ISOTOPE EFFECTS ON CHEMICAL EQUILIBRIA

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A Thesis

by

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submitted in partial fulfillment of the requirements for the degree of Master of Science

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Notes on thesis - D.J. Barnes

p.	Comment
4.	Manhattan mis-spelt.
5.	Description of "zero-point energy" is confusing.
7.	In diagram the k(D)'s and k(H)'s will not be the same?
8.	(a) Suggest rewording of 1st paragraph: "Effects of the first kind where the H/D substituent is linked to a cation undergoing a change of hybridization......processes in which no spatial reorganization involving the H/D substituent takes place (......."
	(b) " $\Sigma_i pK_a$ " could be defined here.
	(c) to what are Wolfsberg and Stern's observations similar?
14.	Since σ^* is not the same as σ^* in $\Sigma\sigma^*$ could it be indicated what theoretical basis there is for the latter function.
15.	$\Sigma\sigma^*$ on this page differs from that of p.14. This is very confusing.
16.	What is the Halevi-Streitwieser-Taft treatment?
34.	τ should be defined. OMe on wrong line.
38.	Barnstead mis-spelt., Teflon, Pyrex and Amberlite are all trade names.
39.	Units of specific conductivity? Nalgan tubing. "three weeks before determining....." soaking in H_2O or left dry?
41.	"Volumetric" is not a noun, see also p.60. "Complete removal of ions", perhaps, substantially complete.
43.	Jones-Josephs bridge?
46.	Comparator mis-spelt.
49.	Copper cooling coils (3"x 1/2"): what dimensions are these?
56.	Honeywell (potentiometric) recorder? Type No.?

..2/

57. a) Why did the resistances of acid solutions change by only 0.1% in 12 hrs., whereas KCl solutions changed by the same fraction in 2 hrs.?

b) Reference missing.

58. a) V_o^o and V_o^o both appear on this page.

b) What is the source of equation (10)? Units of $\emptyset_1$.

c) Can the last term in equation (12) be correct?

d) Ref. (49) should be "Fuoss et al".

60. Ref. (60) should be "Feates and Ives".

80. "Electrolytes of type AB dissociate".

83. $f_{\pm}^2$ is "the mean square ionic activity coefficient of the ions" and should be defined here.

84. Born charging.

85. C_i not c_i.

87. a) "E is ...... as B and" Should this be ?

b) relevant

c) "can" is superfluous in "conductance data can have certain features ...."

89. Total ion concentration is 2 C for uni-univalent electrolytes. I = C.

88. Ref. (27) is "Ives and Pryor".

90. " " omitted in line above equation (36).

92. Ives' method or Ives's Method.

94. What sense does first sentence of the second paragraph make?

96. a) Equation (55) $A \doteq 10^3 K \Lambda_o$ doesn't make sense.

Why subscripts K_c?

b) Might not the results of Streitwieser and Klein have been quoted!

99. α'_s omitted.

112. Λ'_s omitted again.

..3/

113. Λ's omitted.

114. I = IIM is a confusing symbolism!

119. 'Final slope and intercept ..... are sensitive".

123. Table XXXII refers to which acid?

126. a) Acetic and Cyanoacetic Acids.

b) Ref. (30) is Feates and Ives..

128. "of an weak electrolyte".

"A summary .... is recorded........

129. I 'K(H)/K(D) = 1.004" for nitrophenylacetic acid a misprint?

132. Equations (69) and (70), not (60).

134. R=H, NO_2 ....

139. Misprint in 17, 1.0068?

141. "K_t " is the same as K_a?

142. omitted.

146. Average Deviatia x 10?

150. This work?

153. MacInnes and Shedlovsky?

Say so!

163. $p\text{-}RC_6H_4CH_2COOH$ and $4\text{-}NO_2$ superfluous.

169. In what experiments has C an average value of 1.35?

170.

171. Fig.XXXII is rather barren unless acids with suitable pK's are indicated.

Summary: This omits specific reference to $p\text{-}NO_2$ and p-MeO acids.

Frank R. Smith/RB

Frank R. Smith,
Ass't. Professor

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ABSTRACT

A modified synthesis of phenylacetic-α,α-d_2, 4-methoxyphenylacetic-α,α-d_2, and 4-nitrophenylacetic-α,α-d_2 acids is described. The pK_a's of these substances relative to that of the protium analogues have been determined. The ratio of the ionization constants of phenylacetic acid and phenylacetic-α,α-d_2 acid in aqueous solution at 25° was found to be $K(H)/K(D) = 1.007 \pm 0.002$. The new value differs considerably from that originally reported by Halevi but the redetermined ratio is shown to be more consistent in some respects with a modified Halevi-Streitwieser-Taft treatment of secondary isotope effects, based on a greater inductive electron release from deuterium relative to hydrogen. The $K(H)/K(D)$ ratios appropriate to the acids studied show an approximate linear correlation with the pK_a of the related protium acid. The evaluation of $K(H)/K(D)$ ratios from conductance data appropriate to the pairs of isotopically substituted weak electrolytes is considered in detail. The most precise method for determining the $K(H)/K(D)$ ratio does not require determination of the absolute pK_a values of the carboxylic acids but can be made by a comparison of the slopes of a least squares fit to the appropriate conductance equations.

INTRODUCTION

General.

In 1932 Urey, Brickwedde and Murphy (1) established the existence of a new isotope of hydrogen by a spectroscopic study of a sample of ordinary hydrogen which had been concentrated to a small volume by a distillation technique. The usual Balmer lines were duplicated by faint companions with the required wave length for deuterium (^{2}H or D)*.

Shortly afterwards, Washburn and Urey (2) reported that deuterium is enriched in the liquid phase during the electrolysis of ordinary water. The electrolysis method was developed further by Lewis (3,4) and by Taylor (5). This method depends on the fact that ordinary water contains trace amounts of deuterium oxide and that the evolved gas generated electrolytically has a smaller D/H ratio than is present in the liquid. Deuterium was also separated from hydrogen by Seaborg (6) using a thermal diffusion method introduced by Clusius and Dickels (7).

The availability of deuterium from the electrolytic method provided sufficient material for the study of hydrogen-deuterium isotope effects on a variety of rates and equilibria. The interest in the separation of isotopes during World War II in the Manhatten Project (8) increased the availability of the isotopes of a wide variety of elements and led to an increasing interest

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* Both ^{2}H and D are used as symbols for deuterium. In the present thesis the latter will be used.

in the effect of isotopic substitution on chemical reactivity.

The magnitude of hydrogen-deuterium isotope effects can be crudely estimated by considering the complete dissociation of the pseudo-diatomic molecules R-H and R-D, where R may be an atom or a complex molecular group. To a very high approximation, the potential energy curves for the R-H and R-D bonds can be considered identical for any given internuclear distance. This is sometimes known as the Born Oppenheimer Principle (9). However, since the minimum point on the potential energy curve exceeds the lowest energy by the vibrational zero point energy $E_0 = \frac{1}{2} h\nu$, the lowest states for R-H and R-D will differ by an amount equal to the difference in their respective zero point energies. Since the frequency of vibration will be lower for the heavier isotope, it follows that more work will be required to separate R-D than R-H. If this argument is now considered in thermodynamic terms, it is evident that both rates and equilibria should favor the lighter isotope leading to what is described as a normal isotope effect, i.e. $K\ (\text{light})/K\ (\text{heavy}) > 1$.

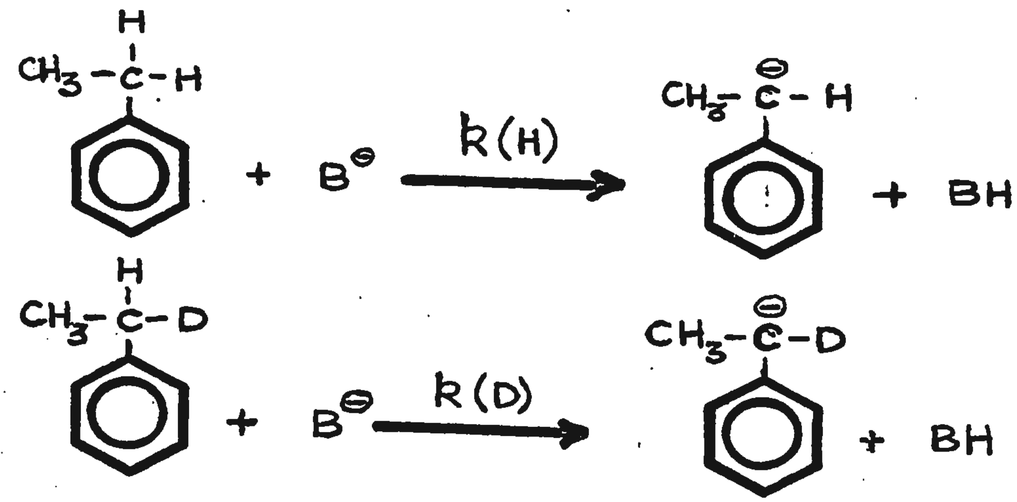
However, the fission of a diatomic or a pseudo-diatomic molecule is a poor model for most chemical reactions, which usually involve a complex sequence of bond making and bond breaking processes. Furthermore, the isotopic atoms may not be intimately involved in the reaction because isotopic substitution may be remote from the reaction site. In certain cases, so called inverse effects are observed, i.e. $K\ (\text{light})/\ K\ (\text{heavy}) < 1$, which would superficially seem to invalidate the simple zero-point treatment outlined above.

It is clear from the above considerations that some sort of classification of isotope effects is necessary so that these subtle effects on reactivity can be considered in a systematic manner. The problem of classification has been thoroughly discussed in an important review by Halevi (10).

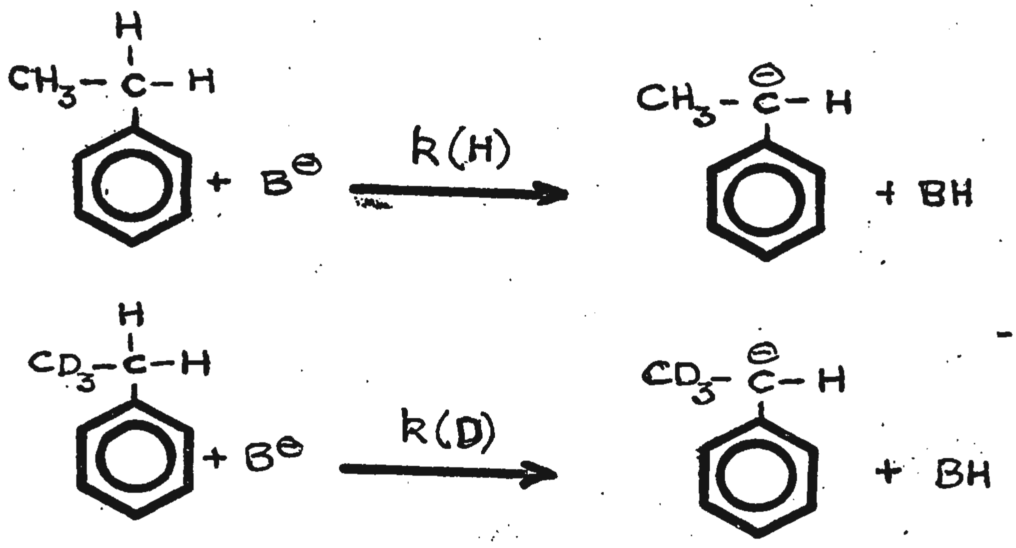
A rigorous theoretical treatment of isotope effects, based on the statistical theory of rates and equilibria, has been developed by Bigeleisen. This theory is available in numerous publications (11-15), and since no direct application of the theory has been made in the present thesis, it will not be elaborated. The work described in this thesis is primarily concerned with secondary hydrogen-deuterium isotope effects on the acidities of carboxylic and ammonium acids,and it would appear to be more useful to review critically the current status of this particular aspect of secondary isotope effects, which has not, so far, proved a particularly fruitful area for the application of the detailed theoretical treatments mentioned above.

Secondary Hydrogen-Deuterium Isotope Effects on the Strengths of Acids and Bases.

The substitution of deuterium for hydrogen in the side chains of carboxylic and ammonium acids has been shown to produce varying effects on the aqueous dissociation constants of these molecules. Isotope effects of this kind are generally small and may be usefully classified in terms of the position of the isotopic substitution with respect to the reaction site. A further classification considers the effect of the reaction on the spatial orientation of bonds which link the isotopic atoms to the rest of the molecule. This subclassification is best considered with reference to some definite examples. Streitwieser (16,17) and co-workers have studied the following proton abstraction reactions:-



--- (1)



---- (2)

Isotope effects in which the spatial orientations of the bonds linking the isotopic atoms to the molecule are altered (as in the processes represented by Equation (1) where the carbon atom of the methylene group changes its hybridization from $sp^3 \rightarrow sp^2$) are described by Streitwieser as secondary isotope effects of the first kind. On the other hand, processes in which no spatial reorganization takes place (e.g. the processes represented by Equation (2)) are described as secondary isotope effects of the second kind. The replacement of deuterium for hydrogen in the side chains of ammonium and carboxylic acids leads to isotope effects which are in the latter category.

In general the complete theory has not been applied to secondary isotope effects of the second kind but a notable exception is provided by Bell and Crooks (18), in their calculation of the pK_a difference between HCOOH and DCOOH. In this calculation Bell and Crooks used observed vibrational frequencies and assumed harmonic vibrations and the experimental $\delta_i pK_a$ was reproduced without the necessity of invoking anharmonicity. A detailed evaluation of this calculation has been given by Halevi (10). Similar observations have been made by Wolfsberg and Stern (19) who have given a theoretical account of secondary isotope effects in C-heavy atom cleavage reactions and have shown that the effects arise primarily from force constant changes affecting zero point energy differences in the various C-H or C-D bond vibrations which are coupled with the cleaving bond.

A less restrictive treatment of these secondary isotope effects has been proposed by Streitwieser and Halevi and their respective coworkers (20, 10) who have postulated that isotope effects of the second kind behave like inductive effects. This hypothesis has been supported by the effect of deuteration at carbon atoms α or β to the carboxyl group on the equilibria of carboxylic acids listed in Table I. A similar picture is presented by a few nitrogen bases (21,22,23,24) although the effect of deuteration on the acidity of the related ammonium ion acids is more pronounced than that observed in the case of the carboxylic acids. This has been rationalized by Halevi (10) in terms of opposing inductive and hyperconjugative effects in the carboxylic acid series, although this explanation is not particularly convincing.

The postulate that isotope effects of the second kind behave like inductive effects suggests that the variation of secondary hydrogen-deuterium isotope effects , with both structure and the position of deuteration, should be amenable to a linear free energy treatment such as that proposed by Taft (25) for 'large scale' inductive effects. The Taft equation has already been used by Streitwieser (20) to estimate the magnitude of isotope effects in certain ring deuterated aromatic compounds from the size of isotope effects which have been observed in the aliphatic series. For this particular application of the inductive treatment the effects predicted are of the correct order of magnitude but when applied to a wider range of structures, this model gives results which are only in qualitative agreement with experimental observations. The limitations of the simple inductive linear free energy model are best illustrated by the following slight modification of the Streitwieser-Taft treatment previously mentioned.

TABLE I

Secondary Isotope Effects on the Dissociation Constants of some Carboxylic Acids in Water

Acid Pair	K(H)/K(D)	Reference
DCOOH/HCOOH	1.06	10
CD_3COOH/CH_3COOH	1.035	20
$C_6H_5CD_2COOH/C_6H_5CH_2COOH$	1.12	22
$CD_3CH_2COOH/CH_3CH_2COOH$	1.01	22
$(CD_3)_3CCOOH/(CH_3)_3CCOOH$	1.04	20
$CH_3CD_2COOH/CH_3CH_2COOH$	1.08	22

TABLE II

pKa Values and Related Data for a Series of Substituted Acetic Acids

Acid**	pKa(b)	σ^*(a)	X_1	X_2	X_3	$\Sigma\sigma^*$
CH_3COOH	4.76	0.00	H	H	H	1.47
CH_3CH_2COOH	4.88	-0.10	CH_3	H	H	0.98
$(CH_3)_2CHCOOH$	4.86	-0.19	CH_3	CH_3	H	0.49
$(CH_3)_3CCOOH$	5.05	-0.30	CH_3	CH_3	CH_3	0.00
$CH_2ClCOOH$	2.87	1.05	Cl	H	H	3.88
$CHCl_2COOH$	1.29	1.94	Cl	Cl	H	6.29
CCl_3COOH	0.65	2.65	Cl	Cl	Cl	8.70
$PhCH_2COOH$	4.31	0.215	Ph	H	H	1.58
$Ph_2CHCOOH$	3.94	0.45	Ph	Ph	H	2.45
Ph_3CCOOH	3.96	-	Ph	Ph	Ph	2.94
CH_2FCOOH	2.59	1.10	F	H	H	4.08
CHF_2COOH	1.24	2.05	F	F	H	6.69
CF_3COOH	0.23	-	F	F	F	9.30
CH_2ICOOH	3.18	0.85	I	H	H	3.38
$CH_2BrCOOH$	2.90	1.00	Br	H	H	3.78
CH_3COCH_2COOH	3.58	0.60	CH_3CO	H	H	2.63

(a) Taken from ref. 25.

(b) Taken from ref. 26 apart from the monohalogenoacetic acids which were taken from ref. 27

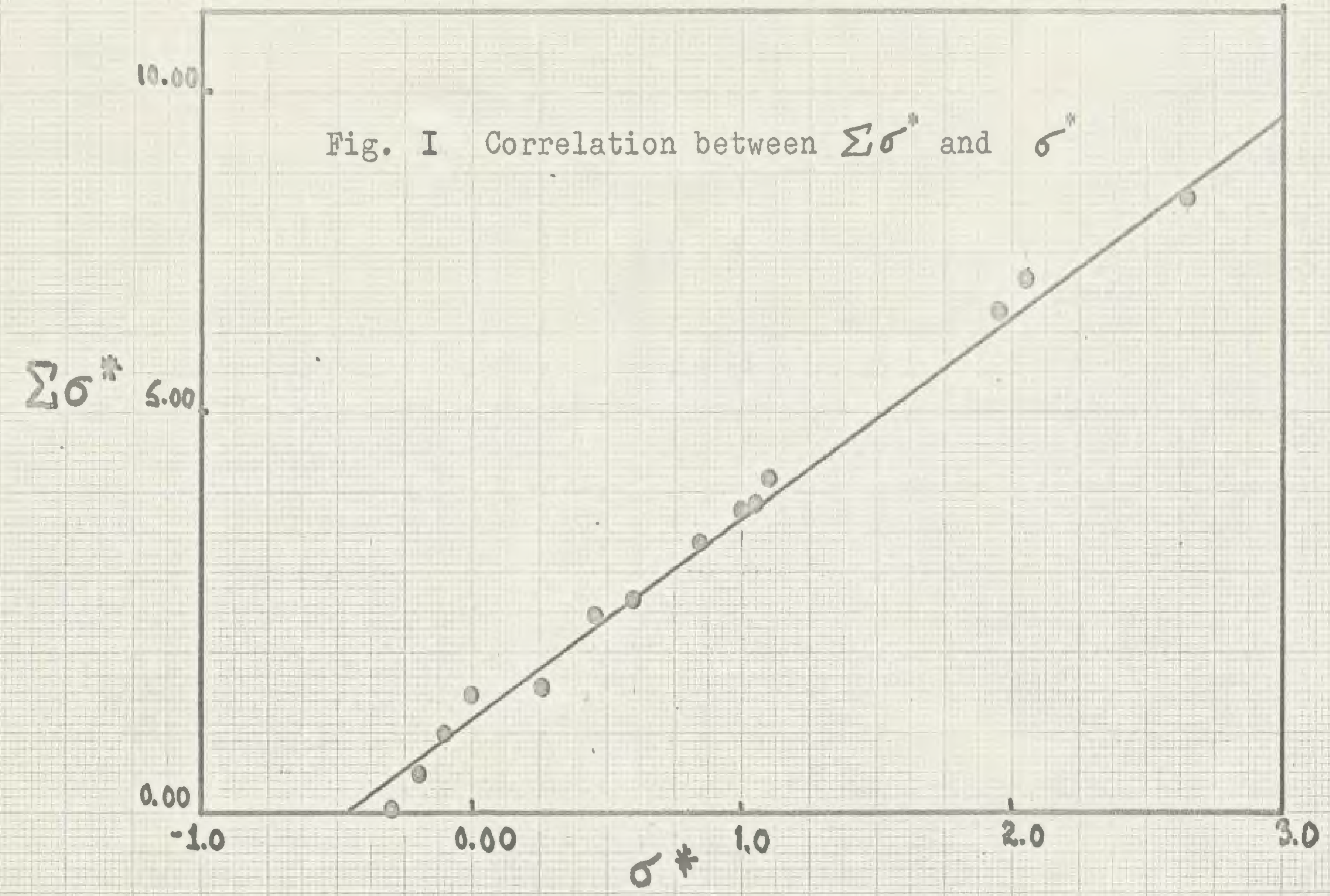


Fig. I Correlation between $\Sigma\sigma^*$ and σ^*

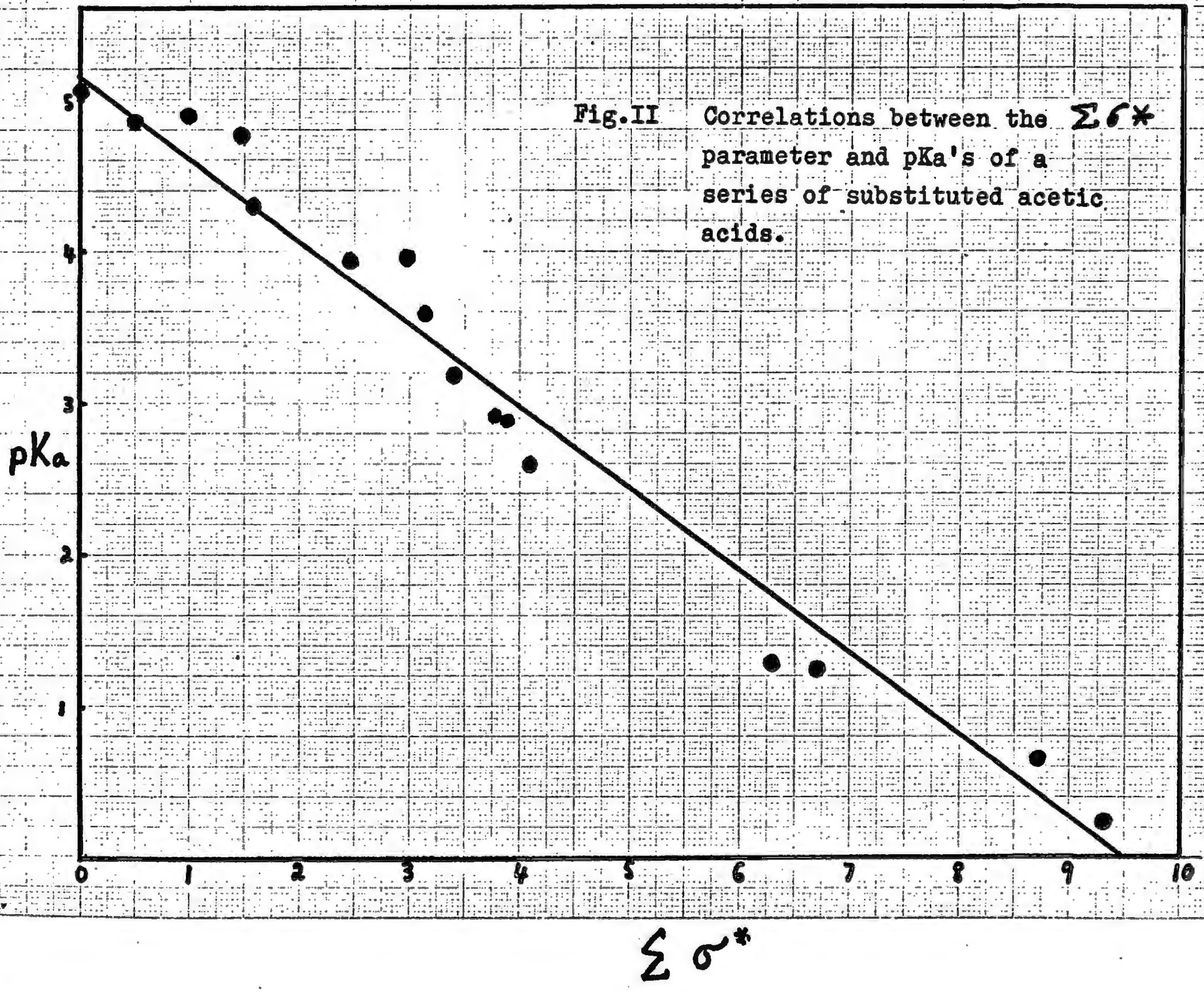


Fig.II Correlations between the $\Sigma\sigma^*$ parameter and pKa's of a series of substituted acetic acids.

The original correlation presented by Taft (25) for the pK_a's of a series of substituted carboxylic (XCOOH) acids was of the form:-

$$\log K/K_o = 1.721\sigma^* - 4.65 \quad \ldots\ldots\ldots (3)$$

where σ^* is the Taft inductive parameter for a substituent 'X' attached to the carboxyl group. In cases where group 'X' can be considered as a substituted methyl group ($-CX_1X_2X_3$) it is possible to set up a modified version of Equation (3) which is more useful for discussing isotope effects. In the modified version of Equation (3) the inductive effect of the substituted methyl group is measured by the sum of the individual contributions from the substituents X_1, X_2 & X_3, leading to a quantity $\Sigma\sigma^*$ which is defined by the equation:-

$$\Sigma\sigma^* = \sigma^*(X_1) + \sigma^*(X_2) + \sigma^*(X_3) \quad \ldots\ldots\ldots (4)$$

The new treatment introduces a scale factor into Equation (3) because although an adequate correlation exists between $\sigma^*(-CX_1X_2X_3)$ and $\Sigma\sigma^*$ (see Fig.1 and Table II) the slope of the line is not unity and the line does not pass through the origin. The new version of Equation (3) using the $\Sigma\sigma^*$ parameter and the related pK_a values is of the form:-

$$pK_a = (-0.558 \pm 0.016)\ \Sigma\sigma^* + 5.19 \pm 0.07 \ldots (5)$$

The relevant data for this correlation is listed in Table II and it is illustrated in Fig.II. This correlation is slightly inferior to that given by Taft but it covers a more extensive range of structures than were used in establishing Equation (3).

The $\delta_i pK_a$ values measured by Streitwieser and Klein (20) for the isotopic weak acid pairs CH_3COOH/CD_3COOH and $(CH_3)_3CCOOH/(CD_3)_3CCOOH$ when substituted in Equation (8) give the following values: $\sigma^*(D-) = 0.482$ and $\sigma^*(CD_3-) = -0.0106$. From the values of σ^* for the deuterium atom and trideuteromethyl group, secondary isotope effects can be predicted for the following systems:- $CH_3CH_2COOH/CH_3CD_2COOH$, $CH_3CH_2COOH/CD_3CH_2COOH$ and $PhCH_2COOH/PhCD_2COOH$. Hall (28) has demonstrated that the pK_a values of primary and secondary aliphatic amines can be correlated with the Taft σ^* parameter by the equations:-

$$pK_a = 13.23 - 3.14\Sigma\sigma^{*\ddagger} \quad ......(6)$$

for primary amines and

$$pK_a = 12.13 - 3.23\Sigma\sigma^{*\ddagger} \quad ......(7)$$

for secondary amines. These equations, when used in conjunction with the value of $\sigma^*(CD_3-)$ calculated above can be used to predict the relative acidities of the isotopic ammonium acid pairs $CH_3\overset{+}{N}H_3/CD_3\overset{+}{N}H_3$ and $(CH_3)_2\overset{+}{N}H_2/(CD_3)_2\overset{+}{N}H_2$. The predictions for all these ammonium and carboxylic acid systems are listed in Table III where they are also compared with experimental values determined by Halevi (22) and Robertson (24) and their respective coworkers. For the propionic acid pair $CH_3CH_2COOH/CD_3CH_2COOH$ the predicted ratio is in excellent agreement with the experimental value, but for the remaining pairs of carboxylic and am-

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$\ddagger$ The $\Sigma\sigma^*$ parameter here refers to the sum of the Taft constants for the groups attached to the nitrogen atom.

monium acids, although the predictions are qualitatively verified, the observed effects generally exceed the predicted ratios by several per cent.

The finer details of the variation of the strengths of ammonium and carboxylic acids with structure remains itself a problem of notorious difficulty (29, 30, 31) and it is doubtful whether a rigorous discussion of the deviations observed in Table III is possible solely from the standpoint of inductive effects. The amount of data presently available is not really sufficient to provide for an adequate test of the Halevi-Streitwieser-Taft treatment of isotope effects, and there is an obvious need for more accurate measurements. To partially rectify this situation, the K(H)/K(D) ratios for the isotopic weak acid pair $C_6H_5CH_2COOH/C_6H_5CD_2COOH$ have been redetermined as a preliminary to measurements on the following isotopic pairs:- $4\text{-}NO_2\text{-}C_6H_4CH_2COOH/4\text{-}NO_2\text{-}C_6H_4CD_2COOH$ and $4\text{-MeO-}C_6H_4CH_2COOH/4\text{-MeO-}C_6H_4CD_2COOH$. These measurements form the main contribution of the present thesis. The inductive treatment mentioned earlier requires that the isotope effect in these three acid pairs should be independent of the nature of the group in the 4-position of the aromatic side chain, and in consequence the above series of compounds provide a further test of the adequacy of this treatment.

Because $\delta_{Ar}\,\delta_i\,pK_a^*$ was expected to be small, a precise method for determining the pK_a values of the individual acids was mandatory. The most precise method

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* δ_{Ar} and δ_i are chemical operators denoting respectively changes in the structure of an aryl group and isotopic changes. This type of notation is now frequently employed, see ref. (32) & (33).

for determining pK_a^* values of carboxylic acids appears to be the conductance method, which is apparently also well suited to the determination of isotope effects without the determination of the absolute pK_a of either isotopic acid. A detailed consideration of these matters also forms an important part of the subject matter in the present thesis.

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[*] The symbols K_t and K_a will both be used to represent thermodynamic equilibrium constants in this thesis.

TABLE III

Secondary Isotope Effects Calculated from a Modified Linear Inductive Free Energy Relationship

Acid pair	Ref.	K(H)/K(D)	
		Obs.	Calc.
$CD_3CH_2COOH/CH_3CH_2COOH$	22	1.016	1.014
$CH_3CD_2COOH/CH_3CH_2COOH$	22	1.08	1.021
$PhCD_2COOH/PhCH_2COOH$	22	1.12	1.02
$CD_3NH_3^+/CH_3NH_3^+$	24	1.13	1.08
$(CD_3)_2NH_2^+/(CH_3)_2NH_2^+$	24	1.32	1.17

EXPERIMENTAL

PREPARATION OF MATERIALS

General:

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian A-60 analytical spectrometer and peaks are reported on the τ scale relative to tetramethylsilane as an internal reference. For analytical purposes integrationsof the peak intensity were recorded several times and separate integrations agreed to within one percent.

Infrared spectra were recorded on a Perkin-Elmer Model 237B grating spectrophotometer and also on a Unicam SP100 spectrophotometer using both the potassium chloride disc technique (2 mg of sample in 200 mg KCl) and the liquid cell technique (10 mg. acid in 1 ml. solvent).

Phenylacetic-α,α-d_2 acid has been prepared previously by Ives (34) using a base-catalysed exchange reaction in a Pyrex bomb and by Halevi and co-workers (22) via the reduction of ethyl benzoate with lithium aluminum deuteride in ether. Saunders and co-workers (35) have prepared 4-methoxyphenylacetic-α,α-d_2 acid using a method similar to that described by Ives. Efforts to prepare phenylacetic-α,α-d_2 acid via hydrolysis and decarboxylation of phenylmalonic ester (36) have also proved successful but yields were erratic when this method was applied to the preparation of 4-methoxyphenylacetic acid (35).

A modified synthesis of deuterated monocarboxylic acids of the type RCD_2COOH (R = phenyl, 4-substituted phenyl,

α and β-naphthyl) has been developed using an exchange reaction involving D_2O and triethylamine. The reaction probably proceeds via the removal of the methylene protons from the free acid by the organic base.

Preparation of Phenylacetic-α,α-d_2 Acid:

Phenylacetic acid (10 g., 0.074 mole), deuterium oxide (15 ml.) and triethylamine (5 ml., 0.036 mole) were heated at 110°C for 52 hours in an oil bath. The nuclear magnetic resonance spectrum of the neat mixture showed, by integration, about 88.2 % methylene deuteration. The mixture was acidified with approximately 6M DCl, prepared by the slow addition of thionyl chloride to cold deuterium oxide. The white acid precipitated was collected by filtration, washed once with cold spectrograde cyclohexane and dried for 24 hours in a vacuum over phosphorous pentoxide. A second exchange was carried out by dissolving the partially deuterated acid in triethylamine (5 ml.) and deuterium oxide (15 ml). The resulting mixture was heated for 96 hours at 82°C. The n. m. r. spectrum indicated methylene deuteration of ca.96.7 %. The solution was then heated for a further 48 hours, acidified with 6 M DCl and the precipitated acid recovered as previously. The recovered acid was recrystallized once from cyclohexane and once from water and dried over phosphorous pentoxide for 24 hours, m.p. 75-76°C, (lit. 76.7°C (37)), yield 75%. A deuterium analysis by n. m. r. of the acid in carbon tetrachloride showed 98% deuteration.

Rate of Deuterium Exchange:

Phenylacetic acid (10 g.) was dissolved in deuterium oxide (15 ml.) and triethylamine (5 ml.) and the mixture heated for 182 hours. During this period of time the extent of hydrogen-deuterium exchange was determined by recording nuclear magnetic resonance spectra of aliquots (1 ml.) of the reaction mixture. A plot of the percentage deuteration against time is shown in Fig. III and the results appropriate to this study are given in Table IV.

Preparation of Phenylacetic -α,α-d_2 Acid from Phenylmalonic Acid:

Diethyl phenylmalonate was obtained from Eastman Kodak and was used without further purification.

Diethyl phenylmalonate (20 g., 0.088 mole) was refluxed for 2 hours in 120 ml of 6N sodium hydroxide. The mixture was cooled, neutralized with dilute hydrochloric acid, extracted with ether and the extract dried for several hours over anhydrous sodium sulphate. Removal of the ether gave an oily solid which was washed with carbon tetrachloride to remove both unhydrolysed ester, and phenylacetic acid, the latter formed via the decarboxylation of phenylmalonic acid during hydrolysis. The phenylmalonic acid was dried in a vacuum over phosphorus pentoxide, m.p. 149-150°C (decomp.) (lit. 152-153°C (decomp.) (38), Yield 6.5 g. A n. m. r. spectrum of the white solid gave no indication of phenylacetic acid being present.

