of the ionic radii. It thus appears that K_2 values can be calculated approximately for solutions of triphenylcarbonium salts in liquid sulfur dioxide if a detailed knowledge of the effective radius of the carbonium ion can be deduced.

Model for Carbonium Ion Pairs

Several models can be considered for the triphenylcarbonium ion in solution. Lichtin and Bartlett (90) used a model for their qualitative deductions which corresponds to that of a carbonium ion fixed in space relative to the approaching gegenion. They considered that since the ion is planar, or shaped like a flat pinwheel (87), with the positive charge uniformly distributed over the surface of the disk the gegenion would approach from the side and the distance of closest approach would be insensitive to meta or para substitution. This "static ball and flat circular disk" model did not lend itself to numerical evaluation of the ionic

association constants since the mathematical treatment based on this model was not available.

Much evidence is available to show that this model is incorrect. The known ability of sulfur dioxide to complex with the benzene ring (5) has been interpreted as involving an O-S-O bridge between para positions of the ring with the center of the sulfur atom on a line through the center and perpendicular to the plane of the ring. Although alternate structures are possible it is nevertheless most probable that (103) the sulfur dioxide will be above the plane of the ring. For the triphenylcarbonium ion which also forms complexes with sulfur dioxide (73) the picture becomes somewhat more complicated. Qualitatively, however, it would seem reasonable to assume that the sulfur dioxide in the complex is above the plane of rings. The overall effect then is to destroy the disk by effectively increasing its narrower dimension thus producing a shape approaching that of a symmetrical sphere. Moreover it would seem reasonable to assume that the triarylcarbonium ion in solution, regardless of its disk like shape in space, is to all intents and purposes spherically symmetric on a time average due to the tumbling motion (107) of the ion resulting from thermal collisions with solvent molecules. Add to this the smearing out effect due to solvent held as complex or as solvation shells and the spherical nature of the ions becomes a very attractive concept.

The model chosen for the calculations in this research avoids the difficulties inherent in the earlier model. Since spherical symmetry is assumed for the triarylcarbonium ion, the model can be used for numerical computations.

Discussion of the New Model

The model used by Bjerrum in the derivation of his equation for ion pair dissociation equilibria consists of rigid spherical ions of ionic radius r_i where

$$\overset{\circ}{a} = r_+ + r_-$$

A very important experimental verification of the Bjerrum theory and a proof of the quantitative adherence of equation 2-12 for sulfur dioxide solutions of 1-1 electrolytes have been presented in Part I of this dissertation. This work constitutes the only sound basis for using the Bjerrum equation for the exact calculation of ion pair dissociation constants in sulfur dioxide and is the underlying justification for the ion pair treatment described below.

For the purpose of the calculations presented here, essentially the same model has been chosen. Since, however, ion pair dissociation constants cannot be measured directly for the majority of triphenylcarbonium salts in liquid sulfur dioxide several assumptions had to be made in selecting $\overset{\circ}{a}$ values for these salts.

It is assumed that the radius of the carbonium ion is equal to the radius of the sphere swept out by the ion and is thus equal to the largest van-der Waals radius about the

center of gravity. The ionic radii for the anions were obtained directly from the values selected by Pauling (105) and those for the carbonium ions were estimated from Fisher-Hirschfelder-Taylor models.

Radii of Triarylcarbonium Ions

Consistent with a free tumbling body of non uniform shape but possessing a relatively uniform density throughout, the radius of any triarylcarbonium ion must be equal to the radius of the volume swept out by such a free tumbling body. This radius will be equal to the largest van-der-Waals radius about the center of gravity of the ion. In the case of unsubstituted or symmetrically trisubstituted triarylcarbonium ions the problem is simple since here the center of gravity is located at the central carbon atom and the radius of the volume swept out by an ion tumbling about this center of gravity is equal to the radius of a plane projection of a molecular model of the ion.

In the case of an unsymmetrically substituted ion the center of gravity is displaced from the central carbon atom and the estimation of the radius of its swept out volume is more difficult. As a first approximation it must be assumed that the mass density throughout the bulk of the ion is constant. That this is not a bad assumption is immediately apparent from molecular models for these ions.

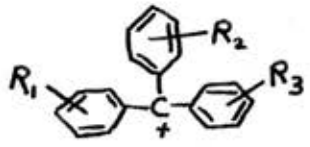
The center of gravity must be found. This can be done quite readily in two ways, namely by direct experimentation

with the molecular model or by geometrical considerations on a plane projection of this model. The former method was chosen for this work. The radius of the unsymmetrical ion is considered as being equal to the distance between the center of gravity and the atom most distant from it.

Table 2-VIII summarizes the radii estimated for the series of triarylcarbonium ions treated by the method of Bjerrum to yield the K_2 values listed in table 2-X.

TABLE 2-VIII

Estimated Ionic Radii for Triarylcarbonium Ions and Corresponding Bjerrum Parameters.

Carbonium ion 			Temp. (°C.)	Cation Radius (Å)	Bjerrum Parameters for the Corresponding Trityl Chlorides.		
R_1	R_2	R_3			a (Å)	b	Q(b)
H	H	H	0.1	7.0	8.8	4.524	0.667
H	H	H	-8.9	7.0	8.8	4.407	0.641
H	H	H	-17.0	7.0	8.8	4.308	0.619
H	H	m-ø	0.1	8.8	10.6	3.757	0.496
H	H	m-ø	-8.9	8.8	10.6	3.658	0.474
H	m-ø	m-ø	0.1	10.2	12.0	3.319	0.398
H	m-ø	m-ø	-8.9	10.2	12.0	3.232	0.378
m-ø	m-ø	m-ø	0.1	10.8	12.6	3.161	0.363
m-ø	m-ø	m-ø	-8.9	10.8	12.6	3.078	0.244
H	H	p-ø	0.1	9.2	11.0	3.619	0.465
H	H	p-ø	-8.9	9.2	11.0	3.526	0.444
H	p-ø	p-ø	0.0	10.8	12.6	3.160	0.362
p-ø	p-ø	p-ø	0.0	11.8	13.6	2.927	0.310
H	H	m-methyl	0.0	7.1	8.9	4.473	0.656
H	H	p-methyl	0.0	7.9	9.7	4.104	0.573
H	H	p-t-butyl	0.0	8.3	10.1	3.942	0.537
H	p-t-bu	p-t-butyl	0.0	9.0	10.8	3.686	0.480

(Tables 2-VIII Continued)

p-t-bu	p-t-bu	p-t-butyl	0.0	9.4	11.2	3.555	0.451
H	H	1-naphthyl	0.0	7.8	9.6	4.147	0.583
H	H	2-naphthyl	0.0	8.5	10.3	3.865	0.520
H	H	H	0.0	7.0	9.4[a]	4.234	0.604
H	H	p-methyl	0.0	7.9	10.3[a]	3.865	0.519

(a) For corresponding perchlorates. Radius of perchlorate ion is 2.36 Å. (136).

The assumptions involved in selecting the above radii can be somewhat substantiated by an examination of the conductivity data of Ziegler and Wollschitt (138) for several triphenylmethylperchlorates. Since these perchlorates are essentially ionic in the crystal (30) the equilibrium constants derived from the conductivity data for these salts in liquid sulfur dioxide should correspond to pure ion pair dissociation constants.

Equilibrium constants from Ziegler's data were calculated by the Shedlovsky method. Ion pair dissociation constants were calculated from equation 2-12 using $\overset{\circ}{a}$ equal to the sum of the ionic radii listed in table 2-VIII. The results of these calculations summarized below illustrates the apparent validity of the imposed assumptions to at least a good first approximation.

TABLE 2-IX

Tentative Ion Pair Dissociation Constants
Triphenylmethylperchlorates in SO_2 at 6°C.

Substituent	$K_{exp.} \times 10^5$ (observed)	$K_2 \times 10^5$ (calculated)
None	350	341
p-Methyl	400	403

The agreement shown above is excellent within the combined experimental and computational errors. It should be pointed out, however, that this agreement may be fortuitous in view of the questionable accuracy of Ziegler's measurements combined with the inherent uncertainties in the K values for strong electrolytes. In this respect it is noteworthy that Lichtin and Bartlett (90) failed to obtain a straight line plot from data for tri-p-methoxyphenylmethylperchlorate. Moreover, they observed discrepancies between their data and Ziegler's data for triphenylchloromethane and its mono-p-methyl derivative.

Figure 2-XIV illustrates the Shedlovsky plots obtained from Ziegler's perchlorate data. The straight lines were plotted by the method of least mean squares and the mean deviations of the points serve as a basis for the estimation of the probable accuracy of the derived Λ_o and K_2 values. The Λ_o values are in error by ± 5% which sets the

SHEDLOVSKY PLOT

TRIPHENYLMETHYL PERCHLORATE DERIVATIVES 0.0°C.

Rate of Ziegler (1938)

(2000-50,000 liters/mole)

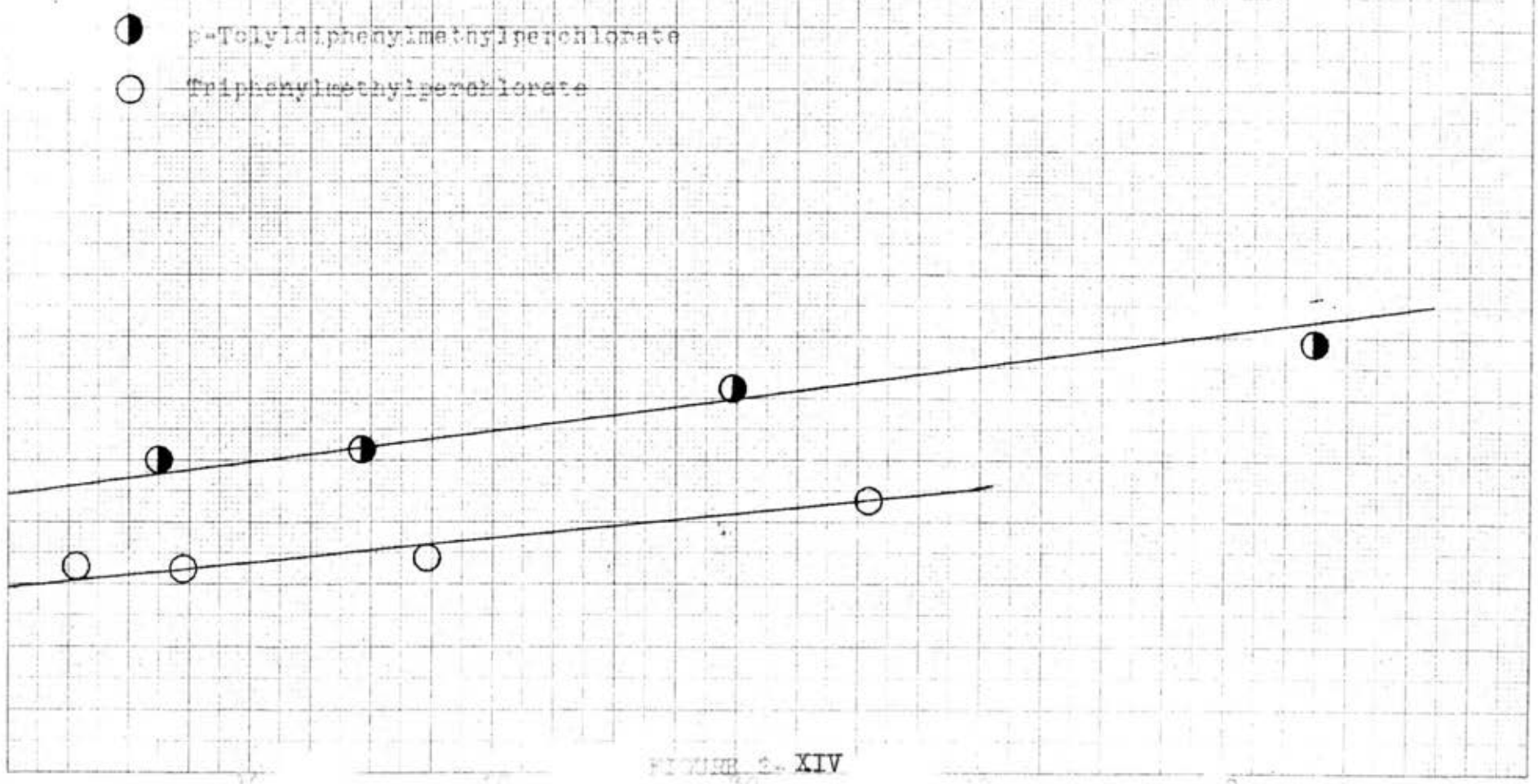


FIGURE 2. XIV

probable error in the slope at about a factor of two. Thus the $K_{exp.}$ values for both compounds lie in the range 2×10^{-3} to 8×10^{-3} and the apparent agreement cannot be weighted very heavily. These data do however suggest that precise experimental measurements of triphenylmethyl perchlorates would be profitable.

One further assumption is implied in the radii tabulated (table 2-VIII), namely, that the values are independent of both temperature and the dielectric constant of the medium. The data of Fuoss and Kraus(42) and those presented in Part I of this dissertation are offered in support of these assumptions. A detailed examination of these assumptions has been presented in Part I.

That the data of table 2-VIII based on the new model are consistent with the limitations imposed on K_2 is at once apparent and can be seen from the structural influence of m-phenyl substituents on the radii of m-phenyl substituted triphenylcarbonium ions. It is seen, that as required by the ratios in table 2-VII, the radius suffers its greatest change in going from 0 to 1 substituent, a smaller change from 1 to 2, and less change from 2 to 3.

Ion Pair Dissociation Constants

Table 2-X summarizes the ion pair equilibrium data calculated for a series of substituted triphenylcarbonium salts in liquid sulfur dioxide solution by the equation of Bjerrum(16).

TABLE 2-X

Summary of Ion Pair Equilibrium Data for Triarylcarbonium Chlorides in Liquid Sulfur Dioxide.

Compound $(R_x\text{-}\phi)_3C^+ Cl^-$			Temp. (°C.)	$10^5 K_2$	ΔF° (K-cal./mole)	ΔH° [a] (K-cal./mole)	ΔS° e.u.
R_1	R_2	R_3					
H	H	H	0.1	314	3.13	-1.86	-18.3
H	H	H	-8.9	353	2.96	-1.86	-18.3
H	H	H	-17.0	393	2.82	-1.80[b]	-18.0
H	H	m-ø	0.1	422	2.97	-1.99	-18.2
H	H	m-ø	-8.9	478	2.81	-1.99	-18.2
H	m-ø	m-ø	0.1	526	2.85	-2.07	-18.1
H	m-ø	m-ø	-8.9	599	2.69	-2.07	-18.1
m-ø	m-ø	m-ø	0.1	576	2.80	-2.15	-18.2
m-ø	m-ø	m-ø	-8.9	659	2.64	-2.15	-18.2
H	H	p-ø	0.0	450	2.94	-2.00	-18.2
H	H	p-ø	-8.9	510	2.77	-2.00	-18.1
H	p-ø	p-ø	0.0	578	2.80	----	----
p-ø	p-ø	p-ø	0.0	675	2.71	----	----
H	H	p-t-C_4H_9	0.0	390	3.01	----	----
H	p-t-C_4H_9	"	0.0	436	2.95	----	----
p-t-C_4H_9	"	"	0.0	464	2.92	----	----
"	"	"	-17.0	587	2.62	----	----
H	H	m-CH_3	0.0	319	3.12	----	----
H	H	p-CH_3	0.0	365	3.05	----	----
H	1-naphthyl	H	0.0	360	3.20	----	----
H	2-naphthyl	H	0.0	403	2.99	----	----

(a) Calculated over the range 0.1 to -8.9°C. ΔH° is assumed to be constant over this interval.

(b) Calculated over the range -8.9 to -17.0°C.

According to the Bjerrum theory of ionic association, the reciprocal of the ion-pair dissociation constant can be calculated from the equation

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|Z_1 Z_2|\epsilon^2}{DkT}\right)^3 Q(b) \qquad (2\text{-}12$$

where,

$$b = \frac{|Z_1 Z_2|\epsilon^2}{\overset{o}{a}\, DkT} \qquad (2\text{-}13$$

and

$$Q(b) = \int_2^b e^y y^{-4} dy = \frac{1}{6}\left\{ e^2 - Ei(2) + Ei(b) - \frac{e^b}{b}\left(1 + \frac{1}{b} + \frac{2}{b^2}\right)\right\} \qquad (2\text{-}14$$

in which Ei(x) is the exponential integral

$$Ei(x) = \int_{\infty}^{-x} e^{-t} t^{-1} dt \qquad (2\text{-}15$$

provided that values of, $\overset{o}{a}$, the distance of closest approach of the ions are known.

Calculations

Details of the calculation of ionic association constants are described fully in Part I of this dissertation. Briefly, the data reported in table 2-X were obtained by solving equation 2-12 for each compound, employing the physical constants for liquid sulfur dioxide reported in Part I equation 2-12 becomes for 1-1 electrolytes

$$K^{-1} = C_K Q(b) \qquad (2\text{-}16$$

and 2-13 becomes

$$b = \frac{C_b}{\overset{o}{a}} \cdot \qquad (2\text{-}17$$

Values of the constant coefficients C_K and C_b are summarized below.

TABLE 2-XI

Bjerrum Coefficients for 1-1 Electrolytes in Liquid SO_2.

Temperature (°C.)	C_K x100	C_b x 10^7
0.1	4.7802	3.9825
0.0	4.7763	3.9813
-8.9	4.4140	3.8780
-17.0	4.1245	3.7913

Values of the function Q(b) were obtained directly from a large scale plot of Q(b) versus b. The Q(b) values used in the construction of this plot were calculated from equation 2-14 employing W.P.A. Tables (134) of the exponential integral. The plot shows that over the range $3 \leq b \leq 5$, Q(b) is exactly linear with b and can be described by the equation

$$Q(b) = 0.215 + 0.2233(b-2.5) \qquad (2\text{-}18$$

Q(b) values can be obtained from the plot or from equation 2-18. It should be pointed out that for all of the triarylcarbonium-chlorides considered in this work the value of b falls within the range of validity of equation 2-18 and this equation may be used conveniently in the derivation of an equation for ΔH° of dissociation of ion-pairs consisting of triaryl-carbonium chlorides as will be shown below.

Thermodynamic Properties of Ion Pairs

It has been shown that the ion pair dissociation constant is dependent only on temperature, dielectric constant, and the distance of closest approach of the ions. It should therefore be possible to calculate the thermodynamic properties ΔF^{o}, ΔH^{o}, and ΔS^{o} directly from equation 2-12 without recourse to experiment. In principle this can be done by substituting equation 2-12 into the differential Van't Hoff equation and solving for ΔH_2^{o}.

For the special case of triarylcarbonium-chloride ion pairs in liquid sulfur dioxide, where $3 \leq b \leq 5$, equation 2-12 becomes

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|Z_1 Z_2|\epsilon^2}{DkT}\right)^3 \left[0.215 + 0.2233(b-2.5)\right] \qquad (2\text{-}23$$

Equation 2-23 can be substituted into the differential Van't Hoff equation and solved for ΔH_2^{o} as a function of temperature dielectric constant and the distance of closest approach to give

$$\Delta H_2^{o} = 3RT - 3RLT^2 + \frac{RT\ 0.2233b\ (1-LT)}{0.2233b - 0.343} \qquad (2\text{-}24$$

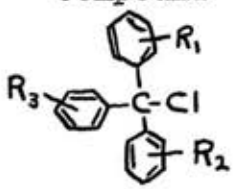
where $L = 6.676 \times 10^{-3}$ is the temperature coefficient of the dielectric constant of liquid sulfur dioxide.

A detailed derivation of a general equation for ΔH_2^{o} is presented in Part I of this dissertation (see equation 1-40).

Table 2-XII summarizes the thermodynamic properties calculated from equation 2-24 for the ion pair dissociation reaction. In column 3 are tabulated ΔF_2^0 values calculated from K_2 values listed in table 2-X. The ΔH_2^0 values in column 4 were calculated from the theoretical equation 2-24, and those in column 5 were calculated by substituting K_2 values into the integrated form of the Van't Hoff equation. Columns 6 and 7 contain the ΔS_2^0 values calculated from the ΔF_2^0 values and the ΔH_2^0 values of columns 4 and 5 respectively.

TABLE 2-XII

Derived and Apparent Thermodynamic Properties of Triarylcarbonium Chloride Ion Pairs in Liquid Sulfur Dioxide.

Compound			Temp. (°C.)	ΔH_2^o (a)	ΔH_2^o (b)	ΔS_2^o(a)	ΔS_2^o(b)
				(K.-calories/mole)		(calories) (deg.-mole)	
R_1	R_2	R_3					
H	H	H	0.10	-2.02	-1.86	-18.9	-18.3
H	H	H	-8.93	-1.82	-1.86	-18.2	-18.3
H	H	H	-17.0	-1.65	-1.80[c]	-17.4	-18.0[c]
H	H	m-ø	0.12	-2.10	-1.99	-18.5	-18.2
H	H	m-ø	-8.93	-1.90	-1.99	-17.9	-18.2
H	m-ø	m-ø	0.12	-2.16	-2.07	-18.4	-18.1
H	m-ø	m-ø	-8.93	-1.96	-2.07	-18.4	-18.1
m-ø	m-ø	m-ø	0.12	-2.21	-2.15	-18.4	-18.2
m-ø	m-ø	m-ø	-8.93	-2.01	-2.15	-17.5	-18.2
H	H	p-ø	0.10	-2.12	-2.00	-18.5	-18.2
H	H	p-ø	-8.93	-1.98	-2.00	-18.0	-18.1

(a) Calculated by equation 2-24.
(b) Calculated by integrated Vant Hoff equation.
(c) Temperature interval from -8.93° to -17.0°C.

It can readily be seen from equation 2-24 that ΔH_2^o is not temperature independent. Since the ΔH_2^o values calculated by the integrated Van't Hoff equation (column 5 table 2-XII) supposes that ΔH_2^o is constant over the temperature range employed, a comparison of colums 4 and 5 should give an estimate of the error in ΔH_2^o introduced by this assumption. These errors range from a few percent to somewhat more than plus or minus ten percent and may be ignored for all practical purposes since they do not change the conclusions which can be drawn concerning the effects of variation in ionic size on the energy of dissociation of ion pairs.

From an examination of ΔH_2^o values in either columns 4 or 5 (table 2-XII) we find, as should be expected for this range of ion sizes, ΔH_2^o is almost independent of the distance of closest approach.

Unfortunately, for the case of experimentally determined ($K_{exp.}$) equilibrium constants direct comparison of ΔH^o values calculated by the integrated Van't Hoff equation may lead to erroneous conclusions since the logarithm of the ratio of equilibrium constants at two temperatures is a very sensitive function of errors in the individual equilibrium constants employed. Experimentation with equation 2-2 for a given compound demonstrates that as little as a five percent error in one or both of the experimental equilibrium constants can

result in an apparent error in ΔH° of the order of 2 to 20 percent. Table 2-XIII summarizes the results of such experimentation with the data for triphenylchloromethane at 0.12°C. and -8.93°C. In this table the ΔH° values were calculated by 2-2 using several values of K_{exp} to which were assigned an error of ≠ or - 5 percent of K_{exp}.

TABLE 2-XIII

Influence of Errors in $K_{exp.}$ on ΔH° Values Calculated by Equation 2-2. (Trityl Chloride in Liquid Sulfur Dioxide.)

Error in $K_{exp.}$		ΔH°	Apparent Error in ΔH°.
0.12°C.	-8.93°C.	(K.Cal./Mole)	(%)
none	none	-7.63	0.0
≠5%	none	-6.9	8.0
-5%	none	-8.4	10
-5%	≠5%	-9.4	24
≠5%	≠5%	-7.7	2.0
≠5%	-5%	-6.2	18
none	≠5%	-8.4	10
none	-5%	-6.7	12
-5%	-5%	-7.7	2.0

Several more interesting deductions can be obtained from table 2-X. The data clearly indicate that the conclusions of Lichtin and Bartlett (90) are correct to a first approximation. It can be seen from column 2 that the calculated ΔF°_{2} values are approximately constant over the entire range of compounds considered. The essential constancy of ΔH°_{2} and ΔS°_{2} are in agreement with the approximation that K_2 varies little for the series of compounds being compared. There is a variation, however, of about 10 percent in ΔF°_{2} which cannot be neglected since it corresponds to a change of almost a factor of two in the value of K_2 in going from triphenylchloromethane to its tri-m-phenyl substituted derivative. It has been shown that such a factor of two in K_2 has a noticeable effect on the desired proportionality between $K_{exp.}$ and K_1 for the ionization of the covalent compound.

Calculated Ionization Constants for Triarylchloromethanes.

K_1 values for the ionization of the carbon-chlorine covalent bond in triarylchloromethanes can now be calculated from the measured $K_{exp.}$ and calculated K_2 values (see tables 2-I and 2-VIII) by employing the expression relating these three quantities, namely,

$$K_1 = \frac{K_{exp.}}{K_2 - K_{exp.}} \qquad (2\text{-}22$$

Values calculated for the ionization constants K_1 and the apparent thermodynamic quantities ΔH_1°, ΔS_1° for the reaction

$$\phi_3CCl \underset{}{\overset{K_1}{\rightleftharpoons}} \phi_3C^+ + Cl^-$$

are summarized in table 2-XIV. These results constitute the first attempt to evaluate the absolute values of the thermodynamic equilibrium quantities for the ionization of triarylchloromethanes in liquid sulfur dioxide. The values are the composite result of both experimental data and data calculated on a purely theoretical basis.

Although, as has been shown thus far, the assumptions of Lichtin and Bartlett hold fairly well for the compounds which are weaker electrolytes than triphenylchloromethane, and interpretations based on either K_1 or K_{exp} for such compounds agree well with the exception of minor refinements in interpretation which are possible with K_1 values, the major significance of the K_1 values lies in the interpretation of experimental data for compounds which are much stronger electrolytes than triphenylchloromethane.

A final test of the model used for the calculation of ion-pair equilibrium constants lies in an examination of

TABLE 2-XIV

Calculated Ionization Constants and Thermodynamic Properties for the Ionization of Triarylchloromethanes in Sulfur Dioxide.

Compound			Temp. (°C.)	$10^3 K_1$	ΔF_1°	$\Delta H_1^{\circ(a)}$	ΔS_1°
					(K.-cal/mole)		$\left(\frac{\text{Cal.}}{^\circ\text{-mole}}\right)$
R_1	R_2	R_3					
H	H	H	0.10	13.4	2.35	-5.90	-30.3
H	H	H	-8.93	19.4	2.09	-5.90	-30.3
H	H	H	-17.0	34.3	1.74	....	....
H	H	m-ø	0.12	7.35	2.67	-4.55	-26.5
H	H	m-ø	-8.93	9.78	2.43	-4.55	-26.5
H	m-ø	m-ø	0.12	4.25	2.97	-3.71	-24.4
H	m-ø	m-ø	-8.93	5.32	2.75	-3.71	-24.5
m-ø	m-ø	m-ø	0.12	2.36	3.29	-3.60	-25.3
m-ø	m-ø	m-ø	-8.93	2.96	3.06	-3.60	-25.3
H	H	p-ø	0.10	56.8	1.56	-7.50	-33.2
H	H	p-ø	-8.93	90.7	1.26	-7.50	-33.3

(a) Calculated from the integrated van't Hoff equation using K_1 values.

the data of table 2-XIV for its adherence to the expected stepwise influence of the stepwise introduction of meta-phenyl groups on the ionization constant of triphenylchloro-methane. As has been done before, this test can be applied by comparing the ratios K_n/K_{n-1} for all values of n from zero to three using K_1 values listed in table 2-XIV. Table 2-XV summarizes the results of this test.

TABLE 2-XV

The Relative Effects of Meta-Phenyl Substituents on the Calculated Ionization Constant of Triphenyl-chloromethane in Sulfur Dioxide Solution.

n (number of m-phenyl substituents)	K_n/K_{n-1} (0.12°C.)	K_n/K_{n-1} (-8.93°C.)
1	0.55	0.51
2	0.58	0.55
3	0.56	0.55
Mean	0.56 ± 0.010	0.54 ± 0.016

The agreement shown above is excellent within the combined experimental and computational errors.

These data (table 2-XIV) illustrate another interesting fact. Examination of the ΔH_1^o values shows that there exists an apparent parallelism between electrolyte strength and the energy of dissociation. The direction of the ΔH_1^o changes is the expected one, for, those substituents which stabilize the carbonium ion over the covalent molecule will make the ionization more favorable in the sense that it would reduce the energy necessary to effect the ionization thereby increasing the endothermicity of the reaction.

Limiting Conductances

The limiting conductance values summarized in table 2-I appear to adhere to the qualitative demands of Stoke's Law (62) in that the observed values decrease with increasing size of the cations. One exception to this generalization lies in the Λ_o value for p-biphenylyldiphenylchloromethane at 0.12^o compared to the similar quantity for the m-phenyl derivative. According to the ionic radii estimated for triarylcarbonium ions one would predict that the para compound would have a somewhat lower limiting conductance value than the corresponding meta compound. It must be pointed out however, that the observed discrepancy is very close to the experimental error in limiting conductance values and may well be the result of an artifact. Moreover, this apparent reversal is not found in the $-8.93^oC.$ data for these compounds.

Since ionic mobility data are not available for

solutions in liquid sulfur dioxide it is impossible to determine the accuracy of the limiting conductance values by direct comparison with ionic mobilities by the Kohlraush relationship.

$$\lambda^{\circ}_{+} + \lambda^{\circ}_{-} = \Lambda_{o}$$

Such mobility data would be of great value for, as has been pointed out by Belcher (9), the major error in equilibrium constants determined by an extrapolation procedure lies in the Λ_o value obtained by extrapolation. If the limiting conductance values were known accurately from other sources it would be possible to accurately evaluate the equilibrium constant from the slope of the extrapolation plot.

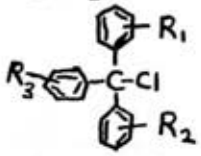
It is possible however, to examine the internal consistency of the limiting conductance values at the two temperatures by testing for deviations from Walden's Rule (127). Walden has established that the relationship

$$\eta \Lambda_{o} = C$$

holds for a given electrolyte in a large number of different solvents or in the same solvent at several temperatures. By applying this rule to the data for the several compounds it is possible to test the constancy of the Walden product at the two temperatures. This test then serves as an estimate of the internal consistancy of the data. Table 2-XVI summarizes the results of this test obtained from the data of table 2-I.

TABLE 2-XVI

A Test of Walden's Rule for Triarylchloromethanes in Sulfur Dioxide Solution.

Compound  R_1	R_2	R_3	$\eta\Lambda_o^{(a)}$ 0.12°C.	$\eta\Lambda_o^{(b)}$ -8.93°C.	Mean	Mean Deviation
H	H	H	0.084	0.082	0.083	0.001
H	H	m-ø	0.074	0.077	0.076	0.001
H	m-ø	m-ø	0.066	0.070	0.068	0.002
m-ø	m-ø	m-ø	0.060	0.064	0.062	0.002
H	H	m-ø	0.076	0.075	0.076	0.000

(a) Viscosity at 0.12°C. = 4.025 millipoise.

(b) Viscosity at -8.93°C. = 4.350 millipoise.

An examination of these data shows that the agreement with Walden's Rule is excellent for the compounds considered. Interestingly, the percent deviation from the mean is of the order of plus or minus two percent which agrees well with the estimate of the precision of these values derived earlier.

A detailed analysis of limiting conductance values must await the availability of precise data for a large number of compounds.

THEORETICAL DISCUSSION

Introduction

The wide variations in the dissociation constants of a series of carboxylic acids in a solvent S must be ascribed to the influence of the group R upon the equilibrium

$$RCOOH \quad \not{} \quad S \rightleftharpoons RCOO^- \quad \not{} \quad SH^{\not{}}$$

The group may either assist or hinder the removal of the hydrogen ion by the solvent molecule; at the same time it may operate in favor of or against recombination. In its influence upon the relative ease of removal of the proton the group exerts its effect by means of pure electrical induction whereby the intrinsic electron affinity of the group polarizes the R-C bond. The direction of the resulting dipole will depend primarily on the group concerned and will result in either an increased or decreased electron density at the reactive site. Ingold (69) has coined the term Inductive Effect ($\not{}$ or -I) to describe this general electrostatic influence of substituents on the reactivity of a parent compound.

The relative magnitudes of the inductive effect can be readily demonstrated by comparison of the relative dipole moments of mono substituted benzenes. The order of increasing dipole moment for the alkyl benzenes closely parallels the

order of decreasing acid strengths of the correspondingly substituted acetic acids in water (130). On the basis of these results it must be concluded that, for example, alkyl groups are electron repelling and can be considered to have a -I effect. A direct and ingenious method of ascertaining the direction of dipole moments has been advanced by Thompson (124) on the basis that the net dipole moment of a disubstituted benzene derivative should be the vector sum of the dipoles of the individual substituents.

Since the inductive effect is coulombic in nature its influence on the free energy of an ionization process, in which ground states of the ions are being compared to the ground states of the undissociated molecules, must be such that the effect will vary inversely as the distance of the group from the reacting center. Moreover, the effect can be transmitted either through the carbon chain (dielectric constant equal to about 2) or through space which may or may not be occupied by solvent molecules. Actually part of the effect will be transmitted through both mediums and the relative amounts through each will depend on the microscopic dielectric constant in the immediate vicinity of the molecule and thus cannot be determined with any degree of certainty. The possibility exists also that the polar group may effectively dissipate some of its inductivity through direct interaction with solvent molecules rather than with the reactive center.

It is therefore virtually impossible to arrive at the absolute magnitude of the inductive effect of substituents on a reactive center without taking into consideration the microscopic as well as the macroscopic variables. Current theory is not sufficiently developed to handle this problem. A noteworthy exception is Kirkwood and Westheimer's (79) application of the electrostatic model of Kirkwood and Scatchard (78) to ionization equilibria*.

It should, however, be a simple matter to determine the relative order and magnitudes of the electronic inductive effects of substituents (relative to hydrogen) by a direct comparison of the relative strengths of the saturated aliphatic acids. This has been amply illustrated in the literature. However, when attempts have been made to predict the course of other reactions on the basis of the inductive effects observed from acid strength measurements, more often than not the results were in complete dissagreement with predictions. Examples of the apparent muddled order of group effects are too numerous to consider here (7), yet we may conclude from these observations that the inductive effect need not be the sole factor contributing to the influence of a substituent on the rate of a chemical reaction or on the position of equilibria. In fact the net influence of a group can have meaning only in terms of the substrate to which it is connected. Thus when the substituent is coupled to an unsaturated or an aromatic substrate conjugative and hyperconjugative resonance

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(*) For a complete discussion of this treatment see reference 133.

effects become important and often completely mask the intrinsic inductive nature of the group.

Influence of Substituents on Reaction Rates and Equilibria

Since the velocity of a chemical reaction can be represented by the Ahrrenius equation, namely,

$$k = PZ\, e^{-E/RT} \qquad (2\text{-}25$$

and the collision frequency Z is essentially constant for most reactions (of the order of $3 \times 10^{+11}$), it is evident that the observed effects of substituents on reaction rates may be due to changes in E, or P, or both. Ingold (70) and coworkers have shown that for several reactions of ring substituted benzene derivatives the influence of meta- and para-substituents on the velocity of the reaction can be ascribed almost entirely to changes in the activation energy. Thus it can be concluded that the probability factor, P, is not significantly altered by the introduction of meta- and para-substituents and may be considered to be a constant for a particular reaction of a series of ring substituted benzene derivatives. It therefore follows that, for a particular value of P, the Ahrrenius equation may be written in logarithmic form as

$$\ln k = \text{Constant} - E/RT \qquad (2\text{-}25a$$

Bradfield and Jones (21) have demonstrated, moreover, that the contributions of groups to the activation energy of poly-substituted benzene derivative are completely and independently additive. The activation energy may then

be represented as the sum of a series of terms.

$$E = E_o + \epsilon_1 + \epsilon_2 + \cdots\cdots + \epsilon_n \qquad (2\text{-}26$$

In this equation E_o refers to the unsubstituted parent compound and ϵ_i are the contributions due to the substituents.

Hammett's Relationship

While variations in reaction velocities resulting from the introduction of groups into the meta or para position of a benzene derivative are usually due to changes in the energy of activation, the variations in log K for the ionization of a series of substituted carboxylic acids are reflections of changes in the free energy of ionization. Hammett (56) has demonstrated that plots of log k for a given reaction of a series of aromatic substitution derivatives against log K for the ionization of the corresponding acids are approximately linear. The plot of log k values for one reaction against those for another reaction are also linear.

These observations led Hammett to propose a general quantitative relationship between the nature of the substituent and reactivity of the side chain. This relationship has become known as the Hammett equation and is usually stated in the form

$$\log k_j - \log k_o = \rho\sigma \qquad (2\text{-}27$$

In equation 2-27 log k_j is the rate constant or equilibrium constant for the reaction or ionization of the aromatic compound which carries substituent, j, in the meta or para position; log k_o being the corresponding value for the unsubstituted compound. Rho is defined as a "reaction constant" dependent upon the reaction and external conditions while sigma is a constant characteristic of the substituent only.

Hammett's linear relationship breaks down when steric factors become involved such as is the case for ortho substituents.

Jaffe (71) has recently presented an excellent review of the Hammet relationship.

The Inductive Effect of the Phenyl Group

Olefinic and acetylenic acids are stronger than the corresponding saturated acids. The electron attracting influence of the multiple bond, like an inductive effect, is transmitted through a chain of saturated atoms and decreases in magnitude with increasing distance from the carboxyl group. Phenyl has a similar effect, the order of decreasing acid strength being $\phi CH_2COOH > \phi CH_2CH_2COOH > CH_3COOH$.

Phalnikar and Bhide (106) found that the introduction of a phenyl group on the beta-carbon of glutaric acid resulted

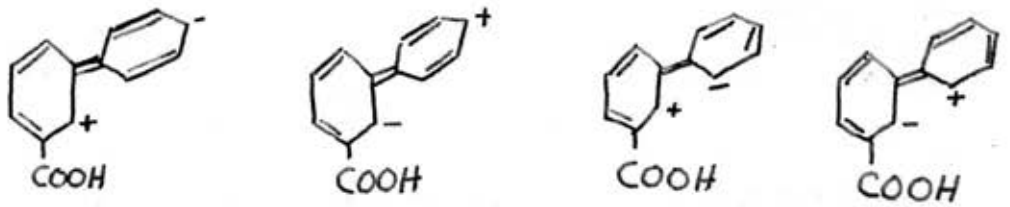
in a decreased ratio of the first and second ionization constants which could not be explained solely on the basis of steric effects but indeed required that the phenyl group be considered as an intrinsic attractor of electrons. It is this inductive effect of the phenyl group which invalidates Bjerrum's (17) equation relating the dissociation constants with the distance between the carboxyl groups in dicarboxylic acids.

Numerous other examples could be cited as evidence of an intrinsic negative inductive effect of the phenyl group. However, due to the coexistent resonance interactions which are usually present, very little evidence of the quantitative aspects of the inductive effect are available. A striking example of this complication arises in consideration of the first order solvolysis rates of phenyl substituted methyl chlorides. For example, the first order rate constants for alcoholysis at 25°C. are 2.5×10^{-8}, 5.06×10^{-5} and 7.44×10^{-1} for benzyl, benzhydryl and trityl chlorides respectively (104). How much of the observed effect is due to the electron attracting influence of the phenyl group and how much to first order conjugative resonance which stabilizes the ground state of the corresponding carbonium ion by distributing the positive charge into the benzene rings cannot be evaluated. This example is further complicated by the possibility of steric effects.

Hammett (58) has assigned a sigma value of $+ 0.218$ to the m-phenyl group. This should constitute excellent

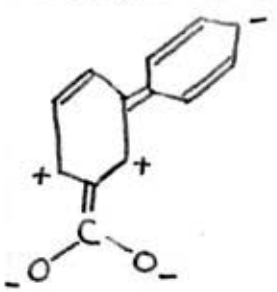
quantitative data on the non-resonance electronic influence of this group. It has recently (91) been pointed out, however, that this value is based on admittedly (23) unreliable data and therefore measurements were carried out in this research which were intended to provide a more reliable sigma value for this group. Acid strengths of benzoic and m-phenylbenzoic acids were determined under conditions which reproduced those employed by Berliner and Blommers (12) for which these workers had accurately established a rho value. The resulting sigma value is $+0.06 \pm 0.03$. Interpretation of this value is relatively simple for neither steric factors nor first order resonance effects can be operative. The possibility that the effect is due to the phenyl group complexed by water or by dibutyl cellosolve can be readily dispelled on the basis of spectral evidence. In this respect it is known (85) that the ultraviolet spectrum of benzene in solution in water, ethanol, or diethyl ether, resembles its spectrum in the gas phase even more closely than does its spectrum in cyclohexane solution. The differences in all of these cases are small.

Higher order resonance interaction between the two rings such as contributions from dipolar structures which are considered important in biphenyl systems cannot account for the increase in acid strength due to the meta-phenyl group. For example contributions from canonical structures I-IV may be considered as



I II III IV

contributing slightly to the resonance stabilization of the unionized acid. On the other hand none of these structures can be of any importance in the stabilization of the anion. Structure I and III would be expected to inhibit direct resonance with the carboxyl group due to the presence of two adjacent positive charges in structures such as V.



V

One should expect on this basis that the resonance interaction of the m-biphenyl system would lead to an overall stabilization of the parent acid over its anion with a consequent slight decrease in strength of the acid.

The observed increase in acid strength upon the introduction of a m-phenyl group into benzoic acid can be due then only to a small but definite electron attracting character of this group.

If such resonance considerations, as have been discussed in this respect, are in fact not of such high order as to be

negligible for all practical purposes then indeed one must conclude that the established sigma value for m-phenyl is at least a minimum estimate of the inductive effect inherent in this group.

It should be pointed out that Wheland (132) has presented a theoretical basis for the electron attracting nature of the phenyl group relative to hydrogen which does not depend on resonance interactions associated with distribution of charge into the benzene ring. Furthermore, the observation that the effect of the phenyl group is reflected on the acid strengths of phenylacetic and β-phenylpropionic acids, in which cases the phenyl group is separated by one and two saturated carbon atoms respectively and therefore cannot be involved in resonance interactions with the carboxyl group, can be considered as direct evidence of an intrinsic negative inductive effect.

In the para position the influence of the phenyl group is complicated by the possible coexistence of direct resonance interaction with the reactive center. Thus while the migratory aptitude (65) of the meta-biphenylyl group in the pinacol rearrangement is 0.4 (phenyl=1) that of the para-biphenylyl group is 3.7. Lichtin and Glazer (91) have interpreted these results as indicating that the p-phenyl is so situated that it can participate in the distribution of a positive charge in the activated complex and thus act as

an electron supplying group while the meta-phenyl, since it cannot participate in such resonance interactions, behaves as an electron withdrawing group in accord with its negative inductive effect. Also it is notable in this respect that while the m-phenyl group has a small effect leading to a decrease in the ionization constant of triphenylchloromethane in liquid sulfur dioxide the para-phenyl exibits a rather large effect in the opposite direction.

The magnitude and direction of the effect of a para-phenyl group is not in accord with the small sigma constant (+0.009) assigned to this group by Hammett. A sigma constant for para-phenyl (+0.01 +0.03) can be calculated from the ionization constants of the corresponding acid (12).

Consideration of possible resonance interactions of the para-phenyl group with the carboxyl group of benzoic acid leads to the conclusion that such interactions cannot contribute substantially to the stabilization of the anion or of the undissociated acid. Dipolar structures can contribute somewhat to the stabilization of the acid; however, the extent of such contributions must be small if not entirely negligible.

If we assume that the para-phenyl, like the meta-phenyl group, exerts an effect on the ionization of benzoic acid which is completely due to its electron attracting

nature then it should be possible to calculate a sigma constant for the para position based entirely on electrostatic considerations. For example, if in the meta position the group exerts an attraction which results in a sigma of +0.06 +/- 0.03 then by invoking an inverse square relationship between sigma and the distance from the carboxyl group it is possible to arrive at a value of about +0.04 +/- 0.03 for sigma at the para position. The actual value observed for the para position lies within experimental error of the calculated value.

It is therefore necessary that another sigma constant be assigned to the para-phenyl group which will account for resonance interactions involving the distribution of charge from the reactive center to the ortho and para positions of the ring. Obviously the dissociation of benzoic acids cannot be used for this purpose. Possibly the acid strengths of substituted phenols would constitute an excellent source for this data.

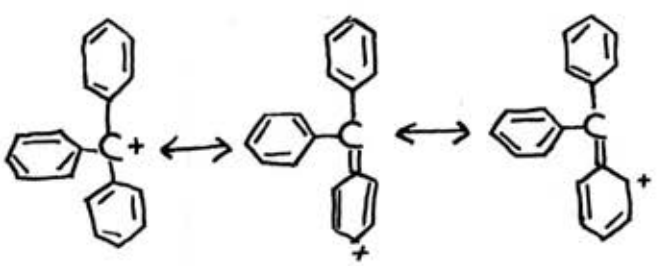
In this research a rho value has been calculated for the reaction

$$(R\text{-}\phi)_3CCl \overset{K_1}{\rightleftharpoons} (R\text{-}\phi)_3C^{+} + Cl^{-}$$

in liquid sulfur dioxide. From the observed effect of a para-phenyl substituent on the ionization constant it is possible to assign a new sigma constant to this group.

The Electronic Influence of the Phenyl Group on the Ionization of Triarylchloromethanes

The effect of a substituent on the ionization equilibrium of triphenylchloromethane cannot be predicted without the assumption that the pronounced stability of the triarylcarbonium ion is due to resonance of the type shown below.



Substituents that assist this resonance either by increasing the number of structures or by stabilizing positive charges on the ortho or para positions increase the ionization constant.

A chemically negative (-I) group is one that attracts electrons. Such a group in the para position reduces the stability of the quinoidal structures having a positive charge

on the para carbon and hence causes a decrease in the ionization constant. A group in the para position can, however, have a tendency to reduce the ionization because of its inductive effect and at the same time have a tendency to increase ionization because it introduces new forms into the resonance. A rigorous prediction is impossible, however, it is possible to determine which of the opposing tendencies is predominant.

In the meta position direct resonance interactions are prohibited and the observed effect is due primarily to the inductive character of the substituent.

Lichtin and Glazer (91) in a study of the effect of one meta-phenyl group on the ionization equilibrium of triphenylchloromethane in liquid sulfur dioxide have produced data which can be interpreted as resulting from a small fundamental electron attracting influence. Alternate explanations however are possible, namely, that the responsibility is due to a sulfur dioxide complex of the m-phenyl group, or that the presence of a positive charge localized in one ring decreases resonance interaction of the two rings.

Consideration of the Possibility of Complexing with Sulfur Dioxide

A small electron attracting influence of the meta-phenyl group has been established in this work and shown not

to be the result of a solvent complex of the group. In liquid sulfur dioxide, however, this possibility cannot be ruled out with any degree of certainty. The known (5)(74) ability of sulfur dioxide to complex with aromatic rings and the observed low limiting conductance value of meta-biphenylyldiphenylchloromethane can be considered as evidence supporting the hypothesis that the phenyl group is solvated. However, since the exact nature of the binding involved in such complexes is obscure it is not possible to predict its influence on the electronic nature of the phenyl group. Some indication of the importance of possible solvent complex formation with the ring on the observed effect of phenyl substituents may, however, be obtained by indirect means. For example, the effects of meta-, and para-phenyl groups on the solvolysis rates of the corresponding trityl chlorides in aqueous alcohol would serve as a quantitative estimate of the effects of these groups in the absence of complex formation with the solvent. These data are, however, not available and therefore as a first approximation it will be assumed in the discussion which follows that the effect of the phenyl group is characteristic of the group itself.

The Influence of Stepwise Introduction of Substituents

Shorter and Stubs (119) compared the effects of several substituents on the free energy of ionization of polysubstituted benzoic acids. In agreement with the conclusions of Bradfield and Jones (cf. pg. 157) these workers were able to demonstrate that the change in ΔF°

of ionization caused by two or more substituents on benzoic acid was the algebraic sum of the effects of the individual groups in all cases except those in which substituents were present ortho to the reactive center.

Recently, Evans and coworkers (10,11,33,34,35) have demonstrated that a similar relationship holds true for the effects of substituents on the ionization of polysubstituted triphenylchloromethanes in nitroalkane solutions. This can be readily seen from their data in nitromethane summarized in table 2-XVIII.

These data demonstrate that in all cases the changes in the free energy of ionization of polysubstituted trityl chlorides are exactly equal to the sum of the effects caused by the individual substituents within experimental error of $\pm$ 0.1 K-cal./mole. These results parallel the data of Nixon and Branch (104) on the solvolysis of substituted trityl chlorides and it is thus possible to conclude that for reactions and equilibria involving the ionization of trityl chlorides the probability factor in the rate equation is not strongly dependent upon the nature of para-, or meta-substituents and that the rate and equilibrium constants therefore reflect only changes in energy of activation or in free energy produced by the electronic influence of the substituent.

A completely equivalent situation should be expected for the ionization of triarylchloromethanes in liquid sulfur

dioxide. The data of this research illustrate that even for the meta-phenyl derivatives, where the relative importance of changes in ionic association are expected to be at a minimum, the expected additivity of group effects as indicated by experimental free energy values is not excellent. On the other hand, however, when the calculated free energy values (table 2-XIV) are compared the expected agreement is indeed excellent and exhibits no individual deviation greater than $\pm$ 0.01 K-cal./mole. In either case, however, the additivity rule is obeyed within the limits of experimental error. This observation strongly suggests that in this investigation the errors in the relative free energy values are extremely small and of the order of $\pm$ 1 percent. It can, moreover, be concluded from these results that the assumptions of Lichtin and Bartlett are a good first approximation for the meta-phenyl derivatives of triphenylchloromethane.

TABLE 2-XVII

Ionization of Triarylchloromethanes in Nitromethane Solution.[a]
20.0° C.

Compound

R	R	R	ΔF° (K.-Cal./M.)
H	H	H	4.5
H	H	p-CH_3	3.6
H	p-CH_3	p-CH_3	2.6
p-CH_3	p-CH_3	p-CH_3	1.7
H	H	p-C_4H_9	3.7
H	p-C_4H_9	p-C_4H_9	2.7
p-C_4H_9	p-C_4H_9	p-C_4H_9	2.0
H	H	p-Cl	5.0
p-Cl	p-Cl	p-Cl	5.9
p-Cl	p-CH_3	p-CH_3	3.1
H	H	p-Br	5.0
H	p-Br	p-C_4H_9	4.0
p-Br	p-C_4H_9	p-C_4H_9	2.9

(a) Data of Evans and coworkers (10,11,33,34,35).

A consequence of the additivity rule is the fact that a plot of free energy against the number of similar substituents should be exactly linear. A comparison of such plots of $\Delta F^{\circ}_{exp.}$ and the calculated ΔF°_{1} values for m-phenyl derivatives should demonstrate the relative importance of ionic association corrections for these compounds.

Figure XV shows a small deviation from linearity for the experimental free energy values and excellent agreement for the calculated free energy values. The excellent agreement shown by the calculated values cannot be purely fortuitous and should serve as an indication of the validity of the ion pair treatment employed in this work. A more rigorous test of the model lies, however, in a comparison of those data for compounds which are stronger electrolytes than trityl chloride and for which the approximation of Lichtin and Bartlett is not valid. Lichtin and Glazer(91) and Lichtin and Bartlett (90) have provided the experimental data needed for this comparison. These values combined with the ion pair dissociation constants calculated in this dissertation make it possible to calculate the desired free energies of ionization for these compounds. These data are summarized in table 2-XVIII.

These data (table 2-XVIII) demonstrate that the additivity principle does not hold for the experimental free energy values while the agreement shown by calculated values is excellent within experimental error.

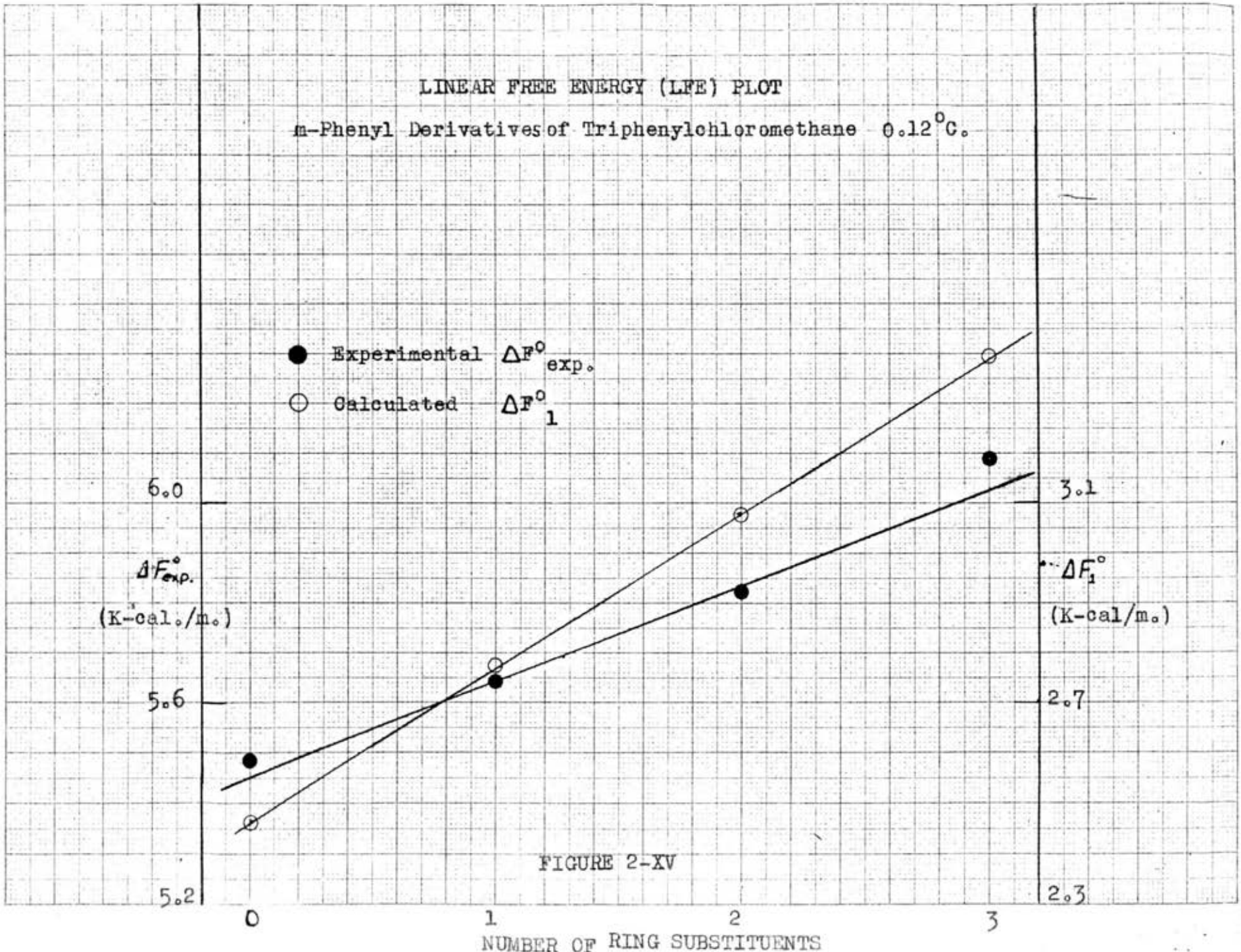
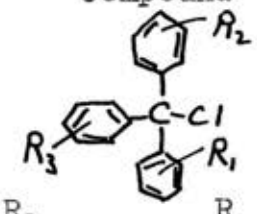

LINEAR FREE ENERGY (LFE) PLOT
m-Phenyl Derivatives of Triphenylchloromethane 0.12°C.
Experimental $\Delta F^{\circ}_{exp.}$
Calculated ΔF°_{1}
6.0
5.6
5.2
$\Delta F^{\circ}_{exp.}$
(K-cal./m.)
3.1
2.7
2.3
ΔF°_{1}
(K-cal/m.)
0
1
2
3
NUMBER OF RING SUBSTITUENTS

FIGURE 2-XV

TABLE 2-XVIII

Experimental and Calculated Free Energies of Ionization of Triarylchloromethanes in Sulfur Dioxide Solution at 0°C.

Compound



R_1	R_2	R_3	10^5K (exp.)	10^2K_1 (calcd.)	$\Delta F^\circ_{exp.}$ (K-cal/m.)	ΔF°_1 (K-cal/m.)
H	H	H	4.15	1.34	5.48	2.35
H	H	p-Ø [a]	23.2	5.68	4.54	1.56
H	p-Ø	p-Ø [a,b]	99	20.7	3.75	0.86
p-Ø	p-Ø	p-Ø [a,b]	290	75.8	3.17	0.15
H	H	m-CH_3 [c]	9.2	2.97	5.04	1.92
H	H	p-CH_3 [c]	71	24.4	4.05	0.72
H	H	p-t-C_4H_9 [c]	76	24.4	3.90	0.72
H	p-t-C_4H_9	p-t-C_4H_9 [c]	340	354	3.08	-0.72
p-t-C_4H_9	p-t-C_4H_9	p-t-C_4H_9 [c]	800	(---)	2.62	(---)
H	H	1-naphthyl [d]	70	30.7	3.96	0.64
H	H	2-naphthyl [d]	14.4	2.70	4.80	1.96

(a) Data of Lichtin and Glazer (91).
(b) Data of Ziegler and Wollschitt (138). Calculated by Lichtin and Glazer (91).
(c) Data of Lichtin and Bartlett (90).
(d) Data of Ziegler and Wollschitt (138). Calculated by Streitweiser (120).

Free Energy Group Factors

A free energy factor can be assigned to each substituent if this be defined as $\Delta F_o^\circ - \Delta F_j^\circ = \Delta\Delta F_j^\circ$; where the subscript, o , refers to trityl chloride and, j , refers to a particular substituent. For polysubstituted compounds the total effect of all the substituents must be equal to the sum of the individual $\Delta\Delta F_j^\circ$ factors of each substituent. Group factors calculated for the stepwise introduction of meta-, and para-phenyl groups are summarized below for both the experimental and calculated free energy data.

TABLE 2-XIX

Free Energy Group Factors for the Stepwise Introduction of Phenyl Substituents.

Number of Groups	Para-Phenyl $\Delta\Delta F^\circ_{exp.}$ (per group)	$\Delta\Delta F_1^\circ$ (per group)
	K.Cal./mole	K.Cal./mole
1	0.94	0.79
2	0.87	0.75
3	0.77	0.74

	Meta-Phenyl			
	0.10°C.	-8.93°C.	0.10°C.	-8.93°C.
1	0.16	0.19	0.32	0.34
2	0.17	0.20	0.31	0.32
3	0.20	0.22	0.31	0.33

From table 2-XIX we note that the group factors for meta-phenyl are exactly identical regardless of the number of times the meta-phenyl group is substituted into the parent compound. In the case of the para substituents there appears to be a small decrease in the group factor as the number of substituents is increased. This departure from ideality is much less pronounced in the calculated $\Delta\Delta F_1^\circ$, group factors than is the case for the experimental values. If this effect is real then it would be suggestive of some sort of interaction between the substituents. Since, however, the group factors for the di-, and tri-, substituted compounds, which are based on the experimental data of Ziegler and Wollschitt (138) and which differ by 0.1 K-cal. per mole, become identical to within 0.01 K-cal. per mole as a result of the correction for ion-pair effects, it would seem not unreasonable to tentatively ascribe the departure from additivity for these two compounds to a consistent error in the experimental data of these workers. This conclusion becomes more attractive in view of the observation of Lichtin and Bartlett that there exist serious discrepancies between Ziegler's data and their own. This apparent discrepancy may be resolved when more accurate data for the di-, and tri-para phenyl compounds become available. In the meantime it is not too unreasonable to assign a $\Delta\Delta F_1^\circ$ value of -0.79 K-cal. per mole to the para-phenyl group at 0.1°C. based on the precise data of Lichtin and Glazer (91).

Correlation of Group Factors

Since the influence of substituents on the free energy of ionization of substituted triarylchloromethanes in liquid sulfur dioxide has been demonstrated to be exactly additive, it follows that the PZ factors of the Arrhenius equation are not significantly different regardless of the nature of the polar substituent in the meta or para position for all reactions involving the ionization of triarylchloromethanes. Thus in any SN-1 reaction of trityl chlorides the effect of a substituent should be reflected completely in the energy of activation. This situation is analogous to that which exists for reactions of meta-, and para-substituted benzene derivatives for which the Hammett relationship $\Delta E^{\neq} = \rho \Delta F^{o}$ has been established.

Consequently, it should be possible to obtain a linear plot of slope ρ if ΔF^{o} of ionization is plotted against $\Delta E^{\neq}$ of any given reaction of a series of substituted trityl compounds. A comparison of such plots using both $\Delta F^{o}_{exp.}$ and ΔF^{o}_{1} should serve as an independent test of the ion pair treatment proposed in this dissertation.

Unfortunately the only extensive data available for such comparisons are the data of Evans (33) in nitromethane solution. Recently doubt (86-a) has been cast on the reliability of these data, however, for the present purposes it is permissible to use these data for qualitative comparison.

In figure 2-XVI the experimental free energies in liquid sulfur dioxide at 0°C. are plotted against the data of Evans for the ionization of the same triarylchloromethanes in nitromethane solution. Figure 2-XVII shows an analogous plot for the free energies in liquid sulfur dioxide calculated on the basis of the ion pair dissociation corrections. While the results thus illustrated are not conclusive, the agreement is qualitatively better for the calculated data than for the experimental values. It can be seen, in either case, that the Hammett relationship appears to be satisfied.

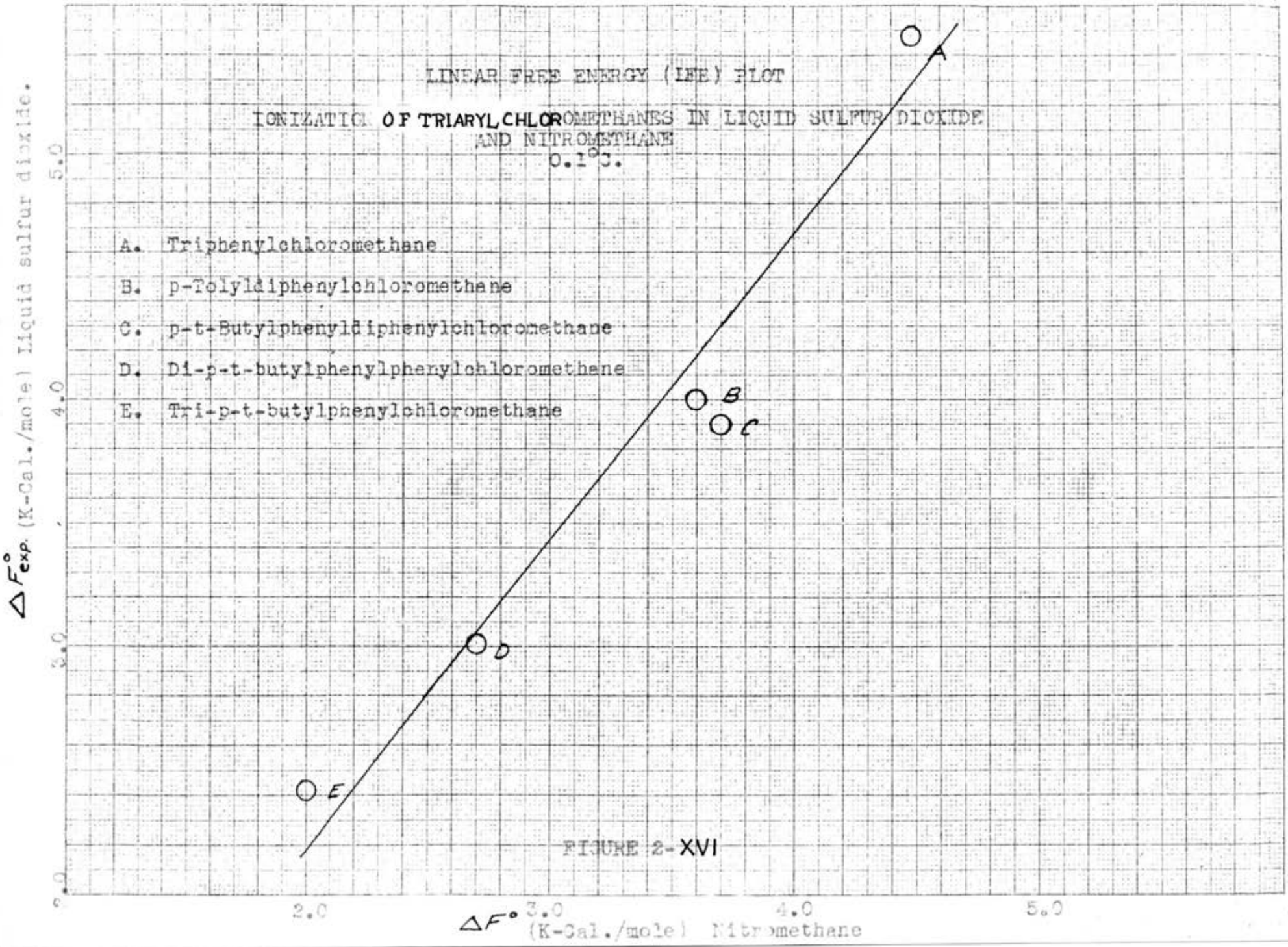

LINEAR FREE ENERGY (LFE) PLOT
IONIZATION OF TRIARYLCHLOROMETHANES IN LIQUID SULFUR DIOXIDE AND NITROMETHANE
0.1°C.
A. Triphenylchloromethane
B. p-Tolyldiphenylchloromethane
C. p-t-Butylphenyldiphenylchloromethane
D. Di-p-t-butylphenylphenylchloromethane
E. Tri-p-t-butylphenylchloromethane
A
B
C
D
E
$\Delta F^\circ_{exp.}$ (K-Cal./mole) Liquid sulfur dioxide.
ΔF° (K-Cal./mole) Nitromethane
2.0
3.0
4.0
5.0

FIGURE 2-XVI

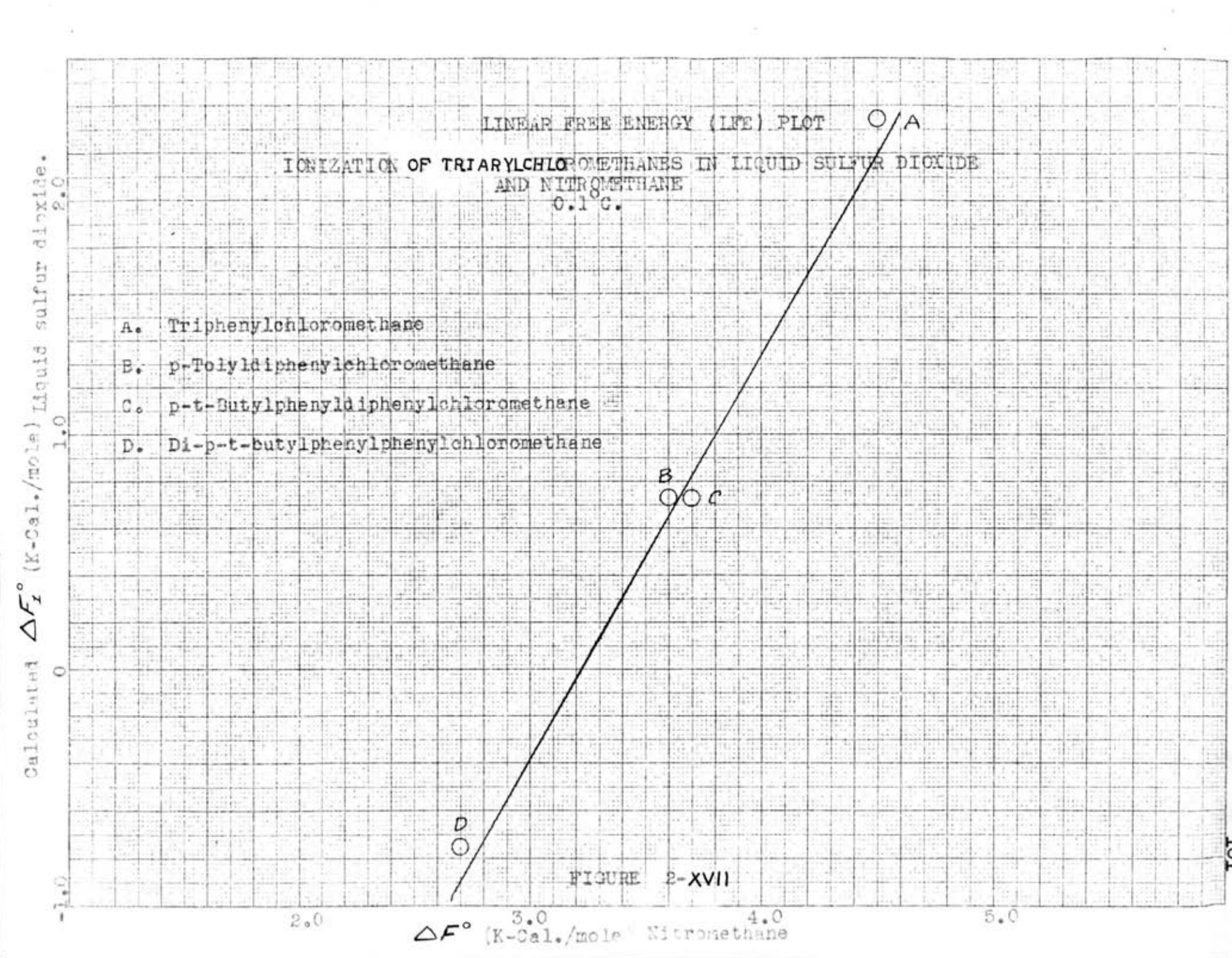


FIGURE 2-XVII

Hammett Rho Value for the Ionization of Triarychloromethanes

An important relationship can be shown to exist between the free energy group factors, $\Delta\Delta F_j^o$, in liquid sulfur dioxide defined as

$$\Delta F_o^o - \Delta F_j^o = \Delta\Delta F_j^o \qquad (2\text{-}28$$

and the Hammett sigma constant defined by the relationship $\log K_o - \log K_j = \sigma_j$ for the ionization of benzoic acids in water at 25°C.

It can be shown from the Hammett equation that in liquid sulfur dioxide

$$\log K_o - \log K_j = \frac{\Delta\Delta F_j^o}{2.303\ RT}. \qquad (2\text{-}29$$

Since for any reaction

$$\log K_o - \log K_j = \rho\sigma \qquad (2\text{-}27$$

it is immediately obvious that

$$\frac{\Delta\Delta F_j^o}{2.303\ RT} = \rho\sigma \qquad (2\text{-}30$$

In words, this equation means that the group factors are directly proportional to Hammett's sigma constants.

In general, for any reaction or equilibrium of substituted aromatic compounds, the rho value is evaluated by plotting log k for a series of substitution derivatives against the corresponding sigma values for the substituents.

A straight line is obtained and the slope of this line determines the rho value for the given reaction under the specified conditions.

An interesting corollary can be deduced from equation 2-30. Since, for the reaction under consideration in liquid sulfur dioxide, we have demonstrated that the free energy group factors are additive and are directly proportional to Hammett's sigma constants it must also be true that for this system the sigma constants are additive.* This should also be the case for those polysubstituted benzoic acids considered by Shorter and Stubs (119). Therefore a plot of log K for the ionization of triarylchloromethanes in sulfur dioxide solution against the summation of sigmas for all substituents should give a straight line of slope equal to rho for this system.

Alternatively, a rho value may be calculated directly from equation 2-27 by substituting the proper values for any given derivative. The values chosen for this purpose are those for the m-phenyl derivative for which a reliable sigma value has been provided in this investigation. Rho values have been calculated in this manner from the experimental

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*) Jaffe' (72) has arrived at a similar conclusion for multi-substituted benzene derivatives. His result is stated in the form of an equation

$$\log K - \log K_o = \rho \Sigma \sigma \qquad (2\text{-}31$$

which can be shown to be identical to equation 2-30 derived in this dissertation for polysubstituted trityl derivatives.

equilibrium constant for m-biphenylyldiphenylchloromethane (table 2-I) and from the calculated ionization constants (table 2-XIV). The resulting rho values are summarized below.

TABLE 2-XX

Hammett Rho Values for the Ionization of Trityl Chlorides in Sulfur Dioxide.

$\rho_{exp.}$ [a]		$\rho_{ion.}$	
0.12°C.	-8.93°C	0.12°C.	-8.93°C.
-2.1	-2.6	-4.2	-4.6

(a) Bartlett (7-a) calculated a value of -6.33 from the data of Lichtin and Bartlett (90).

Sigma Value for p-Phenyl

It was pointed out earlier that the sigma value assigned to the para-phenyl group on the basis of its effect on the ionization of benzoic acid does not accurately describe the effect of this group on reactions in which direct resonance interaction with the reactive center is possible. Indeed, it has been suggested (13,16-a,18,22) that at least two sigma values are needed to adequately define the quantitative aspects of the electronic influence of a substituent. The sigma constant for a group will depend not only upon the nature of the substituent and its location in the ring (meta-, or para-) as required by Hammett's definition, but will also depend upon the nature of the reactive center in so far as

its structure permits or restricts direct resonance interaction with the ring substituent. Moreover, in the case of conjugative resonance between the p-phenyl group and the reactive center, the electronic demands of the reactive center will determine the algebraic sign of the sigma constant (13). Thus sigma will be a positive quantity in those reactions involving the ionization of phenols (83) or anilines where the p-phenyl group can act as an electron withdrawing group. On the other hand, for those reactions involving the formation of a phenyl carbonium ion the sigma constant for a p-phenyl substituent will be a negative quantity indicating that here the phenyl group functions as an electron supplying group.

Thus at least two sigma constants are required to describe the influence of a para substituent except in those cases where the nature of the substituent is such as to prohibit direct resonace interactions with the reactive center. These constants are generally denoted as:(a) the inductive sigma, σ, obtained from dissociation constants of substituted benzoic acids; and (b) the resonance sigma, σ^*, applicable to reactions in which the substituent is involved in direct resonance with reactive centers. Several examples for this reasoning may be found in Hammett's (58) original table of sigma constants where, for example, two values are assigned to the p-nitro group. Jaffe' (71) has summarized several other examples of multiple sigma constants.

The resonance sigma, σ^*, for para-phenyl is further complicated by the fact that this group may act either as an electron supplier or withdrawer. Thus two values are required for the sigma constant of the para-phenyl group, namely: (1) $+\sigma^*$, when the group withdraws electrons from the reactive center and, (2) $-\sigma^*$ when the group supplies electrons.

A tentative value for the electron withdrawing resonance sigma, $+\sigma^*$, for the para-phenyl group can be calculated from the data of Kiefer and Rumpf (76-b) and of Judson and Kilpatrick (76-a) for the ionization constants of p-hydroxybiphenyl and of phenol respectively. Application of Hammett's rho value for this reaction (58) to the above data affords a $+\sigma^*$ value of $+0.15$.

It is now possible, on the basis of the rho value established in this dissertation for the ionization of triarylchloromethanes in sulfur dioxide solution, to evaluate the electron supplying resonance sigma, $-\sigma^*$, for the para-phenyl group. The values summarized below were calculated from the experimental equilibrium data of table 2-I and from the calculated ionization constants of table 2-XIV.

TABLE 2-XXI

Sigma Values for the Para-Phenyl Group.

Rho	Sigma
-2.13 [a]	-0.354
-4.25 [b]	-0.148

(a) Based on experimental data. (b) Based on calculated data.

The value -0.148 is based on calculated K_1 values for p-biphenylyldiphenylchloromethane and triphenylchloromethane and is here proposed as the correct value for the para-phenyl group when direct resonance interactions with the reactive center are possible and when the electronic demands of the reaction are such as to require the substituent to function as an electron supplying group.

At the present time there are no reliable data in the literature with which to test the accuracy of this value for the $-\sigma^*$ value for the para-phenyl group. It may be significant, however, that both the σ^+ and $-\sigma^*$ values appear to be identical except for their algebraic sign.

Hammett Rho-Sigma Plots

Figures 2-XVIII and 2-XIX show Hammett rho-sigma plots constructed for the ionization of substituted triarylchloromethanes in liquid sulfur dioxide at 0°C. The solid lines were drawn through log K for the unsubstituted compound with slopes equal to the appropriate rho values calculated from the experimental values for the mono-meta-phenyl derivatives (figure 2-XVIII) and from the calculated K_1 values (figure 2-XIX). In figure 2-XVIII the log of the experimental equilibrium constants (table 2-I and data from reference 90) are plotted against the summation of Hammett's sigma constants (58) for the various substituents. Figure 2-XIX differs from figure 2-XVIII only in that calculated K_1 values are employed. It can be seen that for all compounds,

HAMMETT RHO-SIGMA PLOT

IONIZATION OF TRIARYLCHLOROMETHANES IN LIQUID SULFUR DIOXIDE 0°C.

Log (experimental equilibrium constant) vs. $\Sigma\sigma_j$

Rho = -2.13.