Phenylacetic-α,α-d_2 Acid.

Phenylmalonic acid (5 g., 0.028 mole) was dissolved in deuterium oxide (10 ml.) and acetonitrile (5ml).

Table IV

Rate of Hydrogen-Deuterium Exchange of the Phenylacetic Acid Extracyclic Methylene Group in D_2O/Et_3N. T=110°C.

Time (hr.)	% Exchange
14	21.8
39	40.5
63	54.1
158	82.5
182	82.4

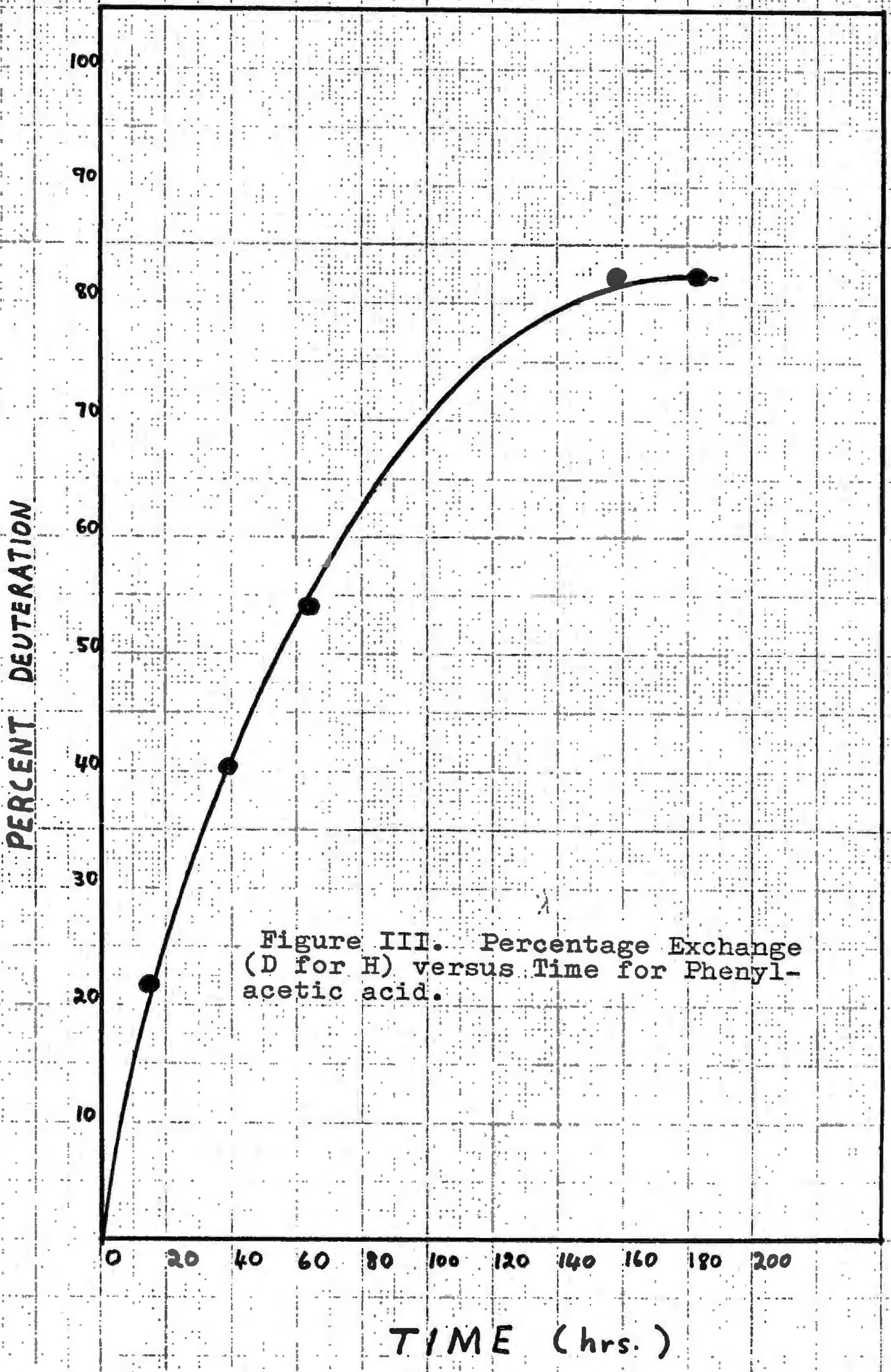


Figure III. Percentage Exchange (D for H) versus Time for Phenylacetic acid.

A n. m. r. spectrum recorded ten minutes after mixing showed 48% phenylmalonic-d_1 acid. The mixture was heated at 40°C for 6 hours; n. m. r. spectrum indicated complete deuterium exchange and some decarboxylation of the dicarboxylic acid giving a weak CH_2/CHD peak at $\tau = 6.45$. The mixture was heated for 17 hours at 84°C and n. m. r. spectrum showed complete decarboxylation of the diacid and, by integration, methylene deuteration 95% complete. The mixture was cooled and two layers separated. Carbon tetrachloride was added and the two layers were separated, the water layer washed with ether and the ether layer dried over anhydrous sodium sulphate. Evaporation of the solvents yielded 4.2 gms. of 95% phenylacetic-α,α-d_2 acid, (m.p. 74-76°C).

Preparation of 4-nitrophenylacetic-α,α-d_2 Acid:

4-Nitrophenylacetic acid was obtained commercially and was used without further purification.

A mixture of 4-nitrophenylacetic acid (10 g.,0.055 mole), deuterium oxide (15 ml.) and triethylamine (5 ml., 0.036 mole) was heated for 11 hours at 50°C in an oil bath; the n. m. r. spectrum indicated 89.6% methylene deuteration. The triethylamine was removed by evaporation, the mixture cooled, acidified with 6N DCl and filtered. The recovered acid was dissolved in ethyl ether and precipitated using cold pentane (b.p. 35-50°C). The acid was dried over silica gel in a vacuum desiccator, m.p. 149-150°C, (lit. 152°C.) (39).

The process of deuterium exchange was repeated by dissolving the ca. 90% deuterated material in deuterium oxide, (20 ml) triethylamine (7 ml.) and heating at 50°C for 11 hours. The n.m.r. spectrum indicated 98.8% deuteration of the 4-nitrophenylacetic acid; m.p. 148.8 - 150°C, yield 71%.

Exchange reactions were carried out at several temperatures. Heating for two hours at 80°C gave over 90% deuteration of the methylene hydrogens, but resulted in some decarboxylation of the acid giving 4-nitrotoluene; m.p. 47-48.5°C, (lit. 53°C) (37). A small n.m.r. peak at τ = 7.52 showed, by integration, 78% deuteration of the methyl group.

Methylene hydrogen-deuterium exchange was also observed at room temperature. After 7.5 hours at 25°C 42% deuterated acid was obtained, 24 hours resulted in 70% deuteration.

<u>Rate of Deuterium Exchange:</u>

A study of the rate of hydrogen-deuterium exchange on 4-nitrophenylacetic acid at 50°C using earlier experimental conditions was followed using n.m.r. (TableV). The acid (10 g.) was dissolved in triethylamine (5 ml.) and deuterium oxide (15 ml.). Over a period of seven hours, seven aliquots (1 ml.) were removed from the reaction flask and n.m.r. spectra recorded. The percent deuteration was plotted against time (Fig. IV).

TABLE V

Rate of Hydrogen-Deuterium Exchange of the 4-Nitrophenylacetic Acid Extracylic Methylene Group in D_2O/Et_3N; T= 50°C.

Time(hr.)	% Exchange
0.25	11.6
1.00	44.2
1.55	57.0
2.25	67.2
4.30	81.7
6.88	86.7
6.95	85.1

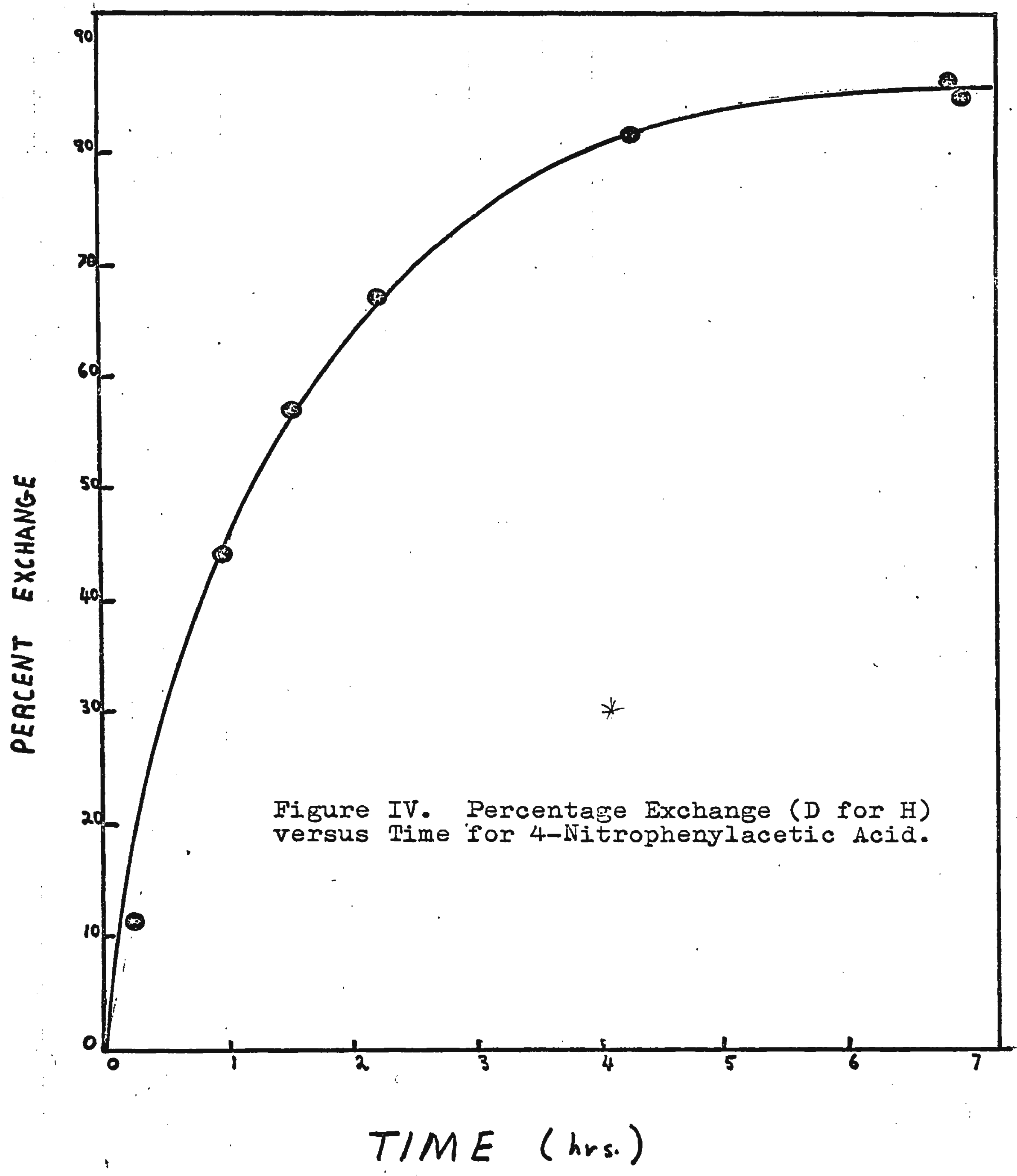


Figure IV. Percentage Exchange (D for H) versus Time for 4-Nitrophenylacetic Acid.

Preparation of 4-Methoxyphenylacetic Acid and 4-Methoxyphenylacetic-α,α-d_2 Acid.

4-Methoxybenzyl Chloride:

4-Methoxybenzyl chloride was prepared by the method of Lee et al (40). The 4-methoxybenzyl alcohol was obtained commercially and used without further purification.

4-Methoxybenzyl alcohol (93.5 g., 0.68 mole) was dissolved in benzene (1000 ml) dried over sodium for several days. HCl gas, dried by passing over a long column packed with calcium chloride, was bubbled through the mixture cooled to -5°C to 0°C for 1¼ hours. The benzene layer was separated from the aqueous layer and dried for several hours over anhydrous calcium chloride. The solvent was removed under vacuum at 50°C and the product vacuum distilled; b.p. 71-75°C/1 mm. Lit. 101-3/8-10 mm. (41).

Attempts to prepare the chloride by adding thionyl chloride dropwise to 4-methoxybenzyl alcohol in ethyl ether were unsuccessful. The distillation of the crude material resulted in polymerization.

4-Methoxybenzyl cyanide:

This compound was prepared by an adaptation of the method of preparation of nitriles from aryl methyl halides by Friedman *et al* (42).

4-Methoxybenzyl chloride (43.2 g.) 0.28 mole) was added, dropwise, over a period of thirty minutes to dimethyl sulfoxide (135 ml) and potassium cyanide (19.5g.,0.30

mole), and stirred vigorously at room temperature. After 2½ hours of stirring a peak appearing at $\tau = 6.11$ in an n. m. r. spectrum indicated about 30% 4-methoxybenzyl cyanide formed. An additional four hours of vigorous stirring gave 90% of the required cyanide. The mixture was stirred for 12 more hours, poured into water (200 ml.), the organic layer separated and the water residue washed with four 100 ml portions of ether. The ether in turn was washed with water (200 ml.) to remove any dimethyl sulfoxide present. The ether extracts were combined with the orange organic layer and dried over anhydrous magnesium sulphate. The ether was removed by distillation and the product vacuum distilled: b.p. 98-100°C/ 1 mm. (lit. 131-4°C/ 9 mm. (41), yield 33g., 84 %.

4-Methoxyphenylacetic acid:

4-Methoxybenzyl cyanide (33.3 g.) was dissolved in 95% ethanol (61.9 ml), heated to 87°C, and 50% sodium hydroxide (76.2 ml) added. The mixture was refluxed for 13 hours, cooled, and the resulting sodium salt collected by filtration. The sodium salt of the acid was washed with pentane, dissolved in a minimum amount of water and acidified with 6N hydrochloric acid. The filtered acid was washed with cold water and petroleum pentane and dried in vacuo over P_2O_5, m.p. 85-86°C (lit. m.p.86°C) (43) yield 34.4 g.

4-Chlorophenylacetic Acid:

Commercial grade 4-chlorobenzyl cyanide (32.5g, 0.22 mole) was hydrolysed by the same procedure as 4-methoxybenzyl cyanide giving 4-chlorophenylacetic acid; m.p. 103-105°C, (lit.105°C (39)) yield 30.1 g.

Methylene Hydrogen-Deuterium Exchange:

4-Methoxyphenylacetic, 4-chlorophenylacetic, 1- and 2-naphthylacetic acid were treated with deuterium oxide (15 ml) and triethylamine (5 ml). The temperature of the reaction mixture and the time allowed for isotopic exchange are given in Table (VI). The exchange rates of the methylene hydrogens were studied by integration of the n.m.r. spectra.

Infrared spectra:

Infrared spectra recorded on both the Perkin-Elmer Model 237B grating spectrophotometer and the Unicam SP100 spectrophotometer give inconclusive results as to the isotopic purity of the carboxylic acids studied. Halevi et al (22) reported similar observations on the spectra of phenylacetic-α, α-d_2 acid. As a result the infrared spectra of the acids will not be reported in this present work.

Nuclear magnetic resonance spectra:

The n.m.r. chemical shifts for several compounds reported in the present work are given in Table VII.

TABLE VI

Rate of Methylene Exchange

COMPOUND	Exchange number	Time (hr)	Temp (°C)	Percent Deuteration
4-methoxyphenyl-acetic acid	1	16	100	22.6
		23	120	81.0
		7	120	84.8
		16	120	92.8
	2	17	130	94
		78	116	94*
	3	96	84	-
		48	117	98
4-methoxyphenyl-acetic acid	1	96	117	91.6
4-chlorophenyl-acetic acid	1	26	84	71.4
		50	84	87.2
		96	82	92.5
	2	11.5	117	96.5
		48	117	97.4
4-chlorophenyl-acetic acid	1	120	75-80	88.1
1-naphthyl-acetic acid	1	72	80	40.3
		48	80	55.0
		120	80	63.9
	2	26	84	78.3
		50	84	90.0
		96	82	95.2

*A very small change in the deuteration reaction for the second exchange was observed. This was probably due to incomplete drying of the acid between exchanges.

TABLE VI (Cont'd)

Compound	Exchange number	Time (hr)	Temp. (°C)	Percent Deuteration
2-naphthyl-acetic acid	1	76	84	84.4
		52	84	89.2
	2	72	87	99.0

TABLE VII

Nuclear Magnetic Resonance Spectra

Acid	τ values			OMe	
	CH	CH_2	Aromatic		Solvent
Phenylacetic	-	6.46	2.78	-	CCl_4
Phenylacetic-α,α-d_2	-	-	2.78	-	CCl_4
4-methoxyphenylacetic	-	6.50	2.75,2.90,3.15,3.30	6.25	CCl_4
4-methoxyphenylacetic-α,α-d_2	-	-	2.74,2.90,3.14,3.29	6.25	CCl_4
4-nitrophenylacetic	-	6.23	1.75,1.89,2.42,2.56	-	CH_3CN
4-nitrophenylacetic-α,α-d_2	-	-	1.76,1.90,2.43, 2.57	-	CH_3CN
Phenylmalonic	5.53	-	-	-	CCl_4
1-naphthylacetic	-	5.92	1.9 - 2.7	-	CH_3CN
2-naphthylacetic	-	6.40	2.4 - 3.0	-	CH_3CN
4-chlorophenylacetic	-	6.38	2.74	-	CH_3CN

PURIFICATION OF MATERIALS

(a) Potassium chloride:

Fisher Scientific (A.R. Grade) potassium chloride was precipitated from a saturated aqueous solution by the addition of distilled 95% ethyl alcohol and this procedure was repeated three times. The salt was filtered, washed several times with ethyl alcohol and dried under vacuum at 110°C for two days in a drying pistol. The salt was then powdered in an agate mortar, dried an additional two days in the pistol. The purified KCl was stored in a glass stoppered weighing bottle over silica gel in a vacuum desiccator.

A second specimen of potassium chloride was precipitated from a saturated aqueous solution, twice by the addition of concentrated hydrochloric acid and once by the addition of 95% ethyl alcohol.

(b) Purification of 4-substituted phenylacetic acids:

The 4-substituted phenylacetic acids were purified by recrystallization from conductivity water, spectrograde cyclohexane and sublimation. To ensure the purity of the acids several methods of purification were used on the various batches of each acid. The purification procedure for each batch along with the appropriate conductance run numbers are recorded in Tables VIII. The acids were dried at the temperature of refluxing acetone, in vacuo using silica gel as a desiccant.

TABLE VIII

Acid Purification

Run Numbers	Method of Purification
Phenylacetic 1-6	Recrystallized twice from water, once from pentane. Dried two days over phosphorous pentoxide.
7-8	Recrystallized from water twice, dried over P_2O_5. Acid turned light brown.
9-17	Acid recrystallized from water, sublimed recrystallized twice from cyclohexane, once from water and dried in a pistol for several days.
Phenylacetic-d_2 1-4	Dissolved in carbonate solution, charcoal added, filtered hot and concentrated HCl added. Acid recrystallized twice from water and dried 3 days in a pistol.
5-10	Recrystallized once from water and cyclohexane, sublimed, recrystallized twice from water and dried in a pistol for 4 days.
11-15	Sublimed, recrystallized twice from cyclohexane, once from water and dried in a pistol for 3 days.
4-nitrophenylacetic 1-8	Recrystallized twice from water, sublimed, dissolved in hot water and filtered hot twice, and dried over acetone in a pistol.
8-12	Sublimed, recrystallized twice from water and dried in a pistol.

TABLE VIII (cont'd)

Run Numbers		Method of Purification
4-nitrophenylacetic-d_2	1-5	Recrystallized three times from cyclohexane, once from water and dried 24 hours in a pistol.
4-methoxyphenylacetic	1-6	Recrystallized from water; dissolved in carbonate, charcoal added and filtered hot solution acidified, filtered and acid recrystallized twice from cyclohexane, twice from water and dried in a pistol for 3 days.
4-methoxyphenylacetic d_2		
	1-4	Recrystallized from cyclohexane, sublimed, recrystallized from cyclohexane and dried in a pistol.
	4-7	Above material was recrystallized from water, and dried in a pistol for 24 hours.

<u>Purification of Acetic Acid(Runs 1 - 8).</u>

A. R. acetic acid was fractionally frozen twice and then distilled using a gold spinning band column (Wester Faust) b.p. 117.5-118°C.

PREPARATION OF SOLUTIONS

(1) Conductivity water:

Conductivity water was prepared by the distillation of deionized tap water from a Barnsted still. The tap water was passed through a deionizer (Ion Exchange Products, Inc.), filled with 3 lbs. of Analytical Grade Amberlite MB-1 (44) (45), before entering the Barnsted still. The still, with Borosilicate Glass Condensing System, is designed to produce a distillate of 0.001 ppm total solid content, with electrical resistances ranging from 1.5 to 5 million ohms per cc. Two 3-necked 10-l round-bottomed flasks, fitted with teflon stoppers were used as water reservoirs. These flasks had previously been cleaned with boiling nitric acid for about three days, after which time they were rinsed with distilled water and steamed for an additional three days. The steam was generated in a 2-l round-bottom flask and forced into the reservoirs through 8 mm pyrex tubing.

The distilled water in the reservoirs was siphoned through three feet of 10 mm pyrex tubing into the second amberlite deionizer. This deionizer was found necessary to remove carbon dioxide dissolved in the water after distillation.

The ion-exchange resin columns were filled by pouring a slurry of Amberlite MB-1 in distilled water into the columns, care being taken to minimize the trapping of air in the resin layer. The columns were washed every day before usage with a minimum of three liters of water. This was necessary to remove possible decomposition products of the resin. The solvent conductance was determined by measuring its resistance in cell 1 using a 10,034 ohm shunt. The specific conductivity of the water was found to vary from 1.8 - 3.0 x 10^{-7}.

(2) Nitrogen purification:

Nitrogen was led successively through a series of cleaning towers to remove any possible carbon dioxide, ammonia and other acid or basic species present. The purification procedure is listed in Table IX.

All joints between the various towers in the purification train were made by butting glass tubing together with either rubber pressure tubing or nalgon tubing. Dust particles were trapped using a tube packed with glass wool.

(3) Cleaning procedures:

The cells were filled with concentrated nitric acid and were heated for three days in a boiling water bath. They were then rinsed with conductivity water, steamed for about 48 hours and given a final rinse with conductivity water. The cells were left for a period of three weeks before determining the cell constants. Subsequent to the above procedures the resistance of conductivity water in the cells was found to remain steady for over a half hour indicating the removal of surface ions was complete.

TABLE IX

Nitrogen Purification

Purification Tower	Reagent
Two gas-washing bottles (one with a sintered glass bubbler).	6N Sodium hydroxide
Column for removing CO_2	Calcium oxide
Two gas-washing bottles with sintered glass butblers.	Conc. sulfuric acid
Two columns for removal of acid spray.	Conductivity water
Two drying towers	Drierite
Drying trap	Liquid nitrogen
Dust removal tube	Glass wool

The cleaning procedure was applied to all flasks used for the preparation of acid and potassium chloride solutions.

(4) Preparation of potassium chloride solutions:

Conductivity water, obtained as previously described, was used in the preparation of potassium chloride solutions. Solutions were prepared by weight and concentrations are expressed in moles/1000 g. The flasks in which the solutions were prepared were fitted with a three-hole teflon stopper. Through one hole was led a teflon stopcock controlling the flow of conductivity water. The second opening was connected to the purified nitrogen line and the third opening accommodated a small pyrex delivery tube. The delivery tube served as a means of flushing out the volumetric and was also used to deliver solutions to the conductance cells. Water was withdrawn from the volumetric, through a cell and into a water pump. Purified nitrogen was kept over the water in the volumetric at all times.

Complete removal of ions from the surface of the glass was accomplished by passing 12-l. of deionized water (tap water passed through Amberlite) through the volumetric. 3-l. of conductivity water was flushed through the system and its specific conductivity recorded. When the conductivity of the water dropped below 3.5×10^{-7} the pyrex probe and teflon stopper were removed and the volumetric was fitted with a ground glass stopper. The pyrex probe and teflon stopper were dried in an oven at 100°C.

A sample of potassium chloride was carefully weighed on a Sartorius Selecta balance in a sample vial weighing about 5g. The vial used had previously been left in concentrated nitric acid for one week, washed with conductivity water and dried in an oven. The vial was manipulated with forceps. The sample and the vial were immediately dropped into the volumetric containing good conductivity water.

After mixing the solution thoroughly the dry pyrex probe was lowered into the volumetric and fresh nitrogen was introduced. The water pump sucked the solution into a cell. The cell was disconnected from the nalgon line and the solution thrown away. This was repeated four times, finally retaining the last filling. The cell with its contents was then capped and placed in the thermostat.

(5) Preparation of Acid Solutions.

Solutions of the solid acids were prepared following the preparation procedure for potassium chloride solutions. Several changes were made in the technique for weighing acetic acid. To minimize evaporation of the acid the sample vial containing acetic acid had to be weighed stoppered. After weighing the stopper was removed and the acid and vial dropped immediately into the conductivity water in the volumetric. Care was taken to avoid contact between the acid and the stopper.

DESCRIPTION OF APPARATUS

(1) Conductivity Bridges:

The resistances of the acid and KCl solutions were measured on a Jones-Joseph type bridge (46) manufactured by the Tinsley Company, and a General Radio Impedance Bridge. The resistance of acid solutions of deuterated and undeuterated phenylacetic and 4-nitrophenylacetic acids were studied using the Tinsley Bridge while conductance values for acetic acid and 4-methoxyphenylacetic acids were recorded on the impedance bridge. A comparison of the bridges over the range (500-12,000 Ω) gave resistance readings which agreed to better than 0.05%.

Tinsley Bridge:

Figure V shows a simplified block diagram of the 4896 Tinsley Bridge with auxiliary equipment. The bridge and accessories were assembled following the current description of Robertson (47) with certain minor modifications made necessary because some of the components described by this author were commercially unavailable.

Oscillator:

The source of 1000 c/sec alternating current was a Hewlett Packard (H.P.) oscillator model 200 AB. The power for the oscillator was supplied by a 120 volt line. No attempt was made to use a voltage stabilized power supply.

Bridge Balance:

Coarse balancing of the Tinsley Bridge (Fig.VI) was detected by observing a Lissajous pattern on an oscilloscope (I), H.P. model 120 B. A second oscillo-

Fig. IV

BLOCK DIAGRAM OF THE TINSLEY CONDUCTANCE BRIDGE

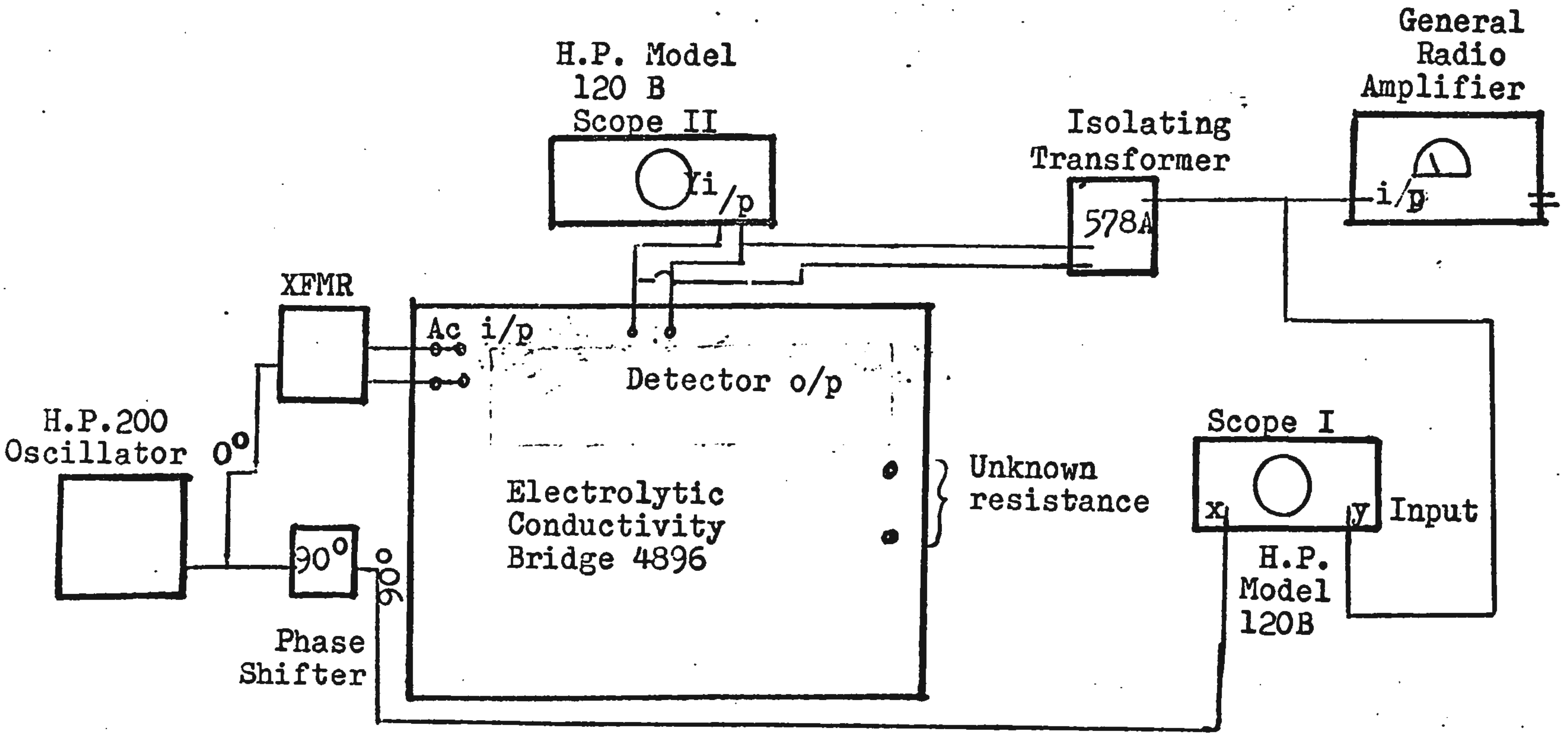
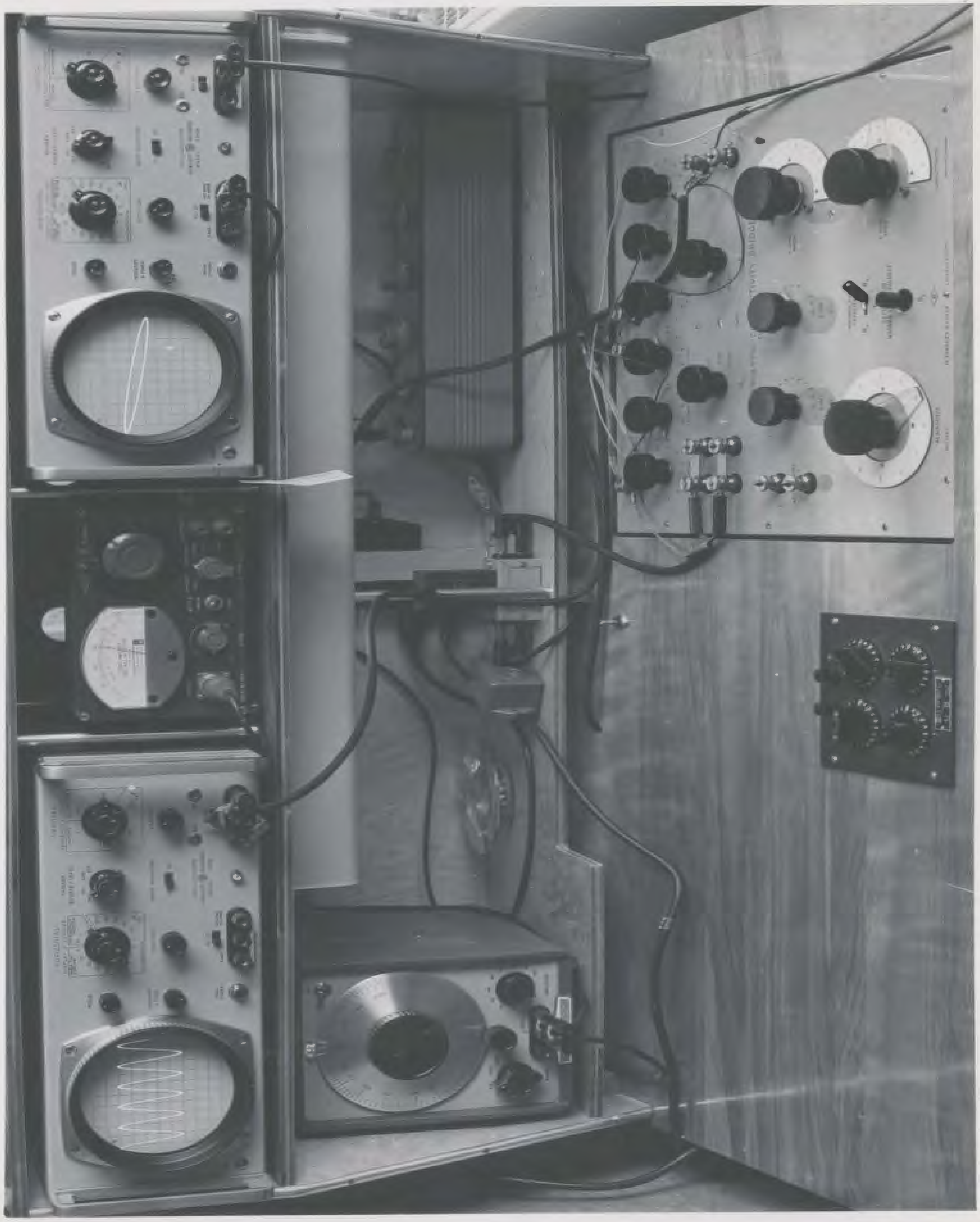


FIGURE VI



scope (II), H.P. 120 B, was used to observe the balance connected across the detector output. Final balance could accurately be obtained by observing the null detector which formed part of the General Radio amplifier, 1232 A. It was recommended that the output (O/P) of the amplifier be used to supply the input (i/P) to the y plates of the oscilloscope (I) but due to the high noise output (even at minimum gain) this was found to be impractical.

High Gain 1000 c/s Amplifier:

During the course of experimental study the General Radio amplifier was replaced by a 1000 c/s high gain amplifier, (Fig. VII). The bridge was connected to the amplifier through the 578-A transformer. The output of the amplifier was fed through shielded leads to the vertical input of the oscilloscope.