A. Tri-m-biphenylylchloromethane
B. Di-m-biphenylylphenylchloromethane
C. m-Biphenylyldiphenylchloromethane
D. Triphenylchloromethane
E. m-Tolyldiphenylchloromethane
F. p-Biphenylyldiphenylchloromethane
G. p-Tolyldiphenylchloromethane
H. p-t-Butylphenydiphenylchloromethane
K. Di-p-t-butylphenylphenylchloromethane
L. Tri-p-t-butylphenylchloromethane
I. Di-p-biphenylylphenylchloromethane
J. Tri-p-biphenylyl-chloromethane

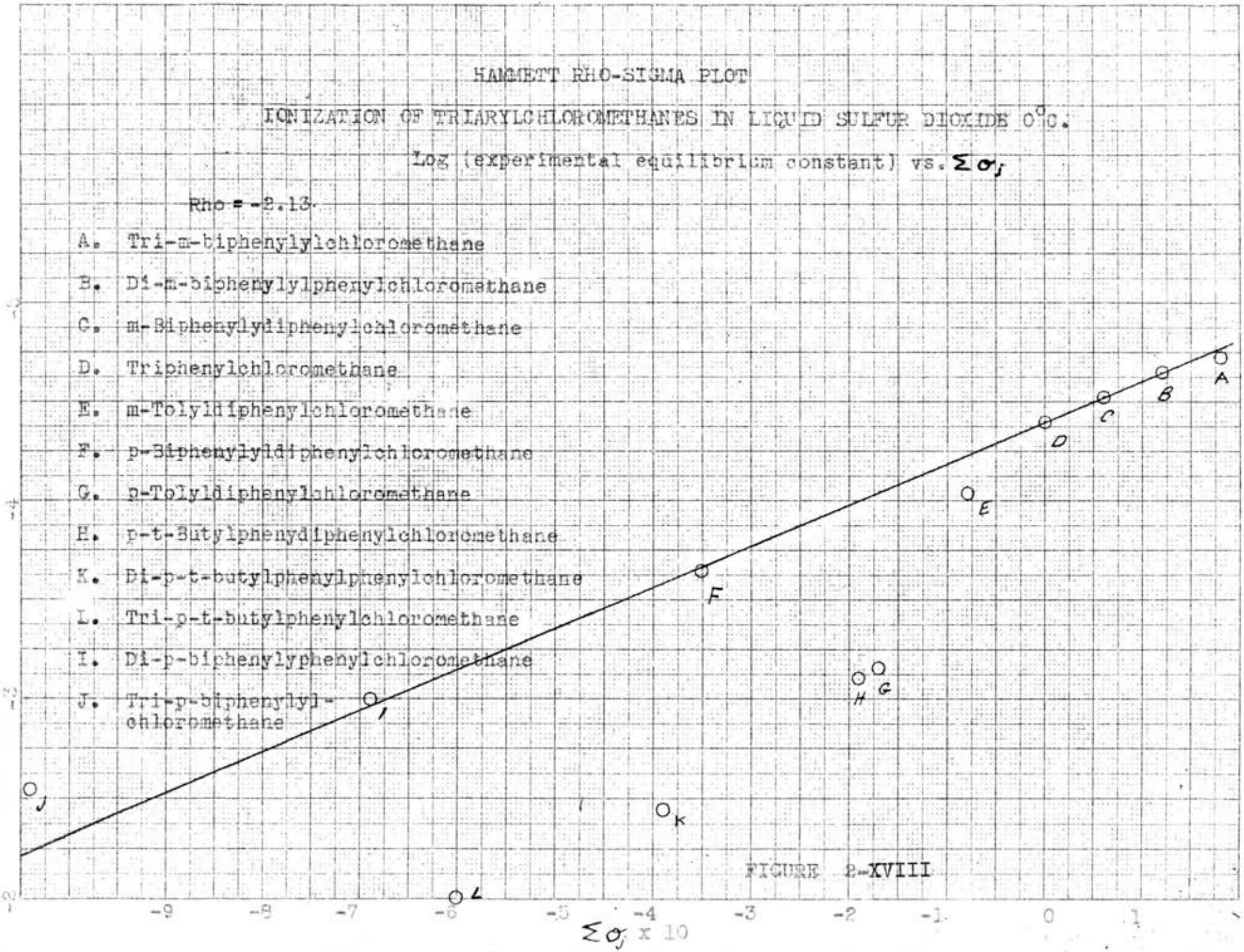


FIGURE 2-XVIII

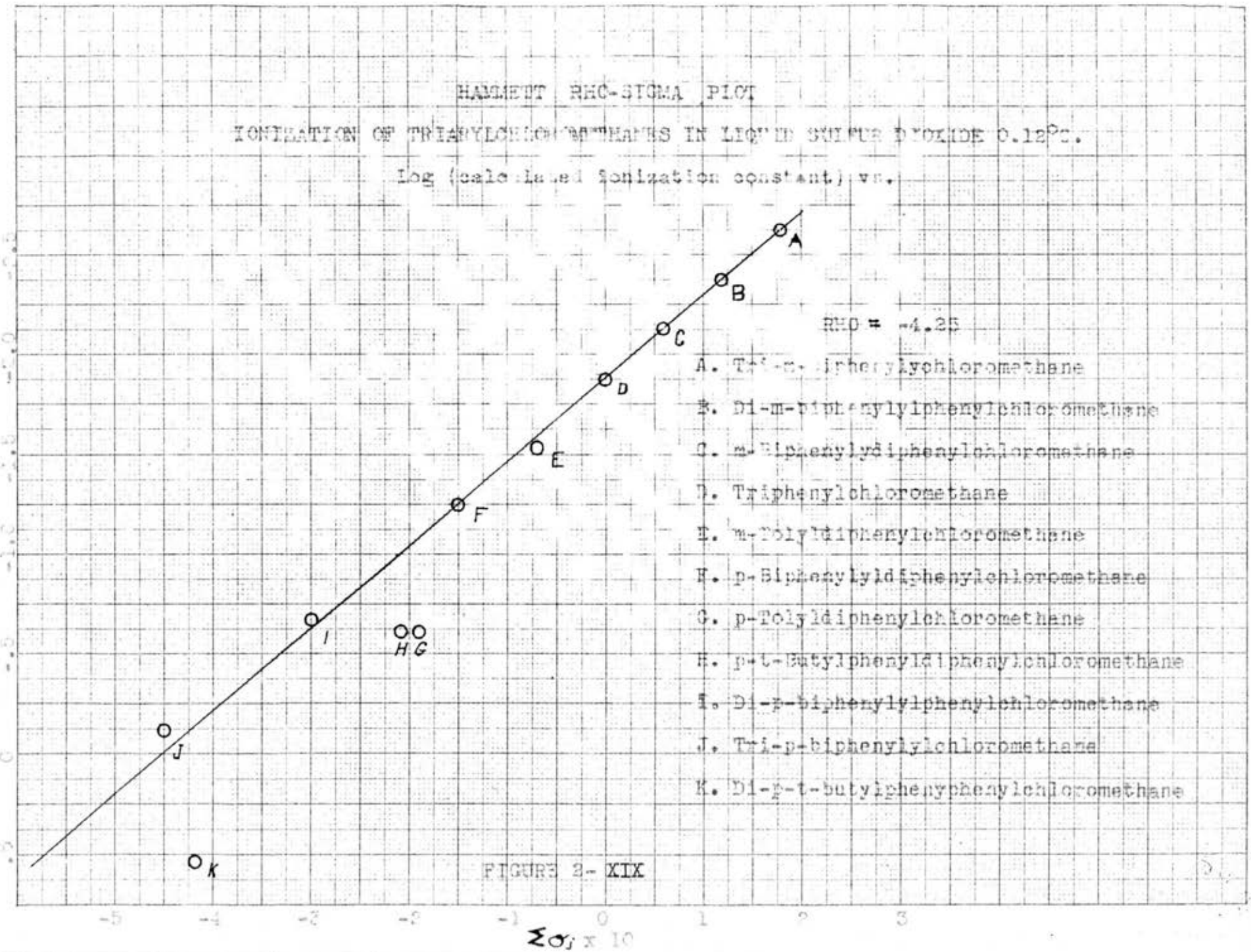


FIGURE 2- XIX

the calculated K_1 values give much better agreement with the theoretical slope than is the case for the corresponding experimental data. The improvement noted here is a direct consequence of the cancellation of the influence of ion pair dissociation on the measured equilibrium constants and therefore serves as a quantitative test of the validity of the ion pair treatment employed.

The divergence of points H, G, and K from the plot (figure 2-XIX) suggests the need for σ^* values for para-alkyl groups where hyperconjugative resonance interactions are important. Values calculated for these groups are $\sigma^* = 0.3$ for both p-methyl and p-t-butyl. If this value were incorporated with the data plotted in figure 2-XIX the observed divergence of all three points would no longer exist.

Resonance Stabilization of Triaryl Carbonium Ions

Calculations (120) of the resonance stabilization of several substituted trityl chlorides and of the ions derived from them on ionization of the carbon-chlorine covalent bond has shown that the meta-phenyl group stabilizes the covalent compound more than it does the corresponding ion. The net effect of the meta-phenyl group then is to decrease the extent of ionization of the substituted compound relative to triphenylchloromethane by virtue of dipolar contributions to the resonance energy which are effective only in the undissociated molecule.

The para-phenyl group, on the other hand, on the basis of similar calculations was shown to stabilize the ion to a much larger extent than it stabilizes the covalent compound. This results in an increased ionization relative to trityl chloride.

The calculated differences in delocalization energy, ΔdE, in terms of the exchange integral β were shown to very closely parallel the measured $\Delta F°_{exp.}$ values for the ionization of the corresponding meta-, and para-phenyl substituted trityl chlorides in sulfur dioxide solution. In this respect Streitweiser (120) demonstrated that a plot of $\Delta F°_{exp.}$ against ΔdE was a smooth plot. It is interesting to note moreover that for the meta-phenyl series each successive meta-phenyl group apparently produces an identical increment in the ΔdE values. While this may well be a direct consequence of the assumptions involved in applying the simple LCAO method to charged ions, it may be argued that these data serve as a theoretical basis, to a first approximation, for the observed additivity of the group effects.

Deviations from additivity for the para-phenyl derivatives are of the order of 4 percent of the calculated stabilization values. This strongly suggests that even here the resonance increments are additive. If this is indeed the case then it is obvious that the smooth curve of dE against $\Delta F°_{exp.}$ is the result of two factors, namely, the fact that only two substituents, meta-, and para-phenyl, are considered and that $\Delta F°_{exp.}$ for the para-phenyl derivatives are not a true

measure of the effect of this group due to the complications of ion pair equilibria.

More exact calculations on a large number of series of stepwise substituted trityl chlorides may well demonstrate that no such smooth correlation curve exists between $\Delta F°_{exp.}$ and ΔdE. A definite relationship may be expected however for the $\Delta F°_1$ values.

Intuitively it seems reasonable that relationship between $\Delta F°_1$ and ΔdE to be expected will consist of a series of straight lines all of which begin at a point corresponding to values of the variables for the unsubstituted parent compound. The slopes of these lines should differ depending upon the nature of the substituent being considered. This follows from the fact that while ΔdE is a measure of the resonance interactions of the group, the free energy of ionization reflects both this effect and the electrostatic effects due to the intrinsic inductive nature of the group.

Figure 2-XX shows an example of a plot of $\Delta F°_1$ against Streitweiser's ΔdE values for meta-, and para-phenyl derivatives which serves to illustrate the above hypothesis. Extensive measurements and calculations are needed to test the soundness of this proposal.

CALCULATED FREE ENERGY OF IONIZATION IN LIQUID SULFUR DIOXIDE VERSUS DELOCALIZATION ENERGY FOR DERIVATIVES OF TRITYL CHLORIDE

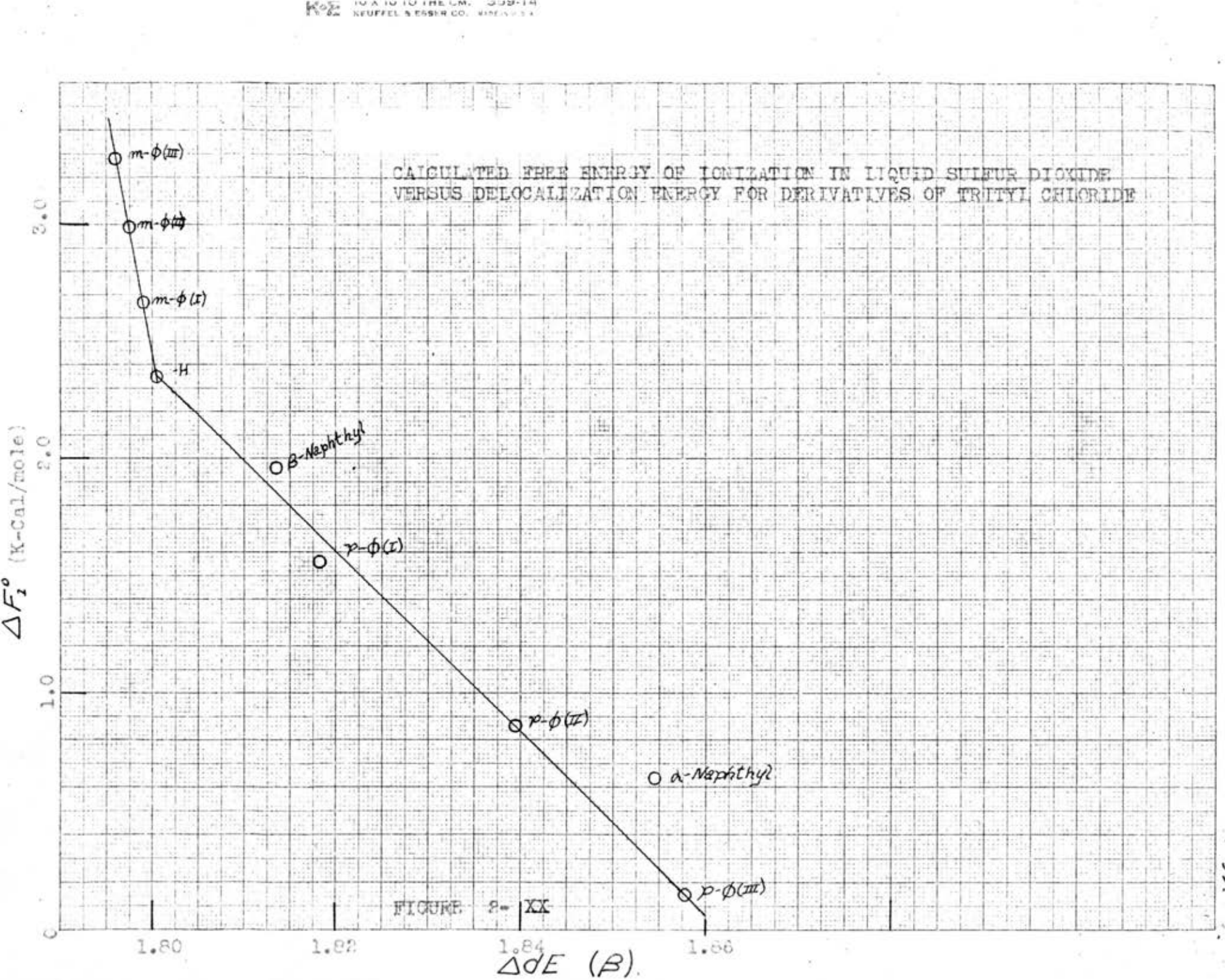


FIGURE 8- XX

FUTURE WORK

Conductivity of triarylchloromethanes in liquid sulfur dioxide solution can serve as a powerful tool for the quantitative evaluation of substituent effects only if it is possible to accurately determine the free energies of ionization of ring substituted derivatives. Since, however, conductivity measurements supply only an experimental free energy value which is a composite of the free energy of ionization and of the free energy of ion pair dissociation, a method of accurately determining the ion pair association constant must be developed. A theoretical treatment of ion pair equilibria based on the statistical theory of Bjerrum has been presented in this dissertation. Very satisfying results have been obtained by application of this treatment to the experimental data of this research. Direct experimental verification of the accuracy and limitations of this treatment for triarylcarbonium chlorides is, however, lacking at this time. The required data are easily accessible and can be obtained from the measured equilibrium constants of a series of substituted triarylmethylperchlorates. A series consisting of triphenylmethylperchlorate and its mono-, di-, and tri-para-phenyl derivatives would amply test the accuracy and validity of the model and would indicate whether refinements in the treatment are required.

Experimentally the measurements must be of the highest

precision and in view of the limited validity of the Shedlovsky treatment the experiments must be designed to yield accurate data over a very limited concentration range. In order to accomplish this, a new cell must be designed which will incorporate the features of a small dilution ratio and an electrode bulb of rather large volume. With such a cell it will be possible to accurately prepare a solution of low initial concentration, of the order of 5×10^{-4} moles per liter and obtain a reasonable number of experimental dilutions within a region extending to a concentration of about 2×10^{-5} moles per liter.

The first order rates of solvolysis of a series of ring substituted triarylchloromethanes should be determined in order to establish a rho value for this system and thereby permit an unequivocal determination of the $-\sigma^*$ value for the p-phenyl substituent. This value would serve both as an independent check for the value proposed for $-\sigma^*$ in this dissertation and also as a test for the ion pair corrections.

EXPERIMENTAL PART

Synthetic

All compounds used in this research were prepared by the author with the exception of triphenylchloromethane and its mono-para-phenyl derivative which were supplied by Professor Norman N. Lichtin to whom the author is indebted. Table 2-XXII summarizes the physical properties and analytical data for all the compounds. The numbers in the last column indicate the conductivity runs in which the particular compound was employed. Experimental data summarized in Appendix II-A (tables 2-A to 2-H) are tabulated under run numbers corresponding to those in the last column of table 2-XXII.

Meta-phenyl substituted triphenylchloromethanes as well as m-phenylbenzoic acid were prepared by reacting m-phenyl Grignard reagent with the proper carbonyl compounds.

TABLE 2-XXII

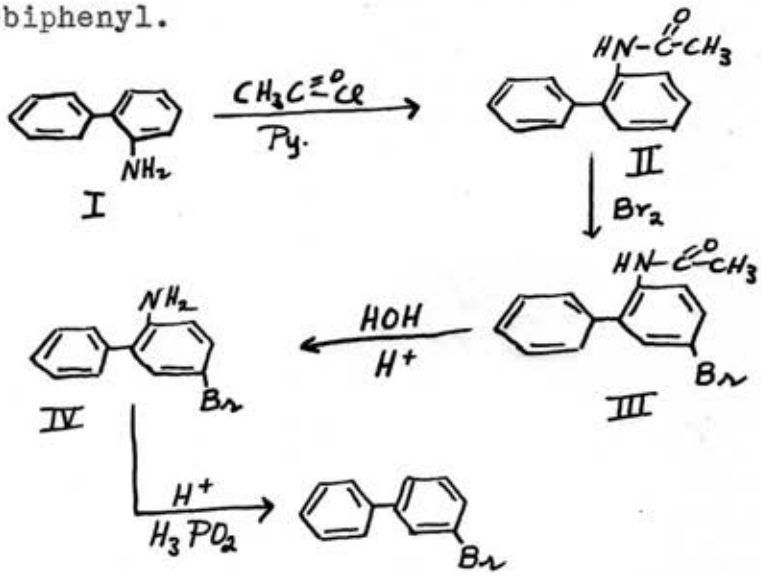
Physical Properties of Compounds.

Compound $R_2-\phi-C(\phi-R_1)(\phi-R_3)-Cl$			Melting Range[a] (°C.)		Analysis[b]						Runs
					Found			Theory			
R_1	R_2	R_3	Found	Lit.	C	H	Cl	C	H	Cl	
H	H	H[e]	111-2	112-3			12.9[f]			12.7	HL-50,55,18
H	H	m-ø	85-87	86-87	84.4	5.5	9.9	84.6	5.4	9.99	HL-63,79,80
H	m-ø	m-ø[c]	113.6-114.4	-----	86.1	5.5	8.3	86.4	5.4	8.2	HL-4,5,6,14,40
H	m-ø	m-ø[d]	117.6-118.4	-----	---	---	8.2			8.2	HL-15
m-ø	m-ø	m-ø[c]	199.8-200.6	200-201	87.1	5.8	7.1,7.0	87.6	5.4	7.0	HL-7,8,9,16 40
m-ø	m-ø	m-ø[d]	201.2-202	"	86.7,88.2	5.3,5.2	6.7	"	"	"	HL-42,43,44
H	H	p-ø[e]	147.0-147.8		84.7	5.4	9.8	84.6	5.4	9.99	HL-20,21,22

(a) Anschutz Type thermometers. (b) Microanalysis by Dr. Carol K. Fitz, Needham, Mass.
(c) Designated as sample I. (d) Designated as sample II.
(e) Compounds supplied as chlorides by Professor N. N. Lichtin.
(f) Hydrolyzable chloride indicated 99.2% of theoretical.

Synthesis of m-Bromobiphenyl

m-Bromobiphenyl (V) was synthesized from 2-aminobiphenyl (I) by the method of Huber (66) employing the modifications of Woods and Reed (135). The following is an outline of the sequence of experimental steps employed in the preparation of m-bromobiphenyl.



The deamination was carried out according to the general procedures for hypophosphorus acid deamination described by Kornblum (80).

Experiment 1: Preparation of 2-acetaminobiphenyl

214 ml. (3.0 moles) Baker's C.P. acetyl chloride were added slowly to a stirred solution of 340 grams (2.0 moles) Eastman Kodak Co., Yellow Label 2-aminobiphenyl in 800 ml. Matheson Co. pyridine. During the addition the temperature was maintained between 10° and 15°C. by means of an ice bath.

When the addition was complete (one hour) the reaction mixture was stirred for one hour at room temperature. The crude product was isolated by slowly pouring the pyridine solution into a mixture of concentrated hydrochloric acid and cracked ice. The crude product was washed free of acid and then dried on a Buchner funnel. Two recrystallizations from 50% aqueous acetic acid following decolorization with animal charcoal afforded a 71.0% yield (310 grams) of straw colored needles melting sharply 118°-119°C.*

Experiment 2: Preparation of 2-acetamino-5-bromobiphenyl.

A solution of 53.4 ml. (1.04 moles) Baker's C.P. bromine in 1 liter of glacial acetic acid was added rapidly to a stirred solution of 220 grams (1.04 moles) of 2-acetaminobiphenyl in 1.8 liters glacial acetic acid. The reaction mixture was allowed to stand for 36 hours after which the product was separated by pouring the reaction mixture into 6 liters of water. The crude product was washed free of acetic acid and air dried. Crystallization from aqueous ethanol furnished 290 gms (97.2% yield) of colorless needles melting sharply between 127.5°-128.5°C. In two other runs the product was prepared in 84% and 92% yields the melting points being 128.5°-129.0 C. and 127.0-128.5°C. respectively.

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* All melting points are recorded with Anschutz type total immension thermometers in a stirred electrically heated bath.

Experiment 3: Preparation of 2-amino-5-bromobiphenyl.

A solution of 287 grams (0.989 moles) of 2-acetamino-5-bromobiphenyl and 300 ml. concentrated hydrochloric acid in 500 ml. 95% ethanol was refluxed for 5 hours. The hot, clear, orange liquor was poured into 4 liters of cracked ice and water. This was allowed to stand for 12 hours and was then diluted with 3 liters of water and neutralized with 20% sodium hydroxide solution. The crude product was triturated with water and finally washed and air dried to give 207 grams (84.5% yield) of poorly defined white crystals melting in the range 53°-57°C.

In two other runs this product was prepared in 89% and 90% yields.

Experiment 4: Preparation of m-bromobiphenyl.

A cold solution of 40 grams of sodium nitrite in 100 ml. of water was added to 400 ml. (4.04 moles) Mallinkrodt U.S.P. 50% hypophosphorus acid which had previously been cooled to -5°C.

Forty ml. of concentrated sulfuric acid cooled to 5°C. was added very slowly to a solution of 75 grams (0.302 moles) of 2-amino-5-bromobiphenyl in 700 ml. glacial acetic maintained at 20°C. This solution was then added slowly to the solution of sodium nitrite in hypophosphorus acid while maintaining the temperature between 0° and 5°C. with a salt-ice mixture.

When the addition was complete the solution was stirred for two hours and an additional 40 grams of sodium nitrite dissolved in 100 ml. water was added slowly. Stirring was continued for two hours at 0°C. after which the ice bath was removed and the reaction mixture was warmed to room temperature. Since evolution of gases at room temperature was not appreciable the reaction mixture was warmed by immersing a hot copper steam coil into the reaction vessel. Instantly the evolution of gases increased and the reaction was soon out of control. Fortunately, however, the reaction beaker was still standing inside of the large galvanized iron tub which was previously used as an ice bath and therefore none of the reaction mixture was lost. In about ten minutes the vigorous reaction had subsided and the mixture was diluted with 2 liters of water and extracted twice with 300 ml. diethyl ether. The ether was removed and the dark oily residue was dissolved in petroleum ether and washed several times with 20% sodium hydroxide solution and then with distilled water.

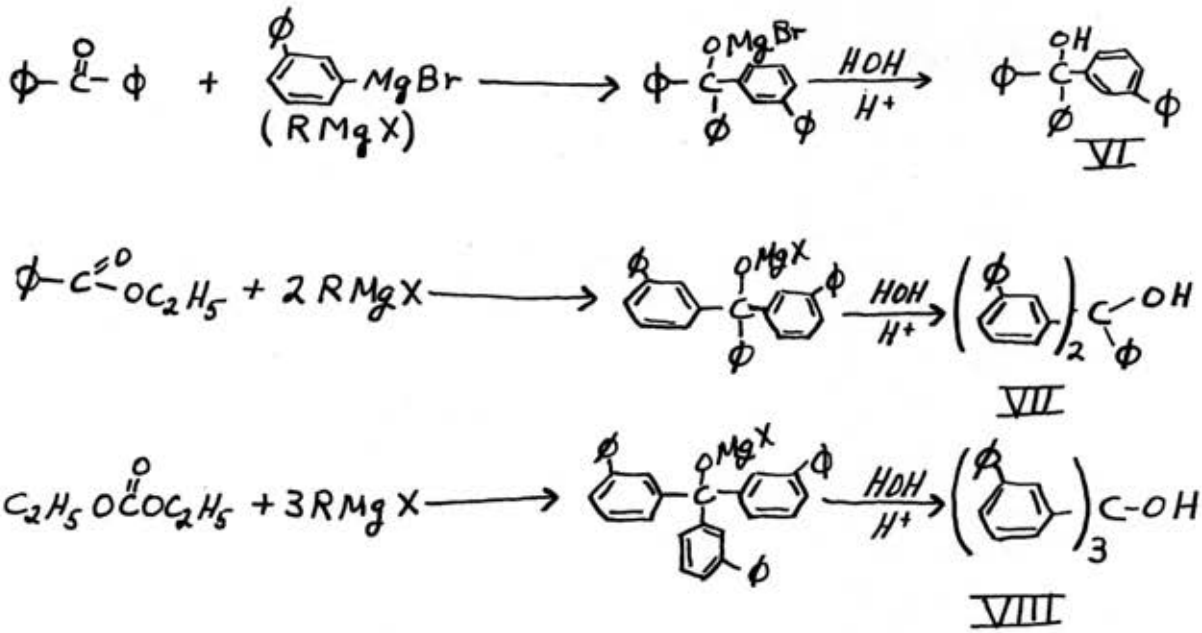
The petroleum ether layer was dried over anhydrous potassium carbonate and chromatographed by passing it through a 2 x 75 cm. column of 80-200 mesh activated alumina (City Chemical Corp. grade F-20). The column retained a deep orange band and the eluate was completely colorless. The column was washed with petroleum ether until the colored band was eluted to the bottom. Solvent was removed by ordinary distillation and the slightly yellow product was distilled under reduced

pressure to give 50.3 grams (72% yield) of colorless oil, $n_d^{25} = 1.6394$, boiling at 104°C. at 0.2 mm. pressure.

In earlier experiments a 22% yield of m-bromobiphenyl was obtained using a 5 to 1 mole ratio of hypophosphorus acid and an 82% yield when the ratio was 12 to 1. These experiments differed from the one described above only in that a steam bath was used in place of a steam coil to warm the reaction mixture and since under these conditions the reactions were mild the mixtures were heated for 3 hours.

Synthesis of meta-phenyl derivatives of triphenylchloromethane.

m-Biphenylyldiphenylcarbinol (VI) was prepared by the addition of one mole of m-biphenylmagnesium bromide to benzophenone followed by acid hydrolysis according to the method of Marvel et. al. (97). Tri-m-biphenylylcarbinol VIII was prepared by the addition of three moles of the Grignard reagent to ethyl carbonate as described by Marvel (96). Di-m-biphenylylphenylcarbinol, (VII) not previously described in the literature, was prepared by the addition of two moles of the Grignard reagent to ethyl benzoate. The reactions involved in these preparations are summarized below.



The carbinols were converted to the corresponding chlorides by reaction with acetyl chloride under anhydrous conditions.

Experiment 5: m-Biphenylyldiphenylchloromethane.

a. Preparation of m-biphenylmagnesium bromide.

The apparatus used was essentially that described by Fieser (36) for the preparation of Grignard reagents under an atmosphere of dry nitrogen. The reaction flask and auxilliary equipment were carefully dried by flaming while being flushed by a steady flow of dry nitrogen.

Dow Chemical Corporation "Super-Pure" magnesium turnings (1.824 grams., 0.075 mole) were dried in the reaction vessel by flaming and flushing with dry nitrogen. When cool, 200 ml. of Baker's C.P. diethyl ether (dried over CaH_2) was added.

A solution of 16.31 grams (0.070 moles) of m-bromobiphenyl (freshly distilled $n_d^{25} = 1.6394$) in 100 ml. anhydrous ether was added through a dropping funnel. Localized heating with the lighted end of a cigarette and scratching failed to initiate the reaction. A crystal of iodine added to the reaction mixture followed by heating had no visible effect. The reaction was finally started by adding a small amount of activated magnesium prepared by heating a mixture of powdered magnesium and iodine in an open test tube over a Bunsen burner.

The reaction proceeded very slowly accompanied by the formation of a white precipitate. The reaction appeared to stop and at this point the mixture was refluxed for two hours.

An aliquot of the reaction mixture was hydrolyzed in aqueous ethanol and titrated with standard hydrochloric acid to a methyl red end point.

A 2.0 ml. aliquot of a total of 350 ml of the etheral solution required 0.94 ml. of 0.116 N hydrochloric acid. This titre corresponds to 0.019 moles of Grignard reagent or 25% conversion.

b. Preparation of m-biphenylyldiphenylcarbinol.

Working on the assumption that the Grignard reagent is only slightly soluble in ether and was present in the observed

precipitate, the addition reaction was carried out as if complete conversion had been obtained.

A solution of 12.84 grams (0.070 mole) Eastman Kodak Co. White Label benzophenone (dried over anhydrous calcium sulfate) in 80 ml. anhydrous ether was added dropwise over a period of 20 minutes to the Grignard solution. An immediate precipitate was formed and the solution became a bright cherry red color which gradually changed to yellow as the addition continued. No heating was observed. The solution was stirred for 30 minutes and then hydrolyzed by pouring into 1 liter of cracked ice containing 100 ml. of concentrated hydrochloric acid.

The ethereal layer was separated and washed three times with 100 ml. of water. The ether was removed by ordinary distillation and the yellow oily residue was purified by steam distillation. When a clear distillate was observed, the residue was dissolved in ether and separated from the water layer. The ethereal solution was dried over calcium chloride and the crude product was isolated on removal of the ether. The crude product was triturated with petroleum ether to give 2.4 grams (10.5% yield, based on m-bromobiphenyl) of yellow powder, m.p. 103-105°C.

Crystals were obtained from aqueous acetic acid after standing in the refrigerator for 8 days. The crystals

(1.0 gram., 5% yield) were pale yellow and melted between 104-106°C. This material was not converted to the chloride.

Since it was believed that the poor yield obtained in the preperation of m-biphenylyldiphenylcarbinol was the result of incomplete conversion of m-bromobiphenyl to the corresponding Grignard reagent, several experiments were performed to determine the optimum conditions for the preparation of this intermediate.

Experiment 6: Preparation of m-Biphenylmagnesiumbromide.

6-a. Fresh turnings of Dow Chemical Co. "Super Pure" magnesium (3.65 grams 0.15 moles) were activated by flaming in a nitrogen filled reaction flask containing a small crystal of iodine. Flaming was continued until the flask was completely filled with purple iodine vapors and it was then allowed to cool under a stream of dry nitrogen. When cool, 400 ml. of anhydrous ethyl ether (dried over sodium wire) was added.

A solution of 34.95 grams (0.15 moles) of m-bromobiphenyl in 100 ml. anhydrous ether was added dropwise. After adding about 10 ml. of the bromide solution the reaction was initiated by localized heating. The reaction proceeded slowly accompanied by the formation of a white precipitate. Within several minutes the reaction stopped. The reaction could be started again by the usual methods but in each case failed to maintain itself for more than a few minutes. The mixture was

refluxed for three hours and stirred overnight at room temperature, after which a considerable quantity of the white precipitate was present.

Since it was believed that the white precipitate may have been m-biphenylmagnesium bromide the next reactant (ethyl benzoate) was added in an attempt to prepare di-m-biphenylyl-phenylcarbinol. No reaction was apparent and the mixture was refluxed for two hours and hydrolyzed in the usual manner. Steam distillation of the residue from the ether layer gave 27 grams (80%) of unchanged m-bromobiphenyl. None of the desired carbinol was obtained.

Experiment 6-b:

Twenty grams (0.086 mole) of m-bromobiphenyl (dried over anhydrous calcium sulfate) in 200 ml. dry ether was added to a mixture of 2.2 grams (0.091 mole) Eastman Kodak Co. White Label magnesium turnings and 100 ml. dry ether. The reaction started on the addition of a crystal of iodine but failed to reach an appreciable rate and stopped completely following the formation of the white precipitate as had been observed in previous experiments. Other standard techniques for starting Grignard reactions also failed to give satisfactory results.

Addition of 20 ml. C.P. benzene (dried over calcium hydride) to the reaction mixture resulted in the complete dissolution of the white precipitate. The reaction was again

started and was now able to maintain itself at a slow but steady rate. Analysis of two aliquots after a three hour reflux period indicated 96.5% and 97.6% conversion to the desired Grignard reagent.

Since excellent results could be obtained by preparing the Grignard reagent in the presence of about 5 percent (by volume) of dry benzene as described in experiment 6-b, this procedure was adopted as the standard procedure for the preparation of this intermediate. It was found, moreover, that with Dow Chemical Co. "Super pure" magnesium which had been turned on the lathe immediately before use, better than 90% yields of Grignard could be obtained repeatedly by refluxing for less than two hours. The increased rate is believed to be due to the greater surface available in the very fine turnings which were used.

Experiment 7: Preparation of m-Biphenylyldiphenylchloromethane.

Meta-biphenylmagnesium bromide was prepared in 97% yield from 16.1 grams (0.069 moles) of m-bromobiphenyl and 1.68 grams (0.07 moles) of freshly turned, extra fine, Dow "Super Pure" magnesium turnings.

A solution of 11.83 grams (0.065 moles) Eastman Kodak Co. White Label benzophenone in 100 ml. of anhydrous ether was added over a period of one hour to the ether solution of

the Grignard. The mixture was stirred and refluxed for two hours. The cooled reaction mixture was hydrolyzed with a cold solution of 30 grams of ammonium chloride in 100 ml. of ice water. The ether layer was washed with water, 5% sodium bicarbonate solution, and finally with water. The residue, after removing the ether, was purified by steam distillation which was continued until a clear distillate was obtained. The crude product, which was a yellow glass, was dissolved in hot ligroin and twice recrystallized from this solvent following decolorization with charcoal to give 15.42 grams (75% yield) of pure white crystalline m-biphenylyldiphenylcarbinol, melting range 104.5°-106°C. The carbinol was converted to the chloride by reaction with acetyl chloride under rigorously anhydrous conditions.

All glass apparatus was used throughout the preparation and purification of all triarylmethylchlorides employed in this research. Glassware was thoroughly cleaned before use as follows: Treatment for at least four hours in a hot acid bath was followed by profuse rinsing with tap water. Traces of acid were then removed by soaking the glass in 10% ammonium hydroxide solution for several minutes. Final washing with tap water and distilled water was followed by oven drying at 120-130°C. for at least four hours. The hot glassware was cooled either in an atmosphere of dry nitrogen or in a desiccator.

Twenty-five ml. of C.P. acetyl chloride was distilled directly onto 6 grams of the carbinol in a 50 ml. erlenmeyer

flask equipped with a 24/40 standard taper joint. The flask was removed from the column and a reflux condenser equipped with a soda-lime drying tube was immediately inserted. The carbinol dissolved completely to form an amber solution which was refluxed for three hours then filtered rapidly through a medium porosity sintered glass funnel. (All filtrations were performed under an atmosphere of dry nitrogen by working directly below a large inverted funnel through which a fast stream of nitrogen flowed.). The volume of solution was reduced to 10 ml. and white crystals were obtained after standing in the refrigerator twenty four hours. The product was recrystallized twice from C.P. acetyl chloride and once from a solvent consisting of three parts dry C.P. petroleum ether and one part C.P. acetyl chloride followed by trituration with C.P. petroleum ether and vacuum drying for forty eight hours at room temperature to give 0.446 grams of pure mono-m-biphenylyldiphenylchloromethane, melting range 87.4°-88.2°C. with slight preliminary sintering at 85°C. The melt was colorless.

Analysis* ; Calculated for $C_{25}H_{19}Cl$: Cl, 9.99%. Found: 9.9%.

Experiment 8: Preparation of Di-m-biphenylylphenylchloromethane

8-a: Preparation of sample B-I

A solution of 7.15 ml. (0.05 mole) Eastman Kodak Co.

* All semi micro analyses, unless other-wise specified, were carried out by Dr. Carol K. Fitz, Needham Heights, Massachusetts.

White Label ethyl benzoate (dried over anhydrous calcium sulfate) in 50 ml. dry ether was added to an ether solution of m-biphenylmagnesium bromide prepared in 90% yield from 0.10 mole of m-bromobiphenyl. The reaction mixture was refluxed for one hour followed by hydrolysis and isolation in the usual manner. The crude carbinol was a yellow glass which did not yield to crystallization. Trituration with petroleum ether finally gave 15.4 gms. of sticky yellow powder, melting below 60°C., which was converted directly to the chloride.

Five grams of the crude carbinol was refluxed for four hours with 15 ml. of freshly distilled acetyl chloride. The carbinol dissolved readily and failed to crystallize even after standing in the freezing compartment for seventy two hours. The acetyl chloride was replaced by petroleum ether but this failed to give a solid material. Benzene also failed to give the desired result. A solid was finally obtained after eleven days in the freezing compartment from a solvent consisting of three parts acetyl chloride and five parts petroleum ether. The solid oiled out on filtration. Most of the solvent was removed by suction and the oil was triturated with petroleum ether. Standing with petroleum ether for three days gave a brownish powder which, when filtered and washed with petroleum ether, gave 2.33 grams of slightly yellow powder. Some of this material was saved for seed and the rest was dissolved in 1:1 acetyl chloride-petroleum ether. Seeding

the concentrated solution gave a crystalline product after twenty four hours in the freezing compartment. This material was essentially white and melted between 114.4° and 116.2°C.

The impure chloride was twice recrystallized from acetyl chloride-petroleum ether to give a pure white crystalline product. The product was triturated and washed with petroleum ether and dried at room temperature under high vacuum to yield the pure product as a white powder. This compound was designated as sample B-I. Melting point 113.6° to 114.4°C. (uncorrected).

Analysis: Sample B-I

Calculated for $C_{31}H_{23}Cl$: C, 86.4%; H, 5.4%; Cl, 8.24%.

Found: C, 86.1%; H, 5.5%; Cl, 8.3%.

8-b: Preparation of Sample B-II

Di-m-biphenylylphenylcarbinol was prepared by the same procedure employed in experiment 8-a. The carbinol was obtained as a pale yellow crystalline solid by recrystallization from heptane. The material melted over a wide range below 65°C. and since all attempts at further purification failed to improve the melting point the crude carbinol was converted directly to the chloride by refluxing a solution of 5.2 grams of carbinol in 20 ml. acetyl chloride for two hours. Standing in the freezing compartment for ten days gave 2.9 grams of a white crystalline solid, melting 117.6°-118.4°C. (corrected). This material was twice recrystallized from acetyl chloride, washed and triturated with petroleum ether and vacuum dried

to produce 1.20 grams of white product.