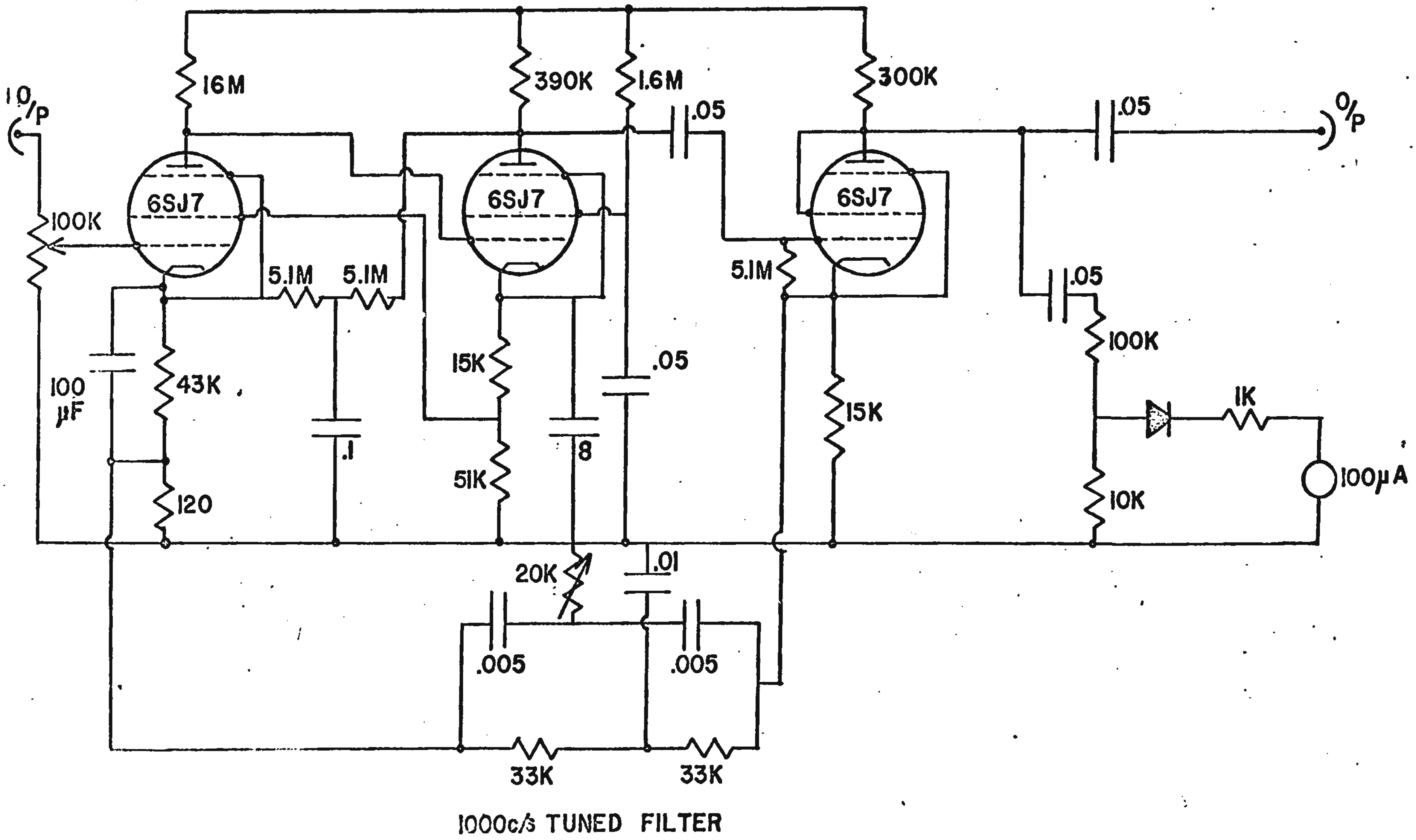
General Radio Impedance Comparator:

The General Radio Impedance Comparator, type 1605-A (Fig. VIII)is designed to measure and indicate on meters the magnitude and phase angle differences between two external impedances. The instrument is essentially a special self-contained bridge measurement system, consisting of a signal source, a bridge and a detecting circuit. The bridge proper consists of two external impedances to be compared and two highly precise 1:1 ratio arms. Since these ratio arms are equal to within 0.0001%, the accuracy of the impedance measurements depends largely on the precision of the external standard.

A description of the oscillator, amplifier and bridge circuit is given in the General Radio operating instructions for an Impedance Compartor,type 1605 - A,

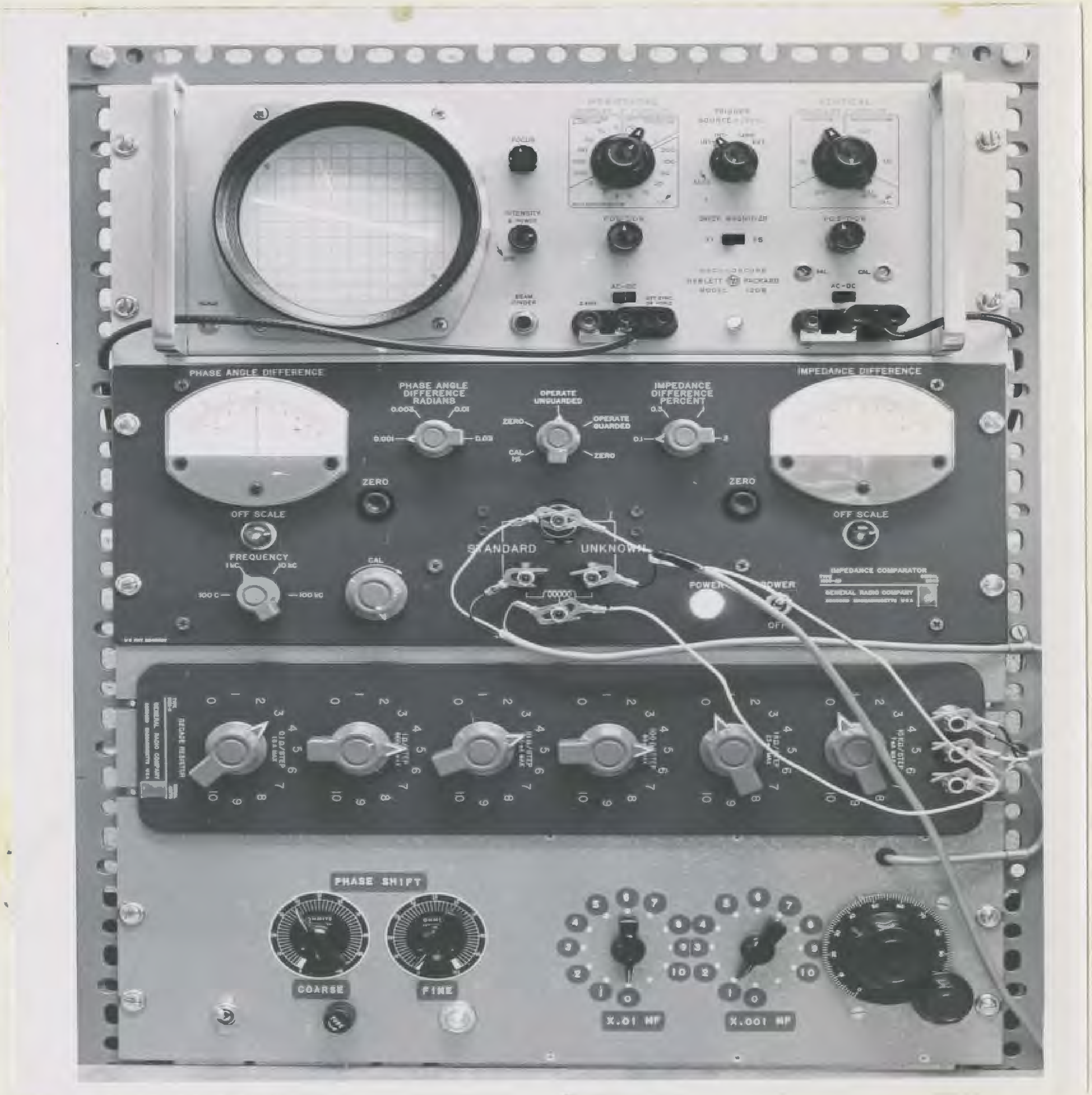
FIGURE VII

1000c/s AMPLIFIER



GAIN AT 1000 c/s 20,000
NOISE 100MV.

FIGURE VIII


FOCUS
INTENSITY & POWER
BEAM FINDER
TRIGGER SOURCE
SWEEP MAGNIFIER
POSITION
AC-DC
OSCILLOSCOPE
HEWLETT PACKARD
MODEL 120B
PHASE ANGLE DIFFERENCE
PHASE ANGLE DIFFERENCE RADIANS
0.002
0.01
0.001
0.03
OPERATE UNGUARDED
ZERO
OPERATE GUARDED
CAL
ZERO
IMPEDANCE DIFFERENCE PERCENT
0.3
0.1
3
IMPEDANCE DIFFERENCE
ZERO
ZERO
OFF SCALE
OFF SCALE
FREQUENCY
1 KC
10 KC
100 C
100 KC
CAL
STANDARD
UNKNOWN
POWER
POWER
OFF
IMPEDANCE COMPARATOR
GENERAL RADIO COMPANY
DECADE RESISTOR
GENERAL RADIO COMPANY
PHASE SHIFT
COARSE
FINE
X.01 MF
X.001 MF

Standard Impedance:

A General Radio resistance box, type 1432, was used as a standard with a range of 0.1 ohms to 111,111 ohms. The accuracy of the resistance increments is given as ± 0.05 %.

Assembly:

The General Radio Impedance Bridge was assembled by Mr. Ralph Parsons of the Technical Services Department of Memorial University and is illustrated in photographs given in Figs. VIII and X (ancillary circuit Fig. IX).

(2) Constant Temperature Bath:

The constant temperature bath (Fig. X.) consisted of a 34" x 32" x 36" metal-framed unit supporting two stainless steel tanks of dimension 28" x 13" x 18". One of the tanks, designed for temperatures from 0° to 50°C, was completely insulated by a one inch covering of styrofoam on the outer surface. To maintain the bath at 25°C it was necessary to heat and cool the bath simultaneously. Cooling was effected by passing cold water (ca. 17.5°C) through a copper cooling coil (3"x½") placed at the bottom of the tank. The auxiliary equipment required to produce the cooling will be described below.

A third stainless steel tank, 28" x 13" x 16", was installed under the 25°C temperature bath. Copper cooling coils from a Tecumseh 1/4 h.p. refrigerator were supported in the second tank on a metal frame. The cooling coils were made of ca. 100 ft. of copper tubing, wound in six spiral coils, placed ca 8" apart.

FIGURE IX

IMPEDANCE BRIDGE CIRCUIT

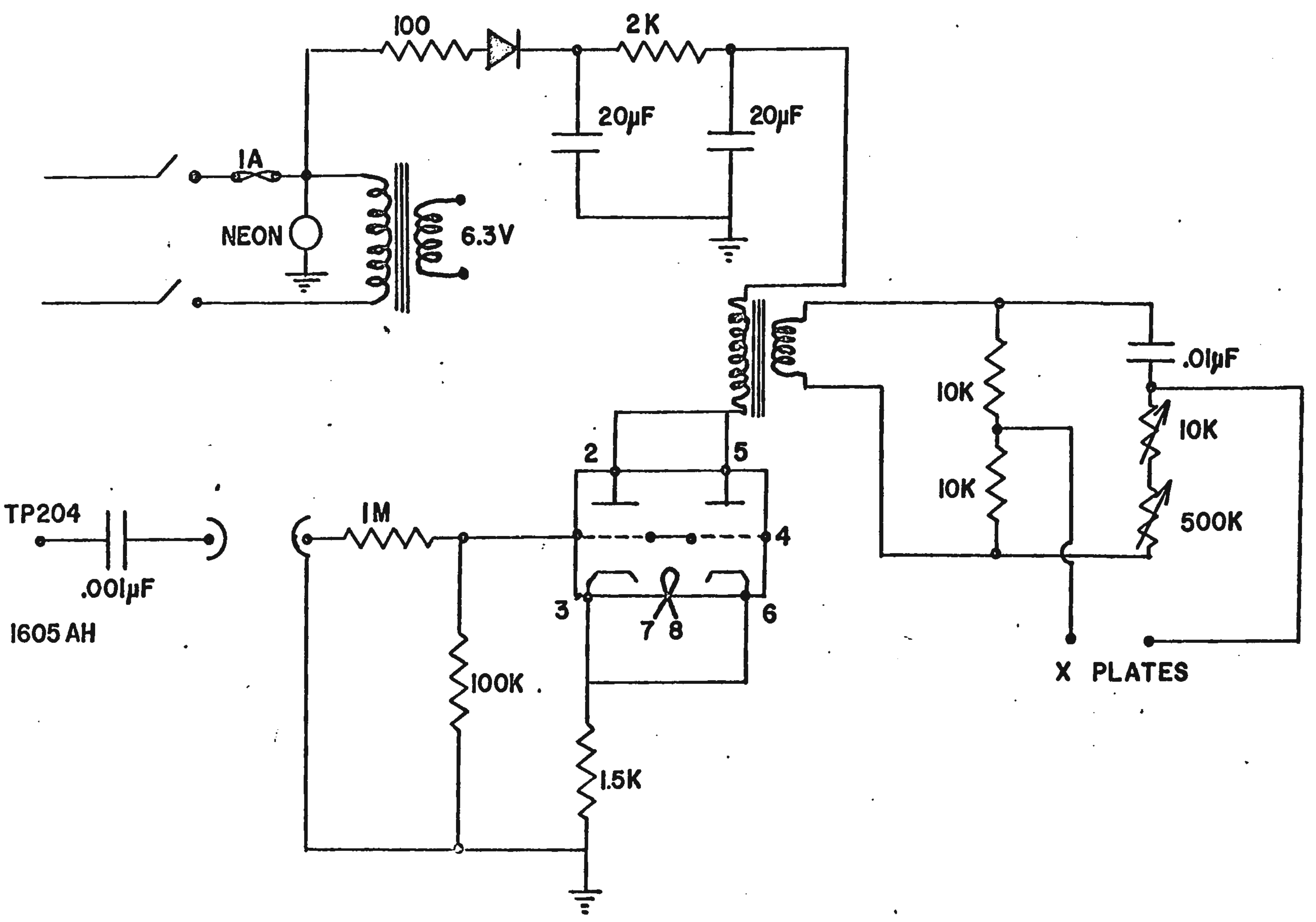
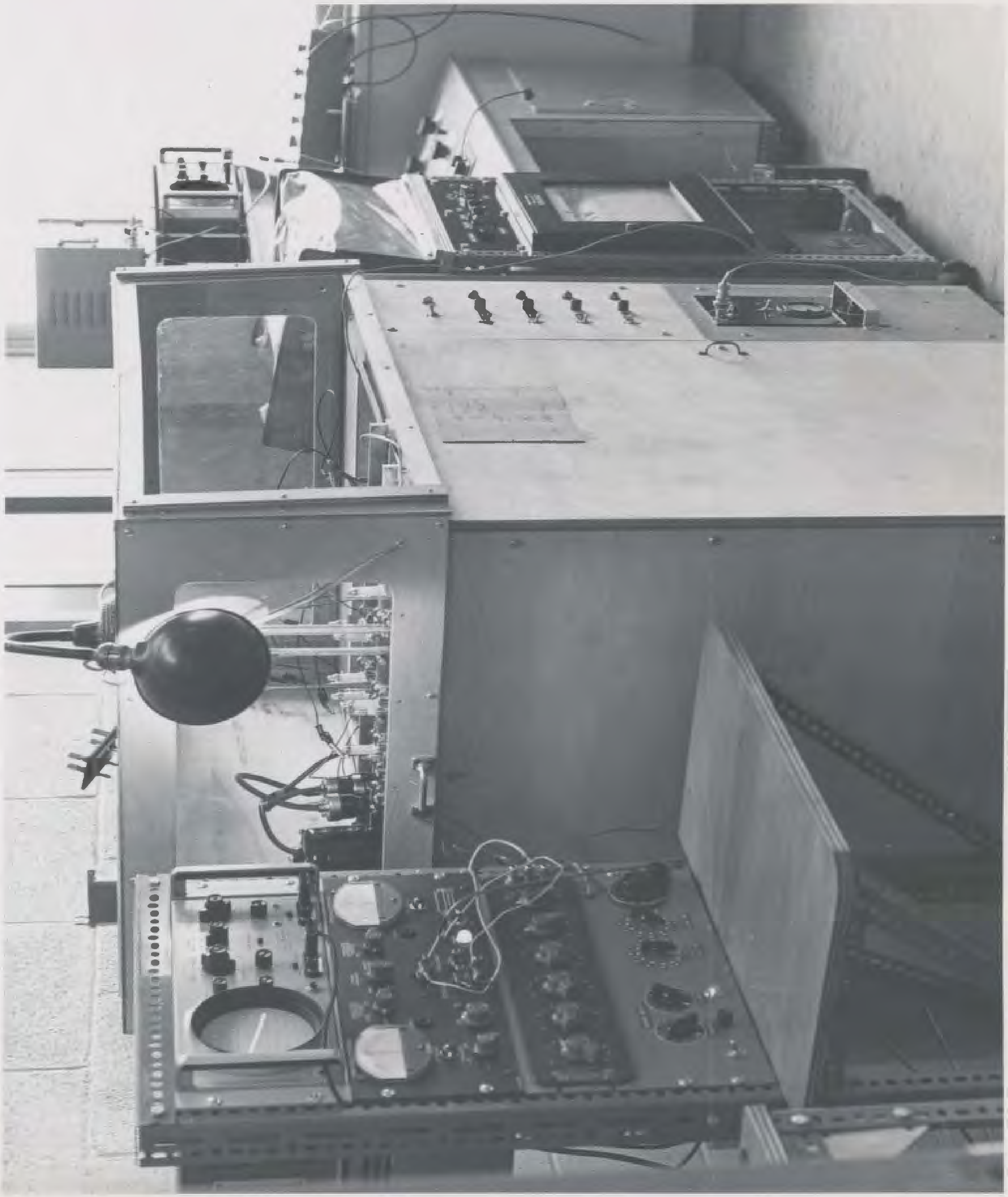


FIGURE X



Water in the cold bath was cooled to 17.5 ± 0.5°C. and pumped through heavy rubber tubing into the cooling coil of the upper constant temperature bath using a circulating pump. The rate of flow of the cold water was controlled by a by-pass arrangement using two control valves.

The temperature of the cold water bath was measured by installing a Fenwal Electronics thermistor (LB21J1) in a Wheatstone bridge circuit. The bridge detector was a microammeter and served as a rough guide to the actual temperature of the cold water bath.

The temperature of the cold water bath was controlled by a second Fenwal Electronics thermistor (GB32J2) in conjunction with a Wheatstone Bridge circuit (Fig. XII).

The oil bath was agitated by a 1/20 h.p. Cenco Centrifugal Electric stirrer (rated circulating capacity for water, 105 gal./min.), mounted on one end of the bath which was filled with 20 gal. of transformer oil (44).

The temperature of the bath was regulated by a Sargent Thermonitor (S-82050). This, in its essentials, consists of a background heater (125 watts) which can be controlled by a variac on the control box of the Sargent unit and an intermittent knife heater (250 watts), which is controlled by a Thermistor-Wheatstone Bridge circuit coupled to a variable reactor. During the course of the work the voltage across the bridge was reduced from 6 volts to 4 volts with a considerable improvement in the performance of this unit. A photograph of the thermostat bath is shown in Fig. XI.

FIGURE XI

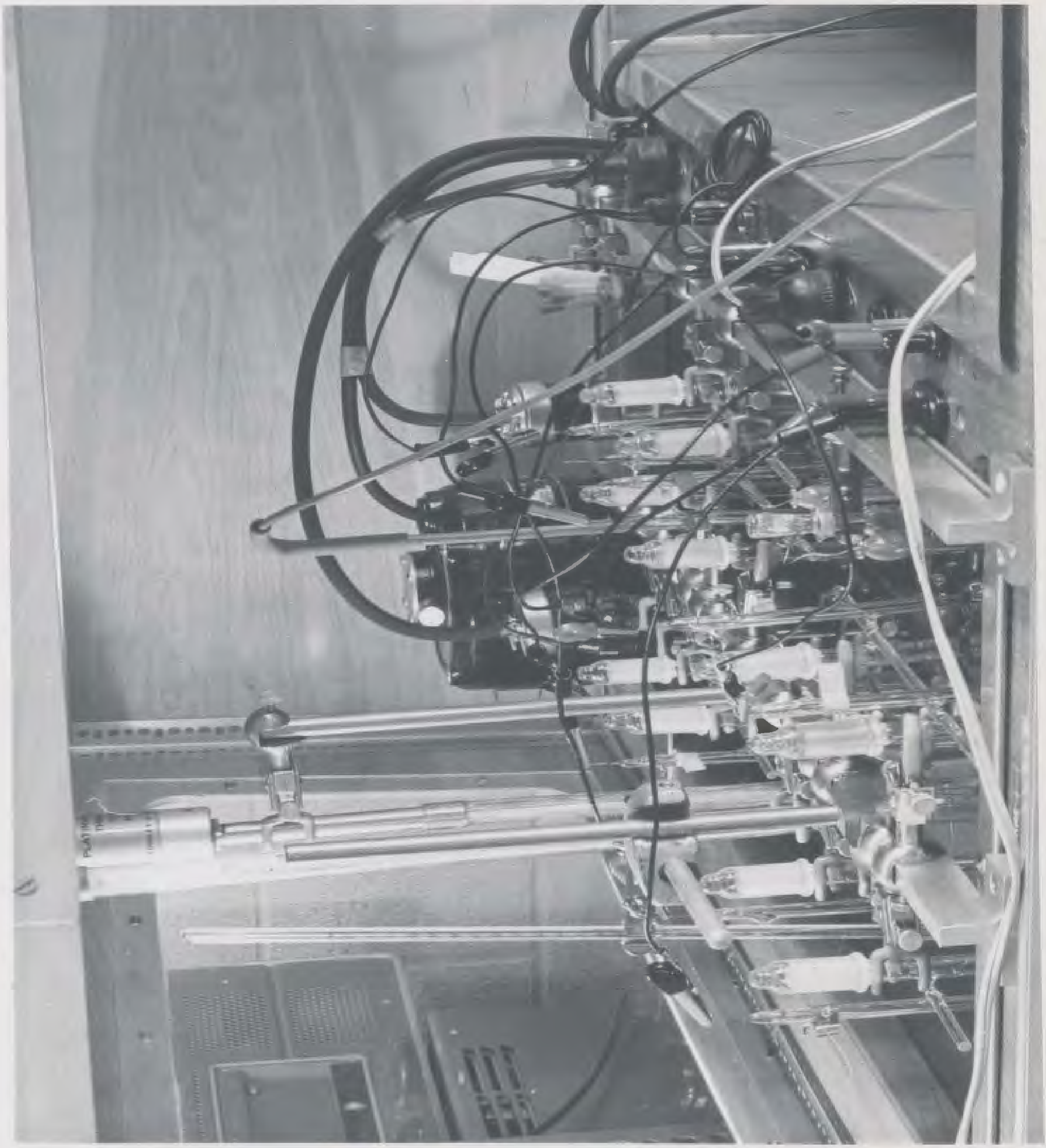


FIGURE XII

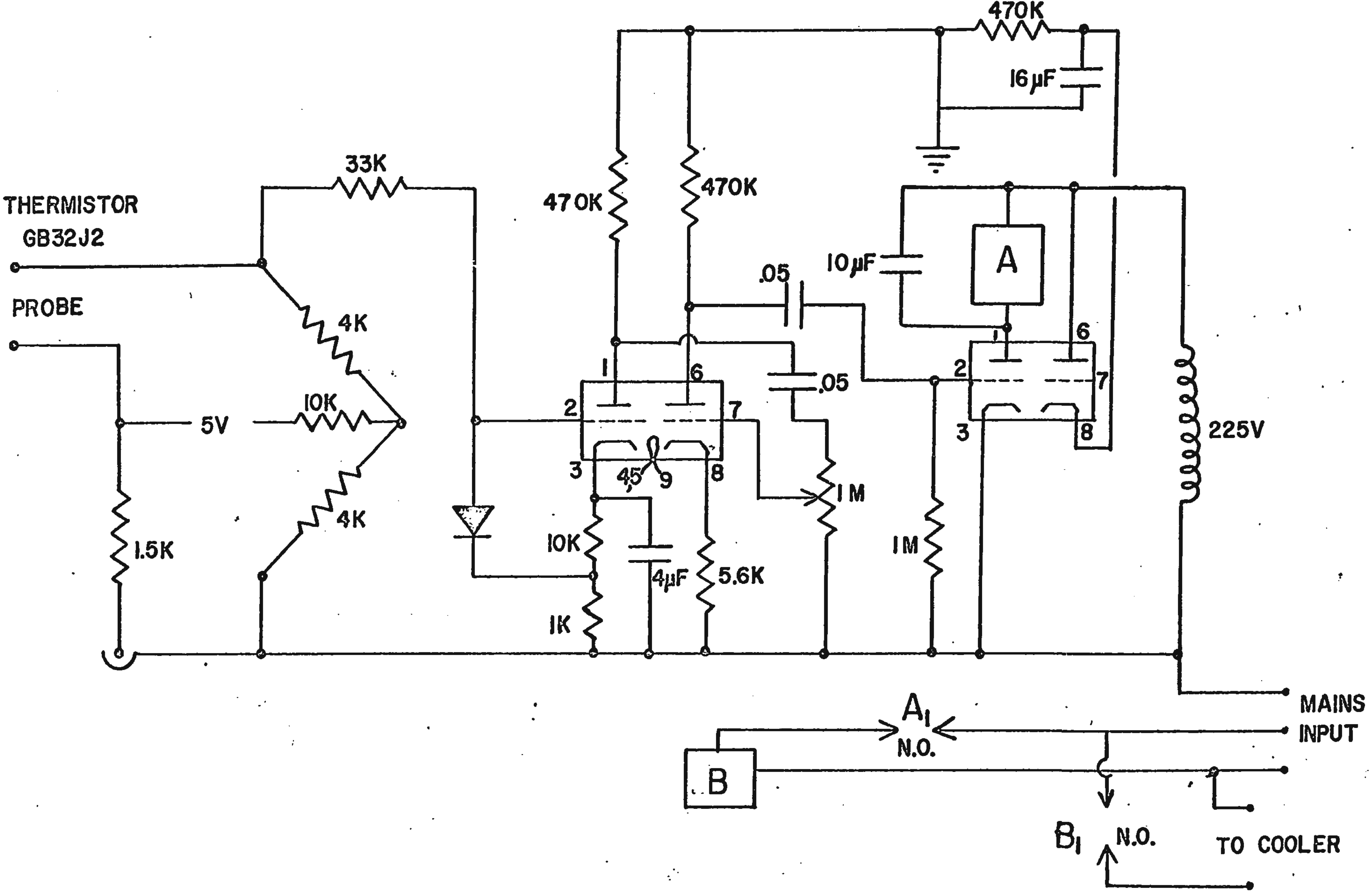
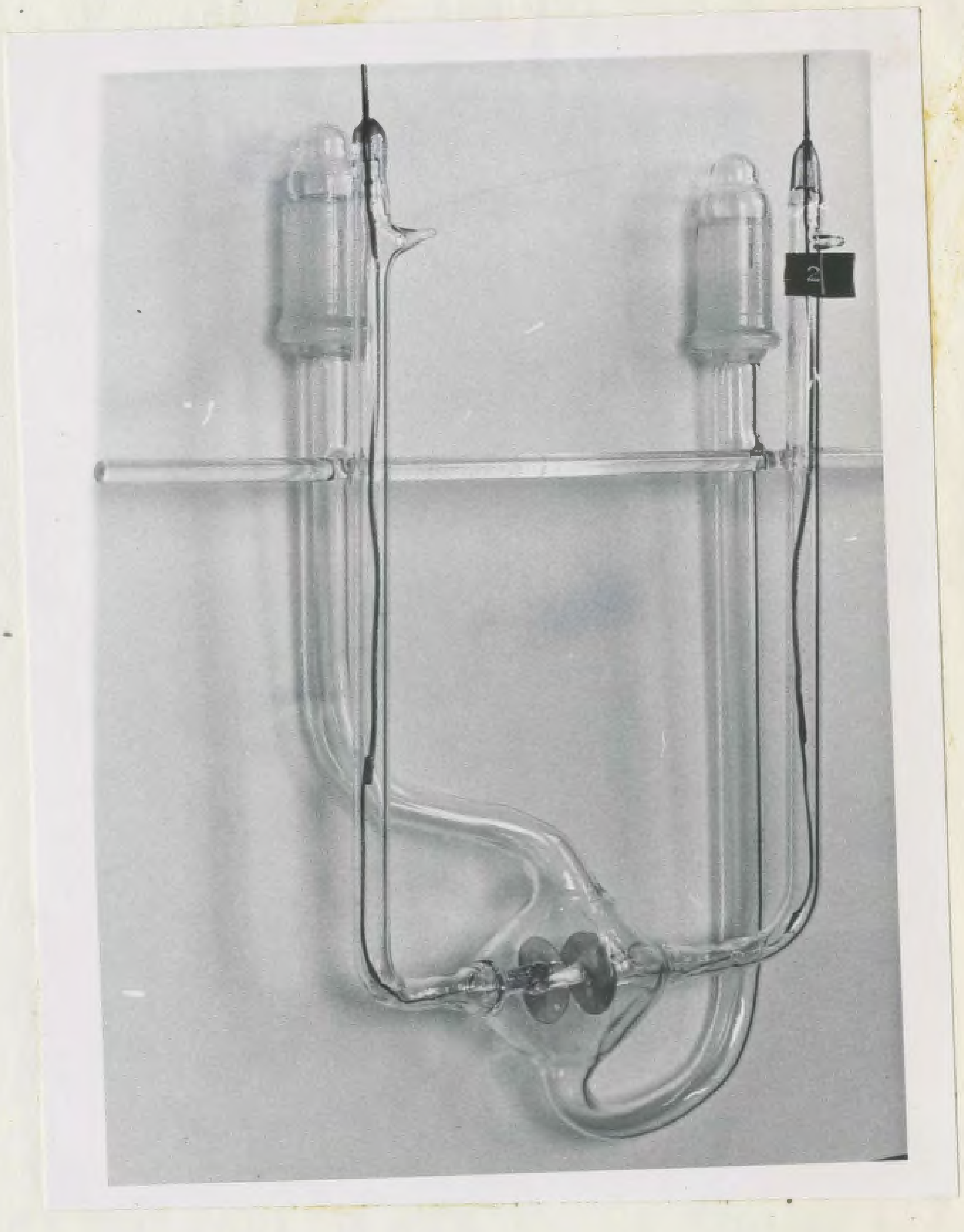

THERMISTOR
GB32J2
PROBE
33K
4K
10K
4K
5V
1.5K
470K
470K
470K
16µF
10µF
.05
.05
A
1
6
2
7
3
45
9
8
10K
4µF
5.6K
1K
1M
1M
225V
MAINS
INPUT
A1
N.O.
B
B1
N.O.
TO COOLER

FIGURE XIII



The constant temperature bath was controlled to better than 25.00 ± 0.01°C. over long periods of time. For periods up to several hours the temperature varied by less than 0.0022°C.

(3) Thermometry:

The constant temperature bath was adjusted to 25° ± 0.01°C using a mercury thermometer (range 0°-50°C) calibrated by the National Bureau of Standards. A Beckman Thermometer, calibrated at the National Research Council by Dr. J. M. W. Scott, indicated the temperature of the bath to be at 25° ± 0.005°C.

A platinum resistance thermometer, calibrated by the National Physical Laboratory, England, was used in conjunction with a Mueller Temperature Bridge, type 4772, manufactured by Tinsley and Company. Temperature readings recorded on the platinum resistance thermometer at 25°C differed by 0.001°C from the values observed using the calibrated Beckmann thermometer.

A Honeywell recorder was used to monitor the bath temperature over long periods of time. The recorder served as a detector in a Wheatstone Bridge circuit. A Fenwal thermistor served as one arm of the bridge. Five resistors (62.5 Ω to 10KΩ) were used to control the sensitivity of the recorder. The 625Ω resistor gave a sensitivity of 0.02°C for 10 small divisions on recorder chart paper.

(4) Conductivity Cells:

Conductivity cells (Fig. XIII), were constructed with shiny platinum electrodes. Cells were designed to give cell constants ranging from approximately 0.08 to 0.2.

Resistance measurements.

Resistances of solutions were recorded twenty-five minutes after the cell entered the constant temperature bath. In most cases resistances were again rechecked after the solutions had remained in the bath for a further period of time (30-60 min.). For potassium chloride solutions resistances were found to change by less than 0.1% over a two hour period and in the case of the acid solutions a change of 0.1% corresponded to a period of **over 12 hours.**

Cell Constants.

Cell constants were determined from two independent samples of purified potassium chloride. Both conductivity bridges were employed to measure the resistance of the salt solutions. The preparation of the salt solutions for determining cell constants has been described earlier ( ). The weights of the potassium chloride and the solvent in air were corrected for buoyancy effects using the expression,

$$M = W + [W(\frac{1}{\rho} - \frac{1}{D})\sigma] \qquad (8)$$

where M is the true mass of a body in vacuum, W the mass of the body measured in air, D the density of the standard weights, ρ the density of the mass M, and σ the density of air at room temperature.

Since the equation relating the equivalent conductance of KCl to concentration is given using the molarity scale and our solutions were prepared on the molal scale, conversion from the molal to the molarity scale was required (48). This was accomplished using the expression

$$V = N_0 V_0^{\circ} + N_1 \phi_1 \qquad (9)$$

where V is the volume of the solution, N_0 the number of moles of water, N_1 the number of moles of KCl and Vo° the volume of a mole of water at 25°C. The density of the water was taken as 0.997075 g ml^{-1}. The molal volume ϕ_1 was obtained from the equation

$$\phi_1 = 26.52 + 2.327 (C_2)^{1/2} \qquad (10)$$

where C_2 is the approximate concentration of the solution.

The equivalent conductance of an electrolyte in solution is defined by the equation

$$\Lambda = \frac{10^3 L}{C} = \frac{10^3 K^{\ddagger}}{RC} \qquad (11)$$

where L is the specific conductivity of the solution and C the concentration of the solute in 1000 ml. of solvent. The true specific conductivity L^* of the KCl solution is obtained by subtracting the specific conductivity of the pure solvent from that of the solution (L).

The equivalent conductance at each concentration of KCl was obtained from an equation proposed by Fuoss (49),

$$\Lambda = 149.93 - 94.65C^{1/2} + 58.74C \log C + 198.4C \qquad (12)$$

Equivalent conductance values at each concentration are applied to Equation (12). Thus the cell constant K can be evaluated from the expression:-

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‡ K is the cell constant.

$$L^* = \frac{K}{R} \qquad (13)$$

R being the resistance of the solution in ohms.

Cell constants of cells 3 and 5 (Table X) were not measured from potassium chloride solutions using the Tinsley Bridge, but were determined from the relationship $K = \Lambda CR/10^3$, where R is the resistance of a phenylacetic acid solution in these cells and Λ the equivalent conductance calculated from measurement of resistances of the same acid solution in cells 1, 2, and 4.

The cell constants of the five cells were redetermined with KCl after completion of the acid studies. These values (Table Xl), measured on the General Radio Impedance Bridge, are compared with earlier cell constants.

All equivalent conductances determined for the seven acids measured were calculated using the cell constants recorded in Table X.

Conductance Results.

The conductance data measured for acetic, phenylacetic, phenylacetic-α,α-d_2, 4-nitrophenylacetic, 4-nitrophenyl-acetic-α,α-d_2, 4-methoxyphenylacetic and 4-methoxyphenylacetic-α,α-d_2 acid in conductivity water at 25.00 ± 0.01°C are listed in Tables XIII to XIX. Column one of each table lists the experimental run numbers, column two, the cells used in each run; column three, the concentration expressed in moles per 1000 gms. of solvent, column four, the resistance value for each cell, and column five lists the equivalent conductance for each resistance measurement, determined by Equation (11).

Results are printed directly from computer cards. Equivalent conductances calculated by the computer were checked with the values determined using a bench calculator. The concentration column is kept in computer format and the symbols 2.8424E-03 signify a concentration of 2.8424 x 10^{-3} moles / 1000 g.

Some further comments on the following data are required.

(a) Phenylacetic acid dried over phosphorus pentoxide.

Conductance runs 7 and 8 are not tabulated with the resistance measurements on phenylacetic acid. It appeared that phenylacetic acid is unstable to extensive desiccation with phosphoric oxide. It decomposed with the formation of a brown, deliquescent material. Similar observations were made by Ives (30) on cyanoacetic acid.

(b) Photochemical decarboxylation of 4-nitrophenylacetic acid.

While attempting to determine the equivalent conductance of 4-nitrophenylacetic acid in water, resistance measurements of the prepared solution were found to vary with the length of time exposed to light. Once the solution was placed in the constant temperature bath the resistance would remain steady. After several hours the smell of 4-nitrotoluene was very pronounced in the volumetric exposed to light. This suggested that the photocatalysed decarboxylation of 4-nitrophenylacetic acid was being observed.

A small ultraviolet lamp was used on conjunction with the constant temperature bath (25°C ± 0.01°) to observe the decarboxylation of the acid. The cell containing acid solution (approximately 2×10^{-4}M) was exposed to ultraviolet light for short periods. The solution required 15 minutes to come to equilibrium in the bath, the resistance remaining constant after that period of time. The kinetic results (Table XII) are plotted in Fig. XIV, time-vs-resistance. During the preparation of solutions of this acid aluminum foil was used at all times to prevent any photochemical decarboxylation.

Density Values for Buoyancy Corrections.

The density values used for buoyancy corrections were:- acetic acid (1.05 ref. 37), phenylacetic acid (1.09 ref. 37) and potassium chloride (1.98 ref. 37). The densities of 4-methoxyphenylacetic acid (1.22) and 4-nitrophenylacetic acid (1.41) were measured by weighing cylindrical blocks of the fused acid or large crystals in air and in a solvent of known density e.g. cyclohexane or water. The measurements were made rapidly so that dissolution of the acid in the solvent was negligible. The densities of the deuterated specimens were assumed to be equal to those of the protium analogues in all cases.

TABLE X

Summary of Cell Constants (K) using Tinsley Bridge

Concentration x 10^3 M	Cell 1		Cell 2		Cell 4	
	R(Ω)	K	R(Ω)	K	R(Ω)	K
1.3964	668.3	.13652	970.8	.19832	805.7	.16459
1.3892	668.5	.13587	976.5	.19847	810.1	.16465
1.3939	666.2	.13591	972.2	.19832	807.6	.16474
1.7385	535.9	.13594	782.6	.19852	649.6	.16478
Average k		.13590		.19841		.16469
Deviation		±.00004		±.00012		±.00010

Cell 3 K = 0.086872 ±0.00002	Cell 5 K = 0.18175 ± 0.00009

TABLE XI

Cell Constants using General Radio Impedance Bridge

Cell	Cell * Constant	K (Table X)	Deviation
1	0.13590	0.13590	0.00000
2	0.19823	0.19841	0.00018
3	0.086881	0.086872	0.000009
4	0.16464	0.16469	0.00005
5	0.18160	0.18175	0.00015

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* Concentration of potassium chloride solution 1.617 x 10^{-3}M

TABLE XII

Resistance-Time Data for the
Photochemical Decarboxylation of
4-Nitrophenylacetic Acid.

Time (minutes)	Resistance (Ω)
0	9,605.8
24	15,922.4
60.2	25,696.4
108.0	40,255.0
160.5	55,224.0

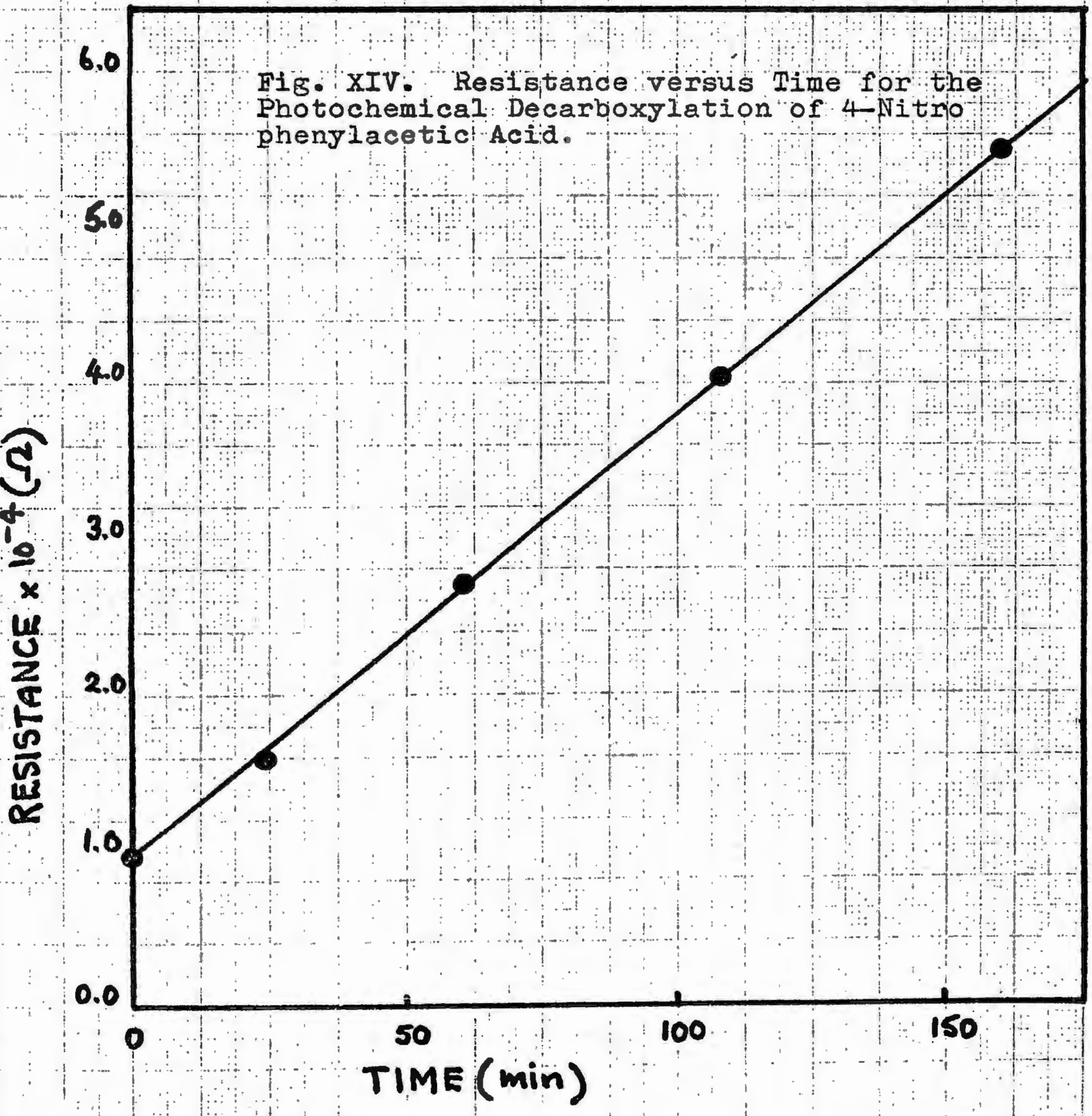

Fig. XIV. Resistance versus Time for the Photochemical Decarboxylation of 4-Nitro phenylacetic Acid.

TABLE XIII

Acetic Acid Results

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
1	1	2.8424E-03	1608.1	29.7321
	2	2.8424E-03	2347.8	29.7311
	3	2.8424E-03	1027.4	29.7476
	4	2.8424E-03	1949.5	29.7207
	5	2.8424E-03	2149.5	29.7478
2	1	2.3264E-03	1784.3	32.7398
	2	2.3264E-03	2605.8	32.7293
	3	2.3264E-03	1140.0	32.7561
	4	2.3264E-03	2163.0	32.7291
	5	2.3264E-03	2386.6	32.7351
3	1	1.4326E-03	2304.8	41.1598
	2	1.4326E-03	3364.9	41.1593
	3	1.4326E-03	1472.3	41.1872
	4	1.4326E-03	2793.5	41.1530
	5	1.4326E-03	3082.4	41.1591
4	1	5.9920E-04	3680.5	61.6239
	2	5.9920E-04	5375.2	61.6020
	3	5.9920E-04	2351.5	61.6543
	4	5.9920E-04	4462.9	61.5861
	5	5.9920E-04	4943.4	61.6084
5	1	4.0555E-03	1334.9	25.1036
	2	4.0555E-03	1948.5	25.1083
	3	4.0555E-03	852.7	25.1212
	4	4.0555E-03	1618.0	25.0986
	5	4.0555E-03	1784.8	25.1098
6	1	1.1103E-03	2635.3	46.4468
	2	1.1103E-03	3848.7	46.4307

TABLE XIII(cont'd)

Acetic Acid Results

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
6	3	1.1103E-03	1683.7	46.4701
	4	1.1103E-03	3195.4	46.4199
	5	1.1103E-03	3525.4	46.4329
7	1	1.0133E-03	2771.4	48.3957
	2	1.0133E-03	4048.6	48.3655
	3	1.0133E-03	1770.9	48.4133
	4	1.0133E-03	3359.8	48.3767
8	1	4.1870E-04	4479.4	72.4610
	2	4.1870E-04	6543.2	72.4216
	3	4.1870E-04	2862.5	72.4823
	4	4.1870E-04	5431.4	72.4197

TABLE XIV

Phenylacetic Acid Results

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
1	2	2.2612E-03	1668.0	52.6039
	4	2.2612E-03	1385.3	52.5752
2	1	1.8720E-03	1264.9	57.3898
	2	1.8720E-03	1846.1	57.4117
	3	1.8720E-03	809.7	57.3117
	4	1.8720E-03	1531.9	57.4287
3	1	3.6858E-03	877.8	42.0038
	2	3.6858E-03	1281.1	42.0179
	3	3.6858E-03	561.2	42.0008
4	1	2.7574E-03	1024.9	48.0906
	2	2.7574E-03	1495.4	48.1168
	3	2.7574E-03	654.7	48.1169
	4	2.7574E-03	1241.5	48.1067
5	1	6.3076E-03	662.3	32.5288
	2	6.3076E-03	966.4	32.5486
	3	6.3076E-03	432.3	32.5357
	4	6.3076E-03	802.5	32.5353
6	1	4.4067E-03	799.7	38.5639
	2	4.4067E-03	1166.9	38.5840
	3	4.4067E-03	511.0	38.5742
	4	4.4067E-03	968.8	38.5741
9	1	4.7217E-03	769.6	37.3991
	2	4.7217E-03	1123.5	37.4013
	3	4.7217E-03	491.9	37.4027
	4	4.7217E-03	932.8	37.3922
	5	4.7217E-03	1029.0	37.4076
10	1	5.8984E-03	685.7	33.6012

TABLE XIV(cont'd)

Phenylacetic Acid Results

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
10	2	5.8984E-03	999.7	33.6475
	3	5.8984E-03	437.8	33.6370
	5	5.8984E-03	915.5	33.6573
11	1	6.9879E-03	626.8	31.0274
	2	6.9879E-03	914.7	31.0405
	3	6.9879E-03	400.5	31.0403
	4	6.9879E-03	760.0	31.0102
	5	6.9879E-03	837.8	31.0444
12	1	1.7139E-03	1324.5	59.8648
	3	1.7139E-03	846.2	59.8969
	4	1.7139E-03	1605.6	59.8453
	5	1.7139E-03	1771.0	59.8761
13	1	2.8300E-03	1010.4	47.5263
	2	2.8300E-03	1475.0	47.5301
	3	2.8300E-03	645.5	47.5538
	4	2.8300E-03	1224.9	47.5085
	5	2.8300E-03	1351.2	47.5288
14	1	2.5118E-04	3984.6	135.7817
	2	2.5118E-04	5821.9	135.6734
	3	2.5118E-04	2544.7	135.9075
	4	2.5118E-04	4832.4	135.6773
15	1	1.3591E-04	5862.4	170.5637
	2	1.3591E-04	8575.4	170.2319
	3	1.3591E-04	3744.2	170.7093
	4	1.3591E-04	7111.7	170.3855
	5	1.3591E-04	7850.3	170.3431
16	1	2.7688E-04	3754.4	130.7311

TABLE XIV (cont'd)

Phenylacetic Acid Results

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
16	2	2.7688E-04	5487.5	130.5805
	3	2.7688E-04	2398.7	130.7969
	4	2.7688E-04	4554.6	130.5910
	5	2.7688E-04	5025.4	130.6163
17	1	1.0855E-04	6790.8	184.3525
	2	1.0855E-04	9925.3	184.1449
	3	1.0855E-04	4335.8	184.5672
	4	1.0855E-04	8236.5	184.1922
	5	1.0855E-04	9091.7	184.1507

TABLE XV

Phenylacetic-α,α-d_2 Acid Results

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
1	1	1.1034E-03	1690.9	72.8346
	2	1.1034E-03	2469.1	72.8200
	3	1.1034E-03	1080.7	72.8458
	4	1.1034E-03	2049.9	72.8060
	5	1.1034E-03	2261.4	72.8328
2	1	2.3347E-03	1122.4	51.8597
	2	2.3347E-03	1639.3	51.8385
	3	2.3347E-03	717.1	51.8862
	4	2.3347E-03	1360.7	51.8393
	5	2.3347E-03	1500.9	51.8650
3	1	2.4213E-03	1100.8	50.9862
	2	2.4213E-03	1606.8	50.9956
	3	2.4213E-03	703.2	51.0195
	4	2.4213E-03	1334.4	50.9705
	5	2.4213E-03	1471.7	51.0023
4	1	2.7031E-03	1039.8	48.3510
	2	2.7031E-03	1517.5	48.3682
	3	2.7031E-03	664.1	48.3923
	4	2.7031E-03	1260.2	48.3460
	5	2.7031E-03	1390.2	48.3645
5	1	3.1922E-03	950.7	44.7801
	2	3.1922E-03	1388.1	44.7756
	3	3.1922E-03	607.4	44.8031
	4	3.1922E-03	1152.7	44.7566
	5	3.1922E-03	1271.1	44.7917
6	1	3.4855E-03	906.6	43.0069
	2	3.4855E-03	1323.7	43.0028

TABLE XV (cont'd)

Phenylacetic-α,α-d_2 Acid Results

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
6	3	3.4855E-03	579.4	43.0159
	4	3.4855E-03	1099.2	42.9854
	5	3.4855E-03	1212.6	43.0016
7	1	4.9732E-03	751.9	36.3434
	2	4.9732E-03	1097.7	36.3442
	4	4.9732E-03	911.6	36.3266
	5	4.9732E-03	1005.2	36.3565
8	1	6.2284E-03	668.3	32.6493
	2	6.2284E-03	975.6	32.6518
	3	6.2284E-03	427.3	32.6412
	4	6.2284E-03	810.3	32.6320
	5	6.2284E-03	893.4	32.6624
9	1	1.7765E-03	1302.8	58.7178
	2	1.7765E-03	1902.5	58.7025
	3	1.7765E-03	832.4	58.7448
	4	1.7765E-03	1579.6	58.6873
	5	1.7765E-03	1742.2	58.7216
10	1	4.9034E-03	757.2	36.6028
	2	4.9034E-03	1105.7	36.5950
	3	4.9034E-03	483.9	36.6120
	4	4.9034E-03	918.2	36.5790
	5	4.9034E-03	1012.5	36.6082
11	1	4.2937E-04	2895.6	109.3074
	2	4.2937E-04	4229.9	109.2425
	3	4.2937E-04	1848.7	109.4399
	4	4.2937E-04	3511.5	109.2294
	5	4.2937E-04	3873.3	109.2838

TABLE XV (cont'd)

Phenylacetic-α,α-d_2 Acid Results

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
12	1	4.9907E-04	2652.8	102.6496
	2	4.9907E-04	3873.6	102.6314
	3	4.9907E-04	1695.0	102.6942
	4	4.9907E-04	3215.9	102.6132
	5	4.9907E-04	3548.5	102.6279
13	1	2.8839E-04	3672.3	128.3201
	2	2.8839E-04	5366.1	128.2058
	3	2.8839E-04	2345.7	128.4146
	4	2.8839E-04	4451.5	128.2834
	5	2.8839E-04	4911.3	128.3173
14	1	6.3995E-04	2298.5	92.3918
	2	6.3995E-04	3356.9	92.3576
	3	6.3995E-04	1468.4	92.4459
	4	6.3995E-04	2787.1	92.3356
	5	6.3995E-04	3074.6	92.3715
15	1	3.1564E-04	3475.7	123.8749
	2	3.1564E-04	5077.3	123.8015
	3	3.1564E-04	2219.5	124.0008
	4	3.1564E-04	4215.1	123.7832
	5	3.1564E-04	4650.9	123.8047
16	1	2.0516E-04	4520.9	146.5230
	2	2.0516E-04	6607.2	146.3682
	3	2.0516E-04	2885.8	146.7299
	4	2.0516E-04	5483.2	146.3999
	5	2.0516E-04	6050.8	146.4086

TABLE XVI

4-Methoxyphenylacetic Acid

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
1	1	1.0838E-03	1818.1	68.9711
	2	1.0838E-03	2654.1	68.9764
	3	1.0838E-03	1161.4	69.0169
	4	1.0838E-03	2203.6	68.9598
2	1	4.6775E-04	2919.4	99.5216
	2	4.6775E-04	4263.5	99.4897
	3	4.6775E-04	1865.5	99.5561
	4	4.6775E-04	3540.0	99.4607
3	1	4.2055E-04	3106.7	104.0179
	2	4.2055E-04	4535.5	104.0197
	3	4.2055E-04	1984.1	104.1110
	4	4.2055E-04	3765.6	103.9962
4	1	1.7463E-04	5267.6	147.7379
	2	1.7463E-04	7692.3	147.7003
	3	1.7463E-04	3365.0	147.8332
	5	1.7463E-04	6386.1	147.6770
5	1	8.0969E-04	2137.5	78.5242
	2	8.0969E-04	3121.2	78.5093
	3	8.0969E-04	1365.8	78.5552
	5	8.0969E-04	2858.5	78.5272
6	1	3.2173E-04	3633.6	116.2500
	2	3.2173E-04	5306.8	116.2065
	3	3.2173E-04	2321.6	116.3041
	5	3.2173E-04	4861.4	116.2029

TABLE XVII

4-Methoxyphenylacetic-α,α-d_2 Acid

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
1	1	3.2833E-04	3603.4	114.8688
	2	3.2833E-04	5258.6	114.9154
	4	3.2833E-04	4365.1	114.9119
	5	3.2833E-04	4815.2	114.9607
2	1	1.6582E-04	5460.3	150.0955
	2	1.6582E-04	7977.8	149.9803
	3	1.6582E-04	3486.6	150.2570
	4	1.6582E-04	6621.2	150.0001
	5	1.6582E-04	7306.9	150.0003
3	1	3.6980E-04	3359.2	109.4027
	2	3.6980E-04	4902.2	109.4476
	3	3.6980E-04	2144.0	109.5698
	4	3.6980E-04	4069.2	109.4462
	5	3.6980E-04	4489.9	109.4649
5	1	3.4958E-04	3477.0	111.8075
	2	3.4958E-04	5072.4	111.8911
	3	3.4958E-04	2221.7	111.8606
	4	3.4958E-04	4216.0	111.9020
4	1	1.9913E-04	4869.6	140.1491
	2	1.9913E-04	7114.0	140.0567
	3	1.9913E-04	3109.7	140.2872
	4	1.9913E-04	5903.7	140.0888
	5	1.9913E-04	6515.4	140.0848
6	1	1.0749E-03	1831.6	69.0287
	2	1.0749E-03	2673.2	69.0498
	3	1.0749E-03	1169.9	69.0819
	4	1.0749E-03	2219.5	69.0318

TABLE XVII (cont'd)

4-Methoxyphenylacetic-α,α-d Acid

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
6	5	1.0749E-03	2448.4	69.0601

TABLE XVIII

4-Nitrophenylacetic Acid Results

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
11	1	1.6011E-03	895.0	94.8338
	2	1.6011E-03	1305.6	94.9094
	3	1.6011E-03	571.5	94.9345
	4	1.6011E-03	1084.2	94.8682
	5	1.6011E-03	1195.7	94.9320
5	1	2.8615E-04	2574.0	184.5096
	2	2.8615E-04	3765.2	184.1504
	3	2.8615E-04	1643.9	184.6741
	4	2.8615E-04	3118.0	184.5846
	5	2.8615E-04	3441.1	184.5775
10	1	1.0442E-03	1147.2	113.4450
	2	1.0442E-03	1674.8	113.4475
	3	1.0442E-03	733.7	113.3862
	4	1.0442E-03	1390.7	113.4058
	5	1.0442E-03	1533.7	113.4835
7	1	2.6242E-04	2727.7	189.8557
	2	2.6242E-04	3994.2	189.2883
	3	2.6242E-04	1741.8	190.0535
	4	2.6242E-04	3305.5	189.8572
	5	2.6242E-04	3646.5	189.9296
9	1	1.5010E-04	4014.1	225.5506
	2	1.5010E-04	5866.7	225.3054
	3	1.5010E-04	2564.5	225.6750
	4	1.5010E-04	4868.6	225.3576
6	1	9.4570E-05	5628.7	255.3067
	2	9.4570E-05	8229.7	254.9292
	3	9.4570E-05	3597.2	255.3640

TABLE XVIII (cont'd)

4-Nitrophenylacetic Acid Results

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
6	4	9.4570E-05	6829.2	255.0025
	5	9.4570E-05	7536.4	255.0086
8	1	6.3893E-05	7631.4	278.7199
	3	6.3893E-05	4873.3	278.9981
	4	6.3893E-05	9247.9	278.7231
9	5	1.5010E-04	5372.0	225.3953

TABLE XIX

4-Nitrophenylacetic-α,α-d_2 Acid

RUN No.	CELL No.	CONCENTRATION	RESISTANCE	EQUIVCON.
1	1	2.4238E-04	2881.0	194.6603
	2	2.4238E-04	4205.5	194.6867
	3	2.4238E-04	1839.4	194.8933
	4	2.4238E-04	3490.6	194.6994
	5	2.4238E-04	3851.7	194.7228
2	1	1.1573E-04	4853.5	241.9448
	2	1.1573E-04	7091.8	241.7400
	3	1.1573E-04	3096.7	242.3959
	4	1.1573E-04	5883.7	241.8610
	5	1.1573E-04	6493.1	241.8627
3	1	5.7311E-05	8335.7	284.4752
	2	5.7311E-05	12189.6	283.9789
	4	5.7311E-05	10120.3	283.9472
	5	5.7311E-05	11164.6	284.0484
4	1	1.3102E-04	4441.3	233.5559
	2	1.3102E-04	6480.5	233.6826
	3	1.3102E-04	2833.2	234.0321
	4	1.3102E-04	5377.0	233.7787
	5	1.3102E-04	5932.0	233.8558
5	1	4.8222E-05	9595.0	293.7202
	2	4.8222E-05	14028.5	293.2932
	4	4.8222E-05	11642.8	293.3337

Theories of Electrolytic Conductance and the Calculation of the Dissociation Constants of Weak Electrolytes from Conductance Data.

Introduction.

Most of the early work on the conductance of electrolyte solutions was performed by Kohlrausch (50). These investigations were expanded by Arrhenius (51) who suggested that electrolytes of the type AB dissociated into ions in solution:-

$$AB \rightleftharpoons A^{+} + B^{-} \qquad \ldots\ldots\ldots (14)$$

By applying the Law of Mass Action to the above equilibrium, Arrhenius derived the following equation:-

$$K_c = \frac{[A^{+}]\,[B^{-}]}{[AB]} = \frac{\alpha^2 C}{1-\alpha} \qquad \ldots\ldots\ldots (15)$$

where K_c is the classical equilibrium constant, and $[A^{+}] = [B^{-}] = \alpha C$, C being the total concentration of the electrolyte and α the degree of dissociation. The concentration of the undissociatedportion:- $[AB]$ is equal to $(1-\alpha)C$. By equating the degree of dissociation with the ratio of the equivalent conductance at concentration 'C' (Λ) to the limiting equivalent conductance (Λ_o) i.e.

$$\alpha = \Lambda / \Lambda_o \qquad \ldots\ldots\ldots (16)^{*}$$

Ostwald (52) obtained an equation for K_c in terms of the conductance parameters and the concentration of the electrolyte:-

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[*] The justification for this relationship is given in most elementary physical chemistry texts and need not be elaborated here.

$$K_C = \frac{\Lambda^2 C}{\Lambda_o(\Lambda_o - \Lambda)} \qquad \ldots\ldots\ldots (17)$$

Equation (17) is known as the Ostwald Dilution Law and is a special case of the Law of Mass Action. Equation (17) can be rearranged to the more useful form:-

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_o} + \frac{\Lambda C}{K_c \Lambda^2_o} \qquad \ldots\ldots\ldots (18)$$

Whilst the conductance data obtained from the study of a variety of electrolyte-solvent systems obeyed the Ostwald Dilution Law as represented by Equation (17) or (18), many other systems provided data which was better represented by an equation:-

$$\Lambda = \Lambda_o - A\ (C)^{1/2} \qquad \ldots\ldots\ldots (19)$$

established empirically by Kohlrausch in 1900. Clearly, the Arrhenius Dissociation Hypothesis was partly verified, but the systems which obeyed Equation (19) presented a puzzling situation in terms of the classical theory. Electrolytes which obeyed Equation (19) were subsequently designated 'strong' and those which obeyed Equation (18) were described as 'weak'. The designations 'strong' and 'weak' evolved from a consideration of the relative conductance of the two types of electrolyte at comparable concentrations, the strong electrolytes having a much higher equivalent conductance. However, the distinction between the two types of electrolyte is not a sharp one, and several cases exist where the limiting distinctions merge. The failure to recognize this hampered the early attempts to construct a satisfactory theory of these phenomena. The variation of the equivalent conductance with concentration was invariably interpreted in terms of the variation of the number of ions present mainly because the early workers failed to realize that the Square Root Law was a consequence of the variation of ion mobilities with concentration. For electrolytes which are in the borderline region between the extreme types the situation is evidently complex because both laws (Equations (17) and (19)) must be relevent.

The recognition that the Ostwald Dilution Law and the Square Root Law are both important for all weak electrolytes represents the starting point of more recent treatments of the concentration dependence of the conductance of such species in aqueous solutions. Modern theories of electrolytic conductance classify electrolytes into two broad groups which are known respectively as ionogens and ionophores. The former are typified by covalent molecules, such as acetic acid, which produce thermodynamically stable* ions rapidly in aqueous solutions by some sort of dissociation process. On the other hand, ionophores are typified by substances such as sodium chloride, which exist in the pure form as an ionic lattice. The variation of the equivalent conductance of ionophores with concentration in solvents of high dielectric constant, wherein dissociation is considered complete, is primarily a consequence of the variation of ion mobilities with concentration. For ionogens the mobility factor is still important, but with

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* Certain organic reactions which involve the production of thermodynamically unstable carbonium ions have been described as "ionogenic reactions". The distinction between such substances and acetic acid is obvious.

increasing weakness of the ionogen, is superimposed upon and dominated by the effect of concentration on the degree of dissociation, which was the only factor recognized in the classical treatment. Finally, since activities (a) rather than concentrations are appropriate to ionic equilibria, Equation (15) must be rewritten as:-

$$K_t = \frac{a\,(A^+)\;a\,(B^-)}{a\,(AB)} = \frac{\alpha^2 c f_\pm^2}{(1-\alpha)f_u} \qquad \ldots\ldots (20)$$

where $f_\pm^2$ and f_u are respectively the activity coefficients of the ions and undissociated molecules. In modern compilations of equilibrium constants of weak electrolytes (53) a distinction is drawn between equilibrium constants calculated from Equations (15) - (18) which are described as classical equilibrium constants (K_c) and those calculated from Equation (20) which are described thermodynamic equilibrium constants (K_t).

The determination of thermodynamic equilibrium sonstants from conductance data must clearly involve a combination of Equations (15), (16) and (19). The problem of linking these three equations has received considerable attention over the past three decades by Fuoss, Kraus, Ives, Shedlovsky, MacInnes and others. Several reviews (54) (55) are available of the various methods the most useful and critical being that in a recent monograph by King (56). In the following section the theoretical background to these various treatments will be briefly summarized so that in subsequent sections of the thesis the application of these various methods to the experimental data can be appreciated.

Modern Methods of Calculating Thermodynamic Equilibrium Constants from Conductance Data.

A consideration of activity coefficients of both the ions and undissociated molecules is common to all the methods available for the calculation of thermodynamic equilibrium constants of weak ionogens from conductance data and this aspect of the problem will be considered first.

(i) Activity Coefficients.

Using the concept of 'the ion atmosphere' Debye and Huckel (57) were able to derive an expression for the electrostatic potential at any given distance from a particular ion. From this expression it is possible to calculate the electrostatic free energy of any particular ion at a temperature T in a medium of dielectric constant D relative to that of a neutral particle of the same mass and size*. This electrostatic model provides an expression for the mean activity coefficient ($f_\pm$) of a given electrolyte which is related to the ionic strength (I) of the solution, charges of the ions (Z_1Z_2) and a constant A (sometimes described as the limiting slope) which is related to $(DT)^{1/2}$:-

$$- \log f_\pm = |Z_1Z_2| \; AI^{1/2} \qquad \ldots\ldots\ldots (21)$$

where I is defined by the equation:-

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* This treatment gives both the Born Charging (59) and ion atmosphere terms which in practice are easily separated. Only the latter term is involved in the present considerations.

$$I = \tfrac{1}{2}\Sigma' Z_i^2 c_i \qquad \ldots\ldots\ldots (22)$$

In the latter equation Z_i is the charge on the 'ith' ion at a concentration c_i. Equation (21) is only applicable to very dilute solutions and for higher concentrations it has been empirically modified by altering the denominator and adding a linear term in c_i (see ref. (56) Chap. 1 for further details, and ref. 58).

For equilibria involving weak ionogens such as carboxylic acids, Equation (21) has generally been used in its unmodified form. This is justified when the ionogen concentration is low and dissociation into ions is not extensive. If it is assumed that $f_u \rightarrow 1$ then Equations (20) and (21) can be combined to give an explicit relationship between the thermodynamic and classical equilibrium constants

$$\log K_t = \log K_c - 2A\, C_i^{\frac{1}{2}} \qquad \ldots\ldots\ldots (23)$$

for a 1:1 electrolyte. Hence a relationship between log K_c and the square root of the ionic concentration is to be anticipated and K_t can be calculated by a suitable extrapolation procedure.

<u>Conductance Curves for Weak Ionogens</u>.

In the introductory section it was pointed out that the square root conductance Law was in fact relevent to both ionophores and ionogens. The square root law has been rationalized by Onsager (60) who applied the Debye-Huckel theory to the problem of predicting the constant A in Equation (19). Onsager's treatment involved the postulation of two factors which would influence the motion of any ion in an electric field. The first of these two factors is known as the 'electrophoretic effect' and derives from the opposing motions of the central ion and its oppositely charged ion atmosphere. The second factor, which is known as the relaxation effect, results from the perturbing effect of the external field of the ion atmosphere, which is continually 'decaying' and 'reforming' as a result of the motion of the ion through the solution. The mathematical treatment of this problem, which is outside the scope of the present thesis, yields an equation of the form:-

$$\Lambda = \Lambda_0 - (\beta + \alpha\Lambda_0)C^{1/2} \qquad \ldots\ldots\ldots(24)^{*}$$

where β is the electrophoretic constant and α is the relaxation constant. The numerical values of these constants, which are relevant to the present thesis, are based on values of the dielectric constant and viscosity of water published in 1952 (61) and recommended by Fuoss and Accascina (62). In the case of weak ionogens the value of 'C' in Equation (24) must be replaced by 'α C' where 'α' is the degree of dissociation.

In a more detailed treatment of the same problem, in which the ions are treated as spheres rather than point charges, Fuoss and Onsager (63) have developed an equation of the form:-

$$\Lambda = \Lambda_0 - SC^{1/2} + EC\log C + JC \qquad \ldots\ldots(25)$$

---

[*] Equation (24) is of the same form as the Square Root Law but in the case of this equation it is possible to calculate theoretically values of α and β. The coefficient of $C^{1/2}$ in Equation (24) is often given the symbol S.

where S is the Onsager limiting law coefficient, E is a constant related to the same variables as B and J is a function of the ion size. This equation, involves two arbitrary constants, the limiting equivalent conductance and the ion size which can be obtained by fitting empirical data to the above equation. This extended equation is undoubtedly relevent to the problem of determining the equilibrium constants of weak electrolytes from conductance data, but the final correction terms involving the constants E and J are probably too small to influence the final results to any great extent. However, this speculation remains to be tested, for the Fuoss-Onsager equation has not been applied to this particular problem.