Analysis: Calculated for $C_{31}H_{23}Cl$: Cl, 8.24%. Found: Cl, 8.6%.

It was assumed that the high chlorine analysis was due to occluded acetyl chloride. The sample was again triturated and washed with petroleum ether and was dried by pumping under high vacuum for eight days.

Analysis: Sample B-II
Calculated for $C_{31}H_{23}Cl$: Cl, 8.24%. Found: Cl, 8.2%.

Experiment 9: Preparation of Tri-m-biphenylylchloromethane

Twenty grams (0.086 moles) of m-bromobiphenyl and 2.2 grams (0.09 mole) Dow "Super Pure" magnesium turnings gave a 97.5% yield of m-biphenylmagnesium bromide. The carbinol was prepared by adding a solution of 2.93 grams (0.025 mole) Eastman Kodak Co., White Label ethyl carbonate (dried over calcium sulfate) in 25 ml. dry ether to the ether solution of the Grignard reagent over a period of two hours followed by a two hour reflux period. The reaction mixture was worked up in the usual manner.

The crude carbinol failed to crystallize from the following solvents: acetic acid, benzene, heptane, ethanol, ligroin, ethyl alcohol, ether, ethyl acetate and petroleum ether. A yellow powder was obtained by rapidly cooling a petroleum ether solution to -80°C. The crude carbinol, 10.7 grams (74% yield), melted over a range between 120°-135°C.

and was converted to the chloride without further purification.

Five grams (0.01 mole) of the crude carbinol was treated with 25 ml. of freshly distilled acetyl chloride. After a three hour reflux period a considerable amount of the solid remained undissolved and dry benzene was added in 0.5 ml. portions until a clear solution was obtained. A total of 15 ml. of benzene was required. A crystalline product was obtained after twelve hours in the freezing compartment. The crude chloride was recrystallized once from benzene containing a few drops of acetyl chloride and was vacuum dried to give 2.90 grams of white micro needles melting 201.2°-202°C. Part of this material was designated as sample T-II.

Analysis: Sample T-II
Found: C; 86.7%, 88.2%. H; 5.3%, 5.2%. Cl; 6.7%.
Calculated for $C_{37}H_{27}Cl$: C; 87.6%. H; 5.4%. Cl; 7.0%.

The remaining product was twice recrystallized from benzene containing a few drops of acetyl chloride and once from pure benzene.
Sample T-I: M.P. 199.8°-200.6°C., (yellow melt).

Analysis: Sample T-I
Calculated for $C_{37}H_{27}Cl$: C; 87.6%. H; 5.4%. Cl; 7.0%
Found: C; 87.1%. H; 5.8%. Cl; 7.1%, 7.0%.

Experiment 9: Preparation of m-Phenylbenzoic acid.

Carbon dioxide (generated from dry ice and dried by passing the gas through concentrated sulfuric acid) was bubbled slowly into an ether solution of m-biphenyl Grignard reagent prepared in 97% yield from 16.1 grams (0.069 mole) of m-bromobiphenyl. A large excess of carbon dioxide was used. The mixture was refluxed for two hours followed by hydrolysis with aqueous ammonium chloride. The aqueous layer was acidified with dilute hydrochloric acid and then separated from the ether layer. The ether layer was washed with water and extracted five times with 5% sodium bicarbonate solution. The combined aqueous extracts were acidified with hydrochloric acid and the crude product which precipitated was washed with water and air dried. Recrystallization from aqueous ethanol following decolorization with charcoal afforded 7.0 grams of slightly yellow plates melting sharply between 165.2°-166.2°C. This product was twice more recrystallized from aqueous ethanol to give the pure white m-phenylbenzoic acid, 6.6 grams (44% yield), m.p. 165.4-166.2°C. The acid was vacuum dried at 110°C. over phosphorous pentoxide for two hours before use. Analysis by potentiometric titration indicated 99.7 and 99.5% purity.

Materials.

All other materials used in this research unless otherwise specified were purified as described below.

Benzoic acid.

The benzoic acid used in the acid strength measurements was National Bureau of Standards Acidimetric and Calorimetric Standard No. 39 f and was oven dried at 90-100°C. for two hours before use.

Butyl Cellosolve.

Howe and French Co. technical grade butyl cellosolve was purified by the method of Halford (55) to yield material boiling between 106°-107°C. at 70 mm. pressure. Two liters of butyl cellosolve was allowed to stand over 600 grams of Baker's C.P. calcium oxide for eight days in a tightly stoppered flask. The mixture was mixed thoroughly by vigorous shaking at frequent intervals over this period. Distillation at reduced pressure gave a middle fraction (1.5 liters) boiling over a one degree range. The pure solvent was stored in a tightly stoppered amber bottle.

Sodium Hydroxide in 50% Aqueous Butyl Cellosolve.

Carbonate free sodium hydroxide solution was prepared from Merck and Co. Analytical Reagent grade sodium hydroxide by diluting an aliquot of a clear saturated solution with freshly boiled distilled water. The aqueous solution was diluted with an equal volume of purified butyl cellosolve to give a solution of about 0.07 molar sodium hydroxide in 50%

aqueous butyl cellosolve. The solution was stored in a dark bottle equipped with a syphon and protected from atmospheric carbon dioxide by means of a soda-lime tube. The solution was standardized against primary standard benzoic acid at frequent intervals.

Aqueous Butyl Cellosolve Stock Solvent.

Stock solvent was prepared by diluting 1 liter of 0.098 molar lithium chloride solution with an equal volume of purified butyl cellosolve to give a solution of 0.049 molar lithium chloride (ionic strength 0.05) in 50% aqueous butyl cellosolve. The solvent was stored in a dark bottle protected by a soda-lime tube. A blank was determined for this solvent by titrating 100 ml. with standard base to a pH of nine employing conditions identical to those used in the actual measurements. The blank was about 0.01 ml. and was neglected since the same volume of solvent was used in each of the runs.

Other Materials.

Acetone, petroleum ether and liquid sulfur dioxide used in this work were as described in part I of this dissertation.

Acid Strength Measurements:

Apparatus and Procedure

Thirty to fifty milligram samples of the purified acids dissolved in 100 ml. of 50% aqueous butyl cellosolve (μ = 0.05 LiCl) were titrated with standard base using a Leeds and Nothrup

Co. No. 7662 pH meter and glass electrode sensitive to ± 0.01 pH unit. Asymmetry of the glass electrode was corrected using Coleman Certified buffer tablets of pH 4.00, 5.00, 6.80, and 7.00. Temperature was maintained at 25.10 ± 0.25°C. with a regulated water thermostat and the solution was stirred and maintained under an atmosphere of nitrogen throughout the titration. Sodium hydroxide solution was added from a self-filling micro buret graduated directly in 0.01 ml. divisions and containing a total volume of 5.0 ml. Sample weights were chosen such that a titration could be completed without re-filling the buret.

pH values were recorded after each addition of base. In the buffer region and near the end point readings were taken at 0.05 ml. increments of added base. The end points were determined by the differential plot of the change in pH per unit volume of base added against the total volume of base used. The p K_A values were then determined from enlarged plots of pH against ml. of base in the buffer regions by determining the pH corresponding to exactly one-half the volume of base required to reach the end point. Individual p K_A values were 5.70, 5.68, 5.65, 5.64, 5.63 for benzoic acid and 5.57, 5.57, 5.61, 5.56 for m-phenylbenzoic acid.

Conductivity Measurements.

The apparatus and techniques used in these measurements have been described in part I of this dissertation.

Individual Conductivity Runs:

A brief summary of each conductance run, the data of which are summarized in tables 2-A-2-H in Appendix II-A, is presented below. The runs are described by compound and in the order in which they were performed. The description of the runs therefore parallels the arrangement of the data in tables 2-A to 2-H.

Measurements at 0.12°C.

m-Biphenylyldiphenylchloromethane

Run HL-63 One run was made at 0.12°C. with this compound to check the conductivity data of Lichtin and Glazer (91). The material used was from the same sample used by these workers and had the following properties: It was an off white solid powder, melting range 85-87°C., to give a brown melt. Analysis by titration of acid formed on hydrolysis carried out by Mr. M. J. Vignale indicated a purity of 99.2%. In this run the sulfur dioxide was outgassed for one hour by pumping the liquid at -78°C. Agreement between this run and the data of Lichtin and Glazer was good over the entire dilution range.

Di-m-biphenylylphenylchloromethane

Three runs, HL-4, HL-5, and HL-6 were carried out at 0.12°C. using sample B-I, melting range 113.6°-114.4°C. Excellent agreement was found between the three runs. The sulfur dioxide was not outgassed in these runs.

Tri-m-biphenylylchloromethane

Four runs were performed on two different samples of this material at 0.12°C. There was no visible difference in the data which could be attributed to differences in purity of the two samples. In runs HL-7, HL-8, and HL-9 sample T-I, melting range 199.8-200.6°C. was employed. Sample T-II was employed in run HL-44 and although analysis by Dr. Fitz indicated a rather low chlorine value for this sample (6.7% found; 7.0% calculated) the conductance data failed to reflect any difference when compared to the data for sample I where 7.0 and 7.1% chlorine was reported by the same analyst. The melting ranges recorded for the two samples (199.8-200.6° and 201.2-202°C.) are not consistent with the large differences in chlorine analysis. Sulfur dioxide was not outgassed in these runs.

Measurements at -8.9C.

Triphenylchloromethane:

Three runs HL-18, 50 and 55 were carried out on this compound. Triphenylchloromethane was from a sample supplied by Dr. Lichtin and used previously in the measurements at 0°C. reported by Lichtin and Bartlett (90). The material melted to a colorless melt between 111-112°C. Analysis for hydrolyzable chloride: Found 12.9%; calculated 12.7%. Run HL-50 was carried out jointly by the author and Professor Norman N. Lichtin.

m-Biphenylyldiphenylchloromethane

Two runs HL-79 and 80 were carried out jointly by the author and Professor N.N. Lichtin employing the sample described for the measurements at 0.12°C. Since the agreement between these runs was excellent a third run was deemed unnecessary.

Di-m-biphenylylphenylchloromethane:

Three runs HL-14, HL-15, and HL-49 were made on two different samples of this material at -8.93°C. Sample B-I was used in runs HL-14 and HL-49. Sample B-II was used in run HL-15. Agreement between runs with both samples was excellent.

Tri-m-biphenylylchloromethane

A total of four runs were made on this compound at -8.93°C. using two different samples.

In runs HL-16, and HL-40 sample T-I was employed and the data obtained were in excellent agreement with those found in runs HL-42 and HL-43 in which sample T-II was employed.

p-Biphenylyldiphenylchloromethane

Three runs HL 20, 21 and 22 on this compound at -8.93°C. showed excellent internal agreement. The sample used in this work was supplied by Professor Norman N. Lichtin and was the

same one used in the 0.10°C. measurements reported by Lichtin and Glazer. Melting range 147.0-148.0°C. (uncorrected)

Analysis: Calculated for $C_{25}H_{19}Cl$: Cl, 9.99%.

Found: Cl, 9.8%.

Recovery of Compounds After Runs.

In several of the conductivity runs recovery of the sample was attempted. This was done by opening the cell and pouring the contents into a dry beaker and allowing the sulfur dioxide to evaporate to dryness under an atmosphere of dry nitrogen produced by the inverted funnel technique. Since the liquid sulfur dioxide solution always sprayed out of the cell, partial hydrolysis invariably occured and the significance of the recovery experiments is therefore uncertain. The residues were always pumped in a vacuum disiccator for at least 48 hours before melting points were recorded.

Di-m-biphenylylphenylchloromethane recovered from run HL-6 melted between 63-67° to give a deep brown melt.

Tri-m-biphenylylchloromethane, recovered from run HL-8, was an ivory colored solid melting over the range 190-197°C. to a red brown melt. In run HL-7 the recovered product melted below 150°C. In several other cases where recovery experiments were performed either insufficient material was recovered or the material could not be dried sufficiently to permit a melting point determination to be made.

Experimental Difficulties:

The major source of difficulty in the conductivity measurements was caused by leakage resulting from a pin hole in the electrode bulb of the cell. This pin hole was sealed with De Khotinsky cement and was always checked before and after each run. Whenever a leak developed during a run, evidenced by the presence of a leak in the De Khotinsky seal after the run was completed, the data of that run were discarded. The data from several other runs were also discarded because of accidental errors in weighing, dilution and drainage.

PART III

The Apparent Ionization of Hexaphenylethane.

INTRODUCTION

Walden (126) first observed the apparent heterolytic fission of a carbon-carbon bond in a symmetrical hydrocarbon. This worker observed that solutions of hexaphenylethane in liquid sulfur dioxide exhibited a high equivalent conductance which increased with dilution. This behavior, typical of electrolytes in solvents of low dielectric constant, led Walden to the conclusion that hexaphenylethane had dissociated heterolytically to produce ionic fragments. The lack of reproducibility in Walden's conductivity measurements was attributed to the uncertain purity of the samples of hexaphenylethane which had been supplied to him by M. Gomberg who first discovered the free triphenylmethyl radical (47).

The observation of the anomalous behavior of hexaphenylethane in liquid sulfur dioxide stimulated many investigations all of which failed to adequately explain the phenomenon. Many apparent contradictions and discrepancies now exist in the literature as a result of these investigations.

Gomberg and Cone (50) repeated the conductivity measurements employing only freshly prepared samples of pure hexaphenylethane. The results of several runs by these workers failed to demonstrate that reproducible conductance data could be obtained in this system. Part of the discrepancy was later (52) attributed to the fact that the hexaphenylethane used in the measurements was actually a 1:1 addition complex with petroleum ether which was used in the

purification of the compound.

Subsequently (53) it was demonstrated that the ionization of a symmetrical hydrocarbon was a general property of hexarylethanes in sulfur dioxide solution. In each instance however, it should be noted that precise and reproducible measurements were not obtained. This fact not withstanding, the phenomenon was considered as well established and many authors (4,49,115,128,129,133) attempted to explain the mechanism of the heterolytic cleavage of symmetrical hexaarylethanes in ionizing solvents. Of the many suggested mechanisms, all of which involved some type of radical-solvent interaction, none could account for all of the many pieces of conflicting evidence available in the literature.

The so called dual nature of hexaphenylethane in ionizing and non ionizing solvents is not an accurate description of the system for the ionization does not occur in many well known ionizing solvents. Thus, for example, Gomberg and Sullivan (53) found that although triarylmethyl halides gave conducting solutions in liquid hydrogen cyanide the radical merely decomposed. In this respect it is interesting that no solvent other than sulfur dioxide exhibits the power to promote the heterolytic cleavage of hexaphenylethane. Indeed, liquid sulfur dioxide stands out as the only solvent in which abnormal behavior is observed.

Many examples of the difference between sulfur dioxide and other solvents can be found in the literature. Thus Gomberg

and Sullivan (53) regarded the colors of hexaphenylethane solutions in sulfur dioxide as being qualitatively different from that in other solvents. Anderson (4) observed a reversal in temperature dependence of the spectrum. In non ionizing solvents the absorption increased with temperature while in sulfur dioxide the reverse was observed. The latter effect is typical for electrolytes in solvents of low dielectric constant. Anderson moreover found that the spectrum in liquid sulfur dioxide was significantly different from that in other solvents. This is even more remarkable in view of the small differences (137), if any, observed between the spectra of triphenylmethyl in a large number of organic solvents. The spectrum of hexaphenylethane in liquid sulfur dioxide was found to be essentially identical with that found for solutions of triphenylcarbonium salts in this medium. Anderson (4) noted, however, that the spectra obtained from hexaphenylethane and from triphenylbromomethane differed somewhat in the region of longer wavelength. This led him to conclude that the radical in sulfur dioxide was in equilibrium with its ionized isomer and a solvated electron. Unfortunately Anderson did not disclose the degree of reproducibility obtained with several independent measurements. This omission is suggestive of a lack of agreement between the spectra for several solutions of hexaphenylethane in sulfur dioxide, which, as in the case of the poor results obtained in the earlier conductance work, may have been attributed to uncertainties in the purity of the material.

Perhaps the singly most significant difference observed in liquid sulfur dioxide solutions of the radical is the apparent failure (4) of the radical in this medium to react with oxygen.

Sulfur dioxide solutions differed photochemically from solutions in non ionizing solvents. Many of the early workers reported that hexaphenylethane solutions were decolorized on exposure to direct sunlight. Meyer and Wieland (100) found that triphenylmethyl exhibits its strongest absorption in the blue-green (4000-5300A^{o}) region of the spectrum. Bowden and Jones (20) found that the radical was photochemically unstable to light of this wavelength and that the rate of photochemical decomposition was essentially independent of solvent except in the case of liquid sulfur dioxide in which the radical was photochemically stable. The photochemical stability of solutions in sulfur dioxide was furthermore demonstrated by the observation that the conductivity of the solution did not change appreciably after several hours of irradiation. In more recent studies, Bartlett and Weston (8) obtained data in direct contradiction of the reported photochemical stability. These workers observed a gradual increase in the intensity of absorption with time. The spectrum of sulfur dioxide solutions of the radical which had been irradiated for several hours differed qualitatively from that obtained from rapid measurements on non irradiated solutions.

In view of the conflicting and uncertain nature of the evidence for the heterolytic cleavage of hexaphenylethane in sulfur dioxide solution it is not surprising that no conclusive mechanism has been proposed. It was considered of interest therefore to reexamine this system by means of precise conductivity measurements on sulfur dioxide solutions employing solid samples of pure hexaphenylethane. Experiments employing crystalline samples of hexaphenylethane of purity established by quantitative oxygenation (92) and a refinement of the conductivity technique of Lichtin and Glazer (91) produced evidence that the conductivity of the sulfur dioxide solutions is an artifact of at least two processes, namely, reaction with dissolved oxygen and a phctochemical transformation. On the basis of these findings and data on the solubility of oxygen in liquid sulfur dioxide (31), much of the conflicting evidence of earlier workers may now be resolved.

SCOPE OF THIS INVESTIGATION

This research was devoted primarily to the study of the behavior of pure hexaphenylethane in liquid sulfur dioxide. Since the author was at first unaware of the importance of dissolved oxygen much effort was expended in attempts to relate the non reproducible conductivity measurements to uncertainties in the purity of the hexaphenylethane. Therefore a considerable amount of time was spent on refinement of the method of preparation and analysis of the free radical. The subsequent discovery of the importance of oxygen in this system demonstrated that

much of the earlier work had been unnecessary. However, several significant observations were obtained which are worthy of description.

Although the photochemical instability of hexaphenylethane in sulfur dioxide solution was found at an early stage of this investigation it was not considered judicious to investigate this phenomenon quantitatively until the major problem of the conductivity behavior was resolved. By the time this goal was achieved the photochemical transformation was no longer considered to be within the scope of this research since it was more significant to attempt to identify the nature of the conducting species resulting from the oxygenation process in liquid sulfur dioxide solution. All attempts toward the direct isolation of the product met with little success. It is possible, however, to cast some light upon the nature of the ionic compound from the results of these investigations.

The detailed mechanisms of the photochemical autoxidation and of the direct oxygenation of hexaphenylethane in sulfur dioxide solution remain as yet unsolved problems.

RESULTS and DISCUSSION

The poor quality of the conductivity data obtained by early workers is illustrated in figure 3-I. For the most part these results fail to demonstrate that even a qualitative

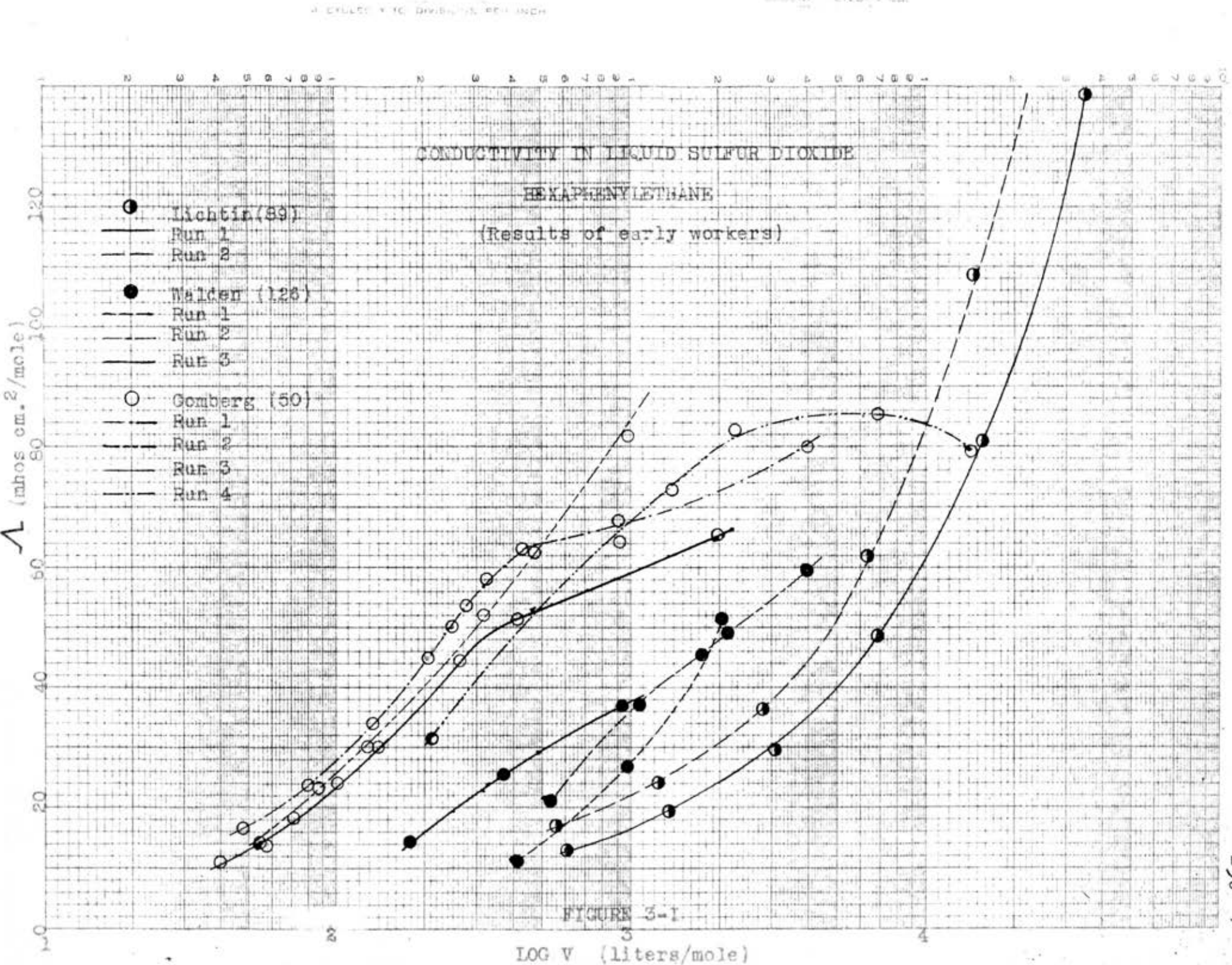

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
HEXAPHENYLETHANE
(Results of early workers)
Lichtin(89)
Run 1
Run 2
Walden (123)
Run 1
Run 2
Run 3
Gomberg (50)
Run 1
Run 2
Run 3
Run 4
Λ (mhos cm.²/mole)
LOG V (liters/mole)
0
20
40
60
80
100
120
2
3
4

FIGURE 3-1

similarity exists between the data of several workers. Indeed, it is not possible to conclude that these results correspond to data for a **single** compound. The striking quantitative differences can be related to the experimental techniques employed by the various workers. The results of Lichtin (89) most closely approach reproducibility. This of course is a consequence of refined technique. In general it is obvious that the results obtained by those workers most experienced in conductivity studies, namely, Lichtin and also Walden exhibit considerably lower conductance values at initial concentrations than were obtained by the less experienced Gomberg (See Table 3-II). Consideration of the techniques employed suggests a possible source of the discrepancies.

Gomberg and Cone (50) employed a conductivity cell which was essentially open to the atmosphere. This technique provided the highest conductance values obtained by any of the early workers. Walden on the other hand used a system which was closed to atmospheric contamination and thus obtained lower conductance values. The most recent of the earlier workers, Lichtin (89) employed a completely closed system with the result that the lowest observed values were obtained.

Neglecting uncertainties in the purity of the hexaphenylethane employed by these workers, the only explanation consistent with the variations in experimental technique is that the magnitude of the conductance is strongly influenced

by some agent present in the atmosphere. Two possibilities can be suggested, namely, water vapor and atmospheric oxygen. On the basis of the results of Anderson (4) and of Bowden and Jones (20) it is possible to eliminate oxygen as the source of the discrepancy. Further support for this is found in the fact (126) that triphenylmethyl peroxide is essentially insoluble and is a nonconductor in liquid sulfur dioxide. Thus if oxygen is at all involved we should expect that the conductivity would be lowest for the most exposed measurements. This is in direct contradiction to observations.

Water vapor, on the other hand, is an attractive possibility. Water will react with the ionized form of the radical to form triphenylcarbinol which is known to give conducting solutions in sulfur dioxide. Thus the most exposed solutions should exhibit the highest conductivity. Although this explanation is compatible with the observed conductance behavior, it can be somewhat discredited on the basis of Lichtin's measurements which involved the rigorous exclusion of atmospheric moisture. It is, moreover, significant that Lichtin observed a time dependence of the conductivity of his solutions and Bartlett and Weston found evidence for the photochemical instability of the radical in sulfur dioxide. Neither of these facts can be related to contamination of the solutions with atmospheric moisture.

It appears then that on the basis of existing evidence both moisture and oxygen can be eliminated as contributors to

the nonreproducibility of the conductance behavior. Only two obvious factors remain to be considered, namely, photochemical decomposition and chemical impurities in the hexaphenylethane. The exact operation of these factors cannot be predicted. For example, the photochemical decomposition may produce either an increase or a decrease in conductance. The former requires the photochemical formation of ions from a solution of the nonconducting radical. On the other hand the photochemical destruction of ionic species would result in a decreased conductance.

Similar difficulty exists in predicting the effect of impurities. First if the impurity is the peroxide, which may have been formed by exposure of the solid samples to air prior to dissolution, a decreased conductance would be expected for impure samples. In this respect, it should be noted that Walden (126) found that part of his hexaphenylethane failed to dissolve.

If, on the other hand, the impurities are of a conducting nature such as unreacted triphenylmethyl halide or the carbinol resulting from its hydrolysis we should expect the conductivity to be highest for the least pure samples.

The Influence of Purity on Conductance

Logical deductions from existing data suggest the possibilities of a photochemical decomposition and chemical impurities as the source of the non-reproducible conductance

behavior. Therefore the early experiments of this investigation were designed to test these possibilities.

Figure 3-II shows the conductance behavior observed in the first run performed in the dark on a sample of hexaphenylethane (Lot II) for which analysis by the oxygenation procedure (92) indicated 95.8% purity. Stable conductance values were obtained at each dilution as indicated by lengthy observations for possible drifts. Table 3-I illustrates a typical drift observation.

Subsequent runs performed under darkroom conditions all yielded stable conductance values, however, reproducible results were not obtained. Table 3-II summarizes the conductance values (at approximately the same concentration) obtained from several runs on samples of high purity. These data fail to demonstrate any relationship between conductance and apparent purity of the samples employed. Indeed it is most disturbing to note that even with runs on several identical samples from the same lot of material completely unrelated values were obtained.

The data of table 3-II serve as a good indication that the difficulty to be resolved does not lie in variations of purity.

Influence of Light on Conductance

Exposure of a dilute solution* of hexaphenylethane in sulfur dioxide to direct sunlight for a short period of time

(*) Refers to Run II-1 at a dilution of 10,740 liters/m.

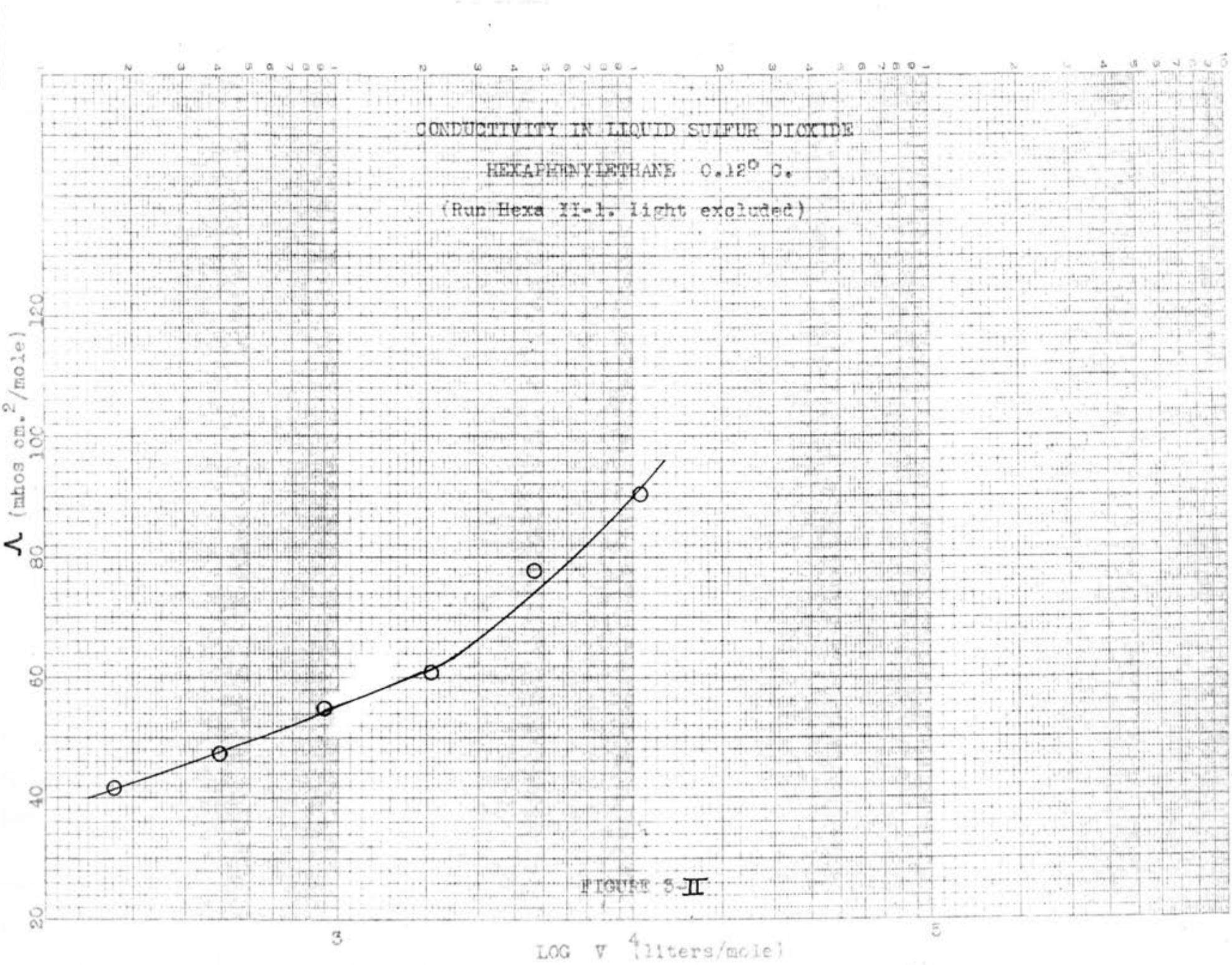

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
HEXAPHENYLETHANE 0.12° C.
(Run Hexa II-1. light excluded)
Λ (mhos cm.²/mole)
120
100
80
60
40
20
3
4
5
LOG V (liters/mole)

FIGURE 5-II

TABLE 3-I

Typical Drift Observation on a Solution of Hexaphenylethane in Liquid Sulfur Dioxide in the Absence of Light.

(Run Hexa II-1, 0.12°C., 168.5 liters/mole.)

Time (min.)	Resistance (ohms)
0	Cell placed in thermostat
11	889.0
17	888.0
24	888.0
32	888.8
48	891.7
82	888.1
101	889.2
200	891.1
215	891.2

TABLE 3-II

Summary of Conductance Data from Early Runs.

Hexaphenylethane in Liquid Sulfur Dioxide
(Light Excluded)

Lot No.	Run No.	Purity[a] (%)	Dilution[b] (liters/m.)	k x 10^6 (mhos-cm.$^{-1}$)	Λ ($\frac{\text{mhos-cm.}^2}{\text{mole}}$)	Temp. (°C.)
II	1	95.8	168.5	249.6	42.0	0.12
II	2	"	208.1	70.4	14.6	-8.93
II	3	"	195.8	84.1	16.5	"
VI-b	1	99.5	218.2	133.3	29.1	"
VI-b	2	"	276.9	141.1	31.6	"
VI-b	3	"	157.6	181.5	28.6	"
VI-c	1	97.2	216.0	58.2	12.6	"
Walden[d]	Ref.126	----	180[c]	77.1	13.9	0.0
"	"	----	412[c]	27.1	11.2	"
"	"	----	526.4[c]	39.3	20.7	"
Gomberg[d]	Ref.50	----	274[c]	195.5	53.6	"
"	"	----	246[c]	200.6	49.4	"
"	"	----	274[c]	160.6	44	"
"	"	----	217[c]	147.0	32	"
Lichtin[d]	Ref.89	----	395.5	29.4	11.5	"
"	"	----	480.6	22.1	10.6	"

(a) Based on quantitative oxygenation by the method of Lichtin and Thomas (92).
(b) Dilution calculated on molar basis. Mol. Wt.= 486.6.
(c) Calculated from data based on Mol. Wt.= 243, converted to Mol. Wt. = 486.
(d) Diffuse daylight.

initiated a slow steady drift towards higher conductance. This drift continued at an approximately constant rate (90 ohms per hour) for the entire period of observation (42 hours). It should be pointed out that irradiation with incandescent, fluorescent and infra-red heat lamps failed to initiate such drifts.

Irradiation of the drifting solution with a Burton mercury vapor lamp produced a ten fold increase in the drift rate. The resistance decreased at an approximately constant rate for thirteen hours and did not reach a steady value until another sixteen hours had elapsed. Further irradiation for an additional sixteen hours failed to produce any further change in resistance. Apparently the photochemical process had gone to completion. Dilution of the totally irradiated solution also provided a solution which was stable to further irradiation.

The drift data summarized in table 3-III clearly demonstrate that, contrary to the results of Bowden and Jones (20) hexaphenylethane is not stable to light in sulfur dioxide solution. Furthermore, the effect of the photochemical process is to increase the concentration of ions in the solution. This may occur either by the decomposition of the conducting species into smaller fragments or, more likely, by the photoionization of the non conducting radical. The exact mechanism, however, remains as yet an unsolved problem.

TABLE 3-III

The Influence of Light on the Conductance of Solutions of Hexaphenylethane in Sulfur Dioxide.

(Run II-1, 0°C., Dilution = 10,740 liters/mole.) (a)

Time (hrs.)	Resistance (ohms)	Remarks
0	22190	U.V.Lamp on
1	21100	"
4	18500	"
8	15630	"
13	13990	Lamp turned off at 13.0 hrs.
36.5	13590	Lamp turned on at 36.5 hrs.
46.5	12330	
61.5	12394	
62.5	12300	

(a) After exposure to sunlight the resistance decreased from an initial value of 26,240 ohms to 22,190 ohms over a forty two hour period in the dark. This solution was then exposed to u.v. light.

Valence Type of the Conducting Species

Figure 3-III illustrates the conductance data obtained from several runs performed in the absence of light. The reader is referred to table 3-II for data concerning the purity of the samples employed in these runs. The conductance and dilution values upon which figure 3-III is based are summarized in tables 3-A to 3-H in the appendix.

Several features of the curves shown in figure 3-III are worthy of mention. First, and most obvious, is the complete absence of reproducibility. More significant, however, is the fact that the curves all appear to have the same shape, and are in no way similar to curves typical of 1-1 electrolytes in this medium.

The significance of the similarity in the shapes in the curves lies in the fact that this strongly suggests that in each run the conductivity is due to the same compound. If we accept this reasoning, then it follows that the discrepancies between runs is merely a reflection of a large uncertainity in the concentration of the electrolyte. It should be pointed out, however, that the magnitude of the apparent concentration error is many times greater than the largest possible experimental errors.

It is possible to demonstrate that the conductance curves shown in figure 3-III can be exactly superposed and therefore

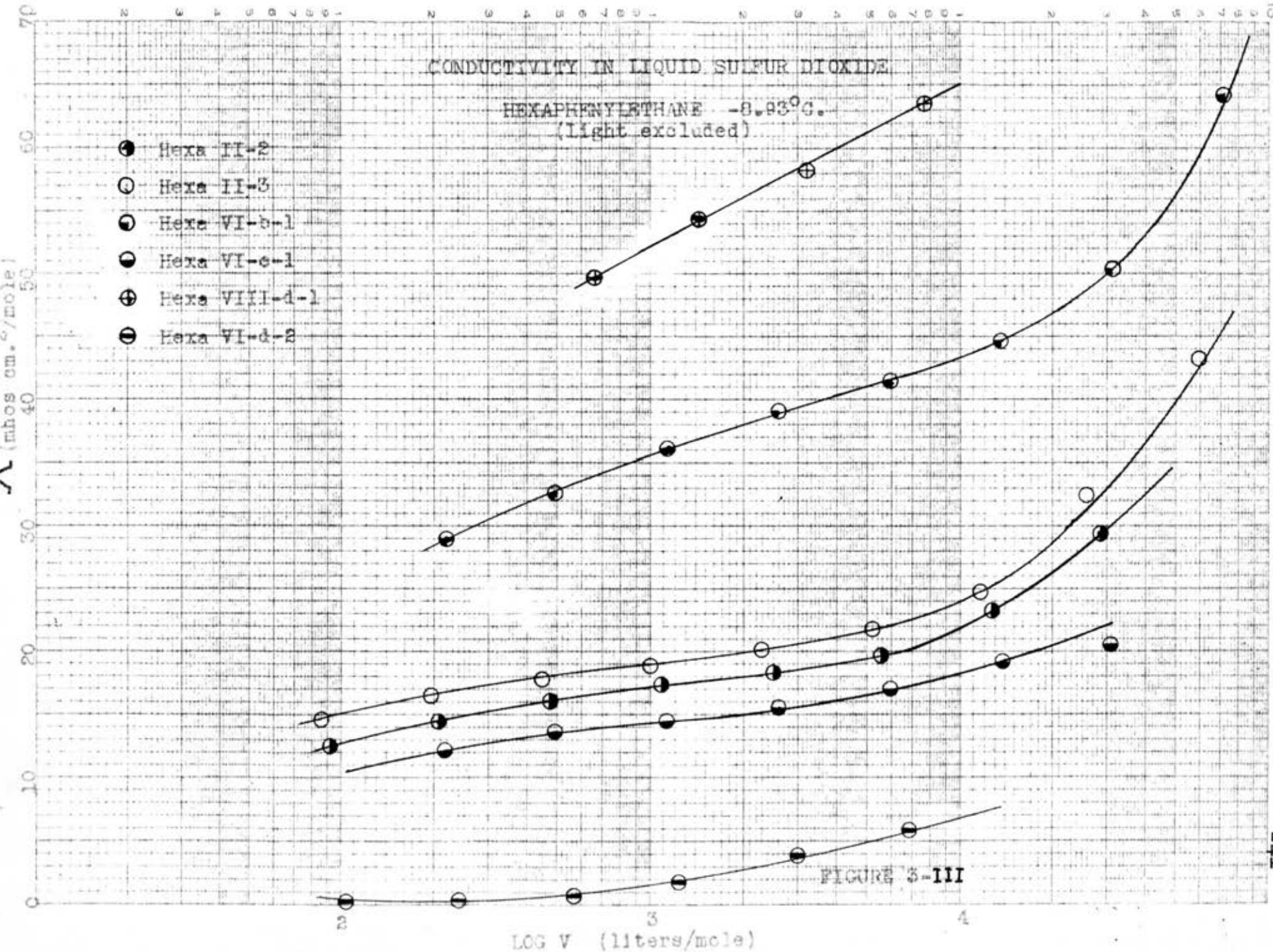

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
HEXAPHENYLETHANE -8.93°C.
(Light excluded)
Hexa II-2
Hexa II-3
Hexa VI-b-1
Hexa VI-c-1
Hexa VIII-d-1
Hexa VI-d-2
Λ (mhos cm.²/mole)
LOG V (liters/mole)
0
10
20
30
40
50
60
70
2
3
4

FIGURE 3-III

represent the conductance behavior of the same compound. Figure 3-IV demonstrates this fact. The curve shown here was constructed as follows: A plot of specific conductivity versus dilution was constructed from the data obtained from a run (VIII d-1) which exhibited the highest observed conductivity. The concentrations of electrolyte (initial concentrations only) of the other runs were then determined directly from the calibration curve by a comparison of specific conductivities. The initial concentrations thus determined were then employed in the calculation of the equivalent conductances and dilution values from the remaining data for each run. This treatment corresponds to an adjustment of the initial concentration of electrolyte for each run considered. The resulting data were plotted as shown in figure 3-IV.