The methods detailed below for calculating the thermodynamic equilibrium constants from conductance data can have certain features in common which have not been previously emphasized. Besides a series of results derived from a study of the variation of the equivalent conductance of the weak electrolyte with concentration a value of Λ_o for the weak electrolyte is required. For a weak acid HB the application of Kohlrausch's Law at infinite dilution gives:-

$$\Lambda_o(HB) = \Lambda_o(H_3O^+) + \Lambda_o(B^-) \quad .... \quad (26)$$

There are two distinct methods of determining Λ_o(HB). In certain favorable cases an accurate value of both Λ_o and K_t can be determined from conductance measurements on the weak acid alone. However, with increasing weakness of the acid it becomes impossible to obtain precise values of Λ_o and K_t simultaneously (64) and under these circumstances Kohlrausch's Law must be used to obtain a value of $\Lambda_o(HB)$. This involves the use of conductance measurements on a salt of the weak acid e.g. NaB. These measurements are then combined with those derived from conductance measurements of a strong acid (e.g. HCl) and the sodium salt of the strong acid (NaCl). The application of Kohlrausch's Law to the Λ_o values obtained from these separate studies gives:-

$$\Lambda_o(NaB) = \Lambda_o(Na^+) + \Lambda_o(B^-) \qquad \ldots\ldots\ldots (27)$$

$$\Lambda_o(HCl) = \Lambda_o(H_3O^+) + \Lambda_o(Cl^-) \qquad \ldots\ldots\ldots (28)$$

$$\Lambda_o(NaCl) = \Lambda_o(Na^+) + \Lambda_o(Cl^-) \qquad \ldots\ldots\ldots (29)$$

and Equations (27), (28) and (29) can be manipulated to give:-

$$\begin{aligned}\Lambda_o(HB) &= \Lambda_o(H_3O^+) + \Lambda_o(B^-) \\ &= \Lambda_o(NaB) + \Lambda_o(HCl) - \Lambda_o(NaCl) \qquad \ldots\ldots\ldots (30)\end{aligned}$$

This is a universal method for the determination of $\Lambda_o(HB)$ provided, as Ives (27) has pointed out, that the anion B^- has sufficient stability for the measurements to be made. Once a value of $\Lambda_o(HB)$ has been established in this way, values of K_t can be calculated from conductance data on the acid HB by direct substitution into the various equations which are considered below.

In cases where both K_t and Λ_o are derived from measurements on the acid alone, Λ_o is found by an iteration process which requires a starting value of Λ_o. This iteration process is probably best approached via the classical plot (Equation (18)) which will now be considered.

The Classical Plot.

The conductance form of the Ostwald Dilution Law (Equation 18) accurately describes the behaviour of strong electrolytes in solvents of low dielectric constant, and the behaviour of weak electrolytes in dilute solution. The very low ionic strength of a solution of a weak acid is the major factor which saves the mass action law. At higher concentration ($C > 0.01$) K_c varies markedly with the rise in the ionic strength of the solution. A linear plot of $1/\Lambda$ against ΛC determines $1/\Lambda_o$ as intercept, and $1/K\ (\Lambda_o)^2$ as the slope. This approximate value of the equivalent conductance at infinite dilution can serve as a starting point in the determination of a thermodynamic ionization constant using the methods which require successive approximations. The Ostwald dilution equation (18) is not exact because of the neglect of the effect of ionic concentration on the mobilities and activities of the ions present in the system.

Fuoss and Kraus Method.

Fuoss and Kraus (65) developed a method which takes account of both the long-range interionic forces and the activities of the ions. The conductance of a completely dissociated electrolyte is given by the Onsager Equation. If the degree of ionization of the electrolyte is α then the ion concentration is $C_i = \alpha C$ and the observed equivalent conductance is given by the relationship:-

$$\Lambda = \alpha[\Lambda_o - S(\alpha C)^{1/2}] \qquad \ldots\ldots (31)$$

which is a cubic equation in α. Rearranging this equation gives:-

$$\alpha = \frac{\Lambda}{\Lambda_o[1-S(\alpha C)^{1/2}/\Lambda_o]} \qquad \ldots\ldots\ldots (32)$$

An accurate value of α can be obtained from Equation (32) by successive substitution of α back into its own correction factor, represented by the bracketed term in the denominator on the R.H.S. of Equation (32). This process rapidly converges to give a correct value of α. The correction term may be expressed in terms of a continued fraction:-

$$F(Z) = 1-Z[1-Z(etc)^{-1/2}]^{-1/2} \qquad \ldots\ldots\ldots (33)$$

where:-

$$Z = (S/\Lambda_o^{3/2})(\Lambda C)^{1/2} \qquad \ldots\ldots\ldots (34)$$

Alternatively, the continued fraction can be expressed in terms of a cosine relationship:-

$$F(Z) = (4/3)\cos^2[(1/3)\cos^{-1}(-3^{3/2}Z/2) \qquad \ldots\ldots (35)$$

It is usual to express α in the contracted form:-

$$\alpha = \frac{\Lambda}{\Lambda_o F(Z)} \qquad \ldots\ldots\ldots (36)$$

Combining Equations (36) and (20) with $f_{ii} = 1$ and then rearranging to a form analogous to Equation (18) gives:-

$$\frac{F(Z)}{\Lambda} = \frac{1}{\Lambda_o} + \frac{C\Lambda f_{\pm}^2}{K_t\Lambda_o^2 F(Z)} \qquad \ldots\ldots\ldots (37)$$

A graphical or least squares correlation of $F(Z)/\Lambda$ versus $C\Lambda f_{\pm}^2/F(Z)$ in which the variables have been calculated from an approximate value of Λ_o gives a new value of Λ_o from the intercept of the curve. The initial value of Λ_o in the variables is replaced by the new value and the correlation repeated, generating a further value of Λ_o. This process is repeated until two successive values of Λ_o are identical within some arbitrarily selected degree of accuracy. The final value of Λ_o from the final correlation is then combined with the final slope ($m_t = 1/K_t\Lambda_o^2$) to give a value of K_t.

The Shedlovsky Method.

Shedlovsky (66) found that replacing α by Λ/Λ_o in the Onsager Equation gave the expression:-

$$\Lambda = \alpha\Lambda_o - \frac{\Lambda}{\Lambda_o} S(\alpha C)^{1/2} \qquad \ldots\ldots\ldots \quad (38)$$

Equation (38) can be rewritten as a quadratic in $\alpha^{1/2}$ to give:-

$$\alpha - \frac{S\ C^{1/2}}{\Lambda_o^2}\alpha^{1/2} - \frac{\Lambda}{\Lambda_o} = 0 \qquad \ldots\ldots\ldots \quad (38a)$$

which can be solved in terms of the variable Z (See Equation (34)) to give:-

$$\alpha = \frac{\Lambda}{\Lambda_o}\left[\frac{Z}{2} + \left(1 + \frac{Z^2}{2}\right)^{1/2}\right]^2 = \frac{\Lambda}{\Lambda_o} S(Z) \quad \ldots\ldots \quad (39)$$

The bracketed term S(Z), is sometimes expressed as a power series in Z:-

$$S(Z) = 1 + Z + Z^2/2 + Z^3/8 \qquad \ldots\ldots\ldots \quad (40)$$

Values of S(Z) have been tabulated by Daggett (67). Combining Equations (39) and (20) with $f_u = 1$ gives after some manipulation (c.f. Equation (18)):-

$$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda_o} + \frac{\Lambda C f_{\pm}^2 \; S(Z)}{K_t \Lambda_o^2} \quad \ldots\ldots\ldots (41)$$

Equation (41) is used in a similar way to Equation (37). The variables in this instance are generated via the S(Z) function rather than the F(Z) function used in the Fuoss Equation.

(6) Ives Method.

Ives (68) developed a method of calculation of dissociation constants and of equivalent conductances at zero concentration using the Ostwald Dilution Law, the Debye-Huckel Limiting Law, and the Onsager Equation. The method is based on the principle that the dissociation constant of a 1-1 electrolyte in dilute aqueous solution is given by the equation:

$$K_t = \frac{\alpha^2 C f_{\pm}^2}{(1-\alpha)} \quad \ldots\ldots\ldots (42)$$

where $f_{\pm}^2$ is the mean ion activity coefficient of the ions and f_u the activity coefficient of the undissociated molecules, is taken as unity. Using the equation for the degree of dissociation $\alpha = \Lambda / \Lambda_x$, where Λ_x is the sum of the equivalent conductances of the ions at concentration C_i; the expression for C_i is:-

$$C_i = \alpha C = \frac{\Lambda C}{\Lambda_x} \quad \ldots\ldots\ldots (43)$$

Substituting Equations (43) into Equation (42) yields:-

$$K_t = \frac{\Lambda^2 Cf_{\pm}^2}{\Lambda_x(\Lambda_x - \Lambda)} \qquad \ldots\ldots\ldots (44)$$

x is obtained by application of the Onsager equation to the ionized part of the solute. Thus:-

$$\Lambda_x = \Lambda_o - S\left(\frac{\Lambda c}{\Lambda_x}\right)^{1/2} \qquad \ldots\ldots\ldots (45)$$

or

$$\Lambda_x = \Lambda_o - S(C_i)^{1/2} \qquad \ldots\ldots\ldots (46)$$

where S is the Onsager slope. Equation (45) may therefore be reformulated:-

$$K_t = \frac{\Lambda^2 c\, f_{\pm}^2}{(\Lambda_o - S(C_i)^{1/2})\ (\Lambda_o - SC_i^{1/2} - \Lambda)} \qquad \ldots (47)$$

The mean ionic activity coefficient, according to the Debye-Huckel theory for a 1:1 electrolyte in water is given by the relationship

$$\log f_{\pm} = -A\,(C_i)^{1/2} \qquad \ldots\ldots\ldots (48)$$

where A is the Debye-Huckel coefficient. Hence the expression for the dissociation constant K_t takes the form:-

$$K_t = \frac{\Lambda^2 c\ 10^{-2AC_i^{1/2}}}{(\Lambda_o - SC_i^{1/2})\ (\Lambda_o - SC_i^{1/2} - \Lambda)} \qquad \ldots\ldots\ldots (49)$$

Rearranging gives:-

$$\Lambda + SC_i^{1/2} = \Lambda_o \ \frac{-\Lambda^2 c\ .\ 10^{-2AC_i^{1/2}}}{(\Lambda_o - SC_i^{1/2})\ K_t} \qquad \ldots\ldots\ldots (50)$$

A plot of $\Lambda + SC_i^{1/2}$ against $\Lambda^2C.\ 10^{-2A(C_i)^{1/2}}/(\Lambda_o - SC_i^{1/2})$ should give a linear relationship with Λ_o obtained from the intercept at C=0 and slope equal to $-1/K_t$. The new value of Λ_o is incorporated in the x and y terms and calculations repeated. Each extrapolation is carried out using the method of least squares. Ives considers that graphical methods are not sufficiently accurate to obtain Λ_o for weak electrolytes.

<u>The Robinson-Stokes Method.</u>

Sherrill and Noyes (69), and MacInnes (70), using both activity coefficients and mobilities on concentration to evaluate K_t in dilute solutions, defined the degree of ionization by the expression:-

$$\alpha = \frac{\Lambda}{\Lambda_i} \qquad \ldots\ldots\ldots (51)$$

where Λ_i is the equivalent conductance of the hypothetical fully ionized electrolyte at ion concentration C_i.

For the weak Bronsted Acid HB which ionizes according to the equation:-

$$BH = H_2O \rightleftharpoons B^- + H_3O^+ \qquad \ldots\ldots\ldots (52)$$

the value of Λ_i was estimated by MacInnes and Shedlovsky (71) by measuring conductances of the electrolytes HCl, NaB, and NaCl as previously described. Thus successive approximations to α in the empirical equations resulted in rapid convergence to give Λ_i(HB).The improved value of α was used to calculate K_t from the Equation (20) with f_u taken as unity.

Robinson and Stokes (72) using a more complete theory divide the square root term of the Onsager Limiting Law by the factor $(1 + \kappa a)$* to allow for the finite size of the ions (a $\mathring{A}$).

$$\Lambda_i = \Lambda_o - (\alpha \Lambda_o + \beta)(\alpha C)^{1/2} / (1 + \kappa a) \quad \ldots (51)$$

Replacing κa by the expression $Ba(\alpha C)^{1/2}$ the Equation (51) becomes:-

$$\Lambda_i = \Lambda_o - (\alpha \Lambda_o + \beta)(\alpha C)^{1/2} / (1 + Ba(\alpha C)^{1/2}) \quad ;\ldots (52)$$

The mean ion size 'a' has been estimated at 4 $\mathring{A}$ (53). The activity coefficient $f_{\pm}$ at an ionic concentration αC is given by:-

$$\log f_{\pm} = -A(\alpha C)^{1/2} / (1 + \kappa a) \quad \ldots\ldots (53)$$

and replacing κa by $Ba(\alpha C)^{1/2}$ as above gives

$$\log f_{\pm} = -A(\alpha C)^{1/2} / (1 + Ba(\alpha C)^{1/2}) \quad \ldots\ldots (54)$$

Since ionization of the weak electrolyte is not usually extensive Λ_i will not be very sensitive to the value of 'a' which is adopted.

---

*κ is the ion atmosphere constant of the Debye-Huckel. Theory which can be put in the form $\kappa^2 = B^2 I$ where I is the ionic strength of the solution and B is a constant at a given temperature for a particular medium.

The Evaluation of Thermodynamic Equilibrium Constants and Isotope Effects from Conductance Data.

Introduction.

A comparison of thermodynamic equilibrium constants from conductance data has previously been made for the isotopic acid pairs:- HCOOH/DCOOH, $CH_3\overset{+}{N}H_3/CD_3\overset{+}{N}H_3$ and $(CH_3)_2\overset{+}{N}H_2/(CD_3)_2\overset{+}{N}H_2$. The formic acid pair was examined by Bell and Miller (73) who calculated the relative strength of the two acids using the Robinson-Stokes method (see pages 94 - 95). The ammonium acid pairs were examined by Robertson and Van Der Linde (24) who used the Ives (68) extrapolation-iteration technique (see pages 92-94). No details of the latter results are available.

In a more extensive study Streitwieser and Klein (20) have used conductance measurements to establish isotope effects for the following acid pairs:- CH_3COOH/CD_3COOH, C_6H_5COOH/C_6D_5COOH, $C_6H_5COOH/2{:}6\text{-}D_2C_6H_3COOH$, $(CH_3)_3CCOOH/(CD_3)_3CCOOH$ and HCOOH/DCOOH. The effect of isotopic substitution on the acid strength was calculated from the expression:-

$$\frac{K_c(H)}{K_c(D)} = \frac{R_D(R_DC_D-A)}{R_H(R_HC_H-A)} \qquad \ldots\ldots\ldots (55)$$

which was derived from Equations (15) and (16). Activity and mobility effects are either implicitly ignored or assumed to cancel. The symbols in Equation (55) refer to the following quantities; $A = 10^3K\Lambda_o$ and K is the cell constant appropriate to the single cell in which the resistances (R_H and R_D) at concentrations C_H and C_D of the electrolyte were measured for the deuterium and hydrogen compounds. For all of the above acid pairs, it was assumed that the limiting equivalent conductances for the isotopic anions were identical ie. $\Lambda_0(B^-_H) = \Lambda_0(B^-_D)$ or $\Lambda_0(HB_H) = \Lambda_0(HB_D)$. This assumption will be considered in greater detail in a later section.

In the present study a variety of methods have been used to calculate both the isotope effects and the individual equilibrium constants from the conductance data. These calculations have all been performed on an I.B. M. 1620 digital computer and the programme appropriate to each type of calculation is recorded in the Appendix.

All linear correlations have been treated by the method of least squares and the probable errors of the slopes and intercepts derived in this way were evaluated from formulae given in Margenau and Murphy (74). In general five values of the equivalent conductance were measured at each concentration of the weak electrolytes studied. These five values were all inserted in the least squares calculation without averaging. Any departure from this procedure will be subsequently noted. The calculations are reviewed in the following sections.

Method I. The Classical Calculation.

Equation (18) has been applied to the conductance data for each acid studied by the method of least squares. The variables $1/\Lambda$ (y axis) and ΛC (x axis) yield a slope m_c and an intercept I_c which are related to Λ_o and K_c by the equations:-

$$m_c = 1/K_c \Lambda_o^2 \qquad \ldots\ldots\ (56)$$

and

$$I_c = 1/\Lambda_o \qquad \ldots\ldots\ (57)$$

Equations (56) and (57) can be combined to give:-

$$K_c = I_c^2 / m_c \qquad \ldots\ldots\ (58)$$

The values of K_c, Λ_o and m_c derived for each acid studied are recorded in Table XX. A typical classical plot is illustrated in Fig. XV.

For an isotopic acid pair Equation (56) gives

$$m_c(H) = 1/K_c(H)\Lambda_o^2(H) \qquad \ldots\ldots\ (59)$$

and

$$m_c(D) = 1/K_c(D)\Lambda_o^2(D) \qquad \ldots\ldots\ (60)$$

Combining Equations (59) and (60) on the assumption that $\Lambda_o(H) = \Lambda_o(D)$ (c.f. Streitwieser and Klein (20)) gives

$$K_c(H)/K_c(D) = m_c(D)/m_c(H) \qquad \ldots\ldots\ (61)$$

Equation (61) shows that the ratio $m_c(D)/m_c(H)$ can serve as an approximate measure of the isotope effect on the thermodynamic equilibrium constants. Values of $K_c(H)/K_c(D)$ calculated according to Equation (61) are reported in Table XXI.

TABLE XX

CLASSICAL RESULTS

Acid	Classical Slope	Deviation	1/Intercept (Λo)	Dissociation Constant
Acetic	0.36438	± 0.00019	359.93	2.1182×10^{-5}
Phenylacetic	0.13622	±0.00005	367.04	5.4488×10^{-5}
Phenylacetic-α, α,-d_2	0.13720	±0.00003	369.35	5.3422×10^{-5}
4-nitrophenyl-acetic	0.052422	±0.000085	376.48	1.3457×10^{-4}
4-nitrophenylacetic-α,α ,d_2	0.052281	± 0.000076	374.49	1.3638×10^{-4}
4-methoxy-phenylacetic	0.15778	±0.00006	370.01	4.6289×10^{-5}
4-methoxyphenyl-acetic-α,α-d	0.15849	±0.00009	367.41	4.6737×10^{-5}

TABLE XXI

K(H)/K(D) from classical slopes

Compounds	K(H)/K(D)	Deviation
$PhCH_2COOH/PhCD_2COOH$	1.0072	±0.0004
$4\text{-}NO_2PhCH_2COOH/4\text{-}NO_2PhCD_2COOH$	0.9973	±0.0020
$4\text{-}MeOPhCH_2COOH/4\text{-}MeOPhCD_2COOH$	1.0045	±0.0007

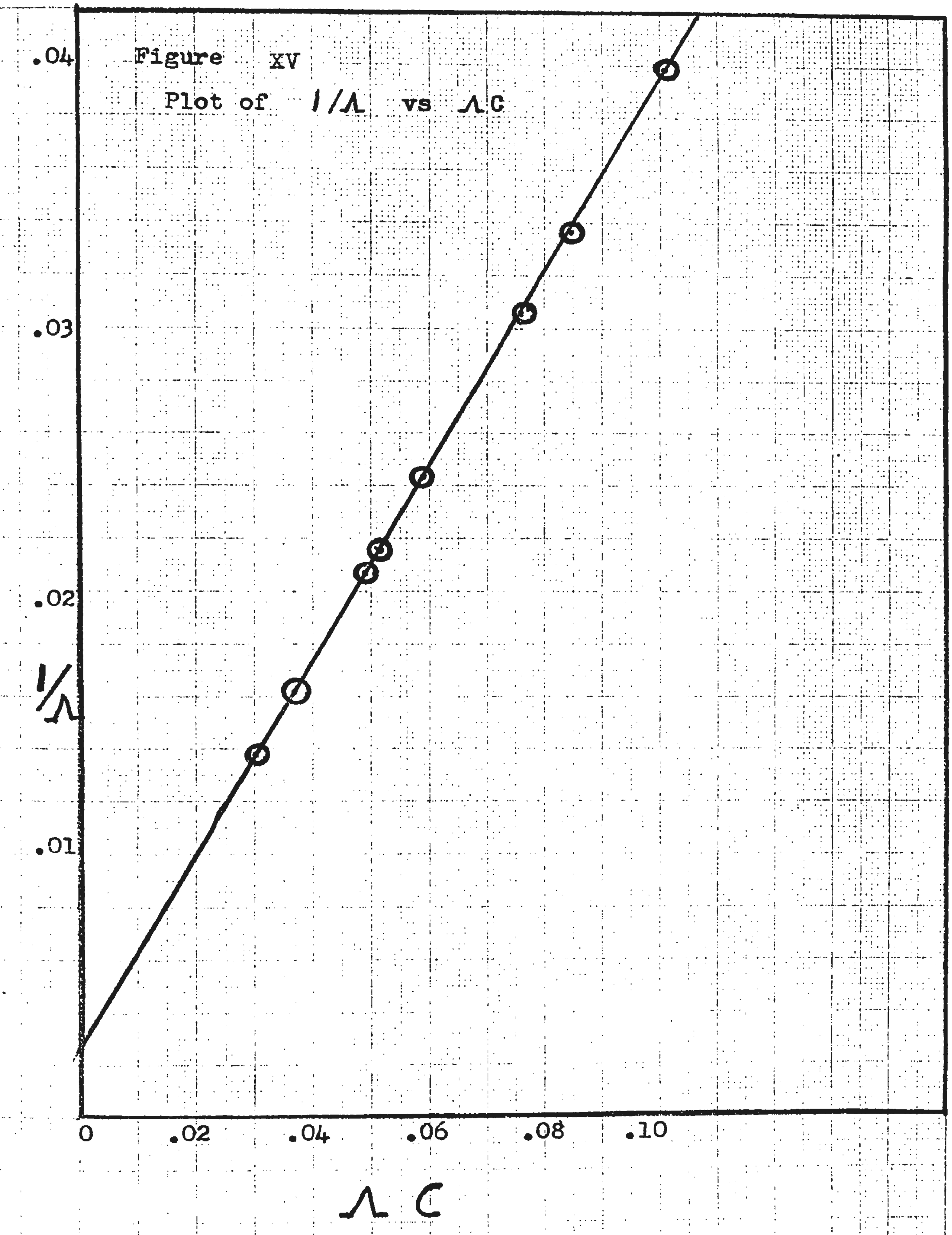


Figure XV
Plot of 1/Λ vs ΛC
.04
.03
.02
.01
1/Λ
0
.02
.04
.06
.08
.10
Λ C

Discussion.

The small probable errors in the m_c values derived from the classical plots for each acid studied, suggest that the variation of K_c over the concentration ranges investigated is not intrinsically large. Ives (68) has observed that errors due to the neglect of mobility and activity factors, while not large, are greatly magnified when the length of the extrapolation is larger than that of the experimental data. This rationalizes the differences between the Λ_o values observed for the deuterium and hydrogen analogues recorded in Table XX. No significance can be attached to these differences for this and other reasons which will be more fully considered in a later section.

The isotope effects calculated from Equation (61) for the phenylacetic acids refer to similar concentration ranges. The least squares fit of the conductance data for 4-nitrophenylacetic acid does not include concentrations in the 10^{-3} molal range. The $K_c(H)/K_c(D)$ ratio for the 4-nitrophenylacetic acids, using the complete concentration range covered for each acid, gave a value of 1.01. On the other,hand a comparison of the slopes for these acids over the same concentration range, gave a value of 0.997 for the isotope effect. This latter value is to be preferred. The curvature of the classical plot which is implied in these observations is not confined to this particular acid and it can be shown that the classical plot tends to be curved for all weak acids.

Method II. The Robinson-Stokes Method (RSM).

The Robinson-Stokes (72) modification of the MacInnes-Shedlovsky (71) method of calculating equilibrium constants (see pages 94-95) was applied to the experimental results of the seven acids studied. This method requires an accurate value of Λ_o in order to calculate, by successive approximations, the equivalent conductance of the hypothetical completely ionized weak electrolyte at a finite concentration (Λ_i). The Λ_o values quoted by Vogel and Jeffery (75) for phenylacetic acid, Dippy and Williams (39) (43) for 4-nitrophenylacetic and 4-methoxyphenylacetic acids and Shedlovsky (71) for acetic acid, were used in the present study. The Λ_o values from these sources recorded in Table XXII. have been converted to the molal concentration scale by the equation:-

$$\Lambda_o(\text{molar}) = \Lambda_o(\text{molal})/\ d_o \qquad \ldots\ldots\ (62)$$

where d_o is the density of pure water at 25°C. Tables XXIII - XXIX list the equilibrium constants calculated in this way. The equivalent conductance and Λ_i at each concentration studied are mean values of the results from the individual cells.

Discussion.

The equilibrium constants determined by the RSM agree very well with previous measurements on these systems (see Table XXX) apart from 4-nitrophenyl acetic acid. The large scatter for the K (classical and thermodynamic) values of this latter acid is almost certainly a consequence of the labile nature of this molecule when it is exposed to daylight. Since the previous workers failed to recognize this fact the value reported in this thesis is to be preferred.

A comparison of the equilibrium constants calculated for different samples of the acids confirms the purity of the individual specimens used. In no case can any discrimination be made between the various samples within the precision of the results of the present study. The redetermined equilibrium constant for acetic acid is also in excellent agreement with previous values (see Table XXX) and offers further confirmation of the precision of the present study.

The thermodynamic equilibrium constants calculated by the R.S.M. reveal a slight residual concentration dependence which is probably outside the experimental error of the present study. This residual concentration dependence (see Figs. XXVI, XXVII, and XXVIII) may be a consequence of the breakdown of the theory at higher concentrations or alternatively may be a consequence of the neglect of the frequency dependence of the electrolyte resistances. In the most precise studies to date (30) (31) the latter factor has been considered important. The possible causes for the breakdown of the theoretical expressions employed to calculate thermodynamic equilibrium constants will be considered in greater detail in the section dealing with the Shedlovsky calculations.

Isotope effects can be evaluated from the equilibrium constants calculated by the RSM. These will be considered subsequently.

TABLE XXII

Limiting Equivalent Conductances

Acid	Λ_o(molality scale)	Λ_o(liter)*	Reference
Acetic	389.6	390.7	(71)
Phenylacetic	379.6	380.7	(75)
4-Nitrophenylacetic	376.6	377.8	(39)
4-Methoxyphenylacetic	377.3	378.4	(43)

* molarity scale

TABLE XXIII

Equilibrium Constant of Acetic Acid (RSM)

Run No.	Conc. x 10^3	Λ	Λ_1	Ka x 10^5
1	2.8424	29.7359	387.34	1.7538
2	2.3264	32.7379	387.44	1.7566
3	1.4326	41.1637	387.69	1.7561
4	0.59920	61.6149	388.06	1.7555
5	4.05555	25.1083	387.13	1.7575
6	1.1103	46.4401	387.80	1.7612
7	1.0133	48.3878	387.84	1.7556
8	0.41870	72.4462	388.19	1.7564

Average Ka(H) 1.7566 ± .0025 x 10^{-5}

TABLE XXIV

Equilibrium Constant of Phenylacetic Acid (RSM)

Run No.	Conc. x 10^3	Λ	Λ_i	Ka x 10^5
1	2.2612	52.5896	377.05	4.9078
2	1.8720	57.3855	377.17	4.9167
3	3.6856	42.0075	376.70	4.9251
4	2.7574	48.1078	376.91	4.9328
5	6.3076	32.5371	376.28	4.8955
6	4.44067	38.5740	376.57	4.9079
9	4.7217	37.4006	376.51	4.9236
10	5.8984	33.6358	376.33	4.9108
11	6.9879	31.0326	376.19	4.9074
12	1.7139	59.8708	377.23	4.9409
13	2.8300	47.5295	376.89	4.9321
14	0.25118	135.7575	378.22	4.9384
15	0.13591	170.4467	378.46	4.9252
16	0.27688	130.6632	378.18	4.9368
17	0.10855	184.2815	378.54	4.9290

Average Ka(H) 4.9227 ± 0.0150 x 10^{-5}

TABLE XXV

Equilibrium Constant for Phenylacetic Acid α: αd_2(RSM)

Run No.	Conc x 10^3	Λ	Λ_i	Ka x 10^5
1	1.1034	72.8278	377.49	4.9204
2	2.3347	51.8577	377.03	4.9151
3	2.4213	50.9948	377.00	4.9148
4	2.7031	48.3644	376.93	4.8922
5	3.1922	44.7814	376.81	4.8936
6	3.4855	43.0025	376.75	4.8976
7	4.9732	36.3427	376.47	4.8796
8	6.2284	32.6473	376.29	4.8692
9	1.7765	58.7148	377.21	4.9067
10	4.9034	36.5994	376.48	4.8836
11	0.42937	109.3006	377.98	4.9226
12	0.49907	102.6426	377.91	4.9202
13	0.28839	128.3082	378.16	4.9110
14	0.63995	92.3805	377.79	4.9208
15	0.31564	123.8530	378.12	4.9187
16	0.20516	146.4859	378.30	4.9175

Average Ka(D) = 4.9055 ± 0.0173 x 10^{-5}

TABLE XXVI

Equilibrium Constant of 4-nitrophenylacetic acid (RSM)

Run No.	Conc. x 10^4	Λ	Λ_i	Ka x 10^4
XI	16.011	94.8956	373.73	1.3212
V	2.8615	184.4992	374.89	1.3277
X	10.442	113.4336	374.06	1.3231
VII	2.6242	189.7969	374.94	1.3260
IX	1.5010	225.4722	375.22	1.3281
VI	0.94570	225.1222	375.44	1.3375*
VIII	0.63893	278.8137	375.60	1.3446*

Average Ka(H) 1.3250 ± 0.0045 x 10^{-4}

* Equilibrium constants not included in average Ka(H)

TABLE XXVII

Equilibrium Constant of 4-nitrophenylacetic-α,α-d_2 acid (RSM)

Run No.	Conc.x 10^4	Λ	Λ_i	Ka x 10^4
1	2.4238	194.7325	374.98	1.3250
2	1.1573	241.7609	375.35	1.3264
3	1.3102	233.7810	375.29	1.3203
4	0.57311	284.1124	375.64	1.3250
5	0.48222	293.4490	375.70	1.3245

Average Ka(D) = 1.3243 ± 0.0048 x 10^{-4}

TABLE XXVIII

Equilibrium Constant of 4-methoxyphenylacetic acid (RSM)

Run No.	Conc. x 10^4	Λ	Λ_i	Ka x 10^5
1	10.838	69.98105	375.27	4.3331
2	4.6775	99.50702	375.69	4.3501
3	4.2055	104.0362	375.74	4.3486
4	1.7463	147.7371	376.10	4.3533
5	8.0969	78.5289	375.42	4.3471
6	3.2173	116.2408	375.85	4.3532

Average Ka(H) 4.3493 ± 0.0053 x 10^{-5}

TABLE XXIX

Equilibrium Constants for 4-methoxyphenyl $\alpha;\alpha d_2$ acetic acid (RSM)

Run No.	Conc. x 10^4	Λ	Λ_i	Ka x 10^5
1	3.2833	114.9142	375.85	=4.3172
2	1.6582	150.0666	376.12	4.3099
3	3.6980	109.4662	375.80	4.3202
4	1.9913	140.1333	376.05	4.3204
5	3.4958	111.8653	375.82	4.3068
6	10.749	69.050	375.28	4.3175

Average Ka(D) $4.3162 \pm 0.0080 \times 10^{-5}$

TABLE XXX

A Comparison of Equilibrium Constants Calculated by the RSM with Previous Values

Acid	Ka x 10^5	Method	Reference
Acetic	1.757 ± 0.003	R-S(m)	(a)
	1.754	EMF(m)	(76)
	1.76	C(c)	(39)
	1.759	I(c)	(68)
	1.758	R-S(m)	(61)
Phenylacetic	4.923 ± 0.015	R-S(m)	(a)
	4.88	C(c)	(39)
	4.88	EMF	(77)
	4.884	C(c)	(75)
	4.95	R-S(c)	(75)
	4.928 ± 0.011	EMF(m)	(78)
	4.887 ± 0.056	C(m)	(79)
4-nitrophenylacetic	13.25 ± 0.05	R-S(m)	(a)
	10.4 (Λ_0 = 414)	C(c)	(80)
	12.94 (Λ_0 = 377.8)	C(c)	(39,80)
	14.1	C(c)	(39)
	11.91 ± 0.36	C(m)	(79)

TABLE XXX (cont'd)

Acid	Ka x 10^5	Method	Reference
4-methoxyphenylacetic	4.349 ± 0.005	R-S(m)	(a)
	4.36	C(c)	(43)
	4.406 ± 0.031	C(m)	(79)

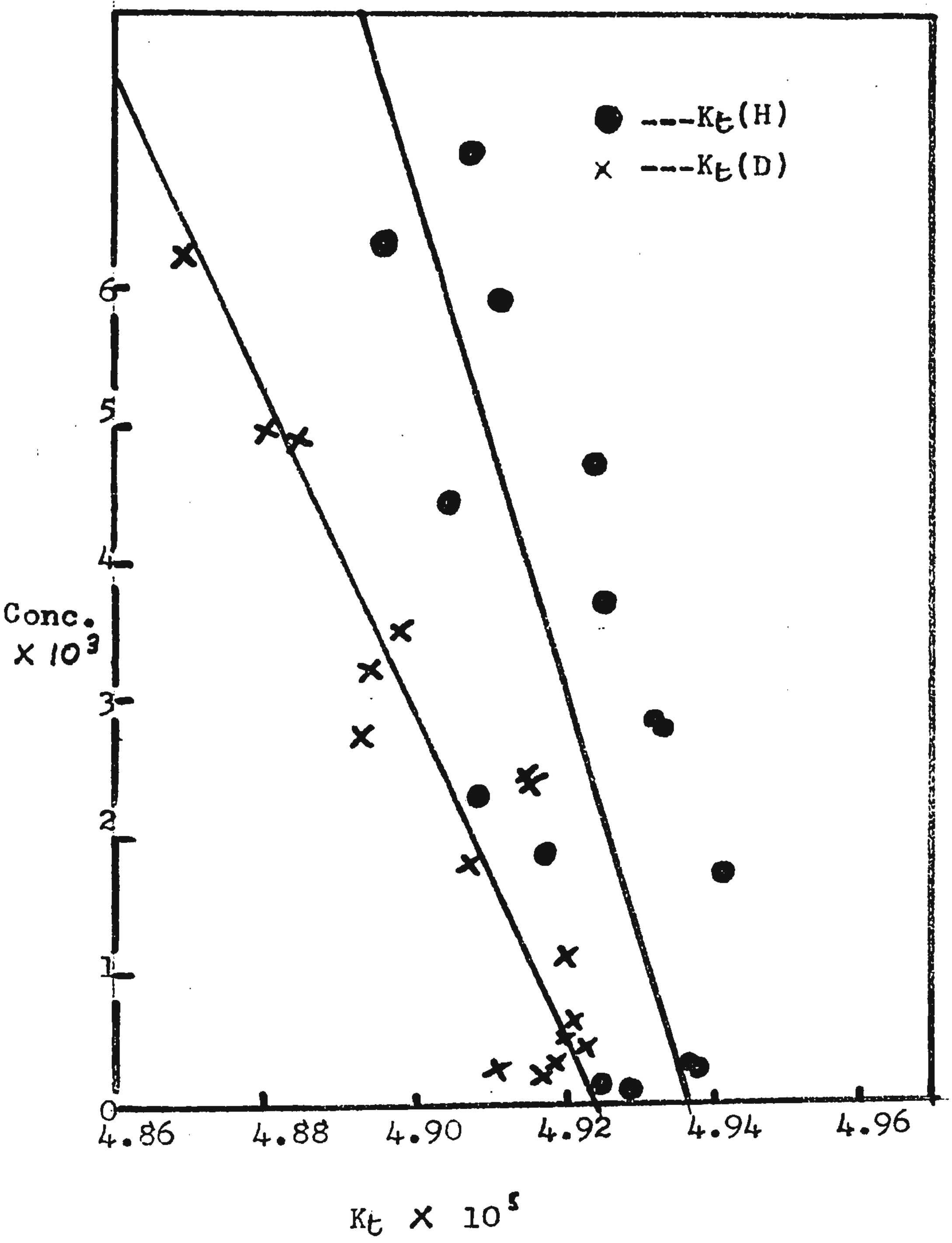
(a) This thesis - Tables XXIII → XXIX, c = mole / liter, m = mole / 1000 g. RS = RSM, C = conductance, I = IIM; EMF has its usual significance.

Figure XXVI. Phenylacetic Acid

Plot of CONCENTRATION

-vs-

EQUILIBRIUM CONSTANT



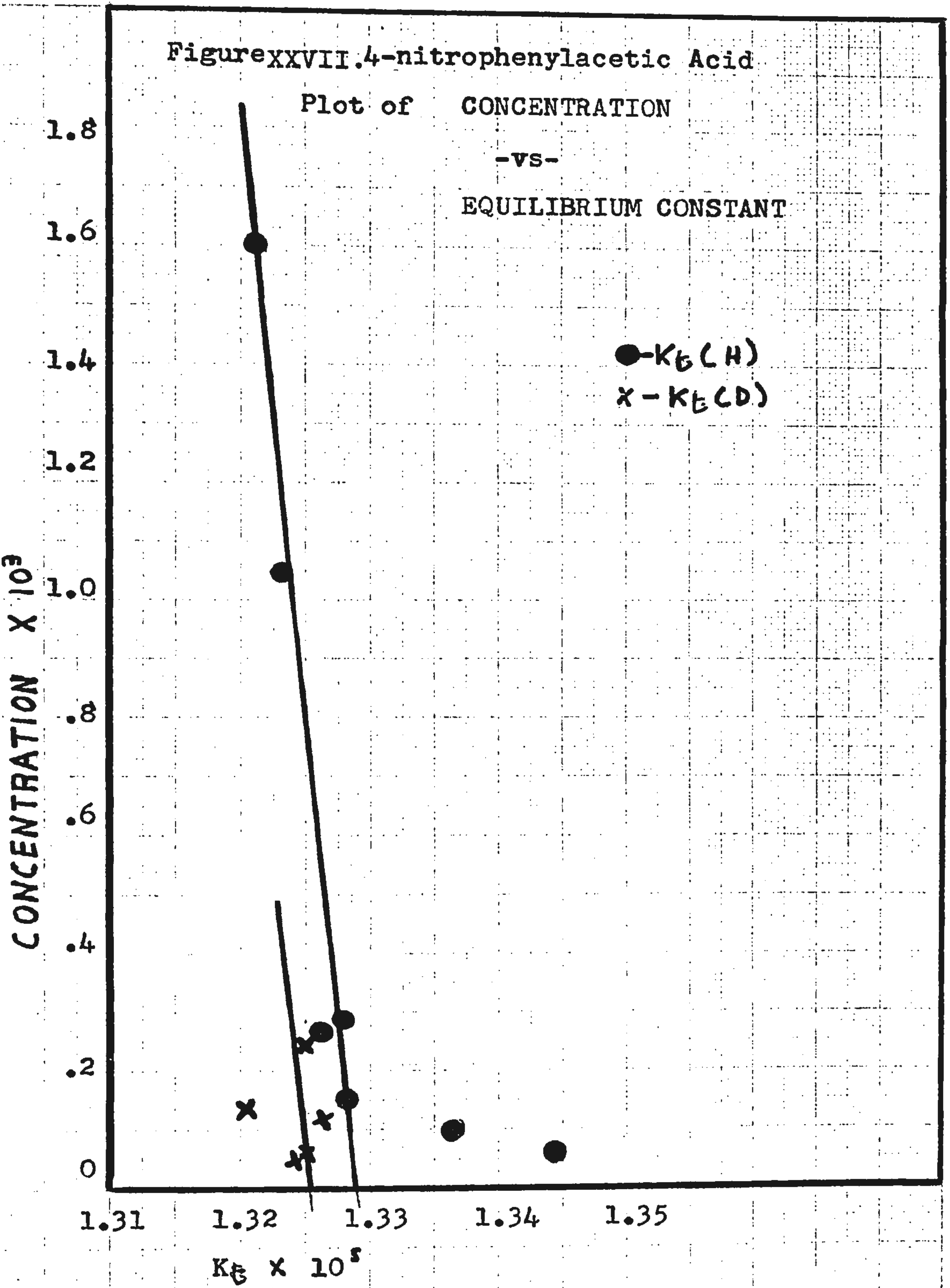


Figure XXVII. 4-nitrophenylacetic Acid

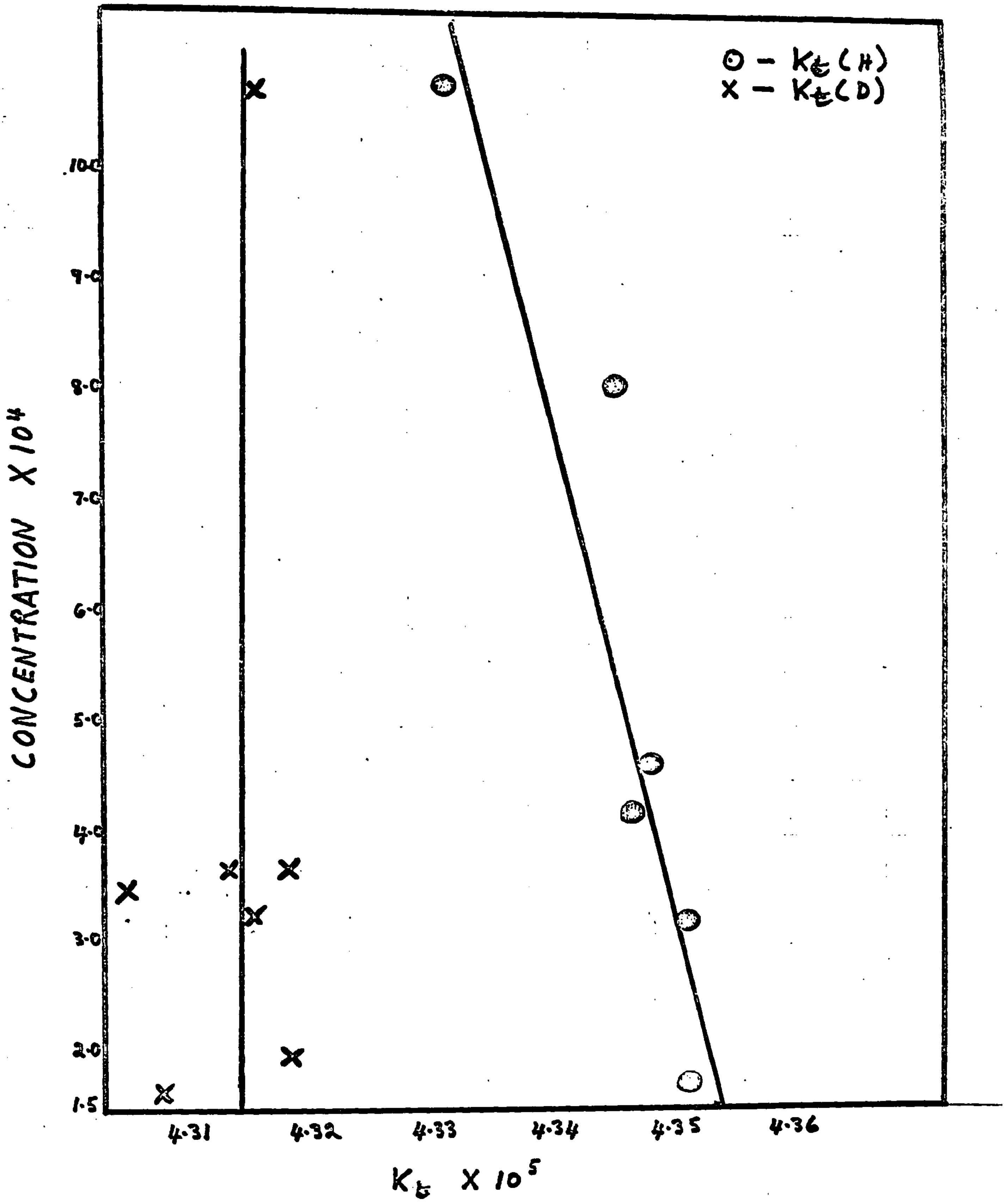
Plot of CONCENTRATION

-vs-

EQUILIBRIUM CONSTANT

Figure XVIII. 4-Methoxyphenylacetic Acid

Plot of Concentrations - vs- Equilibrium Constant



Method III. The Fuoss and Shedlovsky Methods for Determining Thermodynamic Equilibrium Constants and Isotope Effects.

Some initial studies on data for the halogenoacetic acids reported by Ives and Pryor (27) revealed that the Fuoss and Shedlovsky methods of calculating equilibrium constants from conductance data were virtually identical (see Tables XXXI and XXX II). Consequently the Shedlovsky method was arbitrarily selected for a more extended study. Four distinct methods of applying the Shedlovsky Equation were used and these will now be detailed.

Shedlovsky I. The Iteration Method (SIM).

The basis of the SIM has been outlined earlier in this thesis (see pages 89-92) The limiting equivalent conductances used to start the iteration were those obtained from measurements on the appropriate salts (see Table XXII). Since these are the correct values, this should minimize the number of iterations required before a converged value of Λ_o is obtained. One or two iterations were usually sufficient for the Λ_o value obtained from the intercept to converge to a value $<$ 0.01 of its preceeding value. The programme was written to give the following printout: -

```
Results for acetic acid:-
                                   Error in        Error
   Slope         1/Intercept       Intercept       in Slope
3.7565 E-01      391.9416          1.0274 E-05     1.5915 E-04
3.7562 E-01      391.8682          1.0276 E-05     1.5915 E-04
3.7562 E-01      391.8640          1.0275 E-05     1.5915 E-04
```

K_A from the slope = 1733.6873 E-08.
(See also Table XXXII.)

The results obtained from the SIM are detailed in Table XXXIII. Slopes and intercepts for various concentration ranges are also reported to establish that Λ_o tends to increase as the higher concentrations are included in the calculation.

Discussion:-

The application of the SIM to the conductance data of all the acids studied revealed several interesting features. The final slope of the correlation of $1/\Lambda S(Z)$ and $\Lambda CS(Z) f_{\pm}^2$ was found to increase as the range of the data was extended in the direction of increasing concentration. This observation may be a consequence of the breakdown of the theory at high concentrations which leads to a non-linear relationship between the variables. Other factors which merit consideration are:-

(a) the inadequacy of the assumption that $f_u = 1$,

(b) the use of the viscosity of pure water to calculate the constants of the Onsager Conductance Equation rather than the viscosity of the actual solution through which the ions move and finally,(c) the neglect of possible dimerization of the acid at higher concentrations. (c.f. the discussion pertaining to the R.S.M.)

The fact that the final slope and intercept of the SIM is sensitive to the concentration range of the data has important consequences when equilibrium constants are calculated from the slopes (m_t) and intercepts (I_t) of these correlations. Since K_t is given by the expression:-

$$K_t = I_t^2 / m_t \qquad \ldots\ldots\ (62)$$

it is evident that if the parameters m_t and I_t are concentration sensitive, K_t likewise must depend on the concentration range used in the SIM.

In order to clarify this problem, the SIM was applied to the conductance data of Ives (68) and Shedlovsky (71) on acetic acid and Feates and Ives (30) on cyanoacetic acid (see Table XXXIV). For the latter substance, the SIM gave Λ_o values which were distinctly less dependent on the concentration range of the data than acetic acid. The reason for the difference in behaviour of the two acids can be partially understood in terms of their relative strengths. At any given concentration the stronger acid ($CNCH_2COOH$) will display greater dissociation which results in a shorter extrapolation to obtain Λ_o for the stronger acid, and hence Λ_o for this acid will be relatively more precise. At a concentration of 3.2×10^{-4} M cyanoacetic acid has a value of Λ which is 92% of the limiting value. On the other hand, at the same concentration, acetic acid has a Λ value which is only 33 % of the value at infinite dilution. The long extrapolation required for acetic acid to determine Λ_o, combined with possible errors in the data and inadequacy of the theoretical expressions over the whole concentration range, leads to a situation in which it is impossible to determine both Λ_o and K from measurements on the acid alone. In these circumstances an accurate value of K_t from the conductance data can only be obtained if Λ_o for the acid is determined independently.

Belcher (64), using accurate conductance data has examined extrapolation-iteration methods in some detail. He has compared Λ_o values obtained by this technique with those obtained from measurements on the appropriate salt (see Table XXXV). Belcher concludes from his studies that the extrapolation-iteration technique is only reliable if the electrolyte has a dissociation constant $> 10^{-3}$. If the electrolyte is weaker ($K_t < 10^{-5}$) then the value of Λ_o and hence K_t will be in serious error. Belcher states that even if the theoretical expressions are adequate over the complete concentration range studied, the correct Λ_o will not be found unless the random errors are small, and the number of experimental points is very large.

The application of the SIM to the conductance data reported in this thesis bears out Belcher's contentions and no significance can be attached to the observation that $\Lambda_o(H) \neq \Lambda_o(D)$ (converged values) for the various isotopic pairs studied. The SIM method is obviously unsuited to the determination of Λ_o and K_t simultaneously because the phenylacetic acids and acetic acid are all too weak.

Table XXXI

A Comparison of Conductance Methods of Determining K_t Values Proposed by Shedlovsky, Fuoss and Ives.

Acid	Shedlovsky	Fuoss	Ives $\times 10^{+3}$	(Lit. Value) $\times 10^{+3}$	Reference
Fluoroacetic	2.595×10^{-3}	2.597×10^{-3}	2.597	2.592	(27)
Chloroacetic	1.357×10^{-3}	1.358×10^{-3}	1.360	1.356	(27)
Bromoacetic	1.252×10^{-3}	1.254×10^{-3}	1.254	1.253	(27)
Iodoacetic	6.674×10^{-4}	6.679×10^{-4}	6.682	6.680	(27)

The lit. value refers to the values reported by Ives and Pryor (27) using the Ives method of calculation.

TABLE XXXII

Shedlovsky Method

Slope	1/Intercept	Error in B	Error in Slope
3.7465E-01	392.6639	5.6736E-06	9.1548E-05
3.7464E-01	392.6309	5.6288E-06	9.0819E-05
3.7464E-01	392.6317	5.6303E-06	9.0843E-05

Ka from slope is 1731.4554E-08

Concentration	Equil.Const.	O/O Deviation
2.8010E-05	1.7248E-05	.32
1.1135E-04	1.7326E-05	-.12
1.0283E-03	1.7318E-05	-.07
2.4140E-03	1.7326E-05	-.12
5.9120E-03	1.7309E-05	-.02
2.1840E-04	1.7301E-05	.01

Fuoss Iteration Method

Slope	1/Intercept	Error in B	Error in Slope
3.7462E-01	392.5745	5.5126E-06	8.8947E-05
3.7460E-01	392.5430	5.4741E-06	8.8320E-05
3.7460E-01	392.5437	5.4747E-06	8.8329E-05

Ka from slope is 1.7323E-05

Concentration	Equiv.Con.	Equil. Const.
5.9120E-03	20.96	1.7319E-05
1.0283E-03	48.14	1.7327E-05
2.4140E-03	32.22	1.7335E-05
2.8010E-05	210.38	1.7260E-05
1.1135E-04	127.75	1.7336E-05
2.1840E-04	96.49	1.7311E-05

TABLE XXXIII

Shedlovsky Iteration Method

Concentration x 10^3 Range	Slope x 10	1/Intercept	Ka x 10^5
CH_3COOH			
0.41870 to 1.4326	3.7522 ± .0015	389.57 ± 1.34	1.7562 ± .0025
0.41870 to 2.8424	3.7562 ± .0016	391.86 ± 1.58	1.7337 ± .0025
$PhCH_2COOH$			
0.10855 to 6.3076	1.4162 ± .0006	386.39 ± 1.25	4.7296 ± .0222
0.10855 to 2.8300	1.4094 ± .0007	380.46 ± 0.81	4.9015 ± .0127
0.10855 to 0.27688	1.4016 ± .0020	377.51 ± 0.82	5.0060 ± .0125
$PhCD_2COOH$			
0.20516 to 5.2284	1.4260 ± .0006	392.25 ± 1.12	4.5578 ± .0186
0.20516 to 2.7031	1.4172 ± .0006	383.68 ± 0.75	4.7928 ± .0105
0.20516 to 0.63995	1.4086 ± .0012	378.03 ± 0.76	4.9675 ± .0085

TABLE XXXIII (cont'd)

Concentration x 10^3 Range	Slope x 10	1/Intercept	Ka x 10^5
$4\text{-}NO_2PhCH_2COOH$			
0.15010 to 1.6011	5.3495 ± 0.00026	378.90 ± 0.33	13.020 ± 0.037
$4\text{-}NO_2PhCD_2COOH$			
0.048222 to 2.4238	0.53243 ± 0.00062	376.55 ± 0.27	13.246 ± 0.048
$4\text{-}MeO\text{-}PhCH_2COOH$			
0.17463 - 0.80969	1.6184 ± 0.0008	379.26 ± 0.50	4.2975 ± 0.0042
0.17463 - 1.0838	1.6201 ± 0.0006	380.20 ± 0.45	4.2692 ± 0.0044
$4\text{-}MeO\text{-}PhCD_2COOH$			
0.16582 - 1.0749	1.6273 ± 0.0008	377.09 ± 0.50	4.321 ± 0.0079
0.16582 - 0.36980	1.6258 ± 0.0024	376.37 ± 1.14	4.3420 ± 0.0087

TABLE XXXIV

Application of Shedlovsky I Method to Acetic and Cyanoacetic Acid

Concentration Range x 10^3	Slope x 10	1/Intercept	Ka x 10^5
Acetic acid*			
0.028010 to 2.4140	0.37430±0.00007	391.31	1.7447±0.06 %
0.028010 to 20.000	0.38015±0.00079	440.38	1.3564±2.7 %
Acetic acid**			
0.7614 to 4.0724	3.7114±0.0011	393.9	1.7362±0.0006
Cyanoacetic***			
0.32012 to 4.7708	1.9097±0.0027	393.17	338.73±4.12
0.32012 to 1.6651	1.9059±0.0065	393.04	339.64±4.67

*Shedlovsky (71)

**Ives (68)

***Ives (30)

TABLE XXXV

Comparison of Λ_o Values by Belcher (64)

Acid	From Acid and Salt		From Acid alone		Reference
		Ka x 10^5		Ka x 10^5	
Carbonic	394.3	.0431	424	.0365	(81)
Acetic	390.71	1.753	395.3	1.705	(71)
Propionic	385.47	1.343	386.34	1.337	(64)
n-butyric	382.40	1.508	386.05	1.475	(64)
Monochloroacetic	389.52	139.6	389.5	139.6	(82)
O-chlorobenzoic	380.07	119.7	380.0	119.7	(83)
Benzoic	382.21	631.2	382.1	631.2	(84)

Shedlovsky II. The Direct Substitution Method.(SDSM).

Since the degree of dissociation of an weak electrolyte is given in terms of Λ, Λ_o and S(Z) it is possible to calculate K_t directly by combining Equations (20) ($f_u = 1$) and (39) and using a salt value of Λ_o. The SDSM is analogous to the RSM. A summary of the results from the SDSM are recorded in Table XXXVI). The values of Λ_o are those previously used in the RSM given in Table XXII.

Discussion.

The equilibrium constants for the acids studied in this thesis calculated by the SDSM are in excellent agreement with those calculated by the RSM and the isotope effects calculated from the equilibrium constants are of a similar magnitude, and display similar deviations. If a salt value for Λ_o is available, the SDSM represents an acceptable alternative to the RSM.

TABLE XXXVI

Shedlovsky II Results

Acid	Equilibrium Constant x 10^5
Acetic Acid	1.7560 ± 0.0025
Phenylacetic	4.9195 ± 0.0162
Phenylacetic-α,α-d_2	4.9027 ± 0.0187
K(H)/K(D)= 1.0034 ± 0.0050	
4-nitrophenylacetic	13.247 ± 0.047
4-nitrophenylacetic-α,α-d_2	13.242 ± 0.048
K(H)/K(D) = 1.004 ± 0.005	
4-methoxyphenylacetic	4.3481 ± 0.0056
4-methoxyphenylacetic-α,α-d_2	4.3153 ± 0.0080
KK(H)/K(D)=1.0076 ± 0.0023	

Shedlovsky III. The Shedlovsky Isotope Effect Calculation (SIEC).

In the discussion pertaining to the SIM it was pointed out that it is not possible to determine K_t and Λ_o simultaneously for acetic and the phenylacetic acids, since these acids are all too weak. However, the Shedlovsky Equation can be used to calculate isotope effects in the following manner. The correction terms $1/S(Z)$ and $S(Z)\,f_{\pm}^2$ for the classical variables $1/\Lambda$ and ΛC require a value of Λ_o for their calculation. If a salt value of Λ_o is available it is possible to calculate both correction terms for the hydrogen and deuterium acids on the assumption that $\Lambda_o(H) = \Lambda_o(D)$. For both isotopic acids the Shedlovsky variables $1/\Lambda S(Z)$ and $\Lambda CS(Z)f_{\pm}^2$ can be correlated without iteration by least squares to give:-

$$\frac{1}{\Lambda(H)\ S(ZH)} = \frac{1}{\Lambda_o(H)} + \frac{\Lambda(H)C(H)S(ZH)f_{\pm}^2(H)}{K_t(H)\Lambda_o^2(H)} \qquad \ldots\ldots (62)$$

$$\frac{1}{\Lambda(D)S(ZD)} = \frac{1}{\Lambda_o(D)} + \frac{\Lambda(D)C(D)\ S(ZD)f_{\pm}^2(D)}{K_t(D)\ \Lambda_o^2(D)} \qquad \ldots\ldots (63)$$

The slopes of these correlations ($m_t(H)$ and $m_t(D)$) are given by:-

$$m_t(H) = 1/K_t(H)\Lambda_o^2(H) \qquad \ldots\ldots (64)$$

$$m_t(D) = 1/K_t(D)\Lambda_o^2(D) \qquad \ldots\ldots (65)$$

Hence a combination of Equations (64) and (65) gives

$$K_t(H)\ /\ K_t(D) = m_t(D)\ /\ m_t(H) \qquad \ldots\ldots (66)$$

In cases where a salt value of Λ_o is not available these equations are still useful, since Λ_o can be varied over a range of values which fall either side of the true value of Λ_o. In practice the location of this range affords no difficulty since for carboxylic acids Λ_o is relatively insensitive to the structure of the acid (see for instance Table XXXVII). The slopes obtained from setting up the variables $1/\Lambda\, S(Z)$ and $\Lambda C f_{\pm}^2\, S(Z)$ with Λ_o values ranging from 374-390 are shown in Tables XXXVIII and XXXIX for phenyl acetic acid and phenylacetic $\alpha:\alpha$ d_2 acid and it is apparent that the slopes are relatively insensitive to the value of Λ_o used to calculate the correction terms $1/S(Z)$ and $S(Z)f_{\pm}^2$. The isotope effects calculated from Equation (66) are recorded in Tables XL and XLI. These ratios have a further refinement which will now be detailed. Combining Equations (62) and (63) with Equation (11) gives:-

$$\frac{R(H)C(H)}{10^3 K\, S(ZH)} = \frac{1}{\Lambda_o(H)} + \frac{K \times 10^3 S(ZH)\, f_{\pm}^2\,(H)}{R(H)K_t(H)\Lambda_o^2(H)} \quad \ldots\ldots(67)$$

and

$$\frac{R(D)\ C(D)}{10^3 K\, S(ZD)} = \frac{1}{\Lambda_o(D)} + \frac{K \times 10^3 S(ZD) f_{\pm}^2\,(D)}{R(D)K_t(D)\Lambda_o^2(D)} \quad \ldots\ldots(68)$$

Multiplying both Equations (67) and (68) by 10^3K

gives
$$\frac{R(H)C(H)}{S(ZH)} = \frac{K\times10^3}{\Lambda_o(H)} + \frac{K^2 \times 10^6\ S(ZH)f_{\pm}^2\,(H)}{R(H)\ K_t(H)\Lambda_o^2(H)} \quad \ldots\ldots(69)$$

and
$$\frac{R(D)C(D)}{S(ZD)} = \frac{K \times 10^3}{\Lambda_o(D)} + \frac{K^2 10^6\ S(ZD)f_{\pm}^2\,(D)}{R(D)\ K_t(D)\Lambda_o^2(D)} \quad \ldots\ldots(70)$$

Equations (69) and (60) show that if comparison of the slopes of the Shedlovsky Equation is made for conductance measurements in a single cell then the ratio of the slopes (m^1_t(H) and m^1_t (D))will almost be independent of the cell constant, since :-

$$m^1_t(H) = K^2 \times 10^6/K_t(H)\Lambda_o^2(H) \qquad \ldots\ldots (71)$$

and

$$m^1_t(D) = K^2 \times 10^6/K_t(D)\Lambda_o^2(D) \qquad \ldots\ldots (72)$$

or

$$K_t(H)/K_t(D) = m^1_t(D) / m^1_t(H) \qquad \ldots\ldots (73)$$

Thus although a value of K and Λ_o is required to calculate the correction terms 1/S(Z) and $S(Z)f^2_\pm$ (which are small) the main contribution of the terms involving K and Λ_o cancel in the ratio of the slopes. The above treatment can be alternatively considered as a correlation between RC/S(Z) and $S(Z)f^2_\pm$ /R in which the correction terms are calculated from an approximate cell constant K and a variable Λ_o. Since the equilibrium constants calculated in this thesis are in excellent agreement with previous determinations it follows that errors in the correction terms from the cell constant must be small. The insensitivity of the slopes and ratios (Equation (73)) to Λ_o in the immediate region of the true value of Λ_o leads to the conclusion that this method of calculation is probably the best method for comparing thermodynamic equilibrium constants of isotopic acids via conductance data. A final discussion of the data recorded in Tables XL and XLI and illustrated in Fig. XIX will be given subsequently.

Possible errors arising from the approximation $\Lambda_0(H) = \Lambda_0(D)$ for each of the isotopic pairs of acids studied remain to be considered. It is to be noted that the values for substituted phenylacetic acids given in Table XLVIII are relatively unsensitive to gross structural changes. It therefore seems reasonable to assume that the delicate structural change involved in replacing hydrogen by deuterium would produce variations in which are an order of magnitude less than those observed in Table XLVIII. Streitwieser and Klein (20) have also considered this approximation in detail. Their conclusions are identical to those outlined above.

Table XXXVII

Variation of Λ_0 With Para Substituents for 4-Substituted Phenylacetic Acids

	4-R-PhCH$_2$COOH						Refences
	R-H	R-NO$_2$	R-MeO	R-Cl	R-Br	R-phenyl	
Dippy & Williams	380.3	377.8	378.4	383.0	382.6	375.0	(39)(43)
Vogel & Jeffery	380.7	-	-	-	-	-	(75)
	383.7	383.0	383.7	385.0	-	-	(79)

TABLE XXXVIII

SHEDLOVSKY III RESULTS ON PHENYLACETIC ACID

	Slope x 10				
	Cell I	Cell II	Cell III	Cell IV	Cell V
374	1.4185 ± 0.0015	1.4153 ± 0.0013	1.4174 ± 0.0015	1.4173 ± 0.0015	1.4133 ± 0.0016
376	1.418 ± 0.0014	1.4153 ± 0.0013	1.4173 ± 0.0015	1.4173 ± 0.0015	1.4132 ± 0.0016
378	1.4183 ± 0.0014	1.4152 ± 0.0013	1.4173 ± 0.0015	1.4172 ± 0.0015	1.4131 ± 0.0016
380	1.4182 ± 0.0014	1.4151 ± 0.0013	1.4172 ± 0.0015	1.4171 ± 0.0015	1.4130 ± 0.0016
382	1.4181 ± 0.0014	1.4150 ± 0.0013	1.4171 ± 0.0015	1.4170 ± 0.0015	1.4130 ± 0.0016
384	1.4180 ± 0.0014	1.4149 ± 0.0013	1.4170 ± 0.0015	1.4169 ± 0.0015	1.4129 ± 0.0016
386	1.4179 ± 0.0014	1.4148 ± 0.0013	1.4169 ± 0.0015	1.4168 ± 0.0015	1.4128 ± 0.0016
388	1.4179 ± 0.0014	1.4147 ± 0.0013	1.4168 ± 0.0015	1.4167 ± 0.0015	1.4127 ± 0.0016
390	1.4178 ± 0.0014	1.4147 ± 0.0013	1.4167 ± 0.0015	1.4167 ± 0.0015	1.4126 ± 0.0016

TABLE XXXIX

SHEDLOVSKY III RESULTS ON PHENYLACETIC-α,α-d_2 ACID

SLOPES FOR VARIABLE Λ_0

	Slope x 10				
	Cell I	Cell II	Cell III	Cell IV	Cell V
374	1.4277 ± 0.0014	1.4263 ± 0.0014	1.4271 ± 0.0019	1.4275 ± 0.0015	1.4255 ± 0.0014
376	1.4276 ± 0.0014	1.4264 ± 0.0014	1.4270 ± 0.0019	1.4274 ± 0.0015	1.4254 ± 0.0014
378	1.4275 ± 0.0014	1.4261 ± 0.0014	1.4269 ± 0.0019	1.4274 ± 0.0015	1.4253 ± 0.0014
380	1.4275 ± 0.0014	1.4260 ± 0.0014	1.4268 ± 0.0019	1.4273 ± 0.0015	1.4252 ± 0.0014
382	1.4274 ± 0.0014	1.4259 ± 0.0014	1.4267 ± 0.0019	1.4272 ± 0.0015	1.4251 ± 0.0014
384	1.4273 ± 0.0014	1.4259 ± 0.0014	1.4266 ± 0.0019	1.4271 ± 0.0015	1.4251 ± 0.0014
386	1.4272 ± 0.0014	1.4258 ± 0.0014	1.4265 ± 0.0019	1.4270 ± 0.0015	1.4250 ± 0.0014
388	1.4271 ± 0.0014	1.4257 ± 0.0014	1.4265 ± 0.0019	1.4269 ± 0.0015	1.4249 ± 0.0014
390	1.4270 ± 0.0014	1.4256 ± 0.0014	1.4264 ± 0.0019	1.4268 ± 0.0015	1.4248 ± 0.0014

TABLE XL

Isotope Effect for Phenylacetic Acid

Cell No.	Isotope Effect	± Deviation	
1	.10064857E+01	0.1441E-02	374.00
	.10064862E+01	0.1439E-02	376.00
	.10064866E+01	0.1437E-02	378.00
	.10065576E+01	0.1436E-02	380.00
	.10065581E+01	0.1434E-02	382.00
	.10065585E+01	0.1432E-02	384.00
	.10065590E+01	0.1431E-02	386.00
	.10064885E+01	0.1429E-02	388.00
	.10064889E+01	0.1427E-02	390.00
2	.10077722E+01	0.1349E-02	374.00
	.10077728E+01	0.1348E-02	376.00
	.10077021E+01	0.1346E-02	378.00
	.10077026E+01	0.1344E-02	380.00
	.10077032E+01	0.1342E-02	382.00
	.10077744E+01	0.1341E-02	384.00
	.10077750E+01	0.1339E-02	386.00
	.10077755E+01	0.1337E-02	388.00
	.10077760E+01	0.1336E-02	390.00
3	.10066305E+01	0.1734E-02	374.00
	.10066309E+01	0.1732E-02	376.00
	.10066314E+01	0.1730E-02	378.00
	.10066319E+01	0.1728E-02	380.00
	.10066323E+01	0.1727E-02	382.00
	.10066328E+01	0.1725E-02	384.00
	.10066333E+01	0.1723E-02	386.00

TABLE XL (Cont'd).