Shedlovsky Treatment

Figure 3-V shows a plot of the Shedlovsky data based on a representative hexaphenylethane run (II-3). It is immediately obvious that this curve is not typical of those found for uni-uni-valent electrolytes. The curve is, however, typical of behavior expected for 2-1 electrolytes as can be seen by comparison with the curve for tetramethylammonium sulfate (Part I appendix I-C).

It seems not too unreasonable, on the basis of the available evidence of 2-1 electrolyte behavior, to conclude that the conducting species resulting from the apparent

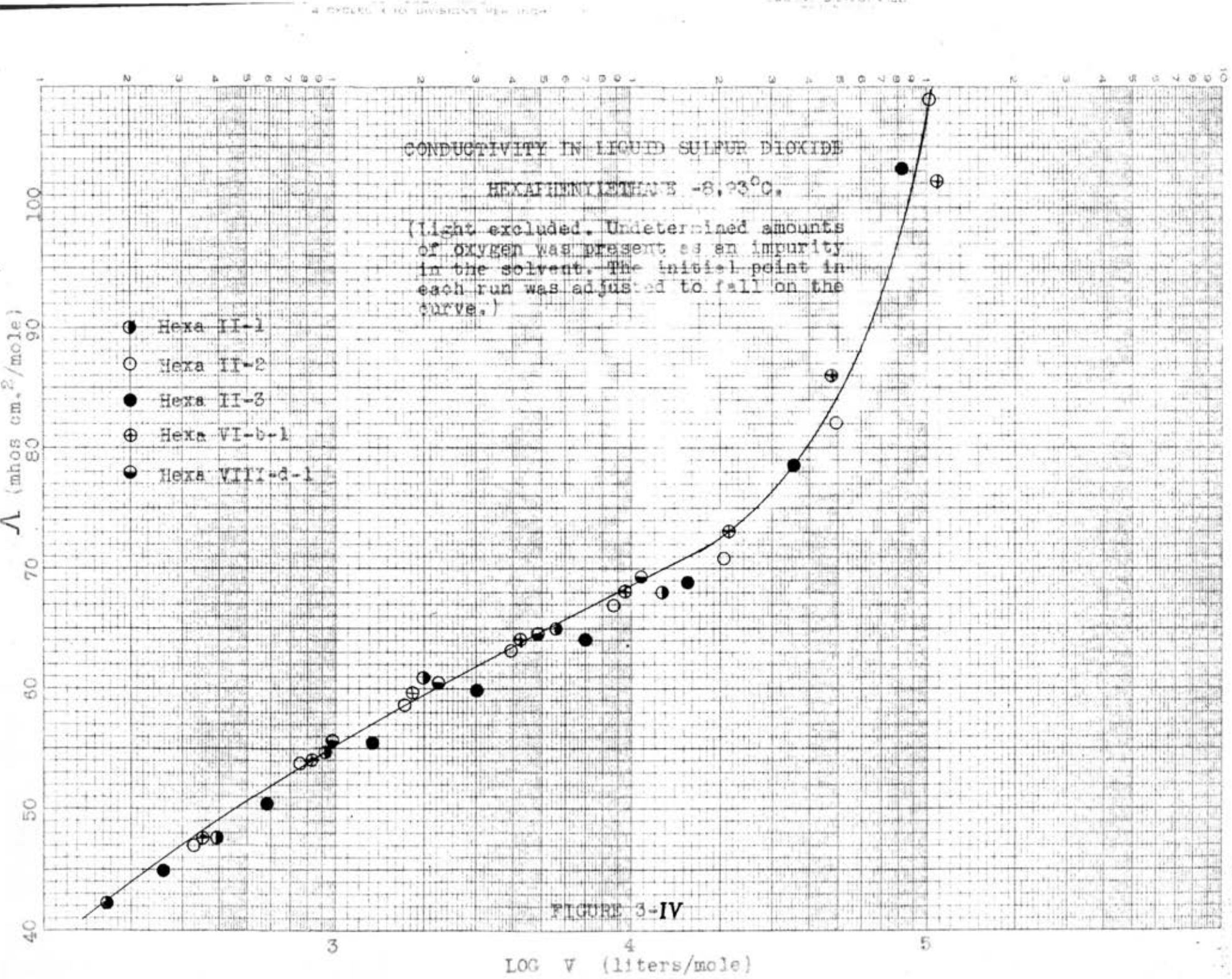

CONDUCTIVITY IN LIQUID SULFUR DIOXIDE
HEXAPHENYLETHANE -8.93°C.
(Light excluded. Undetermined amounts of oxygen was present as an impurity in the solvent. The initial point in each run was adjusted to fall on the curve.)
Hexa II-1
Hexa II-2
Hexa II-3
Hexa VI-b-1
Hexa VIII-d-1
Λ (mhos cm.²/mole)
40
50
60
70
80
90
100
3
4
5
LOG V (liters/mole)

FIGURE 3-IV

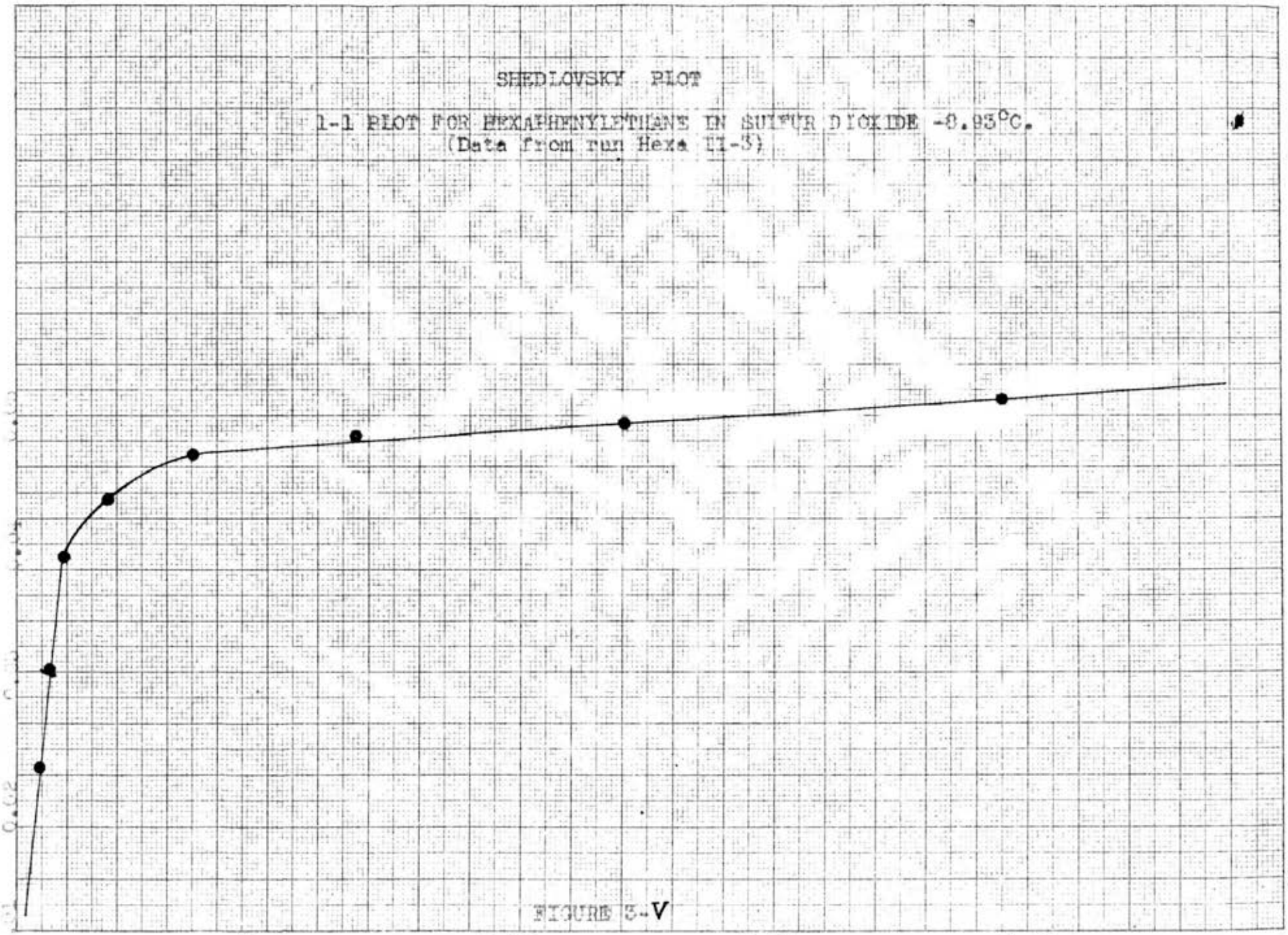

SHEDLOVSKY PLOT
1-1 PLOT FOR HEXAPHENYLETHANE IN SULFUR DIOXIDE -8.93°C.
(Data from run Hexa II-3)
1/ΛS(z)
ΛS(z)Cf±²
0.01
0.02
0.03
0.04

FIGURE 3-V

ionization of hexaphenylethane in liquid sulfur dioxide is a 2-1 electrolyte.

The Influence of Dissolved Oxygen

The next avenue of approach to the problem was to consider possible impurities introduced from the solvent. It was reasoned that since the volume of solvent condensed was known to vary from run to run, this could provide varying amounts of a species promoting conductivity* if this species were volatile.

The sulfur dioxide used in all of this work was of the highest purity available. It was considered possible, however, that certain noncondensible gases may be present probably having been introduced accidentally by the manufacturer while filling the tanks. Therefore a series of runs were carried out in which the solvent was subjected to various treatments.

It was found that increasingly efficient degassing of the solvent prior to dissolution of hexaphenylethane leads to progressive diminution of the conductivity of solutions prepared in the dark. This suggests the production of an electrolyte by reaction with a gaseous impurity present in the solvent. An extremely low specific conductivity (several times that of the pure solvent) was obtained when the solvent was obtained by distillation from a solution of hexaphenylethane.

* This reasoning would also hold if the volatile impurity reduced conductivity by an irreversible reaction with the conducting species.

The gaseous reagent was identified by exposing a solution of the nonconducting radical in sulfur dioxide to an excess of oxygen in the dark and observing a hundredfold increase in conductivity to a level somewhat greater than the highest comparable values obtained without degassing the solvent.

Table 3-IV summarizes some of the relevant data. These data clearly indicate that hexaphenylethane in pure sulfur dioxide does not dissociate heterolytically. In all probability the dissociation is homolytic, as in other solvents, and the apparent ionization is an artifact of at least two processes, namely, reaction with dissolved oxygen and a photochemical transformation.

The Nonconducting Hexaphenylethane

Hexaphenylethane, in the absence of light and dissolved oxygen, forms nonconducting solutions in liquid sulfur dioxide. The dimer dissolves and, as in other solvents, dissociates into free triphenylmethyl radicals. This fact can be demonstrated in several ways, namely, freezing point depression, magnetic susceptibility measurements and product isolation. Only the latter was employed in this research.

Demonstration of the Presence of Radicals

The solvent from a nonconducting solution of hexaphenylethane in degassed sulfur dioxide was carefully removed under vacuum to leave a bright yellow solid residue. The residue

TABLE 3-IV

Conductivity of Hexaphenylethane in Sulfur Dioxide.[a] -8.93°C.

Run	Dilution[b] (liters/m.)	k x 10^6[c] (mhos-cm.$^{-1}$)	Λ ($\frac{\text{mhos-cm.}^2}{\text{mole}}$)	Purity[d] (%)	Treatment of Solvent
II-2	208.1	70.4	14.6	95.8	No degassing
VI-b-1	218.2	133.3	29.1	99.5	"
VI-c-1	216.0	58.2	12.6	97.2	"
VI-d-1	219.2	9.8	2.2	94	Degassed 1 hr.
VI-d-2	236.3	2.7	0.6	94	Degassed 4 hrs.
VI-b-4	226.2	0.9	0.2	99.5	Degassed 3 hrs. and redistilled from hexaphenylethane.
VI-c-2	111.7	3.8	0.4	97.2	Degassed 2 hrs.
VI-c-2	111.7	362	40	97.2	Above solution after treatment with O_2.
VI-c-2	250	206	50	97.2	Above solution diluted.
VIII-d-1	653.6	2.5	1.6	90	Degassed 4 hrs. and redistilled from hexaphenylethane.
VIII-d-1	653.6	77.7	50	90	Above solution after treatment with O_2.

(a) Light excluded.
(b) Based on hexaphenylethane.
(c) Corrected for solvent conductance which varied from 0.15 to 0.3 x 10^{-6} mhos cm.$^{-1}$.
(d) By quantitative oxygenation (92).

dissolved in dry acetone to give a yellow solution in which the presence of free radicals was indicated by the Schmidlin (114) test.* Part of this solution was oxygenated to produce a white crystalline precipitate which was characterized by mixed melting point as being triphenylmethyl peroxide thus proving the presence of triphenylmethyl radical.

The Influence of Light.

Irradiation of a nonconducting solution of hexaphenylethane in degassed sulfur dioxide with u.v. light produced a steady drift toward higher conductivity. Table 3-V summarizes the data of a typical irradiation experiment performed on an initially nonconducting solution.

Contrasting with the behavior shown in table 3-V are the data shown in table 3-VI resulting from irradiation of a conducting solution prepared by oxygenating a nonconducting solution.

The data shown in table 3-VI indicate that the solutions prepared in the presence of oxygen are indeed photochemically stable. This fact lends strong support to the contention that the work of both Bowden and Jones (20) and of Anderson (4) were performed on solutions which contained sufficient oxygen

* According to Schmidlin (114) a positive indication of a hexaarylethane can be demonstrated as follows: The suspected hexaarylethane is dissolved in an organic solvent. Upon standing for a short time the solution develops color. Swirling in air causes the color to disappear by the formation of a colorless peroxide. If this solution is then allowed to stand the color gradually reappears as a result of further dissociation of the hexaarylethane. The phenomenon can be repeated several times.

TABLE 3-V

The Effect of Light on the Conductivity of Solutions of Hexaphenylethane in Pure Sulfur Dioxide.

Time (hr.)	Resistance[a] (ohms)	Remarks
)0	196,600	U.V. Lamp turned on.
3.5	75,000	
4.0	66,200	
5.5	49,100	
6.5	41,500	
8.5	34,600	
9.5	30,800	Observations stopped.

(a) Run VI-d-2 at 0.0°C. 6750 liters/mole dilution.

TABLE 3-VI

The Effect of Light on the Conductivity of the System: Hexaphenylethane- oxygen-sulfur dioxide.

Time (hr.)	Resistance[a] (ohms)	Remarks
0	5500	U.V. Lamp turned on.
1.0	5590	
15	5680	
16	5760	
16.5	5710	Lamp turned off.
27	5820	Lamp turned on
28	6020	
30	6020	

(a) Run VI-c-2 at 0.0°C. 3000 liters/mole dilution.

to convert all or most of the hexaphenylethane. On this basis only, do their results become reasonable.

Color of Solutions of Hexaphenylethane in Liquid Sulfur Dioxide

In the runs in which oxygen was rigorously excluded the solutions were bright yellow and appeared to the naked eye to be similar to solutions of the radical in most organic solvents. The residues obtained from these runs were yellow and reacted with oxygen in organic solvents to form the expected peroxide.

When oxygen was present as an impurity in the sulfur dioxide (evidenced by intermediate conductivity values) the colors of the solutions varied from brownish-red to amber.

In the presence of excess oxygen, both the solution and the residues were blood red. Lengthy irradiation of a nonconducting solution produced a change in color from yellow to redish-orange and the residues were red.

Residues from irradiated or oxygenated solutions did not provide triphenylmethylperoxide when treated with oxygen in an organic solvent.

THEORETICAL CONSIDERATIONS

The Apparent Ionization of Hexaphenylethane

The conductivity which has been observed with solutions of hexaphenylethane in liquid sulfur dioxide has in conjunction with observations of color and spectroscopic data been subject to several interpretations which differ in detail but which all assume an ionization mechanism involving only hexaphenylethane and the solvent. This conductivity is now found to be an artifact of at least two processes, namely, reaction with dissolved oxygen and a photochemical transformation. The results of this investigation now conclusively disprove the long accepted theory which contends that heterolytic cleavage of a carbon-carbon bond can occur in ionizing solvents even when the bonded atoms are symmetrically substituted. It does not seem too unreasonable furthermore to generalize somewhat and include the reported ionization (6) of halogens in liquid sulfur dioxide as another example in which the ionization is more apparent than real. These systems warrant reinvestigation.

A discussion of the interpretations offered in the literature (4,49,115,128,129,133) of the conductivity of hexaphenylethane in sulfur dioxide would not be profitable. These interpretations are no longer of any significance since none of them recognize the importance of oxygen or actinic rays as the essential promotors of the apparent ionization.

The Reaction With Oxygen

Hexaphenylethane in the absence of light reacts with oxygen dissolved in liquid sulfur dioxide to produce ionic species. This reaction is accompanied by a change in the color of the solution from yellow to blood red and the compound produced retains its red color in the solid state. While considerable effort was expended in attempts to isolate and characterize the product of this reaction, very little is known about its nature. It is possible however, to speculate on this subject in the light of qualitative information.

A semi quantitative determination has provided data which indicates the stoichiometry of oxygen in the reaction. Apparently one mole of oxygen is consumed for each mole of hexaphenylethane reacted. It should not be too unreasonable, moreover, to assume that at least one mole of solvent is also involved. Therefore it is possible to write the following reaction:

$$\phi_3\,C\text{-}C\phi_3 + O_2 + SO_2 \longrightarrow \text{ionic compound.}$$

The red substance in sulfur dioxide solution exhibits behavior characteristic of 2-1 electrolytes. Some inference of the nature of the cationic fragment can be gained from spectral data. Anderson (4) found that the spectrum of hexaphenylethane in liquid sulfur dioxide was essentially identical

with that obtained for solutions of triphenylmethyl bromide. Some indication of the presence of a small amount of triphenylmethyl radical was also evident. It appears then, on the basis of the findings of this investigation that Anderson's solution contained almost enough oxygen to convert all of the hexaphenylethane and therefore that the cationic fragment formed in the oxygenated solution is the triphenylcarbonium ion.

A preliminary formula can now be written for the red compound namely, $(\phi_3 C')_2\ S_x O_y^{=}$. Compounds of this type would be expected to be ionic in the crystalline state and hence very unstable toward atmospheric moisture and traces of acid. All attempts to isolate this substance as a pure compound have failed. Such failure is not surprising considering the difficulties inherent in the isolation of highly ionized carbonium salts (25,101).

It is not possible at this time to define the chemical nature of the anion. Several oxides of sulfur can be suggested among which the author prefers and proposes "cum grano salis" triphenylmethyl sulfate.

The mechanism and the products of the oxygenation reaction remain as problems for future workers.

The Photochemical Transformation

The photochemical transformation is by far the more interesting of the two processes. This does not result from

any knowledge of the nature of the process but rather on the basis of the many interesting problems connected with it.

In organic solvents the photochemical reaction product has been shown to be (20) diphenyl-bis-diphenyleneethane. This intermolecular hydrogenation is (20) promoted by light of the wave lengths most strongly absorbed by triphenylmethyl and therefore is a reaction of the radical and not of its dimer. This reaction is not reversible as is indicated by the permanent loss of color of the radical solution. It is interesting in this respect to note that the recent investigations of Linschitz et. al. (94) can be interpreted as contradicting the irreversibility of the photochemical decomposition in organic solvents. These workers found the spectrum of triphenylmethyl radical in a rigid solution of photooxidized triphenylmethide ion. This spectrum is reported to be essentially identical to that found in ether solutions of hexaphenylethane by Anderson (4). Since triphenylmethyl is unstable towards light it is difficult to evaluate Anderson's spectra. However, if the photooxidation of triphenylmethide produces the free radical as claimed by Linshitz, this then should undergo the irreversible photodecomposition to form the diphenylene derivative. Linschitz, however, reports that the photooxidation initiated by light in the 4000-6000 Å region is completely reversible. Apparently the photodecomposition is not a reaction of the

radical alone as suggested by Bowden but rather involves an attack of a radical on a molecule of undissociated hexaphenylethane.

In sulfur dioxide solution the situation is much more complex. Here the photodecomposition, or more likely photooxidation, produces ionic fragments. The initial photochemical reaction may be the oxidation of triphenylmethyl or of sulfur dioxide. If it is the latter then oxygen, which may be produced photochemically, can react with the triphenylmethyl to produce ionic fragments in much the same way they are produced in the oxygenated system. In the photochemical process however the cation would probably be the 9-phenylfluorenyl carbonium ion.

An alternate path could be the initial photooxidation of the triphenylmethyl to the corresponding carbonium ion. The electron could be "solvated" by reaction with sulfur dioxide involving a vacant d-orbital on the sulfur atom (24).

Further investigation of this process will be very rewarding especially to one who is interested in the fundamentals of photooxidation reactions.

Conclusions

Hexaphenylethane dissolves in liquid sulfur dioxide to form solutions containing only free triphenylmethyl radicals in equilibrium with the undissociated dimer. These solutions are nonconducting as one should expect. This observation disproves the long accepted theory that symmetrical carbon-carbon covalent bonds can undergo heterolytic cleavage in ionizing solvents.

The color of the radical solution is yellow and not unlike that observed for solutions of the radical in organic solvents. Contrary to the observations of Bowden (20) the solutions in sulfur dioxide were found to be light sensitive as evidenced both by increased conductivity and a definite color change. The nature of the conducting products formed from the photooxidation of hexaphenylethane in liquid sulfur dioxide has not been established.

Contrary to the reports of Anderson (4) hexaphenylethane in sulfur dioxide solution will react with gaseous oxygen. The reaction with oxygen is different from that observed in organic solvents in that the normal triphenylmethyl peroxide is not the major product observed. In sulfur dioxide solution the oxygenation reaction leads to the production of ionic products probably through a mechanism involving attack on solvent molecules. The oxygenated sulfur dioxide solutions

of hexaphenylethane exhibit a very high conductance characteristic of uni-bivalent electrolytes. These conducting solutions were found to be photochemically stable. The mechanism and products of the oxygenation reaction in sulfur dioxide remain as yet unsolved problems.

On the basis of the findings of this investigation and the data of Dornte and Ferguson (31) on the solubility of oxygen in liquid sulfur dioxide it is possible to reconcile many of the conflicting reports found in the literature concerning this system. The solubility data summarized below clearly indicate that oxygen is a likely impurity in sulfur dioxide. Indeed it can be safely concluded that the heretofore observed conductance resulted from the presence of varying amounts of oxygen in the solvent and /or exposure of the solutions to light. The solutions investigated by Bowden and by Anderson, among others, were essentially completely oxygenated.

This investigation has uncovered several interesting new research problems and it remains for future workers to completely define the system, hexaphenylethane-sulfur dioxide.

TABLE 3-VII

Solubility of oxygen in Liquid Sulfur Dioxide.

(Data of Dornte and Ferguson (31).)

Temp. (°C.)	Solubility[a] (c.c./gm.)
-60	0.12 to 0.59
-50	1.6 to 5.2
-40	10 to 11
-30	25
-20	25
-10	50
0	98
10	183
20	331
30	575

(a) c.c.(S.T.P.)/gm. SO_2 at 1 atm.

Suggestions for Future Work

The research described in Part III of this dissertation has raised many more questions than it has answered. While it has been established that hexaphenylethane does not ionize in pure sulfur dioxide solution very little insight has been gained into the nature of those processes which lead to the formation of ionic species in this system. In this respect there are three important questions which must be answered before the final chapter to this problem can be written. It remains for future investigators to determine the nature of the photochemical transformation, the oxygenation reaction and the conductivity behavior of the products resulting from these processes.

EXPERIMENTAL PART

Preparation of Hexaphenylethane

All samples of hexaphenylethane used in this work were prepared by this worker by the methods described below. Table (3-VIII) summarizes the analytical data and physical properties for the various samples. The sampling technique employed required that several distinct sampling operations be performed on each lot of hexaphenylethane. In each sampling operation four identical samples were obtained. Thus the samples are coded according to lot number (Roman numeral); sampling (lower case letter); and sample number. Conductivity runs are coded to correspond to the sample employed in the run.

Apparatus

All glassware employed in the preparative work were made of pyrex glass and were thoroughly cleaned by the following proceedure. Acid bath treatment was followed by profuse washing with tap water. The last traces of acid were removed by treatment with hot Alkanox solution followed by soaking in dilute ammonium hydroxide. After rinsing with tap water and finally with distilled water the clean glassware were dried in an oven for at least four hours at 120-130 ^{o}C.

Vacuum Dry Box

The dry box used throughout this work was a modified version of the controlled atmosphere laboratory described by Thomas and Lichtin (123). The major modification consisted of

replacing the all metal evacuation system (bellows, valves, tubing and couplings) by an all glass system employing only two stopcocks. This resulted in a considerable improvement in the ultimate vacuum which could be obtained. Further improvement in ultimate vacuum was effected by separating the glove port pumping system from the main (bell jar) evacuation system. With these modifications pressures as low as 0.01 micron could be reached after twelve to fourteen hours pumping. When thoroughly outgassed the bell jar was capable of holding a constant pressure of less than one micron when isolated from the pumping system for twenty-four hours. This was considered satisfactory since the average time for a dry box run was of the order of twelve hours. Figure 3-VI shows a schematic drawing of the dry box pumping system.

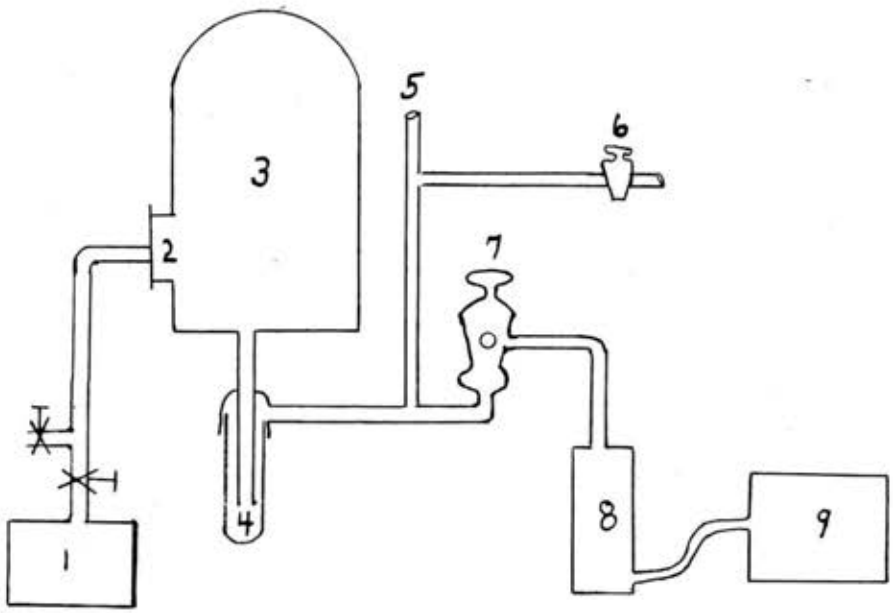
TABLE 3-VIII

Physical Properties of Hexaphenylethane Samples.

Lot No.	Color	M.P.[(a)] (°C.)	Analysis[(b)] (%)
II	Pale yellow	------	95.8
VI-b	White	153.5-154	99.5 ;99.5
VI-c	Buff	153-154	97.2;97.3
VI-d	Pale yellow	146-148	94.02;94.1
VIII-d	Yellow	144-146	90.7;89.9

(a) Sealed Capillary tube. Uncorrected.

(b) Quantitative oxygenation (92).



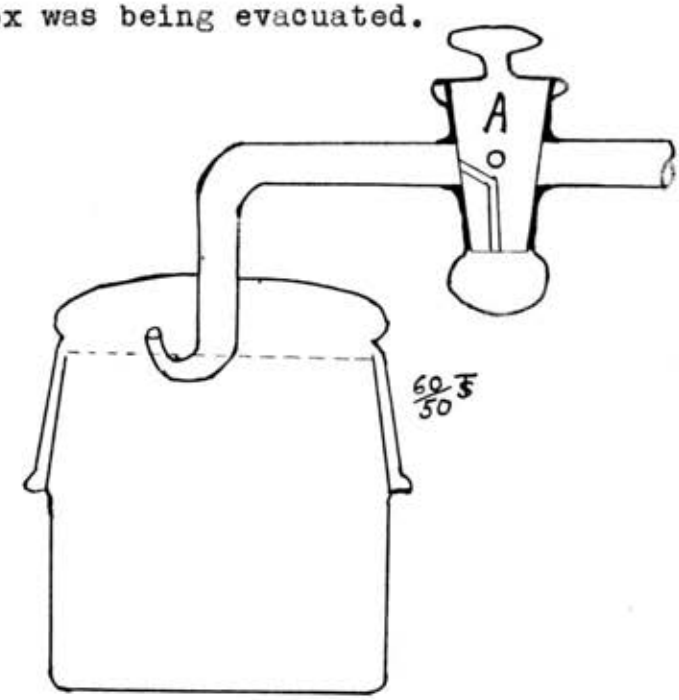
VACUUM DRYBOX

FIGURE 3-VI

1. Mechanical pump for glove port system.
2. Glove port.
3. Main bell jar.
4. Cold trap.
5. Line to manometer and Mc Leod gauge.
6. Line to gas purification system.
7. Main pumping system control stopcock.
8. Mercury diffusion pump.
9. Fore pump for bell jar pumping system.

Sampling Technique

After the final purification, by recrytallization from acetone, the dry hexaphenylethane was stored in a special vacuum storage bulb while the dry box was opened and prepared for the sampling operation. The storage bulb was connected through a base-plate port to an external pumping system and evacuated for several minutes while the dry box was opened. The stopcock A (figure 3-VII) was then closed and the bulb was wrapped in aluminum foil and transferred to the vacuum line where the hexaphenylethane was dried at room temperature by pumping for twelve hours at a pressure of 0.01 micron. During this time the drybox was cleaned and equipped for the sampling procedure. The storage bulb was then returned to the dry box and was further evacuated by an external pump while the dry box was being evacuated.



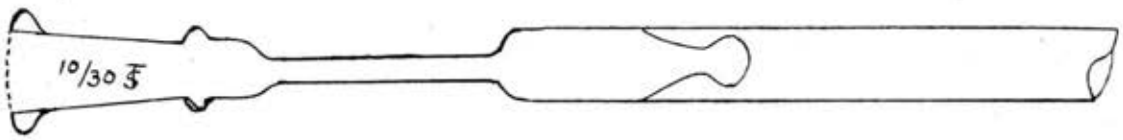
Storage Bulb for Hexaphenylethane

FIGURE 3-VII

The sampling operation was carried out in the dry box as follows:

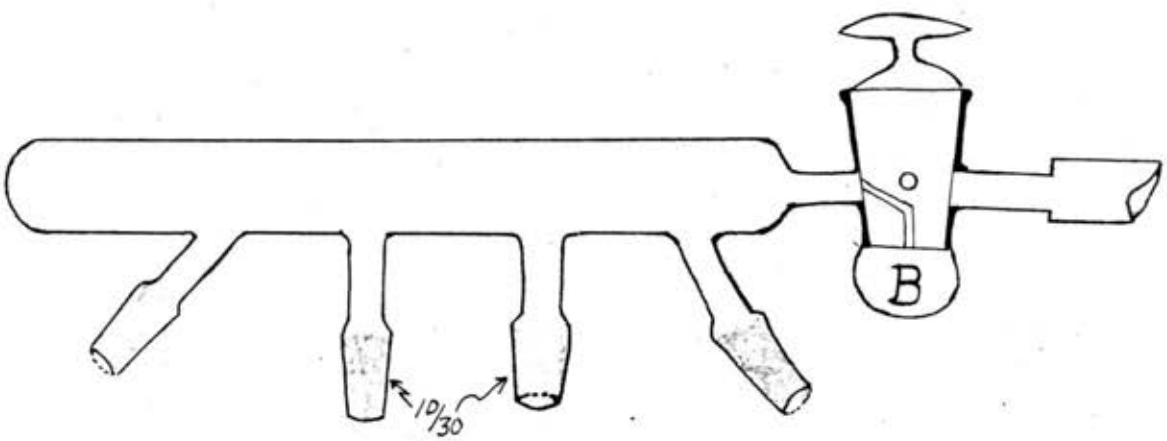
Break-off type sample bulbs (Figure 3-VIII) were placed in the dry box along with a sampling cow (Figure 3-IX). Long stem funnels, spatulas, pipe cleaners and other necessary accessories were included. The dry box was then sealed and evacuated to a pressure of the order of 1 micron after which it was filled with an atmosphere of purified nitrogen. Air Reduction Co. Seaford grade nitrogen was purified by slow passage through a quartz tube filled with freshly reduced metallic copper maintained at 800°C. The hot gas was cooled and dried by passage through a coil of 15 feet of ¼ inch copper tubing immersed in a dry ice acetone slush followed by a 3 x 75 cm. tower containing calcium chloride and indicating Drierite. The atmosphere in the dry box was further purified by exposure to metallic sodium and phosphorus pentoxide which had been stored in the dry box in sealed, evacuated flasks. The getters were allowed to "clean up" the atmosphere until the surface of a freshly cut piece of sodium remained bright for several hours. Not until this condition was reached was the hexaphenylethane allowed to come into contact with the atmosphere in the dry box.

Stopcock A on the storage bulb was closed and the bulb was detached from the external vacuum. The stopcock was opened to relieve the vacuum with dry box atmosphere and the storage



Sample Bulb for Conductivity Samples.

FIGURE 3- VIII



Sample Bulb Filling Cow.

FIGURE 3- IX

bulb was opened. Small quantities of hexaphenylethane were added to each of four sample bulbs. The narrow necks of the filled bulbs were cleaned carefully with pipe cleaners to remove material adhering to the walls. The storage bulb was immediately closed and evacuated and the sample bulbs were installed on the previously lightly greased joints of the cow. The cow and the bulbs were evacuated and the stopcock B turned to a neutral position.

Several samples for oxygen analysis were prepared with each set of four conductivity samples. This was accomplished by the procedure described by Lichtin and Thomas (92) for the preparation of samples for analysis. After the analytical samples were sealed off and stored, the dry box was opened and the sampling cow with four filled sample bulbs was transferred to the high vacuum line where the samples could be conveniently sealed off under high vacuum. All sampling and preparative work was carried out under darkroom conditions where only light from a Kodak Ruby Safelight was employed.

Storage of Hexaphenylethane

Sample bulbs containing pure hexaphenylethane were wrapped in aluminum foil and stored in a closed cardboard box in the freezing compartment. White samples stored in this way remained white for as long as one year unless the sample bulbs contained pinholes in which case the material turned yellow after several hours.

Sample Weights

Sample weights were determined by difference. Buoyancy corrections were avoided by employing a tare consisting of an empty sample bulb. The bulbs were constructed from glass tubing which had been previously cleaned thoroughly as described above. The completed bulbs were washed with distilled water, acetone and petroleum ether and were then dried and annealed at 580°C. They were cooled in a desiccator and weighed after equilibrating with the atmosphere in the balance case. The filled bulbs containing the samples were washed with acetone and petroleum ether and air dried. The connecting joints from which the sample bulbs had been sealed off were cleaned in the acid bath, rinsed with water, dried and then weighed along with the corresponding sample bulb.

A vacuum correction, applied to the weights of the evacuated bulbs, was calculated from the measured volume of the empty bulbs. This correction was usually of the order of 3 to 4 mg. and contained an uncertainty of about 1 mg. due to the volume occupied by the solid sample.

Sample weights were reproducible to within 0.1 mg. and were probably accurate to 1.0 mg.

Melting Point Determination

Several melting point capillaries were prepared for each set of conductivity samples obtained. The capillary tubes (0.5 x 125 mm.Pyrex) were filled in the dry box with 1 to 2 mm.

of hexaphenylethane. The material was packed firmly into the closed end of the tube by gentle tapping and the open end was temporarily sealed with a plug of Apiezon "Q" (vacuum putty). After opening the dry box the tubes were sealed with a small flame. The seal was made between the sample and the temporary plug by first drawing the tube out to a fine tip and then fusing the tip rapidly. In this way it was possible to avoid sample decomposition. Melting points were uncorrected and were determined using an electrically heated, stirred H type bath.

Melting point behavior is worthy of description. The sample remained white and unchanged up to a temperature of about 135°C. Between 135° and 145°C. the sample turned yellow. Above 145°C. the color darkened to orange and finally red. The material melted usually above 150° (see table 3-VII) to a red melt. Further heating failed to produce decomposition. Above 180°C. the sample assumed a deep blue red or purple color. On further heating, up to 300°C, the color became pure blue. Even when heated in an open flame the sample, in the sealed tube, failed to show any signs of charring and the clear blue color remained. The color changes described above were irreversible, the colors formed at any of the several temperatures remained unchanged on cooling. The blue compound formed by the thermal decomposition of hexaphenylethane in the absence of air was strongly fluorescent under ultra violet light. It would be interesting to investigate the nature of the blue decomposition product.

Materials

Triphenylchloromethane was prepared from Eastman Kodak Co. White Label triphenylcarbinol by reaction with acetyl chloride in dry ether. The carbinol (100 gms.) was suspended in 150 ml. C.P. ether (dried over CaH_2) and 40 ml. C.P. acetyl chloride was distilled directly into the mixture which was then refluxed until a clear yellow solution was obtained. The product was crystallized by swirling the solution while it was being chilled with cold tap water. In this way a pure white crystalline product was obtained from the yellow solution. The colored impurities remained in the ether mother liquors.

The rapidly crystallized product was allowed to stand in the refrigerator for one hour. It was found that with a longer digestion period yellow product was always obtained. The product was washed on a sintered glass funnel three times with 10 ml. portions of dry cold ether and then with 50 ml. dry petroleum ether. Recrystallization from ether and vacuum drying gave 93 to 97% yields of pure white triphenylchloromethane M.P. 112.5-113°C.

Mercury was usually triple-distilled C.P. grade which was outgassed by heating and pumping for several minutes before use. The following solvents were of C.P. grade: toluene was dried over calcium hydride and filtered before use; bromobenzene was distilled and small forerun discarded; acetone was stored

over Drierite for several weeks, filtered, refluxed over calcium hydride for several hours and distilled before use; ether was dried over calcium hydride and filtered.

Techniques of Preparation

Lot #II This preparation was carried out in the dry box according to the procedure described by Lichtin and Thomas (92) by shaking a solution of 0.10 mole triphenylchloromethane in 125 ml. of toluene with 1.0 mole of mercury for two hours. The reaction was carried out in a 250 cc. sealed flask shielded from light by wrapping in aluminum foil. Prior to sealing, the flask and contents were cooled in an ice bath and outgassed for thirty minutes. Shaking was carried out at room temperature by means of a Burrell Co. Model CC shaker set at speed 10. The sealed flask was next transferred to the vacuum dry box which contained all equipment needed for the isolation process. The dry box was evacuated to 0.001 mm. pressure and filled with purified nitrogen. During the remaining operations light entering the dry box was kept to a minimum with the aid of a red filter constructed from a 3 inch watchglass made of Corning LA (Low Actinic) glass.

The flask was opened and the contents were filtered on a sintered glass funnel with suction. The filtrate was evacuated to dryness under vacuum and the crystalline hexaphenylethane-toluene complex was subjected to two recrystallizations from acetone to give about 5 grams* of buff colored material.

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* Weights are estimated.

Four samples for conductivity runs were prepared and six samples for oxygenation analysis.

Analysis for Hydrolyzable Chloride

About 0.5 gram of the ethane was dissolved in 50 ml. of acetone and poured into 15 ml. of 10% sodium hydroxide solution. The mixture was evaporated to dryness on a hot plate to assure complete hydrolysis and the residue was extracted with three 10 ml. portions of boiling distilled water thus effecting a separation from organic material. The aqueous extract was acidified with C.P. nitric acid and treated with silver nitrate solution. The test indicated the complete absence of chloride in the solution. Hence it is concluded that hexaphenylethane prepared as described above is completely free of hydrolyzable chloride.

Lot #III

In this run the yield of hexaphenylethane was improved by modification of the procedure employed in the preparation of lot II. Since it was believed that much of the product of lot II was lost as solid retained in the voluminous mercury residue, the reaction mixture was warmed to about 80°C. before filtration in order to increase the solubility of the hexaphenylethane. After filtration of the hot solution the residue was extracted with 50 ml. of hot toluene. This procedure increased considerably the volume of toluene which had to be removed (a tedious operation under dry box conditions) however, when evaporation was complete about 15 gms. of the toluene-

complex remained which was a tolerable increase over that obtained in previous runs.

The toluene complex was decomposed and the product was twice recrystallized from acetone to give about 10 gms. of buff colored solid. Unfortunately the yield was lost by exposure to air as the result of a mishap. The exposed material was canary yellow and melted over a range between 144-147°C. to give a red melt. This melting point is close to that reported by Gomberg (48) and may serve as an indication that Gomberg's material was also partially decomposed by air oxidation.

Oxygen analysis by the method of Lichtin and Thomas (92) met with little success. Three analyses were attempted on the exposed product. Reliable results were not obtained, however, because of the presence of a leak in the oxygenation apparatus.

Lot #IV Molecular Silver

"Molecular" silver was prepared by electrolytic displacement from solution by metallic copper. The precipitated silver was boiled with aqueous silver nitrate solution to remove the last traces of copper. After filtration the silver was washed free of soluble salts and air dried at room temperature. Traces of silver oxide were removed by refluxing for five hours with absolute ethanol. The pure, finely divided product was dried under vacuum at room temperature.

The reaction was carried out by shaking a solution of 50 gms. of triphenylchloromethane in 250 ml. of dry benzene with 53 gms. of "Molecular" silver. After shaking for sixty-five hours at room temperature a considerable quantity of metallic silver remained. The reaction mixture was warmed to about 50°C. and shaking was continued for three hours at this temperature.

The reaction mixture was then worked up in the usual manner and the solid remaining after evaporation of benzene was twice recrystallized from acetone to give about 40 gms. of yellow crystalline solid. Oxygen analysis indicated less than 1% free radical. Part of the residue was recrystallized from dry ether to give pure white crystals of triphenylchloromethane melting between 111.5-113°C.

It is concluded that the reaction with silver prepared as described above is extremely slow under these conditions even though the solution developed an intense yellow color after shaking for one hour. Since Gomberg (49) reports good results by this method it would seem that the surface condition of the silver is extremely critical. In this respect it is important to note that Gomberg's (49) "Molecular" silver was prepared by electrolysis of silver chloride and thus may have differed from that used in the present work in a way which is not readily obvious. In the light of these considerations it seems possible that many of the results of earlier workers, which were based on hexaphenylethane prepared in situe by the silver method, are unreliable.

Lot #V Silver Amalgam

Silver amalgam was prepared by mixing 2 parts of metallic silver with 3 parts of mercury in a mortar. Grinding was continued for several hours to ensure homogeneity and the solid amalgam was dried over P_2O_5 for several days and pulverized before use. A reaction mixture consisting of 50 gms. of 40% silver amalgam 30 gms. of triphenylchloromethane and 350 ml. dry ether was placed on the shaking machine for forty two hours. The solvent was removed after filtration and the solid residue dissolved in 250 ml. of acetone and filtered to remove insoluble material. The volume of this solution was reduced to 100 ml. by suction. About 10 gms. of yellow crystalline solid were removed and stored as lot V-A. The mother liquor was evaporated to dryness under reduced pressure and the residue was dissolved in 100 ml. of ether. Concentration of the ether solution to about 50 ml. gave about 5 gms. of yellow powder which was stored as lot V-E. The residue from the mother liquor was isolated and stored as lot V-R.

The following table summarizes the analytical results obtained for these products.

Analytical Data for Lot V

Lot	% Radical[1]	M.P.
V-A	----------	95-108° C.
V-E	13.7	124-150° C.
V-R	16.5	----------

(1) By quantitative oxygenation (92).

Investigation of Reaction Conditions:

A series of test reactions were carried out in an effort to determine the optimum conditions for the preparation of pure hexaphenylethane.

Reactions were carried out in 4 ounce screw cap bottles fitted with puncture gaskets. Weighed amounts of triphenylchloromethane were added to the carefully dried bottles under a stream of nitrogen. Following the addition of 50 ml. of solvent the solution was deoxygenated by saturation with nitrogen and the bottle was quickly closed with the puncture gasket. The bottles were shielded from light with an aluminum foil wrap and the mercury was introduced through the gasket from a 1.0 ml. hypodermic syringe.

The reaction bottles were placed on the Burrell shaker set at maximum speed and aliquots were withdrawn at various times with a 5 ml. syringe equipped with a 6 inch number 24 hypodermic needle. Before withdrawing the sample the shaker was stopped and sufficient time was allowed for the metal to settle to the bottom. Three ml. aliquots were withdrawn and quenched in an equal volume of ether contained in a 50 ml. beaker. The samples were allowed to react with atmospheric oxygen by standing until all of the solvent had evaporated. The dry residues were leached with acetone, ether and petroleum ether and the insoluble fractions were collected and weighed as peroxide. Melting points recorded for the peroxide residues usually ranged between 180-190°C.

The peroxide residues, which were pale yellow or buff and in some cases almost white, were found to be strongly fluorescent under ultra violet light. The intensity of fluorescence was greatest for the most highly colored residues. Since neither pure triphenylmethyl peroxide, chloride, carbinol, nor triphenylmethane exhibit this behavior under ultra violet light it seems reasonable to conclude that the observed fluorescence is due to the presence of a yellow impurity of unknown composition. The nature of this impurity was not further investigated.

In some cases the soluble fractions from the oxygenated residues were tested for the presence of triphenylmethyl chloride and carbinol. The solvents were evaporated and the Bowden (19) test was applied to the solid residues. Several mg. of the unknown solid was dissolved in 1 ml. of dry benzene on a porcelain spot test plate. One drop of a saturated ethereal solution of zinc chloride was added. Formation of a bright yellow color indicated the presence of a triaarylmethyl halide. If color failed to develop, a glass rod which had been wet with concentrated hydrochloric acid was held over the solution on the spot plate. The formation of a yellow color in the solution when exposed to hydrochloric acid indicated the presence of a triarylcarbinol. Positive tests for carbinol were always obtained.

The results of these investigations are summarized in table 3-IX. The percent conversions were calculated on the basis of the peroxide recovered from the oxygenation of aliquots

TABLE 3-IX

Experiments on the Preparation of Hexaphenylethane Under Various Experimental Conditions.

Exp. No.	Solvent	Metal	Trityl Chloride (gms.)	% Conversion [a] 1 hr.	2 hrs.	4 hrs.	10 hrs.	20 hrs.
S-I	Tetrahydrofuran (THF)	1:1 Ag-Hg 12 gms.	4.0	2.5	8.8	5.4	----	----
S-II	Diethyl oxalate	Hg. 13.6 gms.	4.0	7.0	----	----	79	88
S-III	Ethyl ether	Hg. 10.0 gms.	3.0	----	54	----	75	23
S-IV	Ethyl carbonate	"	"	----	75	----	75	71
S-V	Me-cyclohexane	"	"	11	11	----	12	12 [b]
S-VI	Ethyl formate	"	"	----	71	----	51	37
S-VII	Toluene	"	"	----	78	----	77	81 [c]
S-VIII	THF	Hg. 13.6 gms.	"	----	68	----	68	----
S-IX	Acetone	"	"	----	53	----	65	---- [d]
S-X	Benzene	"	"	67	82	----	82	---- [e]
S-XI	Acetone	"	"	29	47	30	----	---- [f]

(a) Calculated on the basis of weights of solid peroxide obtained on oxygenation.
(b) After 80 hrs. 12% yield.
(c) Solution deep red.
(d) After 60 hrs. 65% yield.
(e) Solution deep red.
(f) Reaction at 60°C.

of the solutions. Since it is known (51) that quantitative yields of triphenylmethyl peroxide cannot be obtained from the oxygenation of pure triphenylmethyl, the conversions tabulated should be considered as minimum values only. The maximum yield of peroxide obtained in this work was 88% (run S-II). This value may be considered to correspond to essentially complete conversion to hexaphenylethane.

The data (table 3-IX) indicate that in all of the solvents tested with the exception of methylcyclohexane good yields of hexaphenylethane can be obtained with mercury. The 10:1 to molar ratio of mercury employed as standard procedure by Lichtin and Thomas (92) can be appreciably reduced (to a 3:1 ratio) without suffering a decrease in the apparent yield. Indeed such a reduction serves to increase the actual yields by reducing losses resulting from retention of product in the bulky metallic residues obtained when a 10 to 1 ratio is employed.

The reaction is generally complete after two hours shaking time, and further shaking does not appear to be detrimental. However, in several cases (runs S-III and S-VI) the yields appeared to suffer a decrease as a result of prolonged shaking. This observation is suggestive of a slow decomposition of hexaphenylethane either by disproportionation or by reaction with the solvent. In this respect it is interesting to note that Thomas (122) failed to obtain any isolatable hexaphenyl-

ethane when the reaction was carried out in toluene by shaking for twenty four hours with a 10:1 molar ratio of mercury. In contradiction to his observation, however, an apparent yield of 81% was obtained in toluene (run S-VIII) after a twenty hour shaking period.

An alternate explanation of the apparent loss of hexaphenylethane with time of reaction lies in the possibilty of a leak arising from a defective gasket. Oxygen introduced in this way would produce triphenylmethylperoxide which, being insoluble, would not be isolated by the sampling techniques employed in these tests. This explanation could also account for the observation of Thomas, for the peroxides thus formed would be removed along with the metallic residue according to the isolation procedure employed by that worker.

Several factors must be considered in selecting an ideal solvent for the preparation of hexaphenylethane. Among these are boiling point, ease of purification, solubility of products and impurities and complex formation. Acetone appears to be the most desirable solvent in many respects. For example, it is readily available and easily purified. Since acetone does not form stable complexes with hexaphenylethane it is possible to prepare and purify the product with the same batch of solvent. This feature allows one to prepare pure hexaphenylethane in an all glass, sealed, system without requiring the use of the vacuum dry box.

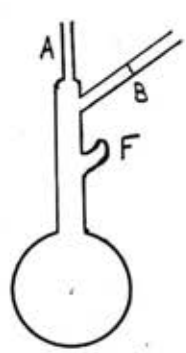
Preparation of Hexaphenylethane in Acetone Solution

Lot VI

Since acetone is one of the few solvents which does not form a molecular complex (52) with hexaphenylethane it is possible to prepare and purify the product in the same batch of solvent. Therefore the solvent removal step of the procedure of Lichtin and Thomas can be eliminated and it should be possible to prepare pure hexaphenylethane in a sealed apparatus without requiring the laborious dry box operations. An apparatus was designed to permit bench top preparation of pure hexaphenylethane. The apparatus consisted of two separate units which could be sealed together as required.

Procedure

The reaction flask, figure 3-X was dried carefully by flaming under vacuum and when cool was filled with dry nitrogen. Eighty grams of mercury added through arm A, was degassed by pumping and flushing with nitrogen.

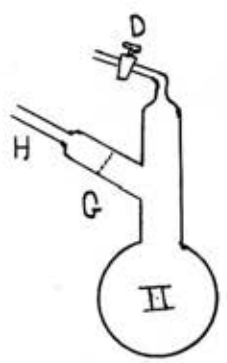


Reaction Vessel

FIGURE 3-X

Thirty grams of pure triphenylchloromethane and 400 ml. of acetone were then added under darkroom conditions and the resulting solution was outgassed by pumping for thirty minutes. The reaction mixture was cooled in a dry ice-kerosene bath (-40°C.), evacuated, and carefully sealed off under vacuum at A. The reaction was carried out in the absence of light for nine hours by shaking on a Burrell shaker set at speed 10.

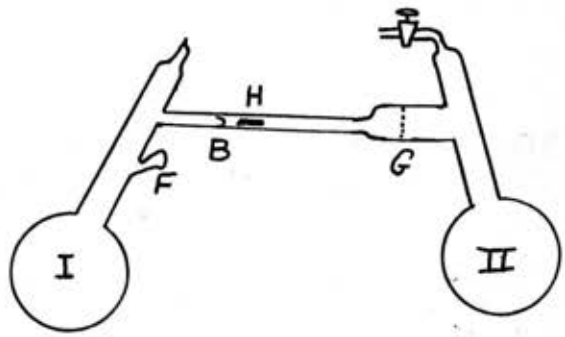
The filtration flask, figure (3-XI), was sealed to the reaction flask as shown in figure (3-XII). This vessel was



Filtration Vessel

FIGURE 3-XI

dried by flaming under vacuum and flushing with dry nitrogen through stopcock D. It was evacuated and removed from the pump after stopcock D was closed. The break-off seal, B, was smashed with a small glass rod which has been placed into the connecting tube for this purpose.



Apparatus for Preparation of Hexaphenylethane.

FIGURE 3-XII

The orange solution in the reaction flask was filtered into flask II by cooling II to -78°C. and rotating the apparatus clockwise so that flask I was above flask II. The side bulb F served to trap out most of the mercury residue in order to prevent plugging of the sintered disk, G. The solvent was then distilled back into flask I in order to wash the mercury residue free of product. The extract was filtered into flask II and the washing procedure was repeated.

The material in flask II was crystallized by concentrating the solution to a volume of about 75 ml. The concentrated solution was chilled in a dry-ice acetone slush until crystallization appeared complete. The mother liquor was filtered into vessel I and fresh solvent (about 300. ml.) was distilled into flask II from flask I. The solid was dissolved and

recrystallized by concentration and cooling. The recrystallization procedure was repeated, and the twice recrystallized product was finally washed with 75 ml. of fresh acetone. The filtration flask, II, was removed from the reaction flask by sealing off on arm H which consisted of a short length of heavy wall tubing. The solid material was dried at room temperature by pumping through stopcock D. After several hours the stopcock was closed and the vessel was transferred to the dry box for final purification and sample distribution.

The hexaphenylethane prepared as described above was pale yellow or buff colored. That the yellow color was due to a surface impurity is evidenced by the fact that washing the solid with dry acetone effectively removed the color and a pure white product was obtained which melted between 153-154°C. Oxygen analysis indicated a purity of 99.50 and 99.47% free radical. The white solid hexaphenylethane did not fluoresce under ultra violet light.

The product stored for further sampling was accidentally exposed to air for a short period as a result of a pinhole in the storage flask. Analysis after the second sampling indicated 97.5% purity. The exposed product was pale buff and showed a weak yellow fluorescence.

The chemical nature of the yellow compound formed by the reaction of solid hexaphenylethane with atmospheric

oxygen is a worthy subject for future investigations. It is obvious that this compound is not the normal peroxide obtained from oxygenation of solutions of triphenylmethyl radical.

Lot VIII

Another batch of hexaphenylethane was prepared by the procedure employed in lot VI. Several samples of white product were obtained which assayed at 90±1% hexaphenylethane.

Analysis of Hexaphenylethane

The method of analysis employed in this work has been adequately described elsewhere (92).

Conductivity Measurements

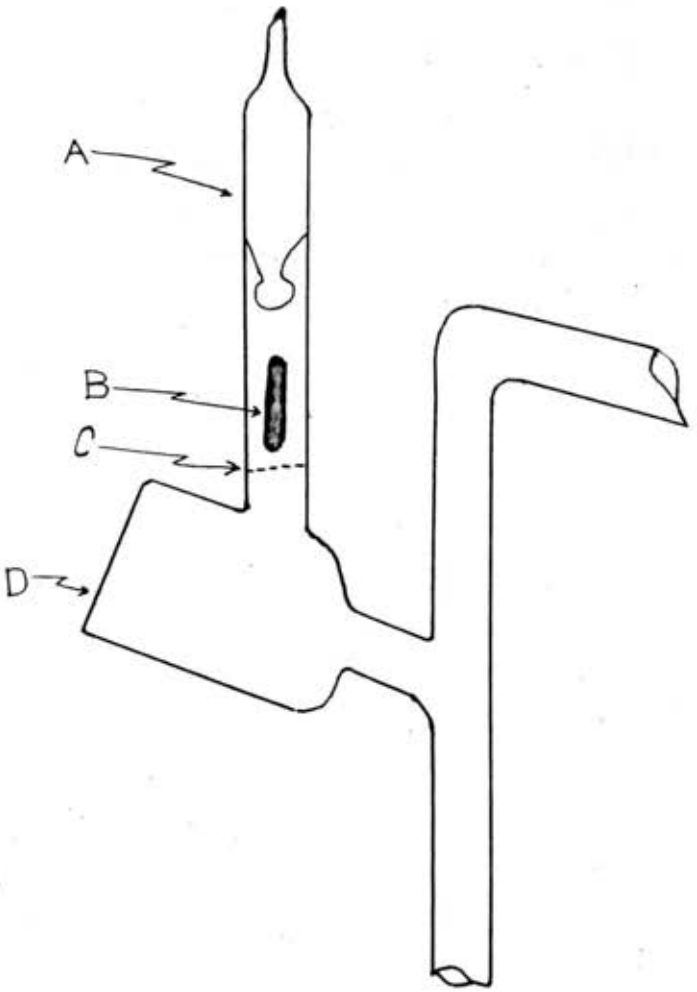
Apparatus, materials and techniques employed in this work were essentially those described earlier in this dissertation. Several modifications and refinements were required in order to prevent exposure of the samples to atmospheric or other contaminants.

Preparation of Solutions in Sulfur Dioxide.

Samples were introduced into the conductivity cell by the following procedure: Special sample bulbs were sealed directly to the inlet arm of the cell. A glass coated, gold or platinum plated, iron rod was used with the aid of a solenoid as a magnetic breaker. In this way the fragile breakoff seal,

which retained the sample, could be broken at the proper time thereby introducing the sample into the electrode bulb. A small quantity of glass fragments were also introduced by this procedure. This, it is estimated, introduces an error of about 0.01 ml. in the apparent volume of the solution. Since an error of this magnitude is negligible a correction was not applied.

Special precautions were required in order to prevent thermal decomposition of the sample during the sealing operation. The sample bulb was inverted and gently tapped so that essentially all of the hexaphenylethane was packed into the upper part of the sample bulb. The breaker rod was then carefully inserted into the open extension tube (see figure 3-VIII) and allowed to rest upon the fragile breakoff membrane. The bulb was carefully immersed in a beaker of ice slush so that only about one inch of the extension tube remained above the water. The sample bulb and ice bath were clamped to the rack and the conductivity cell was inverted and clamped above the sample bulb so that the inlet tube of the cell was directly above the extension tube. The bulb was then carefully sealed to the inlet tube. When the seal had cooled completely the cell was carefully rotated to its normal position and the breaker rod was allowed to slide down into the inlet tube. A glass grid in the inlet tube (figure 3-XIII) prevented the breaker from falling into the cell.



Method of Introducing Hexaphenylethane
into the Conductivity Cell.

FIGURE 3-XIII

A. Sample bulb.

B. Magnetic breaker

C. Glass grid support for magnetic breaker.

D. Mixing bulb of conductivity cell.

The conductivity cell was sealed to the vacuum line and evacuated for 24 hours, followed by the introduction of solvent. The cell was then generally removed from the line and the sample introduced by smashing the breakoff seal.

Conductance measurements were carried out by the method of Lichtin and Glazer (91) with minor modifications which are described below.

Survey of Individual Conductivity Runs

Run Hexa II-1

This run was an exploratory run in which the influence of several factors was tested. The material was from lot II and assayed at 95.8% radical. The cell was pumped at a pressure of 10^{-5} mm. for eight hours after which the bulb was smashed. The sample was then pumped an additional two hours prior to introduction of liquid sulfur dioxide.

The operations described in setting up the run were carried out in diffuse daylight. Attempts were made, however, to protect the sample and solution from exposure to intense illumination.

Conductance measurements were carried out at -8.9° at night under semi darkroom conditions. The first point was stable for a period of three hours. The next three dilution points were each followed for periods of one to two hours and

were perfectly stable. After the fourth point (2000 l./m.) had been followed for two hours in the dark, the cell was transferred from the -8.9°C. thermostat to a battery jar containing ice slush and was allowed to equilibrate in the dark. The influence of light from several sources was then tested.

A 60 watt incandescent bulb focused directly on the solution in the electrode bulb, produced no measurable change in conductance after a forty five minute period of irradiation. Fifteen minutes of intense irradiation with an infra-red heat lamp also failed to produce a change in the conductance of the solution. The conductance remained stable for ten hours in the dark after the irradiation tests.

On the next dilution, the solution was exposed to fluorescent light for ten minutes with no measurable effect.

When on the next dilution the solution was exposed to direct sunlight for five minutes a small steady drift toward higher conductance resulted. This drift was followed for forty two hours during which the resistance changed at an approximately constant rate of 90 ohms per hour. The solution was then irradiated with a Burton mercury vapor lamp and a tenfold increase in drift rate was observed. For the first 800 minutes of irradiation the drift averaged 600 ohms per hour. When the source of illumination was removed the conductance remained essentially constant for an eight hour period. On further

irradiation the drift continued at a rate which steadily decreased from 400 ohms in the first hour to a stable value after sixteen hours. The resistance remained constant for the next sixteen hours of irradiation (see table 3-III).

Irradiation of the next dilution point showed a slow drift from 25,850 ohms to 23,630 ohms over a thirty four hour period. The resistance then remained constant for the next seventy hours.

The next dilution gave a constant value during fifty four hours of irradiation.

At the completion of the run the solution was poured over into the reservoir bulb and it was noticed that some of the solid material would not dissolve. The cell was opened and the residue was collected in a stoppered flask and evaporated to give a red brown amorphous residue. Pumping for one hour at less than 1 mm. failed to decompose the complex. The residue, which was dry and odorless soon became liquid (hygroscopic) on standing in contact with the atmosphere (wet day) and an odor of sulfur dioxide became apparent.

Run Hexa II-2

This run was carried out under strict darkroom conditions at $-8.9^{\circ}C$. The material used was from lot II. The run proceeded smoothly from the start and steady resistance values were reached at each point after a normal (15 minute) thermal equilibration period. In some cases the conductance was watched

for two hours but no drifts were detected. The data fit a smooth conductance-Log V plot. The residue was discarded.

Run Hexa II-3

This run, also at -8.9°C., was plagued from the start by a series of mishaps the worst of which involved an explosion of a sulfur dioxide tank. When the run was finally started the glass jacket on the breaker cracked exposing the iron rod. It was impossible to remove the iron rod from the cell so the run was continued in the presence of the iron rod. It appears that any impurities introduced by the iron rod had no influence on the stability of the ethane solution for steady resistance values were readily obtained. The data fit a smooth conductance plot which differed from Run 2-II by about 10%. It was found that the two curves could be made to coincide by applying a correction of somewhat less than 10% to the initial concentration. This seems to suggest a possible error in weighing of one of the samples.

Run Hexa VI-b-1

This run was carried out at -8.9°C. under strict dark-room conditions. Since the resistance of the initial solution was quite low it was necessary to add a 250 $\mu\mu f$ parallel capacitance to the cell arm of the bridge. The run proceeded smoothly and stable resistance values were obtained at each dilution. After completion of the run, part of the solution

from the reservoir bulb was poured back into the electrode bulb and a segment of the curve was reproduced.

The data obtained in this run failed to reproduce those observed in runs on lot II. The shape of the curve very closely paralleled that of the earlier runs, however, the conductance values were greater by a factor of about two.

The residue after evaporation of sulfur dioxide was a dark brown amorphous semi-solid.

Run Hexa VI-b-2

This run produced conductances which were somewhat higher than those obtained in the previous run. The cell developed a leak after the first dilution and unstable resistance values resulted. The conductance of the initial point was in fair agreement with the comparable data from the previous run.

Run Hexa VI-b-3

Cell leakage again interfered in the measurements, however, the initial conductance value was in fair agreement with other runs on this lot of hexaphenylethane.

Run Hexa VI-C-1

This run proceeded smoothly and stable resistance values were obtained at each dilution. The data obtained however, were lower by a factor of two than comparable values from other runs on the same lot.

Run Hexa VI-d-1

The sample bulb was sealed to the cell in the usual manner under darkroom conditions. The cell was pumped for sixteen hours after which the sulfur dioxide was introduced into the line. The solvent was degassed by pumping for one hour at -78°C. The bulb was then broken and the purified sulfur dioxide distilled into the cell. The cell was sealed off and the run was carried out.

The solution was essentially nonconducting.

Run Hexa VI-d-2

In this run the solvent was purified by degassing for four hours followed by several distillations within the closed cell. In this way a specific conductance of 1×10^{-7} mhos-cm. was obtained for the pure solvent before sample dissolution. The sample bulb was then broken and the homogeneous solution failed to conduct. The increased degassing period employed in this run produced resistance values for the solution which were greater by a factor of four than those obtained with a one hour degassing period in the previous run. The color of the solution was lemon yellow and was not unlike that observed in solutions of hexaphenylethane in organic solvents. The solid residue in the residue bulb of the cell was bright yellow and crystalline.

Irradiation Experiment: Run VI-d-2:

At a dilution of 6750 liters per mole the cell was transfered to an ice-water thermostat and the solution was irradiated with a Burton mercury vapor lamp. After about ten hours of continuous irradiation the resistance of the solution decreased from 200,000 ohms to a stable value of 30,000 ohms. This tenfold resistance change was accompanied by a change in color from bright yellow to amber. Thus evidence is provided that solutions of hexaphenylethane prepared in oxygen free sulfur dioxide undergo a photochemical transformation leading to the production of ionic products.

The results obtained in the irradiation of this non-conducting solution are summarized in table 3-V.

Run Hexa VI-b-4

This run was set up in the usual manner with the following exception. About 1 gram of hexaphenylethane was placed in the reservoir bulb of the cell before the initial pumping procedure. The cell was pumped for sixteen hours after which the line trap was filled with liquid sulfur dioxide . After degassing the solvent for three hours the electrode bulb was filled and the cell was removed from the line. The solvent was poured into the resevoir bulb, which contained hexaphenylethane to be used as a "getter" and then distilled back into the electrode bulb. After introducing and dissolving the sample the conductance of

the solution was determined and found to be about three times that of pure sulfur dioxide.

The residue from this run dissolved in benzene to give a yellow solution which gave a positive Schmidlin Test (114) for free triphenylmethyl. Oxygenation gave a white precipitate which was characterized by mixed melting point and infra-red spectrum as being the expected triphenylmethyl peroxide. These results clearly indicate that in the absence of light hexaphenylethane dissolves in pure sulfur dioxide to give a non-conducting solution containing only free triphenymethyl radical and undissociated hexaphenylethane.

Run Hexa VI-C-2: The Influence of Oxygen

In this run the cell was modified by the addition of a pressurized stopcock on the arm between the residue bulb and the vacuum line. After filling the cell with sulfur dioxide (degassed for two hours) the stopcock was closed and the cell was removed from the line. The sample was introduced and dissolved and the conductivity of the homogeneous yellow solution was measured at $-30^{\circ} \pm 1^{\circ}$C. in a manually controlled dry-ice kerosene thermostat. The cell was returned to the vacuum line and the electrode compartment thermostated at -30°C. in a large dewar. The line was evacuated to the stopcock on the cell and was then filled with one atmosphere of tank oxygen which was dried by passage through four 3.0 x 100cm. columns of magnesium

perchlorate. The stopcock to the cell was then opened and the effect of oxygen on the solution was followed by observing the resistance changes as a function of time. The resistance of the solution changed by a factor of almost one hundred in about two hours. The results summarized below clearly demonstrate that the observed conductance of hexaphenylethane in sulfur dioxide solution is, in the absence of light, due to products formed by a reaction between hexaphenylethane and oxygen and probably involving at least one molecule of solvent.

Table 3-X

The Influence of Oxygen on the Resistance of a Hexaphenylethane Solution in Sulfur Dioxide.

$-30^{\circ} \pm 1^{\circ}C.$

(Run Hexa VI-c-2, 111.7 liters / mole., Light excluded.)

Time (min.)	Resistance (ohms)
	(a)
0 (b)	53560
15	53560
30	38370
35	34870
40	23970
50	12740
53	8790
65	3780
95	2460
135	1160
155	960
170	910
175	880
300	614

(a) Before exposure to oxygen
(b) Oxygen introduced at 16 minutes.

The cell was transferred to the -8.9°C. thermostat and several dilutions were performed. It was not possible to complete this run since the volume of the solution had decreased during the dilutions so that the volume could not be accurately measured.

The solution and the residue from the reaction of oxygen with hexaphenylethane in sulfur dioxide were blood red.

Irradiation Experiment

The cell was transferred to an ice-water thermostat and irradiated with a Burton mercury vapor lamp. Thirty hours of continuous irradiation failed to produce a significant resistance change (see table 3-VI).

Run Hexa VIII-d-1

Sulfur dioxide was purified by degassing for four hours followed by distillation from a solution of hexaphenylethane. After determining the conductivity of the nonconducting solution oxygen was introduced and several dilutions were performed on the oxygenated solution. Again a hundredfold increase in conductivity was noted when oxygen was added to the nonconducting solution. This run was carried out at 0.1°C.

Run Peroxy-I Conductivity of Triphenylmethylperoxide

Triphenylmethylperoxide isolated from lot II was twice recrystallized from hot benzene to give white glistening crystal melting between 186-187°C.

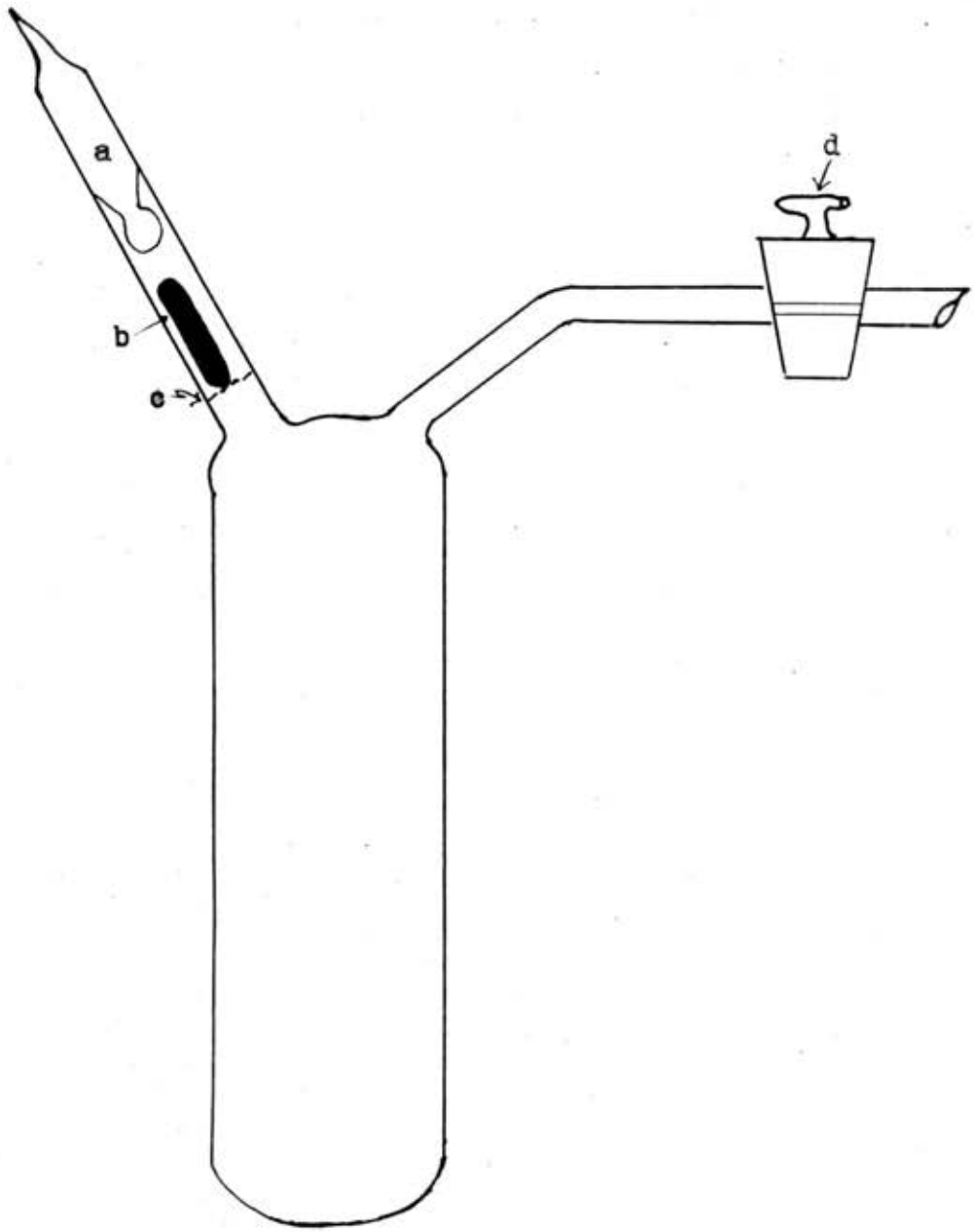
A sample of 3.4 mg. of peroxide failed to dissolve completely in degassed sulfur dioxide (45 ml.). The resistance of the solution remained essentially constant at a value near that of the pure solvent. Throughout the three hour period of observation the solution remained colorless and white solid remained undissolved. It can be concluded from these results that triphenylmethyl peroxide does not form conducting solutions in sulfur dioxide.

Attempt to Determine the Stoichiometry of the Reaction of Hexaphenylethane with oxygen in Liquid Sulfur Dioxide.

One experiment was carried out in an effort to determine the stoichiometry of the reaction between hexaphenylethane and oxygen in sulfur dioxide solution. This work was done under darkroom conditions.

The volume of the vacuum line was determined from the pressure change occuring when a known volume of nitrogen was expanded into an expansion bulb of known volume. A calibrated 1 liter flask was sealed to the vacuum line through a stopcock. The line and expansion bulb were evacuated and after the bulb was isolated by turning the connecting stopcock the line was filled with an atmosphere of nitrogen. The connecting stopcock was then opened and the volume of the vacuum line was calculated from the observed pressure drop. Six determinations afforded a value of 830 $\pm$10 c.c.

A weighed sample of hexaphenylethane (lot VIII-d) was sealed to a reaction bomb as shown in figure 3-XIV. The



Reaction Bomb

FIGURE 3-XIV

a. Sample bulb.

b. Magnetic breaker.

c. Glass grid support for magnetic breaker.

d. Stopcock to vacuum line.

reaction bomb was connected to the vacuum line through a stopcock and a 10/30 ⁸ joint. About 70 ml. of liquid sulfur dioxide (degassed three hours) was condensed into the bomb which was then removed from the line in order to introduce and dissolve the sample. After returning the bomb to the calibrated vacuum line the line was evacuated and filled with a positive pressure of dry oxygen. The stopcock to the bomb was then opened and the reaction was allowed to proceed at 0°C. until a constant pressure was observed. The bomb was then thermostated at -60°C. and the final equilibrium pressure was recorded. The volume of oxygen reacted and dissolved in the solvent was calculated from the observed pressure drop as follows.

P_i = 1148 mm., V_i = 830 cc., (pressure and volume before reaction.)

P_f = 975 mm. V_f = 830 + 120 cc., (pressure and volume of system after reaction.)

V_r = volume reacted.

V_s = volume dissolved.

$$975(950 + V_r + V_s) = 1148 \times 830$$

$$V_r + V_s = 34.2 \text{ cc. at } 771 \text{ mm. and } 23°C.$$

A solubility correction was applied to the total apparent volume change as follows: The solution containing the reaction products was degassed for two hours at -78°C. The bomb was isolated and the line was again filled with oxygen. The volume of oxygen dissolved by the solution was calculated from the pressure drop observed when the bomb was

opened to the vacuum line.

P_i = 1147 mm. V_i = 830 cc. (pressure and volume before solubility experiment)

P_f = 1000 mm. V_f = 950 cc. (pressure and volume after solubility experiment)

V_s = volume of oxygen dissolved by the solution.

The volume of oxygen dissolved in the solution was calculated as follows:

$$1000(950 + V_s) = 1147 \times 830$$

$$V_s = 2.6 \text{ cc. at 771 mm. and 23°C.}$$

The volume of oxygen reacted with 0.958 gms. (0.00197 m.) of hexaphenylethane was calculated as the difference between the apparent uptake observed in carrying out the reaction and that observed in the solubility experiment.

$$V_r = 34.2 - 2.6 = 31.2 = 29.2 \text{ cc. S.T.P.}$$

This value corresponds to 0.7 mole oxygen per mole hexaphenylethane assuming the ethane to be 90% pure as was indicated by quantitative oxygenation by the method of Lichtin and Thomas.

It should be noted that the value obtained for the solubility correction (2.6 cc.) is in fair agreement with the value of 12-50 cc./100 gms. of sulfur dioxide found by Dornte and Ferguson (see table 3-VII).