	.10067043E+01	0.1721E-02	388.00
	.10066337E+01	0.1720E-02	390.00
4	.10070547E+01	0.1517E-02	374.00
	.10070552E+01	0.1515E-02	376.00
	.10071262E+01	0.1513E-02	378.00
	.10070557E+01	0.1511E-02	380.00
	.10070562E+01	0.1509E-02	382.00
	.10070567E+01	0.1507E-02	384.00
	.10070572E+01	0.1505E-02	386.00
	.10070577E+01	0.1504E-02	388.00
	.10070582E+01	0.1502E-02	390.00
5	.10083469E+01	0.1366E-02	374.00
	.10082762E+01	0.1363E-02	376.00
	.10082767E+01	0.1361E-02	378.00
	.10082773E+01	0.1359E-02	380.00
	.10082779E+01	0.1356E-02	382.00
	.10083493E+01	0.1354E-02	384.00
	.10083498E+01	0.1351E-02	386.00
	.10083504E+01	0.1349E-02	388.00
	.10082797E+01	0.1347E-02	390.00

TABLE XLI

Isotope Effects from Shedlovsky III

R-PhCH$_2$COOH	Cell I	Cell II	Cell III	Cell IV	Cell V
R-H 378	1.0065 ±.0014	1.0077 ±.0014	1.0078 ±.0017	1.0072 ±.0015	1.0086 ±.0014
R-H 380	1.0065 ±.0014	1.0077 ±.0014	1.0068 ±.0017	1.0072 ±.0015	1.0086 ±.0014
R-NO$_2$ 376	0.9986 ±.0013	0.9981 ±.0011	0.9951 ±.0025	0.9938 ±.0007	0.9956 ±.0008
R-NO$_2$ 378	0.9986 ±.0013	0.9981 ±.0011	0.9951 ±.0025	0.9938 ±.0007	0.9956 ±.0008
R-MeO 376	1.0051 ±.0013	1.0037 ±.0009	1.0049 ±.0019	1.0036 ±.0009	1.0052 ±.0012
R-MeO 378	1.0051 ±.0013	1.0037 ±.0009	1.0049 ±.0019	1.0036 ±.0009	1.0052 ±.0012

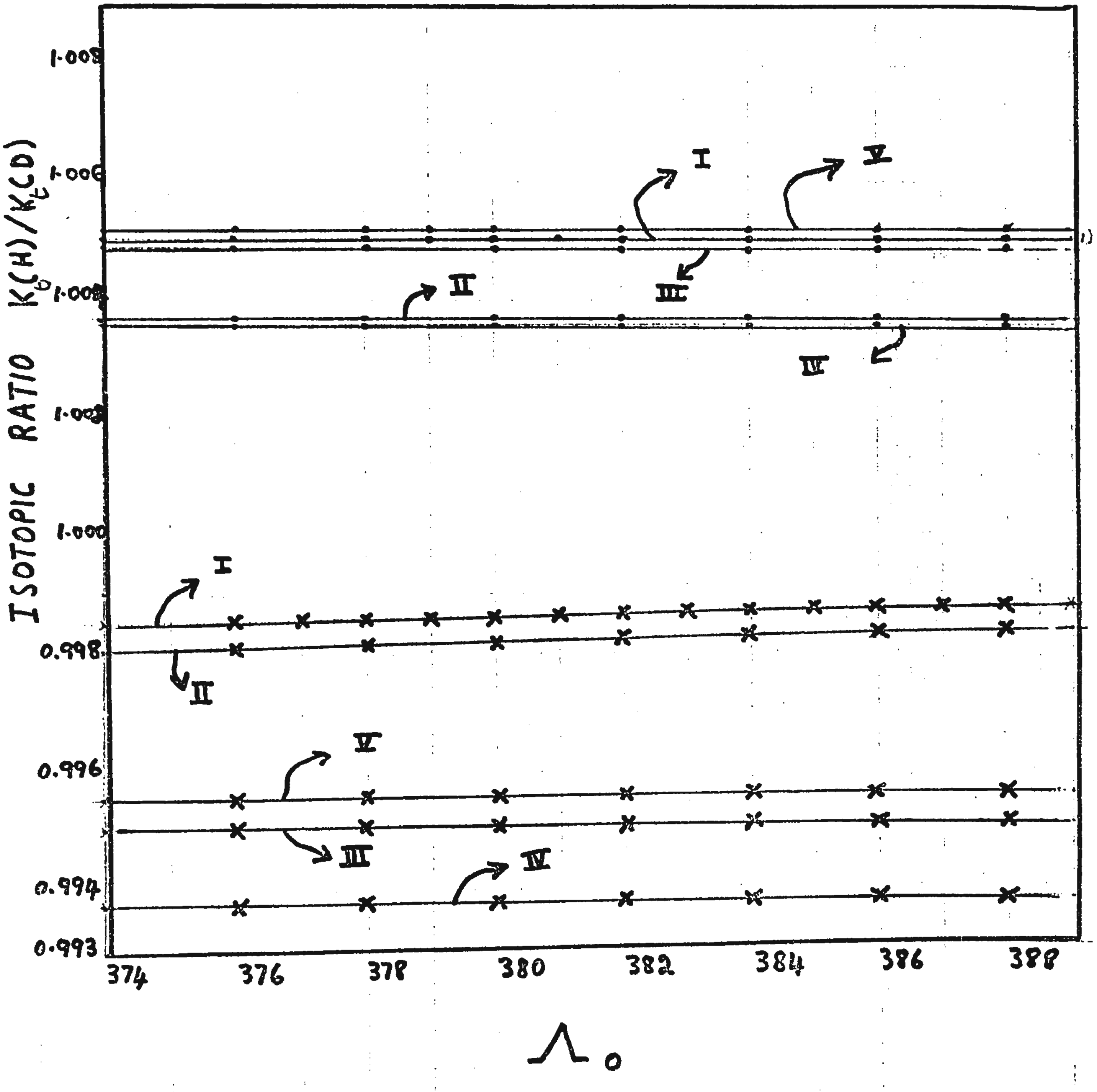
Fig. XIX. Isotope Ratio $K_t(H)/K_t(D)$

-VS-

Λ_o

NB. The Roman numerals refer to the conductance cell numbers.

• - 4-MeO
x - 4-NO2



Shedlovsky IV. The Direct Substitution Method Combined with a Variation of Λ_o (SDSMVL).

The Shedlovsky direct substitution method has already been described (Shedlovsky II). For the SDSMVL the programme for the SDSM was modified so that K_t and the standard deviation associated with this parameter could be calculated for a range of values of the limiting equivalent conductance falling either side of the true value. Such a calculation leads to two interesting relationships:-

(a) The averaged K_t as a function of Λ_o

(b) The standard deviation (δ) of the averaged K_t values at a given Λ_o as a function of Λ_o.

The results of some of these calculations are given in Tables XLII to XLV and are completely illustrated in Figs. XX - XXVII.

Discussion.

The relationship between the average K_t at a given Λ_o and Λ_o is almost linear over the range of Λ_o for which the calculations were made. In the case of $PhCH_2COOH/PhCD_2COOH$ and $4\text{-}MeOC_6H_4CH_2COOH/4\text{-}MeO\text{-}C_6H_4CD_2COOH$ the curves for the deuterium compound fall below and are parallel to the curve for the related hydrogen compound. For the pair $4\text{-}NO_2\text{-}C_6H_4\text{-}CH_2COOH/$ $4\text{-}NO_2C_6H_4CD_2COOH$ the curves intersect. The reasons for this behaviour of the latter substance are not understood.

The plots of δ versus Λ_0 are of considerable interest. All of these curves display minima at values of Λ_0 which are, generally speaking, in better agreement with the salt value than values of Λ_0 obtained from the final intercept using the SIM. Hence a combination of the plots δ versus Λ_0 and K_t versus Λ_0 offers another method of determining K_t values from conductance data.

An application of this method to Ives and Pryor's (27) data on iodoacetic acid gave a Λ_0 value which differed by 0.02 % from that reported by these workers. However, the new method still displays some of the limitations noted for the S.I.M. These can be illustrated from some results obtained from processing the precise acetic acid conductance data measured by MacInnes and Shedlovsky (71). These results have not been tabulated but they are illustrated graphically by the two curves (a) & (b) in Fig. XXVI. Curve (a) was calculated using conductance data over the range $1.11 \times 10^{-5} - 2.41 \times 10^{-3}$ M. The value of Λ_0 at the minimum differs by ca. 0.1 % from the salt value. Curve (b) which includes conductance data in the range $1.11 \times 10^{-5} - 2 \times 10^{-2}$ M gives a curve which has a much shallower minima at a considerably higher Λ_0. The reasons for the change in shape and the position of the minima probably derive from the breakdown of the theoretical expressions over large concentration ranges. The possible causes of the breakdown have already been considered in the sections pertaining to the RSM and SIM.

TABLE XLII

Shedlovsky IV Results for Phenylacetic Acid

Λ_o	Ka(H) x 10^5	Deviation (±)x 10^5	Ka(D) x 10^5	Deviation (±) x 10^5
377	4.9980	0.0231	4.9794	0.0233
378	4.9676	0.0200	4.9497	0.0214
379	4.9374	0.0174	4.9202	0.0196
380	4.9075	0.0156	4.8910	0.0181
381	4.8780	0.0145	4.8621	0.0167
382	4.8487	0.0143	4.8334	0.0155
383	4.8196	0.0151	4.8050	0.0146
384	4.7908	0.0167	4.7768	0.0139
385	4.7623	0.0188	4.7489	0.0136
386	4.7341	0.0218	4.7213	0.0135
387	4.7061	0.0238	4.6938	0.0138
388	4.6784	0.0265	4.6667	0.0144
389	4.6509	0.0293	4.6397	0.0151

TABLE XLIII

Shedlovsky-IV Results for 4-Nitrophenylacetic Acid

Λ_0	Ka(H) x 10^4	Deviation (±) x 10^4	Ka(D) x 10^4	Deviation (±) x 10^4
373	1.3616	0.0096	1.3755	0.0140
374	1.3512	0.0081	1.3623	0.0106
375	1.3409	0.0067	1.3474	0.0076
376	1.3307	0.0054	1.3327	0.0054
377	1.3206	0.0043	1.3183	0.0048
378	1.3107	0.0037	1.3042	0.0062
379	1.3009	0.0037	1.2903	0.0084
380	1.2912	0.0042	1.2767	0.0109
381	1.2816	0.0051	1.2633	0.0135
382	1.2722	0.0062	1.2502	0.0160
383	1.2628	0.0074	1.2373	0.0185
387	1.2146	0.0121	1.1878	0.0276
390	1.2003	0.0156	1.1529	0.0336

TABLE XLIV

Shedlovsky IV Results for 4-Methoxyphenylacetic Acid

	Ka(H) x 10^5	Deviation (±) x 10^5	Ka(D) x 10^5	Deviation (±) x 10^5
370	4.5560	0.0175	4.5283	0.0151
371	4.5266	0.0156	4.4981	0.0135
372	4.4976	0.0137	4.4683	0.0119
373	4.4688	0.0120	4.4388	0.0106
374	4.4403	0.0104	4.4096	0.0095
375	4.4120	0.0088	4.3807	0.0086
376	4.4841	0.0073	4.3521	0.0081
377	4.3564	0.0060	4.3237	0.0079
378	4.3290	0.0049	4.2957	0.0082
379	4.3088	0.0043	4.2679	0.0087
380	4.2749	0.0043	4.2404	0.0095
381	4.2482	0.0049	4.2131	0.0105
382	4.2219	0.0058	4.1862	0.0116
383	4.1957	0.0069	4.1594	0.0128
384	4.1698	0.0081	4.1330	0.0140
385	4.1441	0.0094	4.1068	0.0153

TABLE XLV

Iodoacetic Acid

Average Deviation x 10		Ka x 10^4	Average Deviation x 10		Ka x 10^4
7.49	365	8.239	1.54	385	7.056
8.06	370	8.337	0.94	387	6.912
11.36	371	8.865	0.65	388	6.842
5.42	375	7.866	0.38	389	6.773
4.96	376	7.777	0.12	390	6.705
4.51	377	7.690	0.13	391	6.640
4.09	378	7.606	0.37	392	6.574
3.68	379	7.522	0.61	393	6.510
3.29	380	7.441	0.84	394	6.447
2.91.	381	7.361	1.05	395	6.385
2.55	382	7.282	2.02	400	6.090
2.20	383	7.206	5.21	430	4.722

Fig. XX. $PhCH_2COOH/PhCD_2COOH$
Plot of Equilibrium Constant
Vs - Λ_o

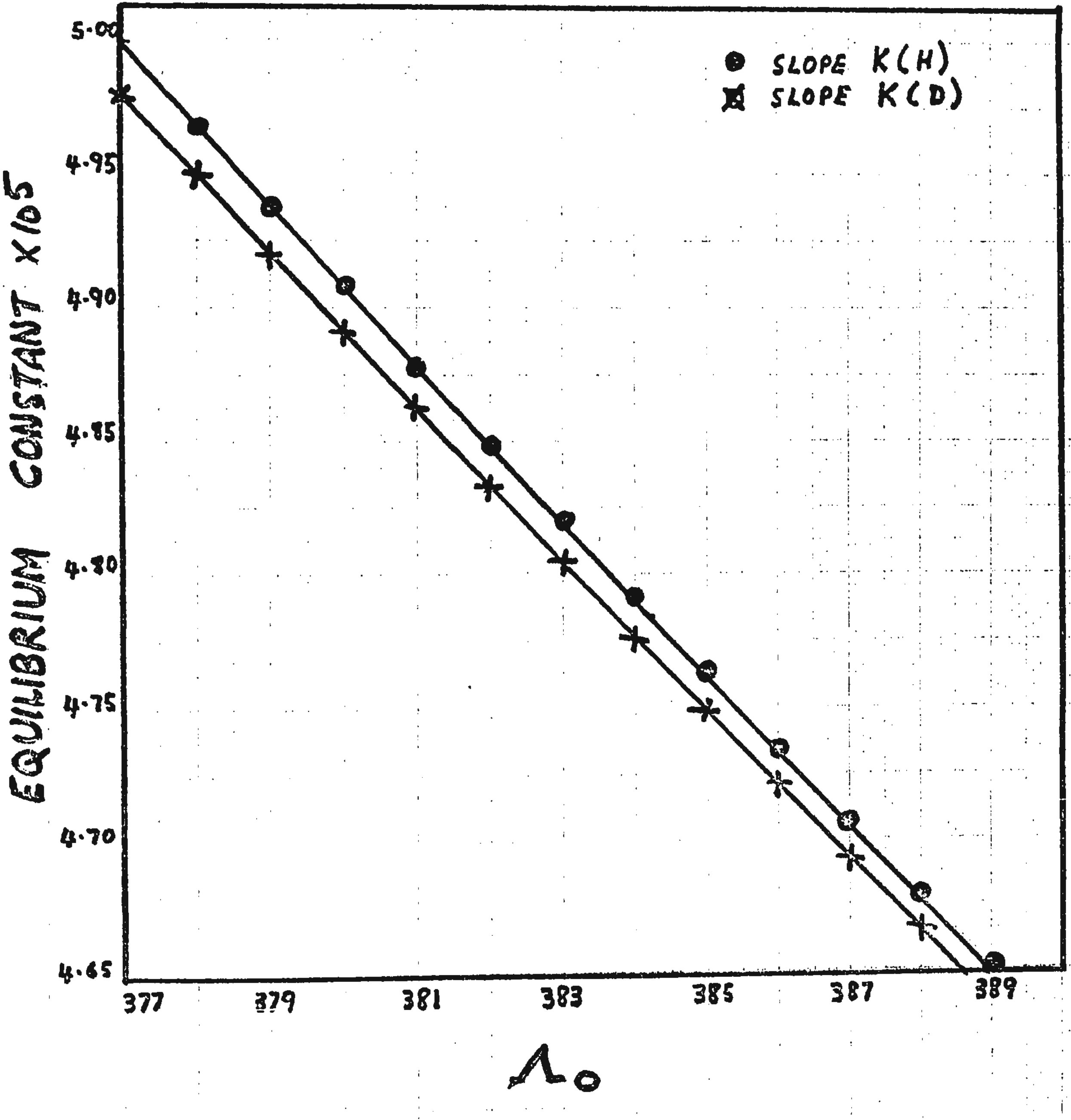
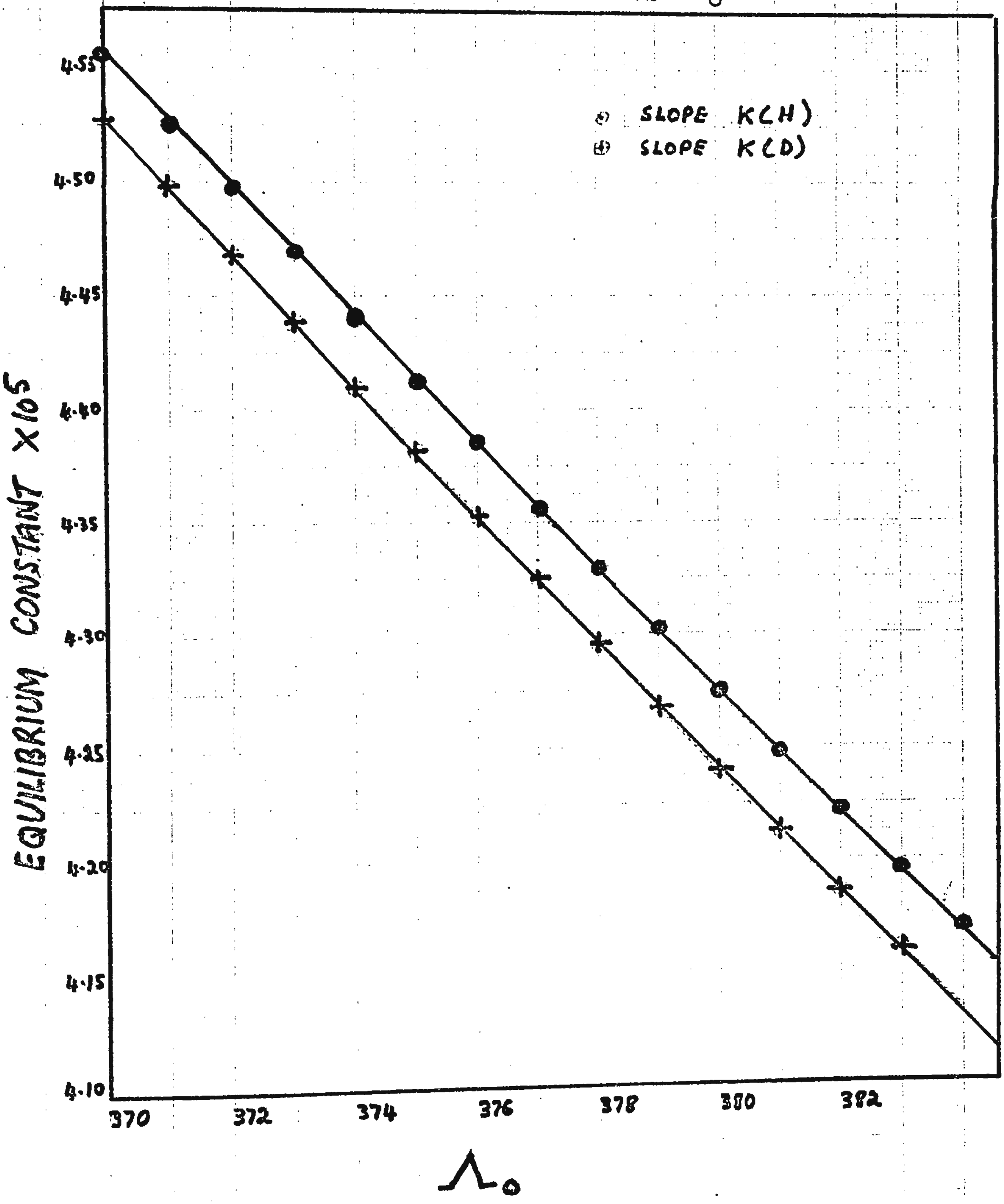


Fig. XXI. 4-$MeOC_6H_4CH_2COOH$ / 4-$MeOC_6H_4CD_2COOH$

Plot of Equilibrium Constant vs o



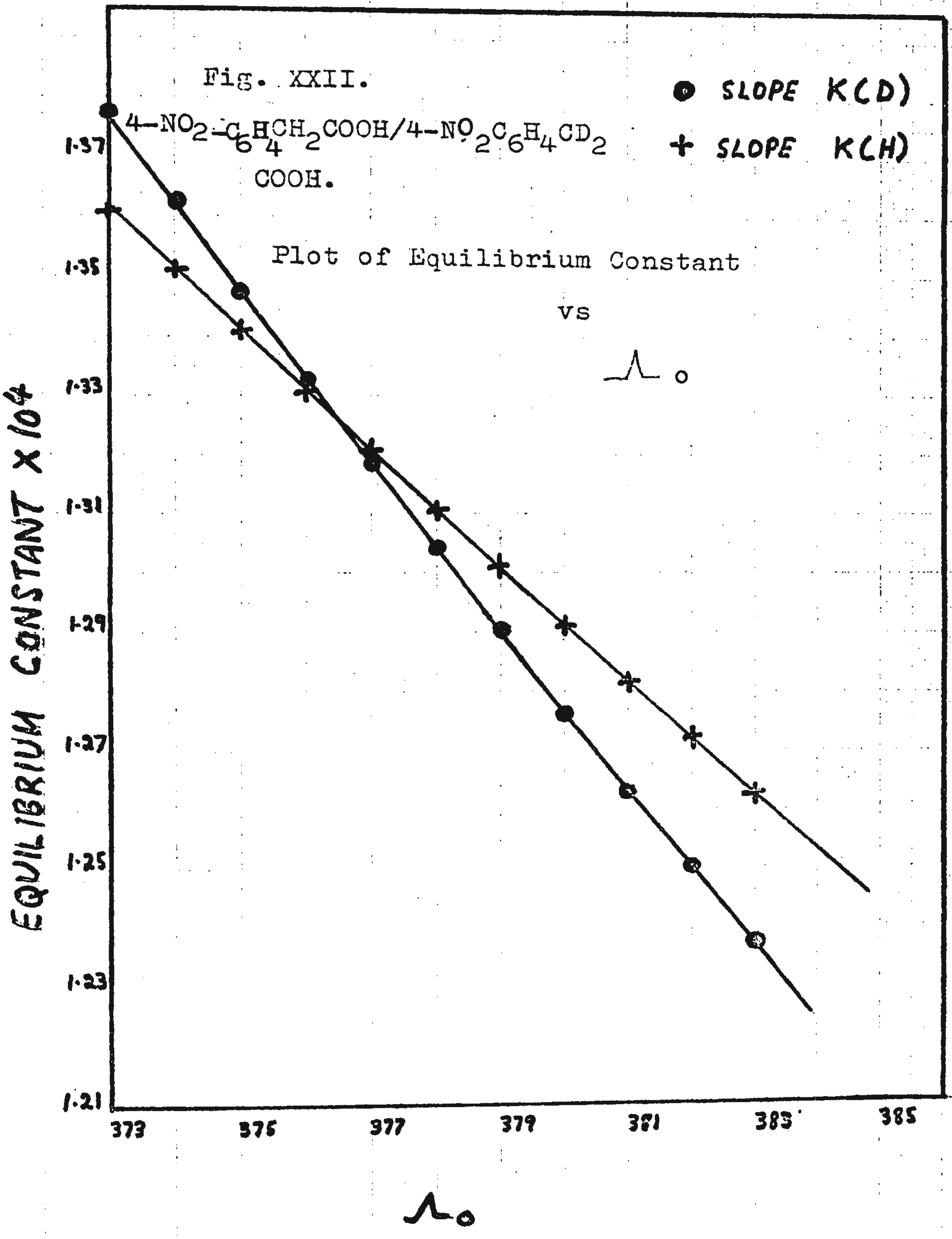


Fig. XXII.

$4\text{-}NO_2\text{-}C_6H_4CH_2COOH/4\text{-}NO_2C_6H_4CD_2COOH$.

Plot of Equilibrium Constant vs Λ_o

Fig. XXIII. Plot of δ vs Λ_o for Acetic Acid

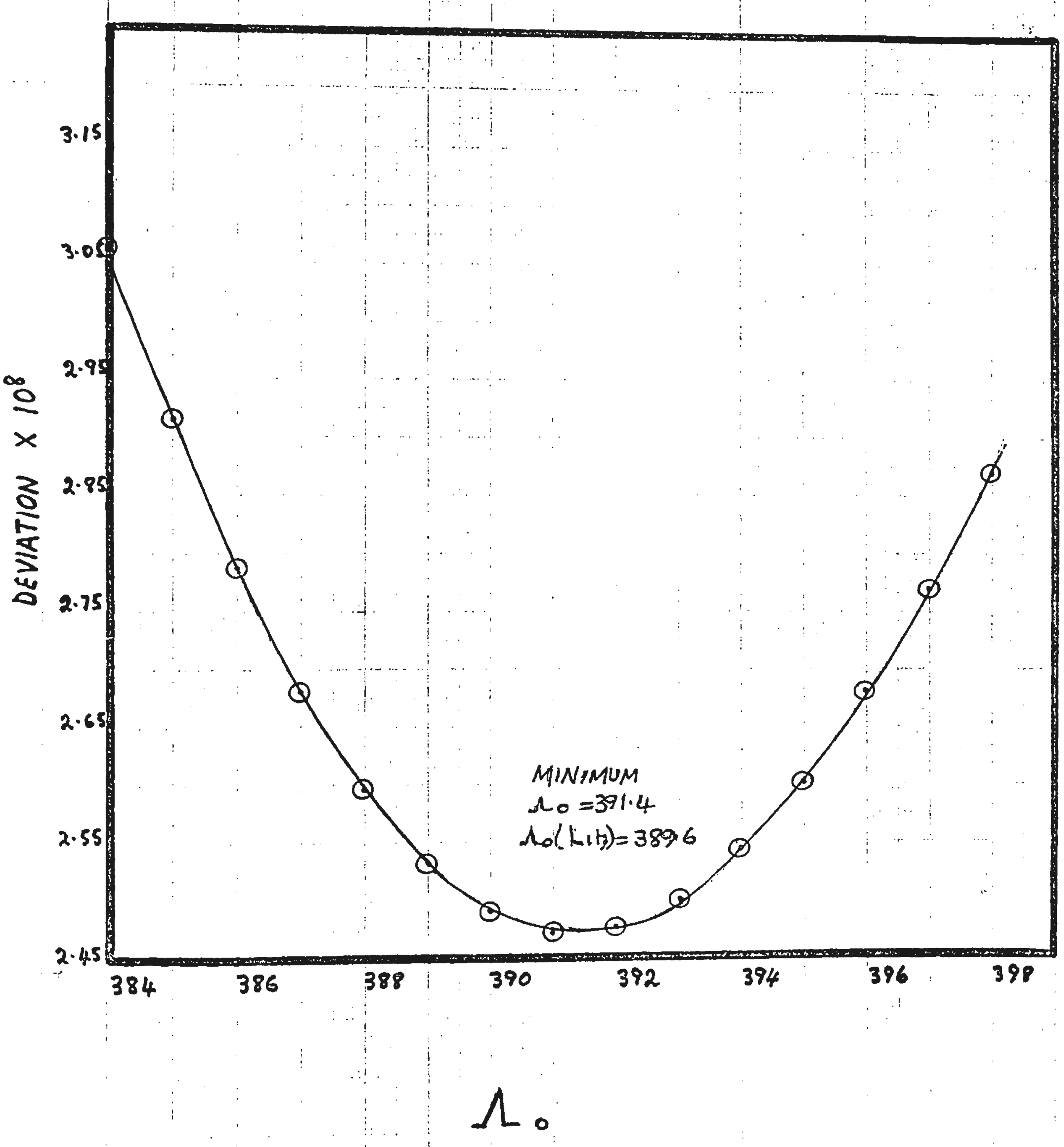


Fig. XXIV. A plot of δ vs Λ_o for $PhCH_2COOH/PhCD_2COOH$.

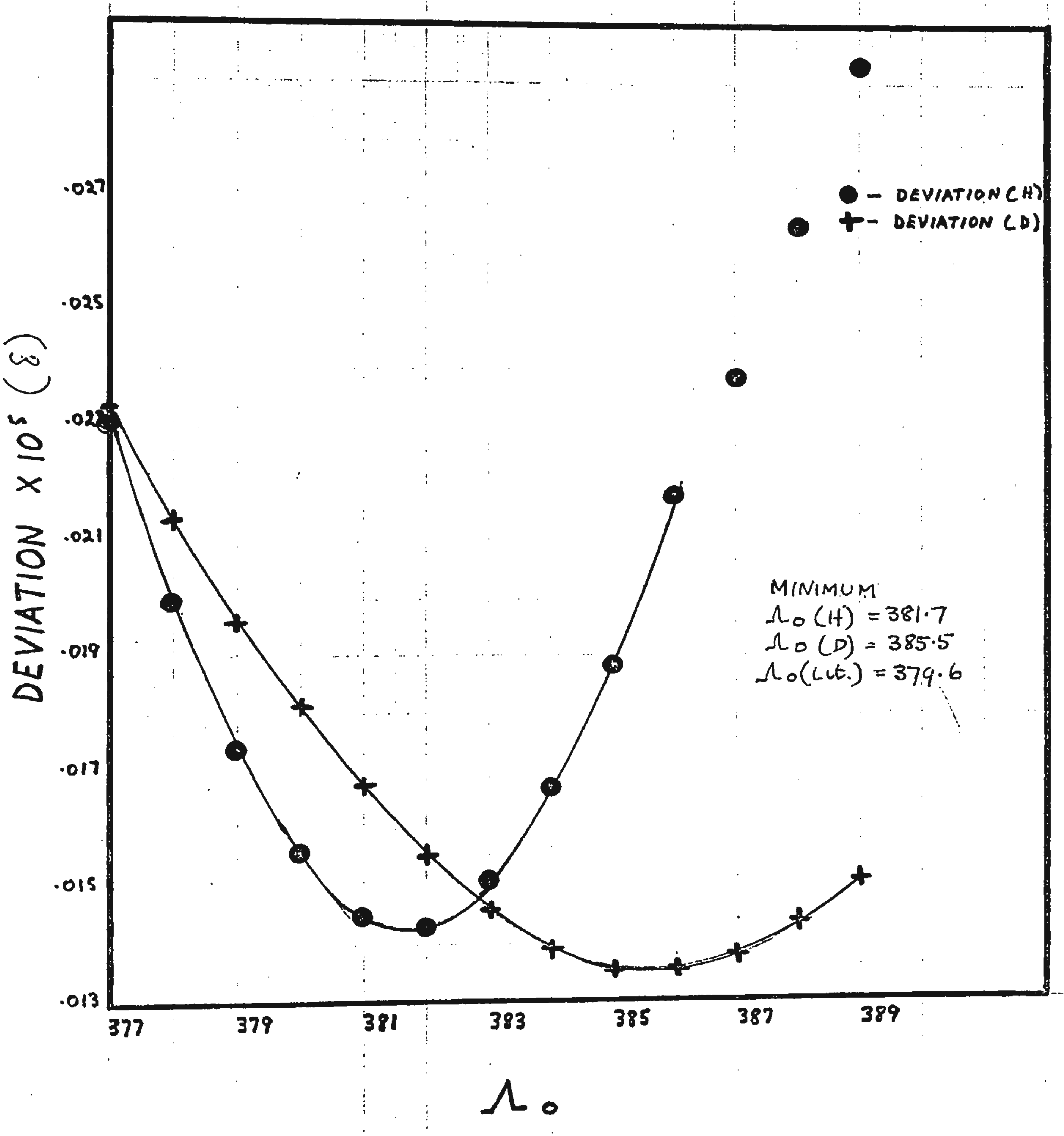


Fig. XXV. A plot of δ vs Λ_o for $4\text{-}NO_2C_6H_4CH_2COOH/\ 4NO_2C_6H_4CD_2COOH$

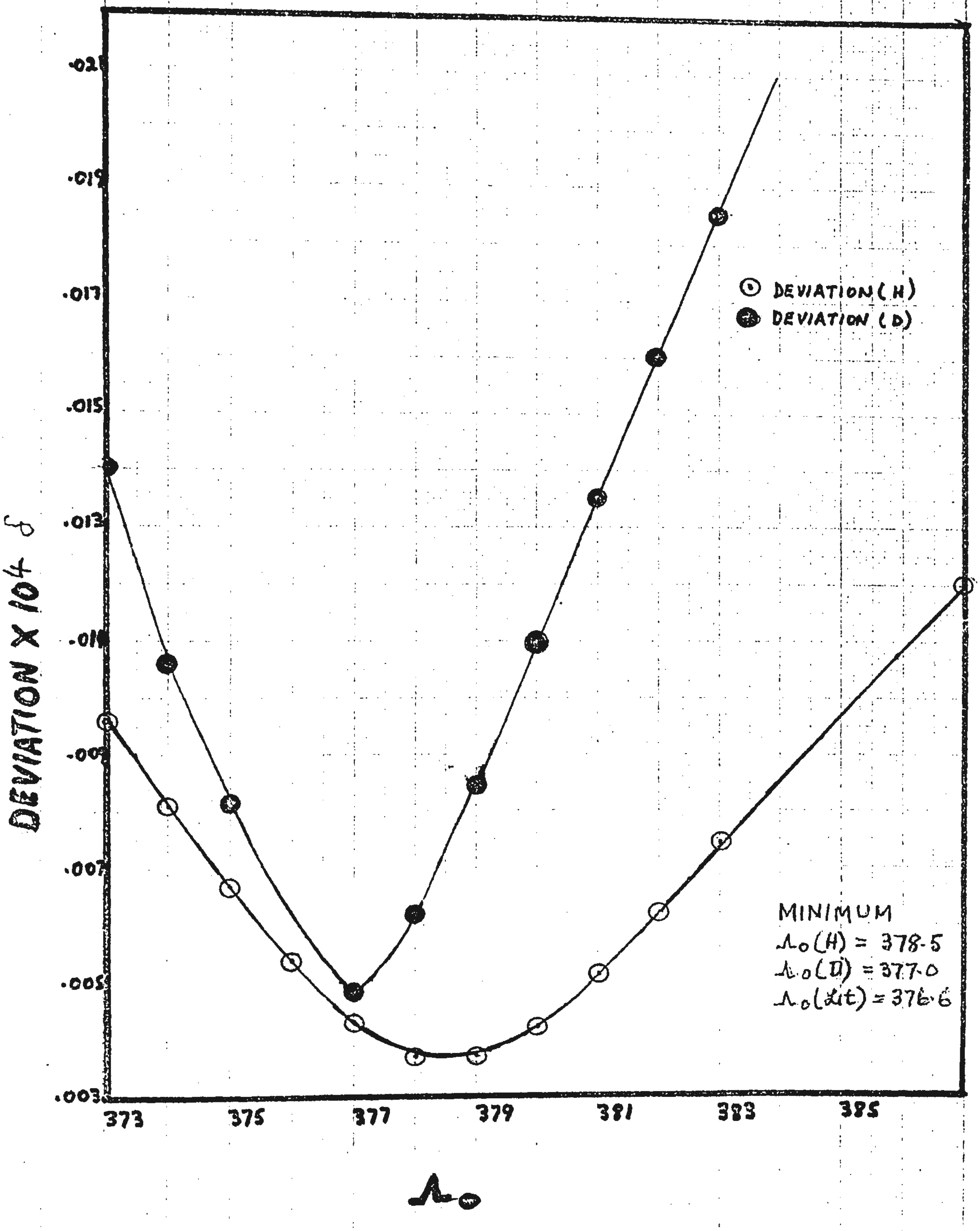


Fig. XXVI. A plot of δ vs Λ_o for Acetic Acid.