In order to obtain a more reliable value of V_r the experiment should be carried out using larger samples of hexaphenylethane. Since larger samples were not available,

the experiment was not repeated and the observed value must be considered as indicating that approximately one mole of oxygen has reacted per mole of hexaphenylethane.

The sulfur dioxide was removed from the bomb and the blood red residue was pumped for twelve hours. When exposed to the atmosphere the color changed from red to dirty brown. A sample of this material was submitted to analysis, however, since the material contained glass fragments from the sample bulb the analytical results are unreliable.

Attempted separation of the Reaction Product

The blood red material was insoluble in the following solvents: petroleum ether, methylcyclohexane, carbon tetrachloride, benzene, toluene and chloroform. Yellow solutions were obtained in methanol, ethanol, acetone and ether, however crystallization could not be effected from these solvents. Addition of water to an alcoholic or acetone solution produced an essentially white curdy precipitate which melted over a wide range between 120° - 150°C. This material gave a positive Bowden test for triarylcarbinol, however, it was not possible to isolate a pure compound.

Crystallization from Acetic Acid.

About 0.2 gms. of the red material was dissolved in 2 ml of glacial acetic acid to give a blood red solution. The solution was solidified by cooling to -78°C. and the resulting solid was triturated with 3 ml. of dry petroleum ether. When warmed slowly to room temperature a yellow

solid remained. This was filtered onto a sintered glass funnel, washed with cold dry petroleum ether and air dried to afford a dry yellow powder which melted sharply between 122-124°C. to give a blood red melt. Sodium fusion on a ten mg. sample of this material afforded a positive test for sulfur.

The yellow solid which was dried overnight under vacuum before being submitted to analysis, decomposed to form a brown solid which melted between 80°- 110°C. Analysis of the decomposed material was as follows:

Analysis: Found: C; 67.7%. H; 5.4%. S; 5.9% O*; 21%.

This corresponds to $C_{31}H_{29}SO_7$ and obviously is not an analysis of a pure compound.

Further work on the separation or identification of the reaction products was not attempted.

(*) By difference.

APPENDIX

TABLE OF CONTENTS

APPENDIX I-A

GLOSSARY OF SYMBOLS

All symbols used in the preparation of this dissertation were chosen to conform with the convention adopted by Harned and Owen (59).

A, empirical coefficients.

a_1, a_2.. activities of components indicated.

$\mathring{a}$, distance of approach of ions in ion pair formation.

a, coefficients of empirical equations.

b, characteristic parameter, Bjerrum's theory of ion pair formation.

C, coefficient of empirical equations.

c, molar concentration in moles per liter of solution.

D, dielectric constant of solvent.

d( ) complete differential.

e, base of natural logarithm.

Ei( ), exponential integral function.

F°, standard free energy.

F(z), special function of Fuoss conductance equation.

$f_{\pm}$, mean rational activity coefficient.

H°, standard heat content, enthalpy.

K, equilibrium constant.

K_A, acid ionization constant

$K_{exp.}$ Dissociation constant obtained from conductance data.

K_1, calculated ionization constant for trityl halides.

K_2, calculated ion pair dissociation constant.

K_1', first dissociation constant of a 2-1 electrolyte.

K_2', second dissociation constant of a 2-1 electrolyte.

k, Boltzmann constant.

k_1, k_0, kinetic constants.

L, coefficient in empirical equation for the dielectric constant of liquid sulfur dioxide.

N, Avogadro's number.

pH($\equiv \log 1/aH^+$)

pK_A($\equiv \log 1/K_A$)

Q(b), function in theory of ion pair formation.

q*, function in theory of irreversible processes.

R, gas constant per mole.

r, distance.

r_+, r_-, r_i, r_j, ionic radii of indicated species.

S, entropy.

$\mathcal{S}$( ), limiting theoretical slopes for quantities indicated.

S(z), special function of Shedlovsky conductance equation.

T(°K) absolute temperature.

T(°C) centigrade temperature.

V, dilution in liters per mole.

z, Shedlovsky variable.

Z_1, Z_2, valences of ions indicated.

$|Z_1|$, $|Z_2|$, magnitudes of valence of ions indicated.

α^*, coefficient of conductance equation.

β^*, coefficient of conductance equation.

γ, conventional activity coefficients.

Δ ( ), finite change in quantity ( ).

∂ ( ), partial differential.

ϵ, electronic charge.

η, viscosity of solvent.

θ, degree of dissociation.

Λ, equivalent conductance of electrolyte.

Λ_o, equivalent conductance of electrolyte at infinite dilution.

λ_+, λ_-, equivalent conductances of ions indicated.

ν_+, ν_-, number of cations, anions produced by dissociation of one molecule of electrolyte.

$\nu (\equiv \nu_+ + \nu_-)$

π (= 3.1416)

ρ, Reaction parameter in Hammett equation.

Σ, summation.

σ, substituent parameter in Hammett equation.

σ^*, substituent parameter in which direct resonance interactions are possible.

APPENDIX I-B

Tables of Experimental Conductivity Data Described in Part I.

Table	Compound	Temperature
I-A	Potassium Chloride	0.12°C.
I-B	Potassium Chloride	-8.93°C.
I-C	Potassium Bromide	0.12°C.
I-D	Potassium Bromide	-8.93°C.
I-E	Potassium Iodide	0.12°C.
I-F	Potassium Iodide	-8.93°C.
I-G	Tetramethylammonium Bromide	0.12°C.
I-H	Tetramethylammonium Bromide	-8.93°C.
I-J	" Sulfate	0.12°C.
I-K	Franklin's data for KBr and KI at 10°, 0°, -10°, -20° and -33.5°C.	
I-L	Potassium Iodide (Data not used in calculations.)	-8.93°C.

TABLE I-A

Conductivity of Potassium Chloride in Sulfur Dioxide Solution.

0.12°C.

V liters/mole	k x 10^{6} (a) mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-30) (b,c)	
2888	33.91	97.93
6602	19.30	127.4
15090	10.54	159.0
34540	5.420	187.2
79170	2.678	212.0
181500	1.268	230.1
416500	0.602	250.5
	(Run HL-31) (b,d)	
2972	33.35	99.12
6821	18.91	129.0
15640	10.26	160.5
35860	5.285	189.5
82230	2.590	213.0
188600	1.250	235.8
433800	0.571	247.9

(a) Sample introduced as an aliquot of a standard aqueous solution.

(b) Corrected for solvent conductance.

(c) $k_{SO_2} = 2.080 \times 10^{-7}$ mhos-cm.$^{-1}$.

(d) $k_{SO_2} = 1.525 \times 10^{-7}$ mhos-cm.$^{-1}$.

TABLE I-B

Conductivity of Potassium Chloride in Sulfur Dioxide Solution.

-8.93°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-25)(a,b)	
1934	46.34	89.62
4452	26.27	117.0
10260	14.22	145.9
23670	7.317	173.2
54510	3.542	193.1
125600	1.665	209.1
289400	0.855	247.3
	(Run HL-26)(a,c)	
2742	36.94	101.3
6309	20.61	130.0
14490	10.97	159.0
33430	5.528	184.8
76890	2.659	204.4
177000	1.252	221.5
406600	0.590	239.7

(a) Sample weighed on micro balance.

(b) $k_{SO_2} = 1.230 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c) $k_{SO_2} = 1.680 \times 10^{-7}$ mhos-cm.$^{-1}$.

(Table I-B. (Cont.)).

V liters / mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2} / mole
	(Run HL-28)[a,b]	
2993	34.20	102.3
6773	19.18	129.9
15360	10.23	157.1
34730	5.158	179.1
78710	2.494	196.3
177800	1.180	209.8
403100	0.574	231.4
	(Run HL-29)[a,c]	
3873	28.79	111.5
8904	15.64	139.3
20500	8.077	165.6
47210	3.987	188.2
108800	1.939	211.0
251900	0.913	230.0
582600	0.436	254.1

(a) Sample introduced as an aliquot of a standard aqueous solution.

(b) $k_{SO_2} = 1.916 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c) $k_{SO_2} = 1.898 \times 10^{-7}$ mhos-cm.$^{-1}$.

TABLE I-C

Conductivity of Potassium Bromide in Sulfur Dioxide Solution.

0.12°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-66)(a,b)	
228.9	236.6	54.16
525.6	139.0	73.06
1208	80.17	96.84
2777	45.16	125.4
6393	24.43	156.2
14720	12.67	186.5
33900	6.172	209.2
78070	2.884	225.2
179800	1.279	230.0
	(Run HL-68)(a,c)	
156.4	304.3	47.59
359.7	176.7	63.56
825.9	102.2	84.41
1898	58.88	111.8
4365	32.57	142.2
10040	17.37	174.4
23090	8.752	202.1
53180	4.217	224.3

(a) The sulfur dioxide was degassed at -78°C. for two hours.

(b) $k_{SO_2} = 2.208 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c) $k_{SO_2} = 1.979 \times 10^{-7}$, mhos-cm.$^{-1}$.

TABLE I-D

Conductivity of Potassium Bromide in Sulfur Dioxide Solution.

-8.93°C.

V liters/mole	$k \times 10^6$ mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-67)[a,b]	
225.6	252.1	56.87
516.8	146.7	75.81
1187	83.41	99.01
2729	46.35	126.5
6309	24.48	154.4
14500	12.42	180.1
33410	5.940	198.4
76860	2.730	209.8
176500	1.199	211.6
	(Run HL-69)[a,c]	
154.6	321.0	49.63
355.4	185.3	65.86
815.6	106.6	86.94
1874	60.65	113.7
4310	32.96	142.0
9925	17.18	170.5
22810	8.470	193.2
52610	3.990	209.9

(a) The sulfur dioxide was degassed at -78°C. for two hours.

(b) $k_{SO_2} = 2.094 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c)n $k_{SO_2} = 1.749 \times 10^{-7}$ mhos-cm.$^{-1}$.

TABLE I-E

Conductivity of Potassium Iodide in Sulfur Dioxide Solution.

0.12°C.

V $\frac{\text{liters}}{\text{mole}}$	k x 10^6 mhos-cm.$^{-1}$	Λ $\frac{\text{mhos-cm.}^2}{\text{mole}}$
	(Run HL-32)[a]	
159.2	435.3	69.30
361.5	243.5	88.02
820.6	136.0	111.6
1863	74.37	138.6
4231	39.38	166.6
9626	20.17	194.2
21920	9.760	213.9
49930	4.567	228.1
113800	2.113	240.5
	(Run HL-33)[b]	
358.4	245.9	88.13
819.7	136.5	111.9
1875	74.22	139.2
4298	38.96	167.4
9851	19.56	193.0
22550	9.373	211.4
51680	4.338	224.2
118600	1.984	235.3
272300	0.893	243.2

(a) $k_{SO_2} = 3.262 \times 10^{-7}$ mhos-cm.$^{-1}$.

(b) $k_{SO_2} = 1.522 \times 10^{-7}$ mhos-cm.$^{-1}$.

(Table I-E., Cont.)

V $\frac{\text{liters}}{\text{mole}}$	$k \times 10^6$ mhos-cm.$^{-1}$	Λ $\frac{\text{mhos-cm.}^2}{\text{mole}}$
	(Run HL-62)(a,b)	
420.2	214.8	90.26
961.4	120.3	115.7
2200	65.89	145.0
5036	34.55	174.0
11520	17.27	199.0
26350	8.269	217.9
60580	3.813	231.0
139200	1.718	239.1

(a) The sulfur dioxide was degassed at -78°C. for two hours.

(b) $k_{SO_2} = 8.96 \times 10^{-8}$ mhos-cm.$^{-1}$.

TABLE I-F

Conductivity of Potassium Iodide in Sulfur Dioxide Solution.

-8.93°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-75)[a,b]	
190.6	372.1	70.92
436.3	210.9	92.02
998.7	116.4	116.2
2286	62.40	142.6
5235	32.07	167.9
12010	15.66	188.1
27550	7.312	201.4
63170	3.315	209.4
	(Run HL-76)[c,d]	
181.7	381.6	69.34
415.5	216.8	90.08
950.2	121.2	115.2
2173	65.94	143.3
4967	33.86	168.2
11360	16.58	188.3
26000	7.744	201.3
59460	3.520	209.3

(a) The sulfur dioxide was degassed for 1.75 hours.

(b) $k_{SO_2} = 1.334 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c) The sulfur dioxide was degassed for 1.25 hours.

(d) $k_{SO_2} = 1.892 \times 10^{-7}$ mhos-cm.$^{-1}$.

TABLE I-G

Conductivity of Tetramethylammonium Bromide in Sulfur Dioxide Solution.

0.12°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-70)[a,b]	
361.4	371.1	134.1
832.3	189.0	157.3
1915	94.18	180.4
4403	45.30	199.5
10130	21.10	213.7
23310	9.536	222.3
53800	4.222	227.1
124000	1.886	233.9
	(Run HL-72)[c,d]	
312.6	416.5	130.2
713.4	216.4	154.4
1623	108.7	176.4
3691	53.32	196.8
8397	25.16	211.3
19120	11.58	221.4
43480	5.361	233.1
99000	2.362	233.7

(a) The sulfur dioxide was degassed at -78°C. for 0.75 hours.

(b) $k_{SO_2} = 1.385 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c) The sulfur dioxide was degassed for 1.3 hours.

(d) $k_{SO_2} = 1.000 \times 10^{-7}$ mhos-cm.$^{-1}$.

TABLE I-H

Conductivity of Tetramethylammonium Bromide in Sulfur Dioxide Solution.

-8.93°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-71)(a,b)	
358.0	353.1	126.4
824.5	180.7	149.0
1897	89.10	169.0
4361	42.59	185.7
10030	19.60	196.6
23080	8.844	204.1
53270	3.915	208.6
122800	1.739	213.5
	(Run HL-73)(c,d)	
309.8	394.6	122.3
707.0	207.3	146.6
1608	102.9	165.5
3657	449.99	182.8
8320	23.42	194.9
18940	10.72	203.0
43070	4.936	212.6
98070	2.172	213.0

(a) The sulfur dioxide was degassed for 0.75 hours.

(b) $k_{SO_2} = 1.237 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c) The sulfur dioxide was degassed for 1.3 hours.

(d) $k_{SO_2} = 1.000 \times 10^{-7}$ mhos-cm.$^{-1}$.

TABLE I-J

Conductivity of Tetramethylammonium Sulfate in Sulfur Dioxide Solution.

0.12°C.

V liters/mole	$k \times 10^6$ mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-77)[a]	
170.0	292.4	49.71
387.2	164.2	63.58
882.7	90.69	80.05
2013	49.21	99.06
4590	25.72	118.0
10470	13.02	136.3
23870	6.547	156.3
54450	3.511	191.2
124100	2.102	260.8
	(Run HL-78)[b]	
315.2	190.7	60.11
722.1	106.4	76.83
1656	57.90	95.88
3797	30.52	115.9
8706	15.54	135.3
19950	7.749	154.6
45760	3.988	182.5
104900	2.207	231.5
240500	1.263	303.8

(a) $k_{SO_2} = 2.812 \times 10^{-7}$ mhos-cm.$^{-1}$.

(b) $k_{SO_2} = 1.924 \times 10^{-7}$ mhos-cm.$^{-1}$.

TABLE I-K

Conductivity in Liquid Sulfur Dioxide.

Data of Franklin (38) used for Shedlovsky and Bjerrum Calculations.

V liters / mole	Λ mhos-cm.^{2}/mole -33.5°C.	-20.0°C.	-10.0°C.	0.0°C.	10.0°C.
		Potassium Iodide			
1000	108.6	115.2	118.8	119.4	117.7
1500	117.7	125.8	131.5	132.7	132.3
2000	124.2	133.0	140.5	142.3	142.3
3000	133.0	143.7	153.7	156.5	157.7
4000	139.0	151.0	162.5	166.3	168.7
6000	147.5	161.5	174.2	179.5	185.0
8000	153.0	168.5	181.8	189.0	196.0
12000	159.5	178.0	192.0	202.0	212.5
		Potassium Bromide			
1000	94.7	97.7	96.0	92.5	86.7
1500	105.4	109.2	108.5	106.0	100.4
2000	113.3	117.4	118.0	116.2	110.3
3000	124.5	129.4	132.3	131.5	127.0
4000	132.0	138.0	142.3	142.5	139.3
4800	137.0	144.0	148.3	149.5	147.8

TABLE I-L (a)

Conductivity of Potassium Iodide in Liquid Sulfur Dioxide at -8.93°C.

V liters / mole	$k \times 10^6$ mhos-cm.$^{-1}$	Λ mhos-cm.^{2} / mole
	(Run HL-34) (b)	
282.7	294.8	83.40
643.4	163.7	105.3
1471	87.07	128.1
3338	45.03	150.3
7604	21.96	167.0
17360	9.930	172.4
39630	4.424	175.3
90400	2.000	180.8
	(Run HL-35) (c)	
334.8	260.9	87.35
760.0	142.8	108.5
1728	75.19	129.9
3924	37.14	145.7
8911	17.72	157.9
20270	8.538	173.1
46260	2.865	132.5
105600	1.069	112.9
	(Run HL-36) (d)	
315.0	274.0	86.31
716.0	150.7	107.9
1632	80.95	132.1
3727	41.66	155.3
8494	20.31	172.5
19350	9.380	181.5
44290	4.133	183.0
101400	1.807	183.2

(a) These data were not used in the calculations.
(b) (c) (d) k_{SO_2} = 6.41, 6.85, 6.54 x 10^{-7} mhos-cm.$^{-1}$ respectively.

APPENDIX I-C

ELECTROLYTES OF HIGHER VALENCE TYPE

Introduction

Since the conductivity data obtained from solutions of hexaphenylethane in liquid sulfur dioxide (Part III) did not lend themselves to interpretations characteristic of normal uni-univalent electrolytes, it became of interest to compare these data with data obtained from electrolytes of higher valence type in this solvent. The behavior of hexaphenylethane could be interpreted in terms of the behavior expected for 2-1 salts in solvents of low dielectric constant. Indeed the results were found to be qualitatively similar to those for barium nitrate in liquid ammonia solution.

Data for 2-1 salts in liquid sulfur dioxide solution are not available in the literature with the exception of data for several salts over a limited dilution range (75). Therefore the conductivity of tetramethylammonium sulfate was measured at 0.12°C. over the dilution range 10^2 to 2×10^5 liters per mole.

Scope of this Investigation

This investigation was not intended to give a quantitative measure of the equilibrium constants or of the limiting equivalent conductance of this salt. Only a qualitative description of the behavior characteristic of 2-1 salts in

solvents of low dielectric constant was desired. Therefore, the data obtained were treated in an approximate manner to produce a conductance curve which was unlike those obtained by the same treatment of uni-univalent electrolytes. This curve is then considered to be characteristic for 2-1 salts and it was furthermore found that the shape of the curve was explicable on the basis of a stepwise dissociation process.

In order to further test the generality of the observed behavior, Franklin's (40) data for barium nitrate in liquid ammonia solution were treated by the same method. From these data a curve was obtained which was in every way similar to those obtained for tetramethylammonium sulfate in liquid sulfur dioxide solution. It has been shown (Part III) that similar behavior is observed in the conducting solutions of hexaphenylethane in liquid sulfur dioxide. This observation is suggestive, if not indicative, that the conducting species formed in this complex system can be assigned to the class of 2-1 electrolytes.

Results and Discussion

Solution of the Onsager limiting law for electrolytic conductance, and of the extrapolation procedures of Fuoss and Kraus (41) or of Shedlovsky (117) based on the Onsager theory, requires a knowledge of the transference numbers or of the limiting ionic mobilities of the ions formed on dissociation of the electrolyte. In the special case of symmetrical

uni-univalent electrolytes the expressions are simplified, since this property of the ions can be exactly cancelled in the expression, (equation 1-6)

$$q^* = \frac{|z_1 z_2|(\lambda_1^\circ + \lambda_2^\circ)}{(|z_1| + |z_2|)(|z_1|\lambda_1^\circ + |z_2|\lambda_2^\circ)} \qquad (1\text{-}6$$

which, in this special case becomes equal to 0.5. Unfortunately, this simplification is not possible in general and, in the case of unsymmetrical 2-1 electrolytes a knowledge of the limiting ionic conductivities is required.

Since ionic mobility data are not available for liquid sulfur dioxide solutions, the available extrapolation procedures cannot be applied to data for 2-1 salts in this medium. Estimations of ionic mobilities could be attempted by intuititive guesswork and by application of such approximations as are possible from Walden's Rule (127) or Stokes Law (62). Efforts in this direction would merely be an indication of the patience of the investigator and therefore a wholely empirical approach offers the advantages of simplicity as well as results of equal qualitative value.

Stepwise Dissociation of 2-1 Salts

A 2-1 electrolyte in solutions of low dielectric constant will dissociate according to the following equations

$$M_2A \xrightleftharpoons{K_1'} M^+ + MA^- \qquad (1\text{-}52$$

$$MA^- \xrightleftharpoons{K_2'} M^+ + A^{--} \qquad (1\text{-}53$$

The overall dissociation will be the algebraic sum of equations 1-52 and 1-53, namely,

$$M_2A \xrightleftharpoons{K_{exp.}} 2M^+ + A^{--} \qquad (1\text{-}54$$

It is more profitable for the present purposes to consider the two steps as essentially independent processes. This in effect will be a good approximation when $K_1' \gg K_2'$ in which case the first step of the dissociation will be essentially complete at a concentration at which the second step has not yet begun to contribute significantly to the observed conductance of the salt. It is possible to deduce several qualitative features of the conductance vs. dilution curve for such a system.

Considering the first step only we would expect a curve similar to that found for normal 1-1 electrolytes. The conductance will rapidly approach its limiting value since K_1' should be large, possibly of the order of 10^{-3}. In the case of tetramethylammonium sulfate the limiting conductance of the ions formed in the first dissociation should be rather low due to the large size of the ions. A value of Λ_o of about 200 would not seem unreasonable for the ions $(CH_3)_4NSO_4^-$ and $(CH_3)_4N^+$.

The curve for the first step of the dissociation process would be expected to follow the behavior of a normal 1-1 electrolyte. In figure 1-XVIII the data for tetramethylammonium sulfate up to a dilution of 20,000 liters per mole are compared to the data for tetramethylammonium bromide. The broken line represents the behavior expected if the second dissociation would not occur in the 2-1 salt. It can be seen from this plot that up to about 20,000 liters per mole the conductance behavior of tetramethylammonium sulfate is similar to that for a simple 1-1 electrolyte. It is apparent, therefore, that the data for this salt up to 20,000 liters per mole can be treated by the Shedlovsky extrapolation method to produce an approximate value for the first dissociation constant. Figure 1-XIX shows the results of the application of Shedlovsky's method to these data. Λ_o assumed for this calculation was 200 which is in fair agreement with the value of 180 obtained from the extrapolation. Recalculation to obtain better agreement was not considered necessary in view of the approximations involved. Franklin's (40) data for barium nitrate in liquid ammonia solution were treated in the same manner in order to afford a further test of the approximate treatment. In this case Λ_o was assumed to be exactly twice the known (39) value of 171 for the nitrate ion in this medium. Only data up to 15,000 liters per mole were used in the calculation upon which figure 1-XX is based. The treatment appears to hold fairly well for both cases tested.

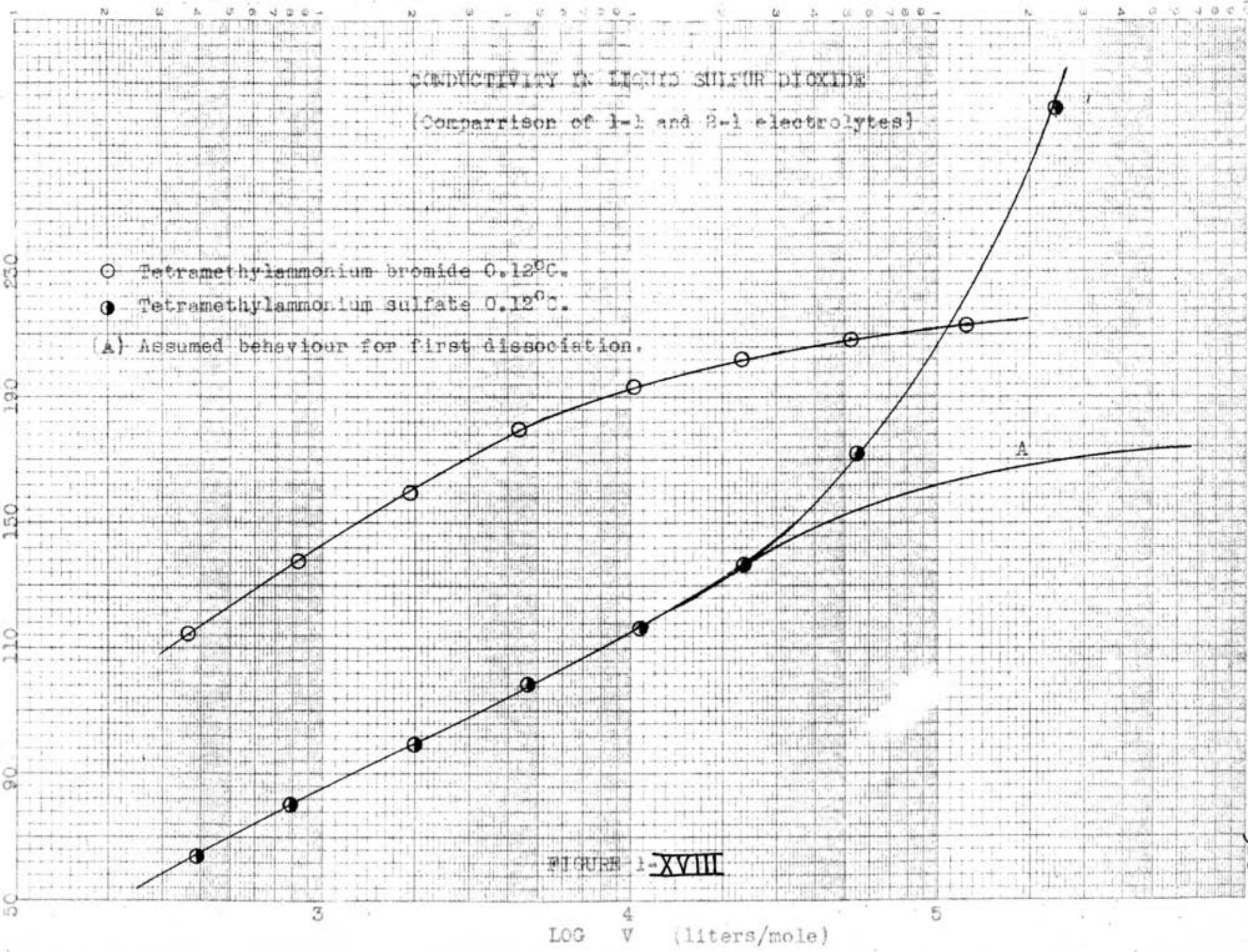


FIGURE 1-XVIII

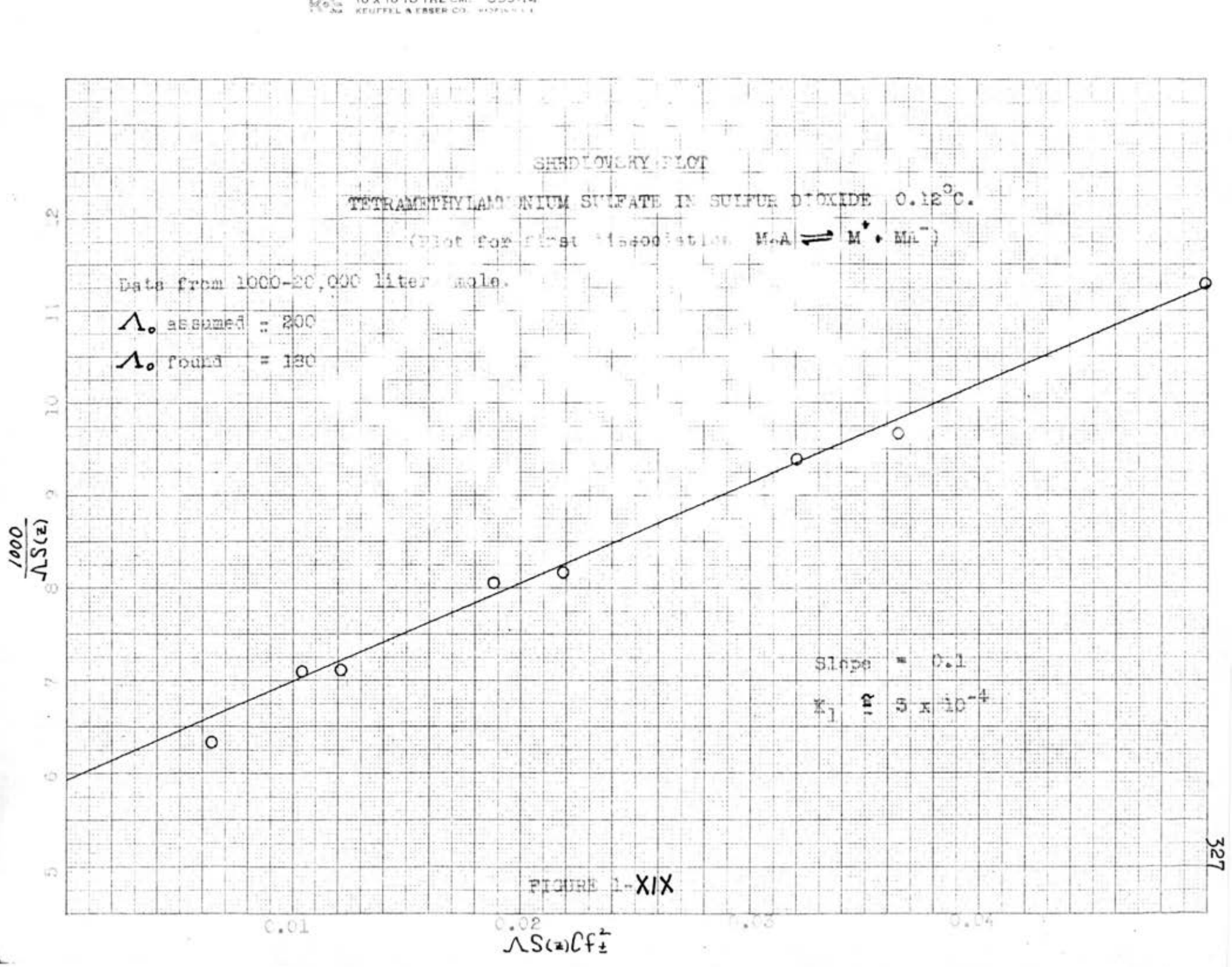

SHEDLOVSKY PLOT
TETRAMETHYLAMMONIUM SULFATE IN SULFUR DIOXIDE 0.12°C.
(Plot for first dissociation M·A ⇌ M⁺ + M⁻)
Data from 1000-20,000 liter mole.
Λ₀ assumed = 200
Λ₀ found = 130
Slope = 0.1
K₁ = 5 x 10⁻⁴
1000/ΛS(z)
ΛS(z)Cf±²
0.01
0.02
0.03
0.04
5
6
7
8
9
10
11
12

FIGURE 1-XIX

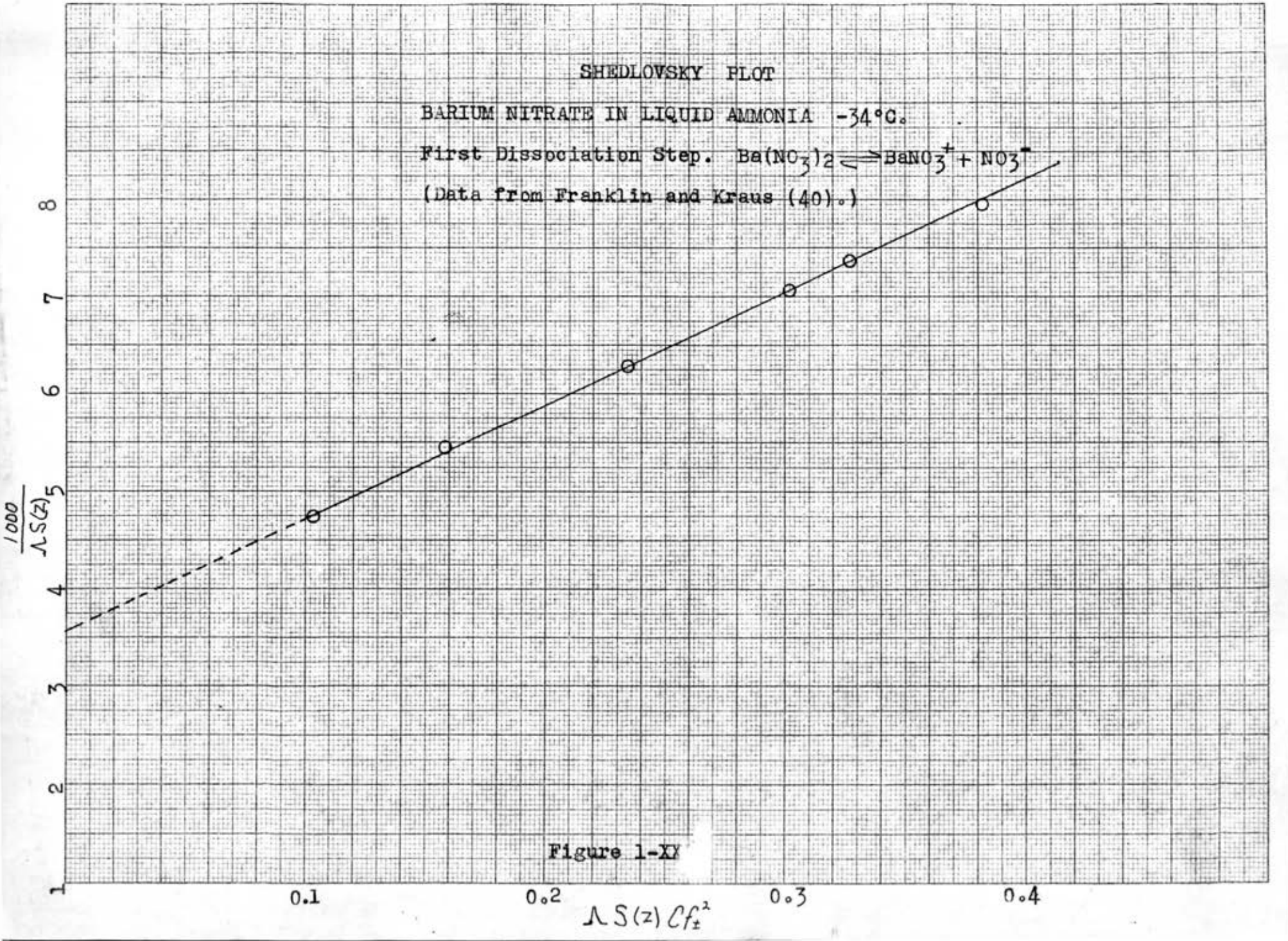


Figure 1-XX

The second step of the dissociation process is somewhat more complicated. As a first approximation to the solution of the problem we may consider the second step by itself as merely another 1-1 dissociation as follows: If we neglect the charge on the MA^- ion, the dissociation can be depicted as a 1-1 dissociation as follows:

$$(MA^-) \rightleftharpoons M^+ + (A^-)$$

Actually this will differ from normal 1-1 electrolyte behavior in two respects. First, the double charge on one of the ions will require a modification in the activity coefficient calculated by the Debye-Huckle limiting law. A valence correction can easily be incorporated into the limiting law, however, such refinement is not necessary in the present system since the qualitative results will not suffer from its omission.

The second effect, due to the presence of a doubly charged ion, will be reflected in the mobility terms. The mobility of the divalent ion will be considerably larger than any observed for univalent ions. Therefore the conductivity of the solution will be expected to increase rapidly even though the dissociation constant in this case is very small.

If we consider the ion MA^- to be a 1-1 electrolyte whose dissociation constant is so small that it can be considered to be essentially undissociated at concentrations greater than 5×10^{-5} moles per liter, and neglect the conductance due to the

presence of this ion and its gegen ion, we would expect the conductivity curve to be similar to that for an extremely weak 1-1 electrolyte. Figure 1-XXI shows curves representative of (1) a strong 1-1 electrolyte, (2) a very weak 1-1 electrolyte and (3) the algebraic sum of curves 1 and 2.

It can be seen that curve 3 is qualitatively similar to the curves observed for 2-1 electrolytes in liquid ammonia and in liquid sulfur dioxide.

On the basis of the assumptions made concerning the second dissociation step it should be possible to apply the Shedlovsky treatment for 1-1 electrolytes to the high dilution data for 2-1 electrolytes in order to estimate the equilibrium constants and limiting conductance values. Figure 1-XXII shows the Shedlovsky plot obtained from the data of tetramethylammonium sulfate at dilutions greater than 20,000 liters per mole with Λ_o assumed to be equal to 450 mhos-cm.^{2}/mole. The plot shows fairly good agreement in the high dilution region in so far as adherence to linearity is concerned.

Dissociation constants

The first and second dissociation constants were not evaluated for the salts considered in this work. In view of the approximations employed, constants obtained from this treatment would be of doubtful value. It is possible, however, to note that constants which can be obtained from these Shedlovsky plots are of reasonable magnitude and in both cases the second dissociation constant is much smaller than the first,

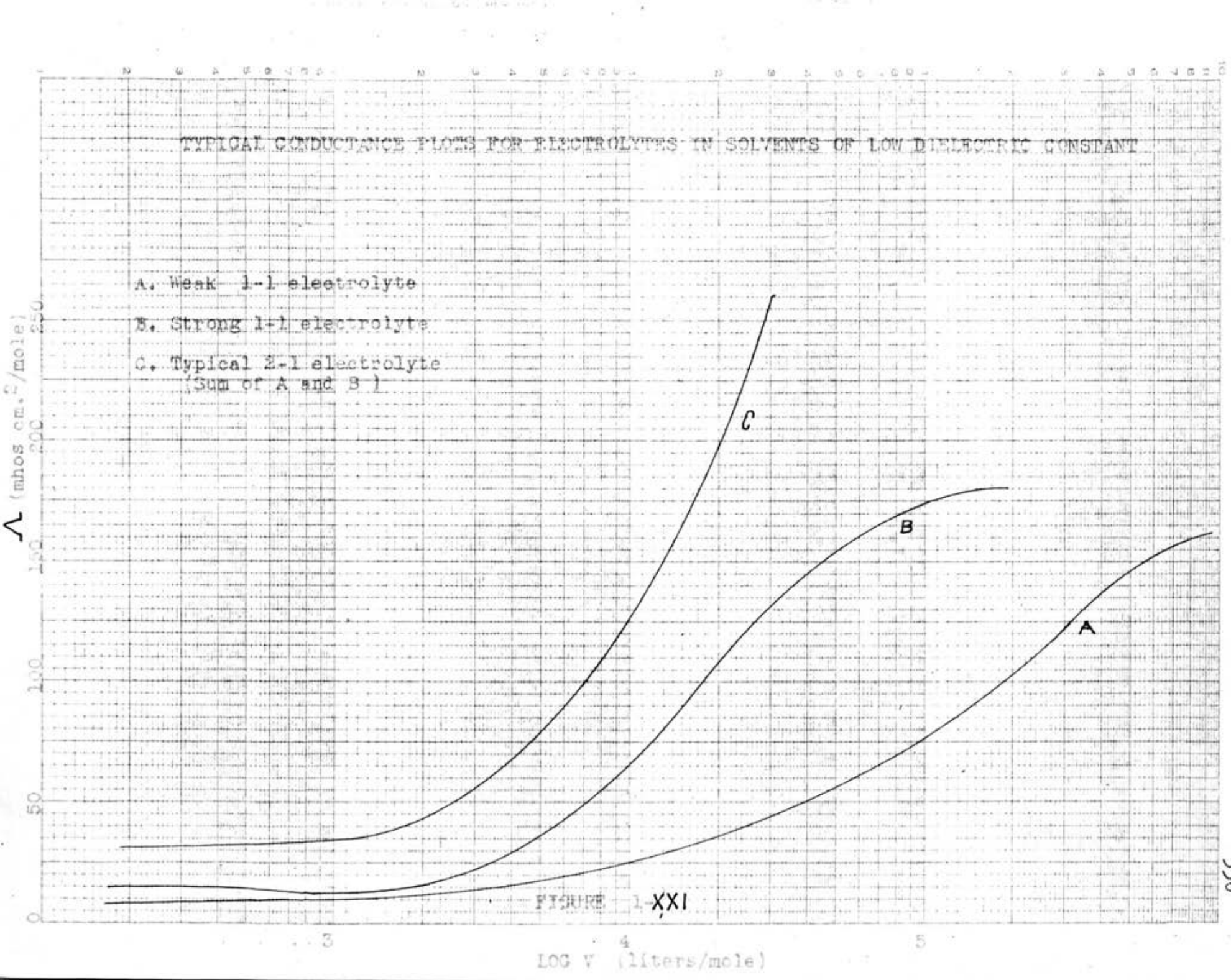

TYPICAL CONDUCTANCE PLOTS FOR ELECTROLYTES IN SOLVENTS OF LOW DIELECTRIC CONSTANT
A. Weak 1-1 electrolyte
B. Strong 1-1 electrolyte
C. Typical 2-1 electrolyte
(Sum of A and B)
C
B
A
Λ (mhos cm.²/mole)
0
50
100
200
250
3
4
5
LOG V (liters/mole)

FIGURE 1-XXI

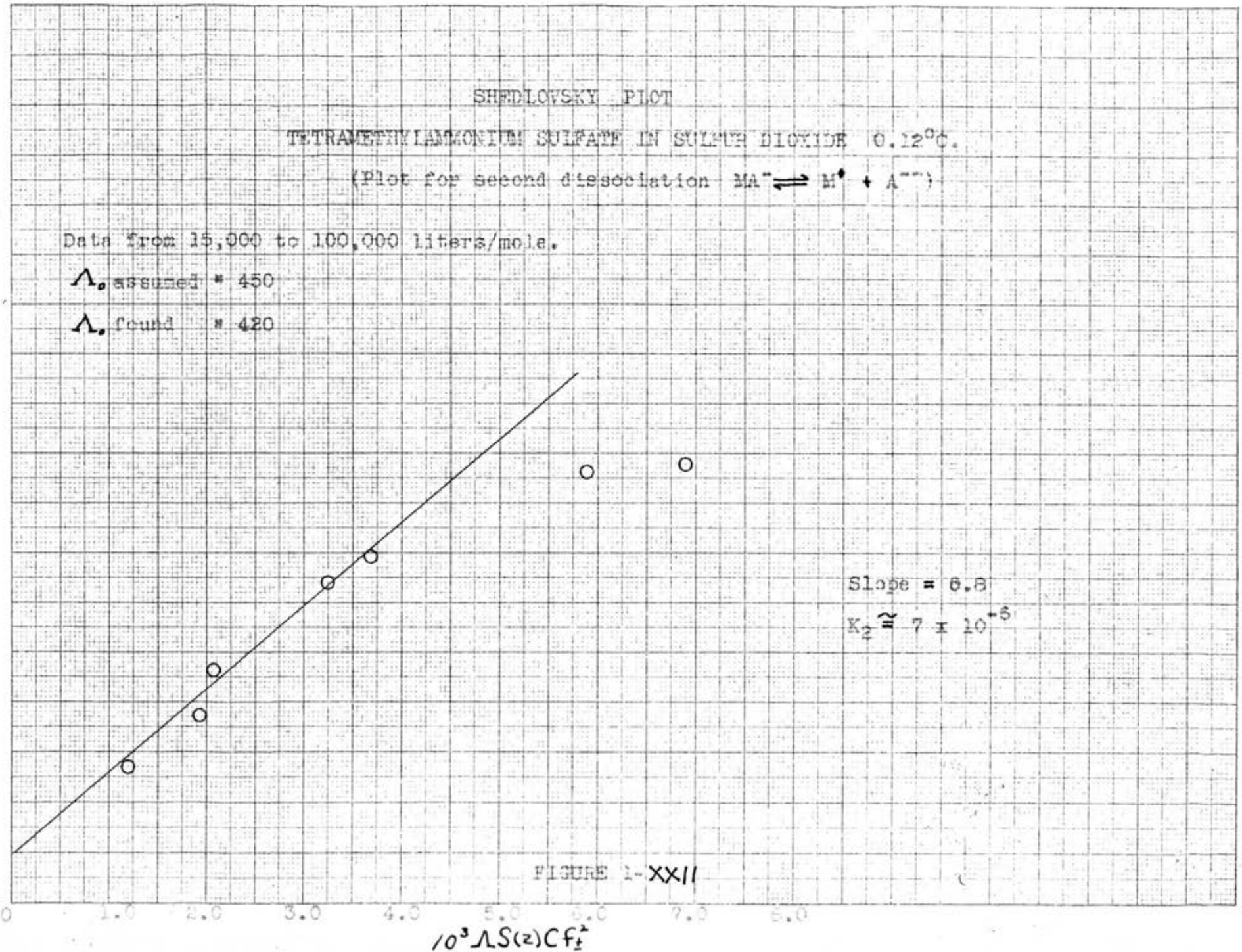


FIGURE 1-XXII

is as should be expected.

Theoretical Considerations

In view of the results obtained from the application of Bjerrum's theory to electrolytes in liquid sulfur dioxide it may be possible to calculate the first and second dissociation constants for 2-1 salts by this method if reasonable assumptions can be made concerning the distance of closest approach. Reasonable results may be expected at least in the case of the first dissociation step. Since, however, there is at present no independent method for checking the results which could be obtained, it would hardly be profitable to use this approach to the problem. The only valid approach requires the knowledge of limiting ionic mobilities in this medium and until such data become available further analysis of unsymmetrical electrolyte behavior in liquid sulfur dioxide solution is not feasible.

Studies of simple 2-1 salts in liquid sulfur dioxide solutions are hindered by the low solubilities of many of these salts in this solvent. The solubility of salts in liquid sulfur dioxide has been the subject of several investigations (73,76,84,116,131). The data available indicate that suitable systems can be studied with no more difficulty than was experienced in the studies of potassium chloride described in this dissertation. Although such data would be of great value at some future time it is more pressing that accurate limiting

ionic mobility data be obtained.

Conclusions

The dissociation of 2-1 salts in solvents of low dielectric constant can be reasonably well described in terms of a stepwise dissociation. The method of Shedlovsky for 1-1 salts, when applied to the data for 2-1 salts, gives a curve which can be reconciled with this interpretation. The qualitative nature of the Shedlovsky curve as well as of the conductance curve for tetramethylammonium sulfate is considered to be characteristic of 2-1 salts in liquid sulfur dioxide. Indeed, similar behavior is found for 2-1 salts in liquid ammonia solution.

The behavior characteristic of 2-1 electrolytes in solvents of low dielectric constant can be described as follows: Application of the 1-1 Shedlovsky treatment to the data will produce a curve which possesses one rather sharp change in slope at an intermediate dilution. The slope, which is essentially constant in the low dilution region, changes over a narrow region to a much steeper slope which then remains constant in the high dilution region. Figures 1-XXIII and 1-XXIV illustrate this behavior. It is concluded that when the Shedlovky treatment produces a curve similar to that shown in figures 1-XXIII and 1-XXIV the data can be considered to be those of a 2-1 electrolyte.

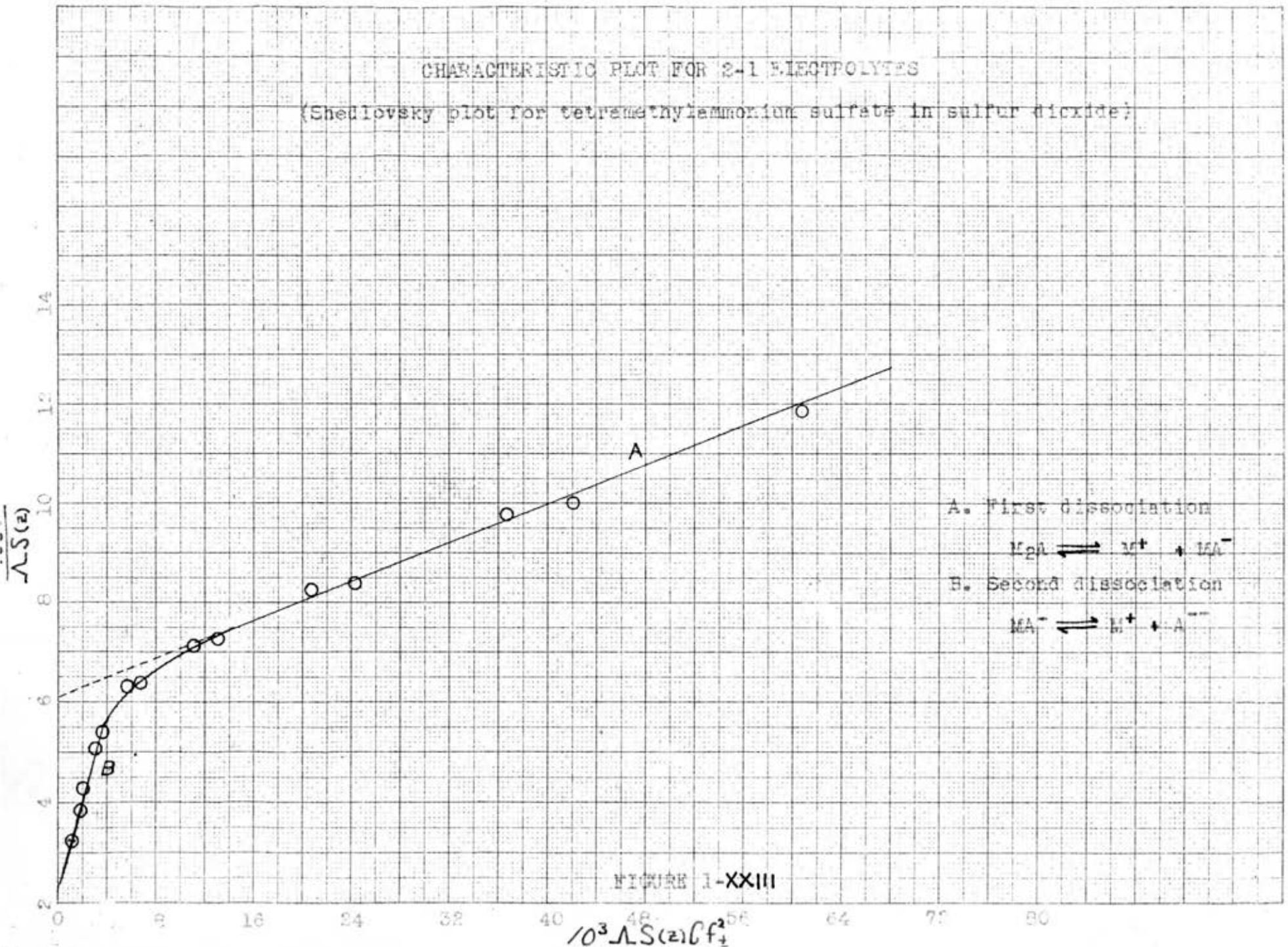


FIGURE 1-XXIII

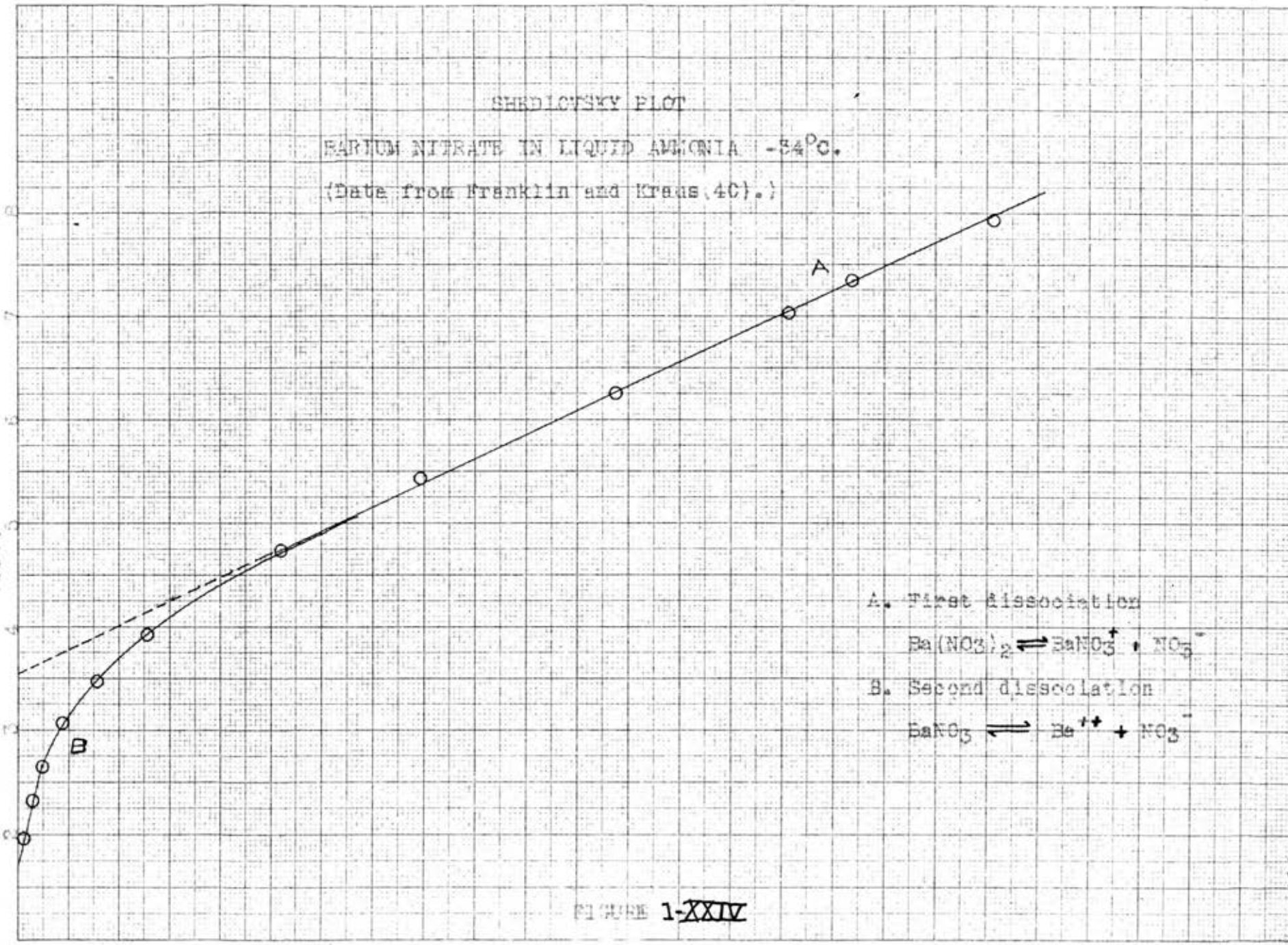


FIGURE 1-XXIV

APPENDIX II

Tables of Experimental Conductance Data Described in Part II.

Table	Compound	Temperature
2-A	m-Biphenylyldiphenylchloromethane	0.12°C.
2-B	Di-m-biphenylylphenylchloromethane	0.12°C.
2-C	Tri-m-biphenylylchloromethane	0.12°C.
2-D	Triphenylchloromethane	-8.93°C.
2-E	m-Biphenylyldiphenylchloromethane	-8.93°C.
2-F	Di-m-biphenylylphenylchloromethane	-8.93°C.
2-G	Tri-m-biphenylylchloromethane	-8.93°C.
2-H	p-Biphenylyldiphenylchloromethane	-8.93°C.

TABLE 2-A

Conductivity of m-Biphenylyldiphenylchloromethane in Sulfur Dioxide Solution.

0.12°C.

V liters/mole	k x 10^6(a) mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-63)(b,c,d)	
689.4	40.89	28.19
1578	25.44	40.14
3617	15.55	56.24
8268	9.283	76.25
18910	5.317	100.5
43250	2.910	125.9
99000	1.501	148.6

(a) Corrected for solvent conductance. $k_{SO_2} = 7.830 \times 10^{-8}$ mhos-cm.$^{-1}$.

(b) Sample from lot prepared by Dr. N.N. Lichtin and used by Lichtin and Glazer (91).

(c) M.P. 85-87°C. Hydrolyzable chloride: Found 12.6%; Theory 12.7%.

(d) The sulfur dioxide was degassed for one hour.

TABLE 2-B

Conductivity of Di-m-biphenylylphenylchloromethane in Sulfur Dioxide Solution.

0.12°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-4)[a,c]	
380.8	43.63	16.61
860.2	27.55	23.70
1944	17.24	33.51
4386	10.61	46.54
9895	6.403	63.36
22330	3.726	83.20
50400	2.078	104.7
113600	1.083	123.0
	(Run HL-5)[b,c]	
309.5	49.07	15.18
711.2	30.57	21.74
1631	18.96	30.92
3742	11.61	43.44
8588	6.956	59.74
19680	4.025	79.21
45110	2.221	100.2
103300	1.160	119.8

(a) $k_{SO_2} = 1.525 \times 10^{-7}$ mhos-cm.$^{-1}$.

(b) $k_{SO_2} = 1.556 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c) Sample B-I.

Table 2-B (Cont.)

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-6)[a,b]	
330.8	47.39	15.68
766.1	29.49	22.59
1773	18.18	32.23
4104	11.06	45.39
9497	6.601	62.69
21980	3.801	83.55
50860	2.069	105.2
117800	1.076	126.8

(a) $k_{SO_2} = 1.566 \times 10^{-7}$ mhos-cm.$^{-1}$.

(b) Sample B-I.

TABLE 2-C

Conductivity of Tri-m-biphenylylchloromethane in Sulfur Dioxide Solution.

0.12°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-7)[a,c]	
851.6	21.14	18.00
1952	13.20	25.77
4478	8.203	36.73
10230	4.971	50.85
23390	2.969	69.44
53420	1.675	89.48
122000	0.900	109.8
	(Run HL-8)[b,c]	
542.9	27.25	14.79
1255	17.05	21.40
2902	10.61	30.79
6704	6.518	43.70
15530	3.928	61.00
35920	2.279	81.86
82940	1.265	104.9
191600	0.6489	124.3

(a) $k_{SO_2} = 1.808 \times 10^{-7}$ mhos-cm.$^{-1}$.

(b) $k_{SO_2} = 1.407 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c) Sample T-I.

Table 2-C (Cont.)

V $\frac{\text{liters}}{\text{mole}}$	$k \times 10^6$ mhos-cm.$^{-1}$	Λ $\frac{\text{mhos-cm.}^2}{\text{mole}}$
	(Run HL-9)[a,b]	
690.0	23.66	16.33
1600	14.79	23.66
3706	9.143	33.88
8583	5.555	47.68
19880	3.279	65.20
46040	1.870	86.09
106700	0.9970	106.4
	(Run HL-44)[c,d]	
813.4	21.92	17.83
1865	13.69	25.53
4275	8.509	36.38
9798	5.165	50.61
22440	3.060	68.67
51430	1.746	89.80
117900	0.946	111.5

(a) $k_{SO_2} = 1.321 \times 10^{-7}$ mhos-cm.$^{-1}$.

(b) Sample T-I.

(c) $k_{SO_2} = 1.150 \times 10^{-7}$ mhos-cm.$^{-1}$.

(d) Sample T-II.

TABLE 2-D

Conductivity of Triphenylchloromethane in Sulfur Dioxide Solution.

-8.93°C.

V liters / mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2} / mole
	(Run HL-18)	
157.2	152.4	23.96
363.9	91.60	33.33
842.1	54.54	45.93
1944	32.24	62.67
4504	18.61	83.82
10430	10.30	107.4
24210	5.411	131.0
56220	2.707	152.0
130400	1.333	173.8
	(Run HL-50)[a,c,d]	
585.8	69.18	40.53
1333	41.59	55.45
3042	24.62	74.89
6942	14.09	97.79
15860	7.697	122.1
36200	3.989	144.4
83750	1.948	161.2

(a) Sample prepared by Dr. N. N. Lichtin and used by Lichtin and Glazer (91).

(b) $k_{SO_2} = 1.900 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c) This run was carried out jointly by the author and Dr. N. N. Lichtin.

(d) $k_{SO_2} = 5.500 \times 10^{-8}$ mhos-cm.$^{-1}$.

Table 2-D (Cont.)

V liters / mole	$k \times 10^6$ mhos-cm.$^{-1}$	Λ mhos-cm.^{2} / mole
	(Run HL-55)[a,b]	
377.3	89.51	33.77
852.3	54.26	46.24
1924	32.07	61.70
4354	19.13	83.29
9827	10.88	106.9
22290	5.857	130.6
50440	2.961	149.4
114300	1.423	162.4

(a) Sample was the same used in runs HL-18 and 50.

(b) $k_{SO_2} = 1.406 \times 10^{-7}$ mhos-cm.$^{-1}$.

TABLE 2-E

Conductivity of m-Biphenylyldiphenylchloromethane in Sulfur Dioxide Solution.

-8.93°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-79)[a,b,c]	
366.8	68.96	25.29
841.8	43.07	36.26
1931	26.22	50.63
4436	15.61	69.24
10200	8.959	91.38
23490	4.906	115.2
54170	2.547	138.0
124400	1.241	154.4
	(Run HL-80)[a,b,d]	
433.5	62.57	27.12
994.7	38.60	38.40
2288	23.40	53.54
5265	13.77	72.50
12110	7.817	94.66
27850	4.235	117.9
64070	2.150	137.8

(a) These runs were carried out jointly by the author and Dr. N. N. Lichtin.

(b) Sample from lot prepared by Dr. N. N. Lichtin and used by Lichtin and Glazer (91).

(c) $k_{SO_2} = 1.123 \times 10^{-7}$ mhos-cm.$^{-1}$.

(d) $k_{SO_2} = 1.295 \times 10^{-7}$ mhos-cm.$^{-1}$.

TABLE 2-F

Conductivity of Di-m-biphenylylphenylchloromethane in Sulfur Dioxide Solution.

-8.93°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-14)(a,c)	
441.7	47.52	20.89
1018	29.29	29.82
2344	17.86	41.86
5398	10.67	57.60
12440	6.159	76.60
28650	3.420	97.98
65970	1.788	118.0
152000	0.8786	133.5
	(Run HL-15)(b,d)	
194.9	76.44	14.90
444.0	47.67	21.16
1012	29.61	29.96
2298	18.18	41.78
5223	10.94	57.14
11910	6.415	76.40
27200	3.617	98.38
62230	1.915	119.2
141700	0.9950	141.0

(a) $k_{SO_2} = 8.343 \times 10^{-8}$ mhos-cm.$^{-1}$.

(b) $k_{SO_2} = 1.094 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c) Sample B-I.

(d) Sample B-II.

Table 2-F (Cont.)

V liters/mole	$k \times 10^6$ mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-49)[a,b]	
1135	27.94	31.71
2607	16.98	44.27
5993	10.16	60.89
13770	5.886	81.05
31640	3.258	103.1
72740	1.697	123.4
167400	0.8567	143.4

(a) $k_{SO_2} = 1.007 \times 10^{-7}$ mhos-cm.$^{-1}$.

(b) Sample B-I.

TABLE 2-G

Conductivity of Tri-m-biphenylylchloromethane in Sulfur Dioxide Solution.

-8.93°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run HL-16)[a,b]	
608.7	29.98	18.25
1400	18.59	26.02
3214	11.42	36.70
7386	6.914	51.07
19690	4.060	68.86
38960	2.278	88.75
89490	1.211	108.4
205500	0.6431	132.2
	(Run HL-40)[b,c]	
2166	14.72	31.88
5006	9.010	45.10
11540	5.371	61.98
26640	3.089	82.29
61720	1.688	104.2

(a) $k_{SO_2} = 1.009 \times 10^{-7}$ mhos-cm.$^{-1}$.

(b) Sample T-I.

(c) $k_{SO_2} = 1.287 \times 10^{-7}$ mhos-cm.$^{-1}$.

Table 2-G (Cont.)

V liters / mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2} / mole
	(Run HL-42)(a,c)	
1032	22.52	23.24
2355	13.92	32.78
5374	8.498	45.67
12270	5.083	62.37
28000	2.916	81.65
63870	1.593	101.7
145800	0.8151	118.8
	(Run HL-43)(b,c)	
734.4	26.92	19.77
1663	16.89	28.09
3763	10.47	39.40
8523	6.375	54.33
19300	3.765	72.66
43680	2.130	93.04
98850	1.142	112.9

(a) $k_{SO_2} = 1.155 \times 10^{-7}$ mhos-cm.$^{-1}$.

(b) $k_{SO_2} = 0.9582 \times 10^{-7}$ mhos-cm.$^{-1}$.

(c) Sample T-II.

TABLE 2-H

Conductivity of p-Biphenylyldiphenylchloromethane in Sulfur Dioxide Solution.

-8.93°C.

V $\frac{\text{liters}}{\text{mole}}$	$k \times 10^6$ mhos-cm.$^{-1}$	Λ $\frac{\text{mhos-cm.}^2}{\text{mole}}$
	(Run HL-20)[a,b]	
509.3	147.7	75.22
1172	80.74	94.63
2702	42.68	115.3
6242	21.56	134.6
14420	10.41	150.1
33370	4.812	160.6
77290	2.136	165.1
179100	0.9820	175.9
	(Run HL-21)[a,c]	
327.8	196.5	64.41
754.3	110.7	83.50
1729	60.24	104.2
3972	31.19	123.9
9120	15.44	140.8
20940	7.279	152.4
48100	3.318	159.6
110400	1.488	164.3

(a) Sample was from lot prepared by Dr. N. N. Lichtin and used by Lichtin and Glazer (91).

(b) $k_{SO_2} = 8.621 \times 10^{-8}$ mhos-cm.$^{-1}$.

(c) $k_{SO_2} = 7.044 \times 10^{-8}$ mhos-cm.$^{-1}$.

Table 2-H (Cont.)

V liters / mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2} / mole
	(Run HL-22)[a,b]	
631.9	124.4	78.61
1448	68.66	99.42
3303	36.28	119.8
7557	18.23	137.8
17300	8.754	151.4
39600	3.992	158.1
90760	1.778	161.4

(a) Sample was the same as used in runs HL-20 and 21.

(b) $k_{SO_2} = 1.749 \times 10^{-7}$ mhos-cm.$^{-1}$.

APPENDIX III

Tables of Experimental Conductance Data Described in Part III.

TABLE 3-A

Apparent Conductivity of Hexaphenylethane in[a] Sulfur Dioxide Solution.

0.12°C.

V liters/mole	k x 10^6 [c] mhos-cm^{-1}	Λ mhos-cm.^{2}/mole
	(Run II-1)	
168.5	249.6	42.06
387.2	123.4	47.78
887.8	61.97	55.02
2040	29.87	60.93
4682	16.68	78.10
10740	8.407	90.20
10740[b]	17.98	193.1

(a) Light excluded.

(b) After prolonged irradiation with u.v.

(c) Corrected for solvent conductance.

TABLE 3-B

Apparent Conductivity of Hexaphenylethane in Sulfur Dioxide Solution.[a]

-8.93°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run II-2)[b]	
91.45	141.8	12.97
208.1	70.42	14.65
480.8	33.80	16.25
1091	16.00	17.46
2477	7.505	18.59
5593	3.510	19.63
12700	1.842	23.39
28900	1.030	29.77
	(Run II-3)[c]	
86.00	171.2	14.72
195.8	84.11	16.47
446.5	40.30	17.99
1011	18.92	19.13
2279	8.911	20.31
5189	4.252	22.06
11760	2.117	24.90
26630	1.224	32.60
60340	0.719	43.38

(a) Light excluded.

(b) $k_{SO_2} = 0.256 \times 10^{-6}$ mhos-cm.$^{-1}$.

(c) $k_{SO_2} = 0.345 \times 10^{-6}$ mhos-cm.$^{-1}$.

TABLE 3-C

Apparent Conductivity of Hexaphenylethane in Sulfur Dioxide Solution.[a]

-8.93°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run VI-b-1)[b]	
218.2	133.3	29.09
498.8	66.03	32.94
1142	31.81	36.33
2610	15.01	39.18
5965	6.992	41.71
13640	3.273	44.64
31220	1.614	50.39
71460	0.898	64.2
164000	0.578	89.8
376200	0.324	122
	(Run VI-b-2)[c]	
125.5	204.7	25.08
269.9	141.1	31.59
628.9	58.60	36.85
1426	29.01	41.37
3239	14.13	45.77
7330	8.614	63.14
16570	5.024	83.24
37530	2.435	91.39

(a) Light excluded.

(b) $k_{SO_2} = 0.0614 \times 10^{-6}$ mhos-cm.$^{-1}$.

(c) Cell developed a leak during this run.

TABLE 3-D

Apparent Conductivity of Hexaphenylethane in Sulfur Dioxide Solution.[a]

-8.93°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	mhos-cm.^{2}/mole
	(Run VI-b-3)[b]	
157.6	181.5	28.60
363.4	95.70	34.78
839.3	47.69	40.02
1935	23.36	45.20
4468	11.13	49.73
10200	5.209	53.13
23550	2.473	58.24
54380	1.244	67.65
	(Run VI-c-1)[c]	
216.0	58.24	12.58
495.9	28.00	13.88
1137	13.06	14.85
2612	6.020	15.72
5994	2.856	17.12
13770	1.390	19.14
31640	0.626	19.80

(a) Light excluded.

(b) The cell developed a leak during this run.

(c) $k_{SO_2} = 0.146 \times 10^{-6}$ mhos-cm.$^{-1}$.

TABLE 3- E

Apparent Conductivity of Hexaphenylethane in Sulfur Dioxide Solution.[a]

-8.93°C.

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run VI-d-1)[b][c]	
219.2	9.860	2.161
507.9	4.914	2.496
1177	2.582	3.039
2731	1.631	4.454
6336	0.974	6.171
14690	0.638	9.370
	(Run VI-d-2)[d][e]	
102.1	5.385	0.550
236.3	2.667	0.630
544.7	1.779	0.969
1257	1.596	2.006
2917	1.402	4.090
6750	0.882	5.954

(a) Light excluded.

(b) The sulfur dioxide was degassed for 1 hr. at -78°C.

(c) k_{SO_2} = 0.192 mhos-cm.$^{-1}$.(x 10^{-6}).

(d) The sulfur dioxide was degassed for 4 hrs. at -78°C.

(e) k_{SO_2} = 0.250 x 10^{-6} mhos-cm.$^{-1}$.

TABLE 3-F

Apparent Conductivity of Hexaphenylethane in Sulfur Dioxide Solution.[a]

V liters/mole	k x 10^6 mhos-cm.$^{-1}$	Λ mhos-cm.^{2}/mole
	(Run VI-b-4)[b,c]	
43.35	3.98	0.17
98.75	2.10	0.20
226.2	0.951	0.21
	(Run VI-b-6)[d]	
111.7	3.76	0.4
111.7[e]	362.5	40.5
250	205.7	51.5
560	97.65	55.0
1200	72.11	86.5
2600	36.71	95.4
	(Run VIII-d-1)[g,f]	
120.5	7.18	----
280.9	4.37	----
653.6	2.50	1.64
653.6[e]	77.74	49.98
1450	37.77	54.77
3254	17.89	58.54
7538	8.46	63.76

(a) Light excluded.

(b) The sulfur dioxide was degassed for 3 hrs. and redistilled from hexaphenylethane.

(c) $k_{SO_2} = 0.345 \times 10^{-6}$ mhos-cm.$^{-1}$.

(d) The sulfur dioxide was degassed for 2 hrs.

(e) Oxygen was added to the solution.

(f) The sulfur dioxide was degassed for 4.5 hrs. and redistilled from hexaphenylethane.

(g) $k_{SO_2} = 0.175 \times 10^{-6}$ mhos-cm.$^{-1}$.

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ABSTRACT

Part I Dissociation of Ion Pairs.

The conductivity of potassium chloride, bromide and iodide and of tetramethylammonium bromide were measured over a dilution range of 10^2 to 10^5 liters per mole in liquid sulfur dioxide solution at 0.12°C. and at -8.93°C. employing the inter nal dilution technique described by Lichtin and Glazer. Similar measurements were carried out on tetramethylammonium sulfate at 0.12°C. Equilibrium constants were evaluated from these data by the method of Shedlovsky. The method of least mean squares was applied to establish the best straight line representing the Shedlovsky equation for each compound at each temperature.

The experimental data and calculations presented in this dissertation clearly demonstrate that the theory of ionic association of Bjerrum is an accurate representation of the behavior of 1-1 electrolytes in liquid sulfur dioxide solution. The distance of closest approach of the ions were calculated from the experimental equilibrium constants by the Bjerrum equation. Values obtained from the data on pure ionic compounds in sulfur dioxide solution are in excellent agreement ($\pm$ 0.1Å) with the sums of crystallographic radii of the corresponding ions. Conversely, ion pair dissociation constants calculated from crystal radii agree closely with the experimental values obtained in this research. In the case of tetramethylammonium bromide, where a crystallographic radius is not available for the cation, a value estimated as the largest Van der Waals

radius from the center of the molecule by direct measurement of a Fisher-Herschfelder-Taylor model gave excellent agreement with experiment.

An equation for ΔH^{o} derived solely from the Bjerrum theory gave values which were in good agreement within the uncertainties inherent in the experimental values of this property.

On the basis of these observations it is possible to conclude that the Bjerrum treatment is quantitatively exact for 1-1 electrolytes in sulfur dioxide solution. This is the first demonstration of quantitative adherence to this theory.

Part II Equilibria of m-Phenyl Derivatives of Trityl Chloride.

All attempts to utilize conductivity data for ring substituted derivatives of triphenylchloromethane in sulfur dioxide solutions for the direct estimation of the electronic influence of the ring substituents have, in the past, met with little quantitative success due to the complications arising from short range ionic interactions which give rise to ion pairs and higher aggregates in solvents of low dielectric constant. In a qualitative manner Lichtin and Bartlett were able to demonstrate that ionic association equilibria introduce only minor errors in the relative equilibrium constants for trityl chloride and those ring substituted derivatives which are weaker electrolytes than trityl chloride. In this way these workers were able to estimate the qualitative electronic influences of those substituents which stabilize triphenylchloromethane more than they stabilize the triphenyl carbonium

ion in sulfur dioxide solution. Since, however, many theoretically interesting substituents exert an effect resulting in an enhanced ionization of triphenylchloromethane it is both interesting and valuable to develop a method of evaluating an ion pair correction term to be used with the experimental data for these compounds.

A method is proposed for the quantitative evaluation of an ion pair correction term to be applied to experimental conductivity data for ring substituted trityl chlorides in sulfur dioxide solution. With this method it is now possible to obtain a quantitative measure of the electronic influence of substituents from conductivity data in this solvent.

The assumptions involved in this treatment are as follows:
(1) The Bjerrum equation is an exact representation of ionic association behavior of 1-1 electrolytes in this solvent. This assumption is supported by the evidence presented in Part I.
(2) The triarylmethyl carbonium ion in solution presents a spherical appearance to the anion by virtue of a tumbling motion about its center of gravity.

The ion sweeps out an effective volume equal to a sphere whose radius is the largest Van der Waals radius from the center of gravity of the ion.
(3) The Bjerrum radius of the triarylcarbonium ion is equal to the radius of the swept out volume and can be estimated directly from molecular models as being the largest Van der Waals distance from the center of gravity.

Experimental equilibrium constants were determined by

applying the Shedlovsky and least mean squares method to the conductivity data for mono-,di-, and tri-m-phenyl derivatives of trityl chloride in liquid sulfur dioxide at 0.12°C. and -8.93°C. obtained in this research.

These values combined with calculated ion pair dissociation constants permitted the calculation of the experimentally inaccessible ionization constants for these compounds. It was demonstrated that the influence of stepwise introduction of m-phenyl substituents on the calculated free energy of ionization of the corresponding trityl chlorides could be described by equal free energy increments for each successive substitution.

A sigma constant for the m-phenyl group was determined from acid strength measurements on benzoic and m-phenyl benzoic acids. With this value it was possible to calculate a Hammett rho parameter for the ionization of trityl chlorides in sulfur dioxide solution. Resonance sigma constants, were calculated for p-phenyl, p-methyl and p-t-butyl groups.

Hammett correlation plots were constructed for the ionization reaction in sulfur dioxide employing all available experimental data from this research and from the literature. It was found that poor correlations could be obtained with experimental dissociation constants while, on the other hand, excellent agreement resulted when ionization constants calculated on the basis of the ion pair treatment were employed.

An electron supplying resonance sigma for the para phenyl group of -0.148 is proposed. Values of -0.3 have been calculated for both the p-methyl and p-t-butyl group.

This research has provided a useful tool for evaluation of substituent effects.

Part III The Apparent Ionization of Hexaphenylethane.

The conductivity which has been observed with solutions of hexaphenylethane in liquid sulfur dioxide has been subject to several chemical interpretations which differ in detail but which all assume an ionization mechanism involving only hexaphenylethane and sulfur dioxide. This conductivity is now found to be an artifact of at least two processes, namely, reaction with dissolved oxygen and a photochemical transformation.

Experiments employing crystalline samples of ethane of purity established by quantitative oxygenation and a refinement of the conductivity technique of Lichtin and Glazer reveal a lack of reproducibility like that apparent in older work. Although irradiation with a Burton ultraviolet lamp produces slow but large increases in conductivity, variable exposure to light cannot be the sole source of the discrepancies since consistent data do not result from experiments performed in the dark. The fact that increasingly efficient degassing of the solvent prior to dissolution leads to progressive diminution of the conductivity suggests production of an electrolyte by reaction with a gaseous impurity. This reagent has been identified as oxygen. The conductivity of an oxygenated solution of hexaphenylethane is somewhat greater than the highest comparable values obtained without degassing the solvent. The conductivity of this solution does not change upon irradiation whereas that of the solutions in degassed sulfur dioxide increases.

About the Author

Harry Paul Leftin the son of Eli Moses and Annie Rose (Davidoff) Leftin was born in Beverly, Massachusetts on October 23, 1926. He graduated from the Public Schools of that city in 1945 and entered the Armed Services of the United States from which he was Honorably Discharged in November of 1946 with the rank of Sergeant. He entered Boston University College of Liberal Arts in September of 1947 and received the A.B. degree in June of 1950. He entered the Graduate School in September of 1950 and was awarded a Research Fellowship from funds provided by a Frederick Gardner Cottrell grant from the Research Corporation for the academic years 1951-52 and 1952-53. He was elected to the Boston University Chapter of Sigma Xi in 1952 . He served as

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