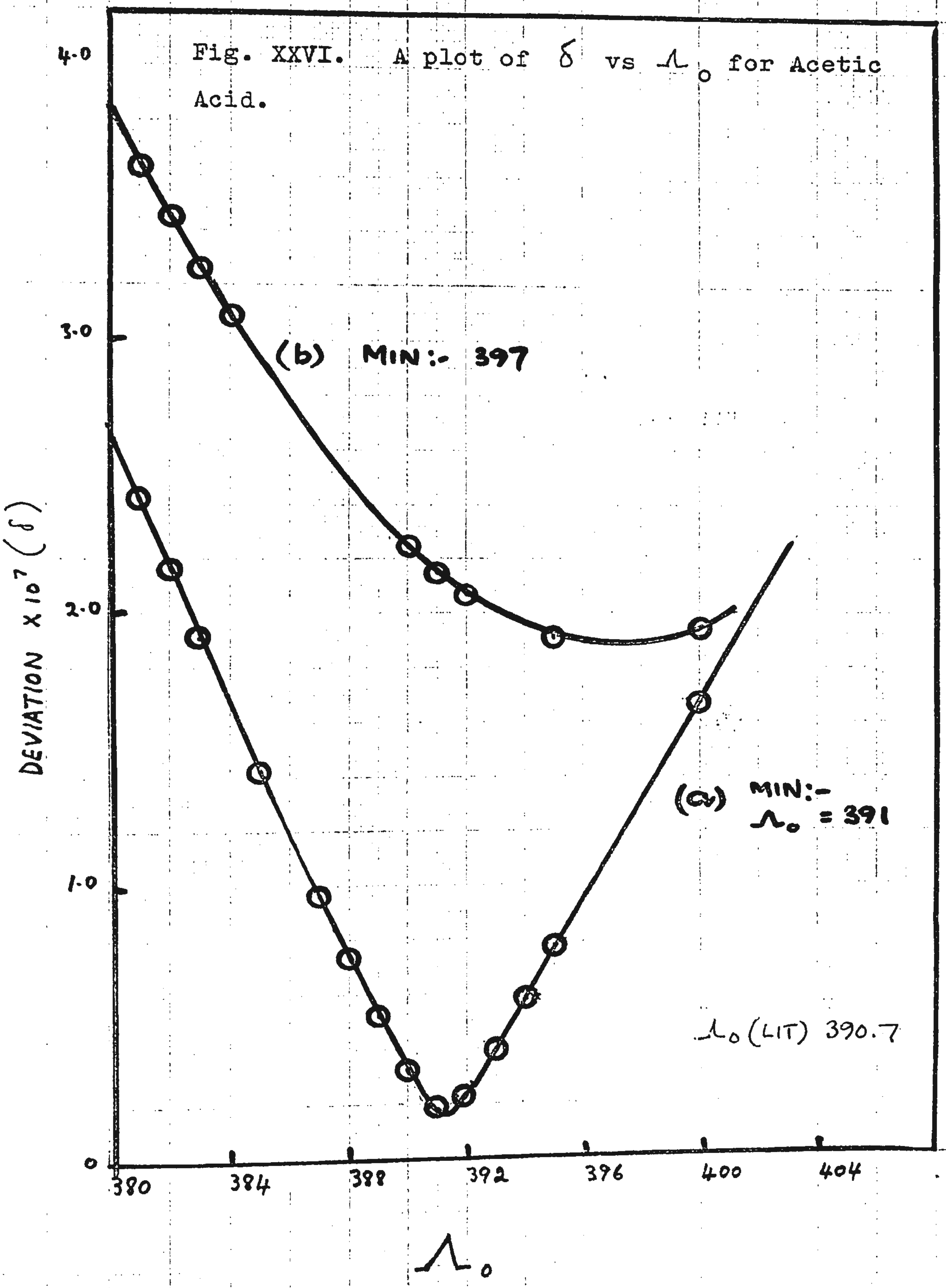


Fig. XXVII. A plot of δ vs Λ_o for
4 $MeOC_6H_4CH_2COOH$/4 $MeOC_6H_4CD_2COOH$

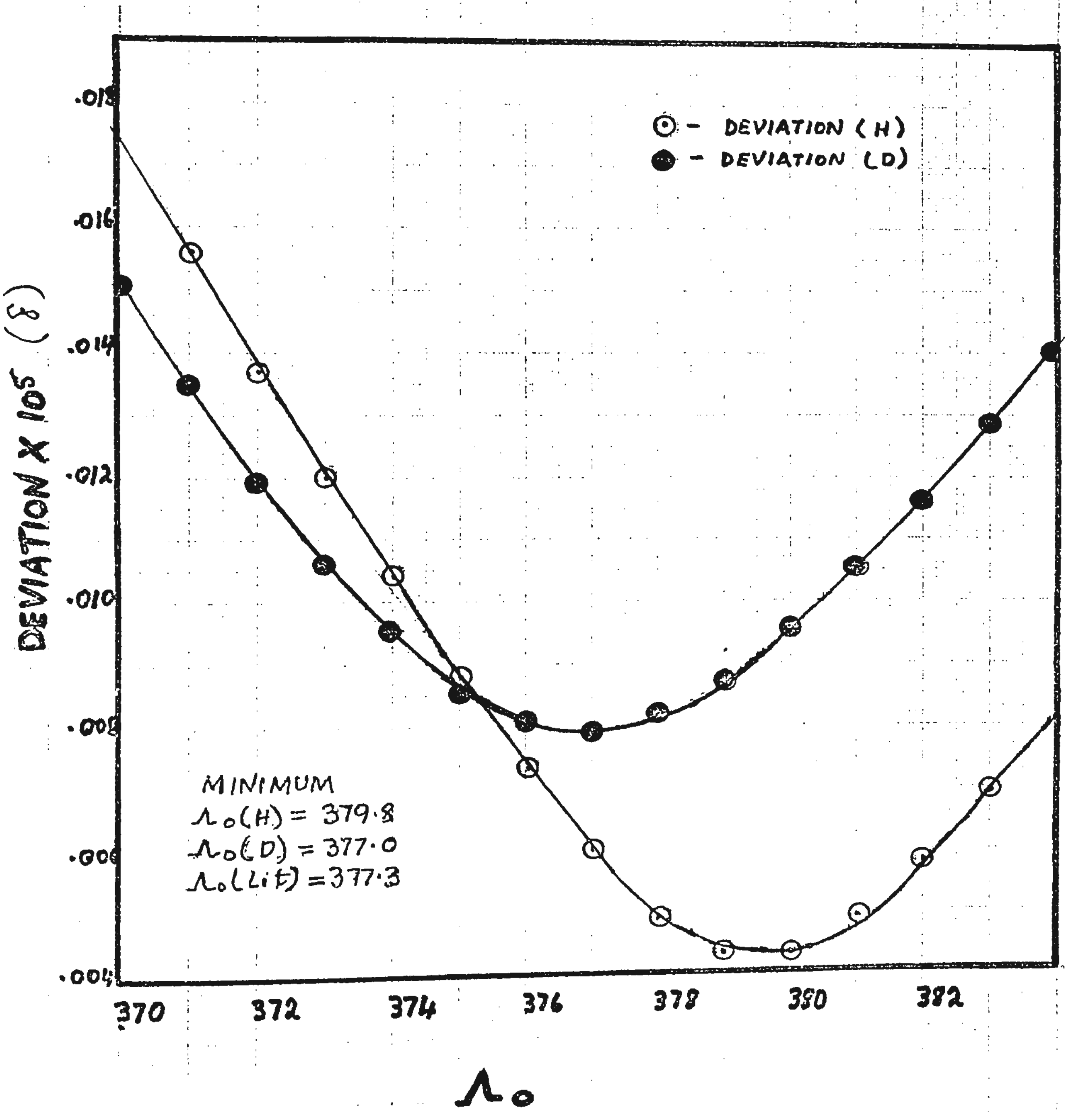
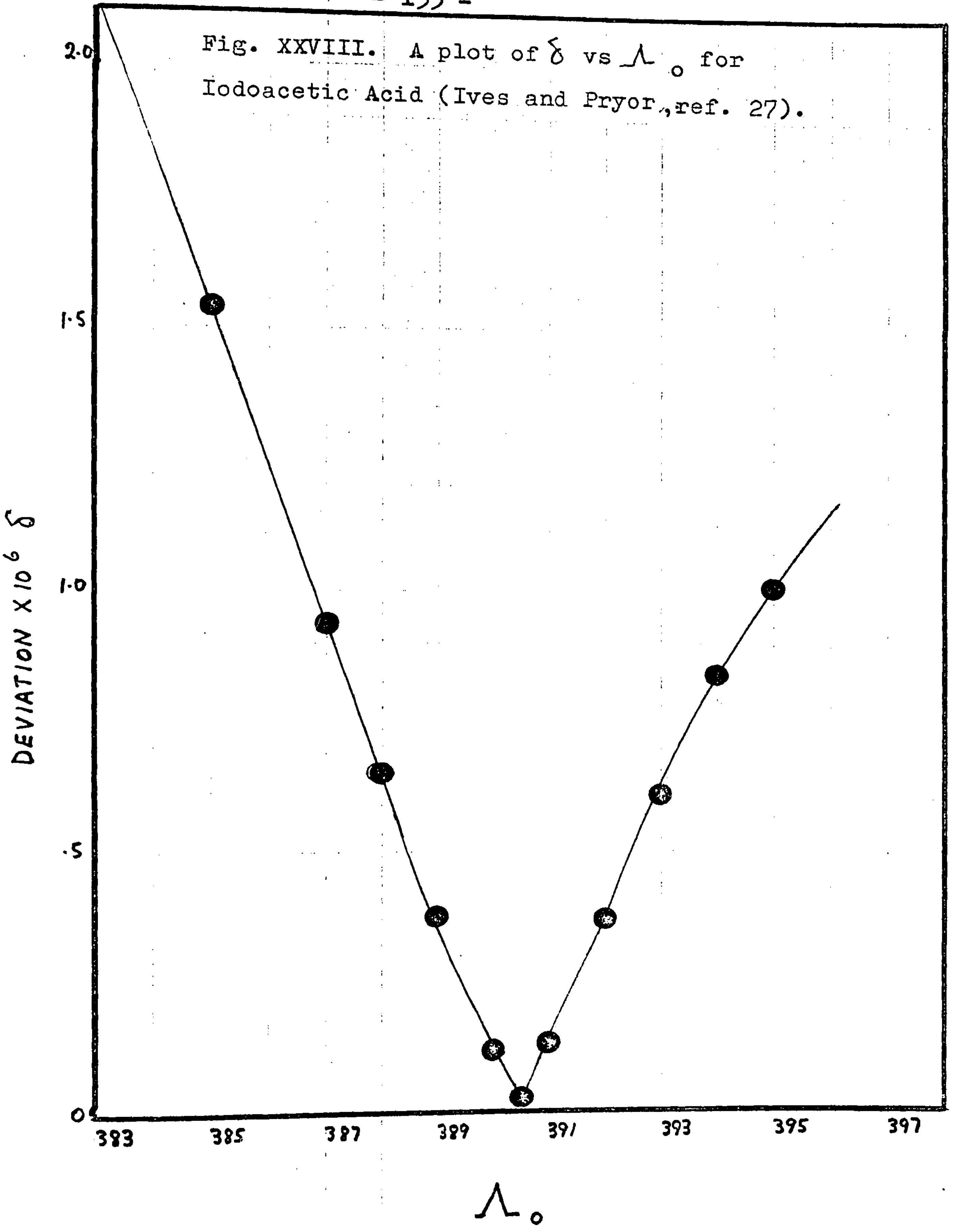


Fig. XXVIII. A plot of δ vs Λ_o for Iodoacetic Acid (Ives and Pryor, ref. 27).



Method IV. The Ives Iteration Method (IIM).

The conductance data was processed by the Ives Iteration Method to determine Λ_o and K_t from the intercept and slope. The results were processed on an individual cell basis for reasons which will be given in the discussion. The computer printout is illustrated in Table XLVI. The salt value of Λ_o was used to commence the iteration and the first slope obtained is designated as the initial slope. The final slopes and intercepts which lead to values of Λ_o and K_t are also recorded. A comparison of the initial slopes for the isotopic acid pairs provides a further method of determining the ratio of $K_t(H)$ / $K_t(D)$. (See Table XLVIII)

Discussion.

The application of the IIM to the conductance data reported in this thesis gave larger errors in the slope and intercept than were observed using the SIM. In consequence the derived parameters Λ_o and K_t appear to be correspondingly less accurate. The squared term in the equivalent conductance in the Ives Equation leads to a magnification of the experimental errors, and consequently the K_t value from the slope will be very sensitive to the precision of the conductance data.

Ives (68) has noted that the IIM when applied to acetic acid gives a value of Λ_o which is not the same as that determined from the salt. He also observed that the multiplication of the experimental equivalent conductance data by a constant factor produces only a slight change in the slope, and hence K_t, but strongly influences the extrapolated value of Λ_o. Thus a systematic error in the cell constant will result only in a small change in K_t, but a large change in Λ_o. The reasons for processing the data from the different cells separately were based on this observation.

The effect of experimental errors on the K_t amd Λ_o values derived from the IIM has been discussed in detail by Kilpatrick (85), but because no corresponding calculations have been made on the Fuoss and Shedlovsky Methods, it is difficult to appraise the relative merits of these methods of calculation from this standpoint. Some results for acetic acid, in which various concentration ranges were used, show the same type of behaviour as was observed with the Shedlovsky method, i.e. K_t is a function of the concentration range studied. The data of Ives and coworkers (27), (30), (31) processed by the IIM appears to give excellent results, but this is partly a consequence of the fact that all the acids studied by these workers have been relatively strong leading to a situation in which only a short extrapolation is required to locate Λ_o.

TABLE XLV

Results from Ives Method

$PhCH_2COOH$	1	20.570	± 0.064	383.1	± 1.0
	2	20.386	± 0.052	380.3	± 0.8
	3	20.632	0.069	384.2	1.0
	4	20.455	0.063	381.3	0.9
	5	20.306	0.066	379.6	0.9
$PhCD_2COOH$	1	20.904	0.086	387.0	1.3
	2	20.749	0.088	384.5	1.3
	3	20.930	0.105	387.9	1.6
	4	20.839	0.086	385.8	1.3
	5	20.756	0.084	384.8	1.2
$4\text{-}NO_2\text{-}PhCH_2COOH$	1	7.6522	0.0097	379.5	0.2
	2	7.5987	0.0254	377.5	0.7
	3	7.6556	0.0086	379.9	0.2
	4	7.6358	0.0105	378.9	0.3
	5	7.6109	0.0117	378.5	0.3
$4\text{-}NO_2\text{-}PhCD_2COOH$	1	7.6241	0.0356	377.9	0.6
	2	7.5502	0.0165	376.3	0.2
	3	7.6481	0.0995	377.9	2.0
	4	7.5428	0.0125	376.3	0.2
	5	7.5447	0.0132	376.4	0.2
$4\text{-}MeO\text{-}PhCH_2COOH$	1	23.220	0.034	379.9	0.6
	2	23.171	0.028	379.2	0.3
	3	23.223	0.033	380.3	0.4
	4	23.284	0.040	380.4	0.5
	5	23.034	0.035	377.9	0.4

TABLE XLV(Cont'd)

4-MeO-$PhCD_2COOH$	1	23.238	0.105	377.9	1.2
	2	23.012	0.086	375.4	1.0
	3	23.259	0.180	378.7	2.0
	4	23.094	0.087	376.3	1.0
	5	2.3014	0.114	375.5	1.3

TABLE XLVI

Ives Results on Cyanoacetic Acid

Lambda (0) = 367.8

Slope	Intercept	Error in B	Error in Slope
-2.9018E+02*	392.9954	3.0323E-01	1.3048E-00
-2.9391E+02	392.9858	3.0305E-01	1.3211E-00

Ka from slope is 3.4023E-03

Concentration	Equil.Const	Deviation
Average Ka is 3.4011E-03		
1.9083E-03	3.4025E-03	-1.3671E-06
1.6651E-03	3.4130E-03	-1.1843E-05
1.2874E-03	3.3811E-03	2.0069E-05
1.2136E-03	3.3925E-03	8.6542E-06
7.9565E-04	3.3952E-03	5.9615E-06
7.3034E-04	3.4003E-03	7.8070E-07
6.1734E-04	3.4390E-03	-3.7919E-05
5.9368E-04	3.4088E-03	-7.7190E-06
4.6651E-04	3.4898E-03	-8.8669E-05
3.7920E-04	3.3849E-03	1.6221E-05
3.2012E-04	3.3053E-03	9.5821E-05

Average deviation is 4.6500E-05

---

*Initial slope

TABLE XLVII

Isotope Effects from the Ives Method

Acid	Cell No.	Ka(H)/Ka(D)	± Deviation
$PhCH_2COOH$	1	1.016	0.005
	2	1.018	0.005
	3	1.014	0.006
	4	1.019	0.005
	5	1.022	0.005
$4\text{-}NO_2PhCH_2COOH$	1	0.9963	0.0048
	2	0.9936	0.0040
	3	0.9990	0.013
	4	0.9879	0.0022
	5	0.9913	0.0023
$4\text{-}MeOPhCH_2COOH$	1	1.001	0.005
	2	0.9933	0.0039
	3	1.002	0.008
	4	0.9919	0.0041
	5	0.9991	0.0052

Summary.

The K(H)/K(D) values for the three pairs of isotopic carboxylic acids which have been investigated in this thesis are summarized in Table XLVIII. Some further deuterium analyses are also reported in this table which were carried out at the NRC Ottawa by Dr. R. E. Robertson and Mr. H. Seguin. These analyses indicate the deuterium content of the deuterated acids to be somewhat lower than was estimated using NMR spectra. The reasons for this discrepancy are not completely understood but the results from Dr. Robertsons laboratory are probably more reliable.

An investigation of the effect of isotopic impurities on the K(H)/K(D) ratios reported in this thesis has been made by Benson and Scott (86) assuming that the measurements were made on all the possible mixtures of $ArCH_2COOH$, ArCHDCOOH and $ArCD_2COOH$ which are consistent with the total deuterium content. The preliminary results of these calculations shows that the effect of the presence of $ArCH_2COOH$ and ArCHDCOOH in the predominantly dueterated acid is ± 0.1 % in the K(H)/K(D) ratio and hence no further discussion of this aspect of the data in Table XLVIII will be given at the present time.

A comparison of the arylacetic acid results with Streitwieser and Klein's (20) K(H)/K(D) value for the isotopic pair CH_3COOH/CD_3COOH (Table I) indicates that the isotope effect is less for the former structures and this observation is qualitatively in accordance with the inductive treatment i.e. as the number of deuteriums decreases

TABLE XLVIII

p-R-C_6H_4-CH_2COOH/R-C_6H_4-CD_2COOH

ISOTOPE EFFECTS

R	% D*	Classical	Robinson & Stokes	Shedlovsky II	Shedlovsky III	S.B.S.**	Ives
H	93.6	1.0072 ± 0.0004	1.0035 ± 0.005	1.0034 ± 0.005	1.0076 ± 0.0015	1.0082 ± 0.0015	1.018 ± 0.005
4-NO_2	92.5	0.9973 ± 0.002	1.0005 ± 0.005	1.004 ± 0.005	0.9962 ± 0.0013	0.9975 ± 0.0017	0.9936 ± 0.005
4-MeO	97.0	1.0045 ± 0.0007	1.0077 ± 0.002	1.0076 ± 0.0023	1.0045 ± 0.001	1.0041 ± 0.0019	0.9975 ± 0.005

* Combustion-V.P.C. Analyses by H. Seguin and Dr. R. E. Robertson.

** SBS Method based on Least Squares of Rc-vs- S(2) $f_{\pm}^{2}/R$ correlations. See Equations (69) and (70).

at a given position with respect to the reaction site, the isotope effect should likewise decrease. (See introduction).

A comparison of the quantity 1/n.log K(H)/K(D), where 'n' is the number of deuterium atoms, is of greater significance* and interest. If acetic acid is included with the data reported in this thesis there seems to be a definite tendency for the magnitude of the isotope effect per deuterium atom to be reduced as the strength of the protium acid increases. (See Fig. XXIX→XXXI). Two important points emerge from these observations:-

(i) The predicted value for the isotope effect for the pair $PhCH_2COOH/PhCD_2COOH$ based on $\sigma^*(D)$ (K(H)/K(D) = 1.02 (see Table III) is now closer to the observed value i.e. the inductive treatment is partially verified.

(ii) The isotope effect per deuterium appears to be variable and depends on the structure of the acid. This is not consistent with the inductive treatment which requires that the inductive effect per deuterium is independent of the molecular environment of the isotopic substituent.

The reasons for the difference between the results reported by Halevi et al (22) for the $PhCH_2COOH/PhCD_2COOH$ pair and the results reported in this thesis are not easily discerned. However, since the present

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*This formula was originally proposed by V.J.Shiner (87), for CH_3COOH/CD_3COOH n = 3 and for the arylacetic acids n = 2.

Fig. XXIX Classical Results
Plot of 1/n . log K(H)/K(D)
vs
pKa (H)

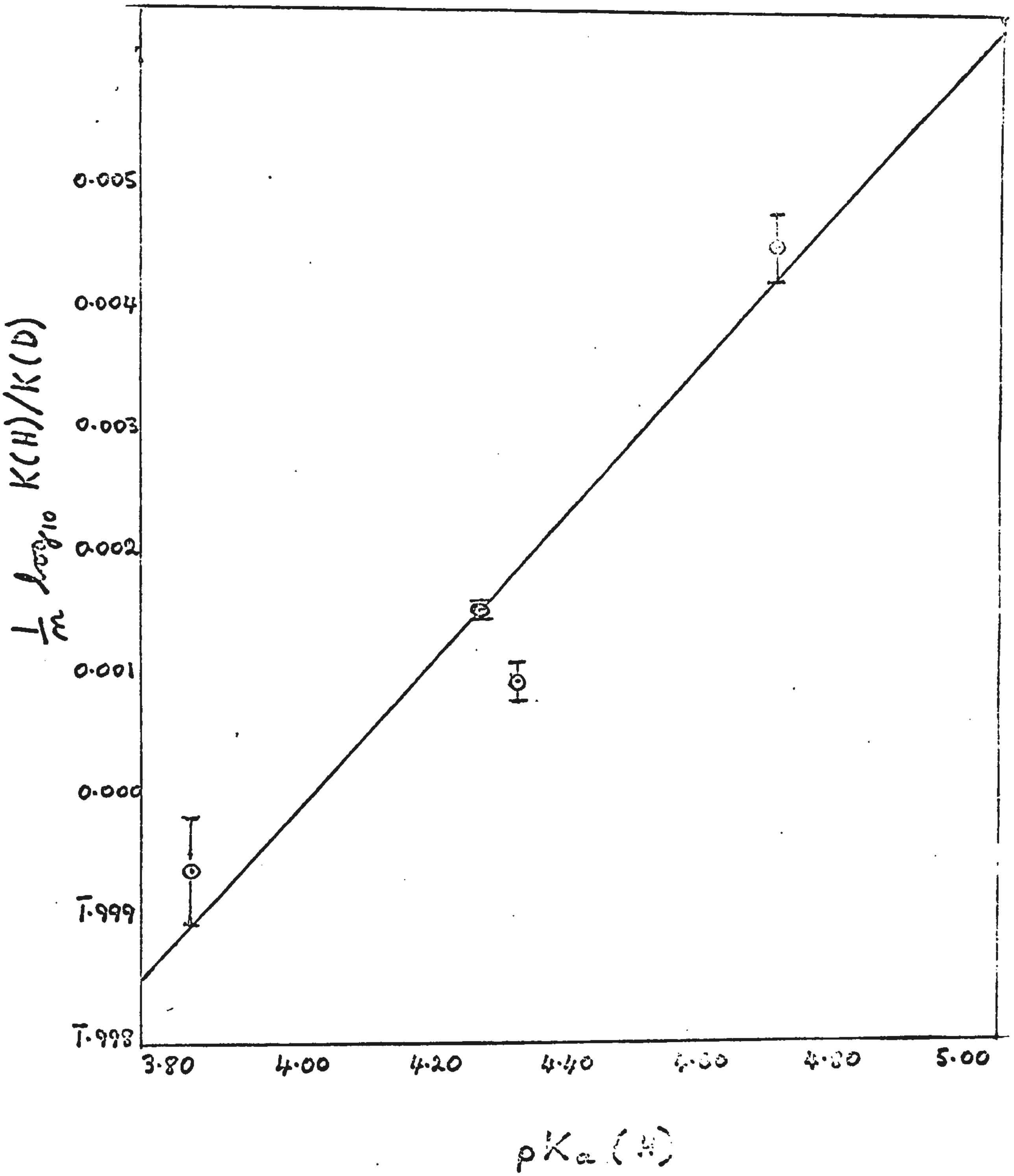


Fig. XXX Shedlovsky II Results
Plot 1/n .log K(H) / K(D)
vs
pKa(H)

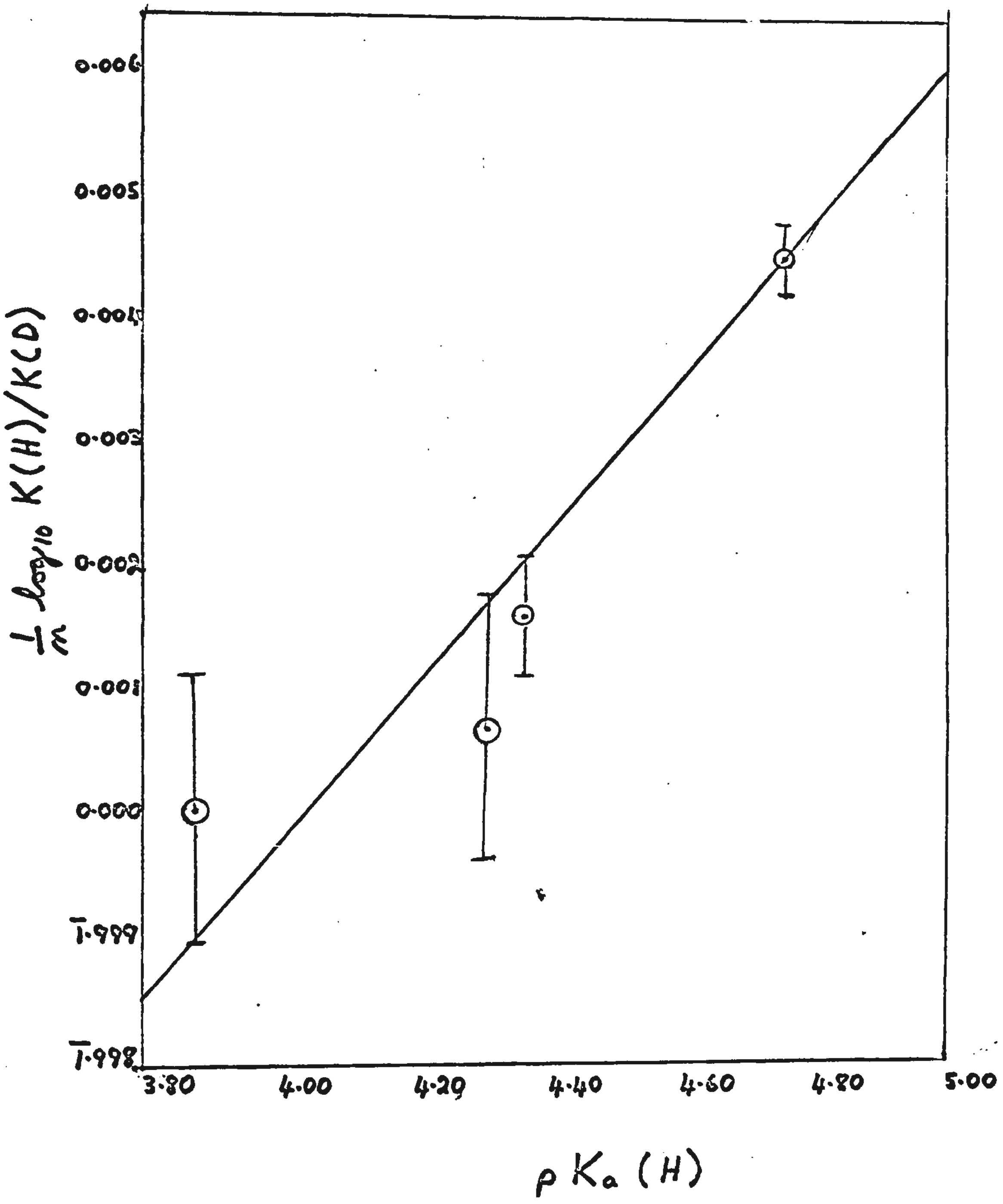
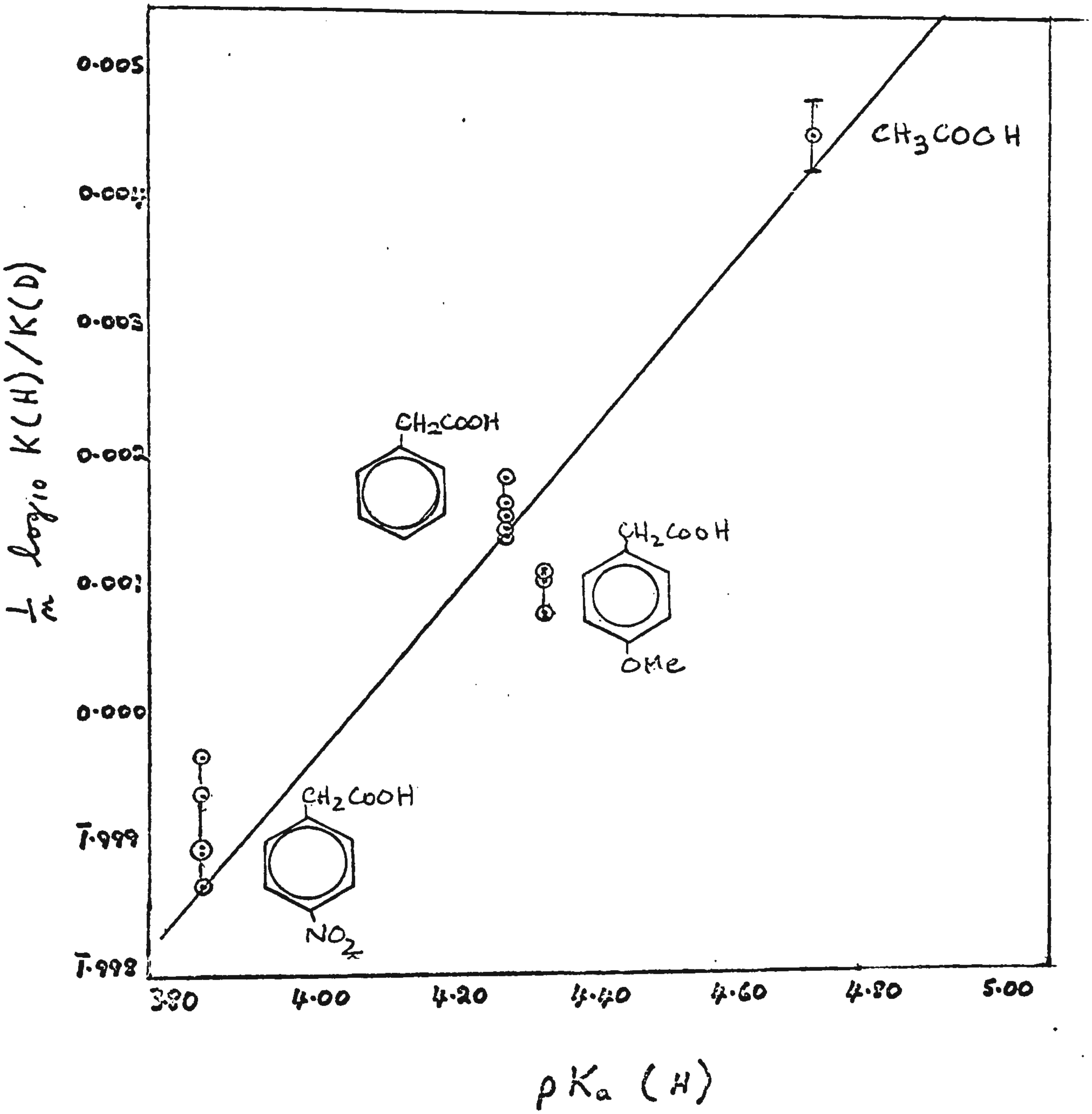


Fig. XXXI Shedlovsky III Results

Plot of 1/n . log K(H)/K(D)

vs

pKa(H)



measurements involve both absolute and relative determinations which are also more extensive, it is felt that the present results are definitely more reliable.

Halevi's result seems unduly large, both in the light of the inductive treatment offered in the introduction and by an alternative treatment based on the pair HCOOH/DCOOH. The inductive effect of a substituent is known to increase as the substituent moves closer to the reaction site (88). A rough calculation shows that the isotope effect for the pair HCOOH/ DCOOH based on Halevi's value of K(H)/K(D) for the pair $PhCH_2COOH/PhCD_2COOH$ would give a value of K(H)/K(D) = 1.15 for the two formic acids. This predicted value is much higher than the isotope effect (K(H)/K(D) = 1.06) reported by Bell and Miller (73).

A variety of explanations have been offered for secondary isotope effects which have all been adequately summarized by Halevi (10). The most important source of secondary isotope effects appears to be changes in zero point energy between the reactants and products. These changes in zero point energy must ultimately depend on force constant changes but since the latter are derived parameters, which depend on the assumptions made in theoretical treatment of observed vibrational data, it is probably preferable to discuss isotope effects in terms of frequencies rather than force constants. Streitwieser et al. (89) have derived a very simple formula for discussing secondary isotope effects:-

$$K(H)/K(D) = \exp.-h/2kT(1-1/C)\left(\sum_{P}{}' \nu(H) - \sum_{r}{}' \nu(H)\right) \quad .....(74)$$

where the symbols h, k and T have their usual significance, $\sum_{r}^{i} \nu(H)$ and $\sum_{p}^{i} \nu(H)$ are the frequency sums for the reactants (r) and products (p) and C is a constant which has a theoretical range $1 < C < 2^{1/2}$ and an average experimental value of 1.35. The application of this equation to experimental data is always uncertain in the absence of temperature dependence data on the K(H)/K(D) parameter but the assumption that $\delta_i \Delta G = \delta_i \Delta E$ (zero point) has ample precedent (see ref. 10).

The application of the zero point equation to substituent effects will be qualitative in the absence of suitable vibrational data. The only other instance of a substituent-isotope effect study is that recently reported by Buddenbaum (90) in which no theoretical analysis was attempted for the same reasons which confine the present discussion to a semiquantitative treatment.

The normal isotope effect observed for the pair CH_3COOH/CD_3COOH has been shown to be consistent with Equation (74) in the sense that the frequency sum for the acetate ion vibrations which involve the methyl hydrogens in an important way is less than the sum for similar vibrations in the undissociated acid (91). Likewise, the increased basicity of CD_3NH_2 relative to CH_3NH_2 is consistent with the Raman spectra of CH_3NH_2 and $CH_3\overset{+}{N}H_3$ (92) (93). Both of these examples suggest that the zero point treatment has some significance.

The application of the zero point treatment to the correlations in Figs. XXIX → XXXI is best considered in terms of the schematic diagram in Fig. XXXII. It may be assumed that electron attracting substituents at the 4-position will have two effects.

(a) Increased electron withdrawal will increase the strength of the acid (decrease the pK_a).

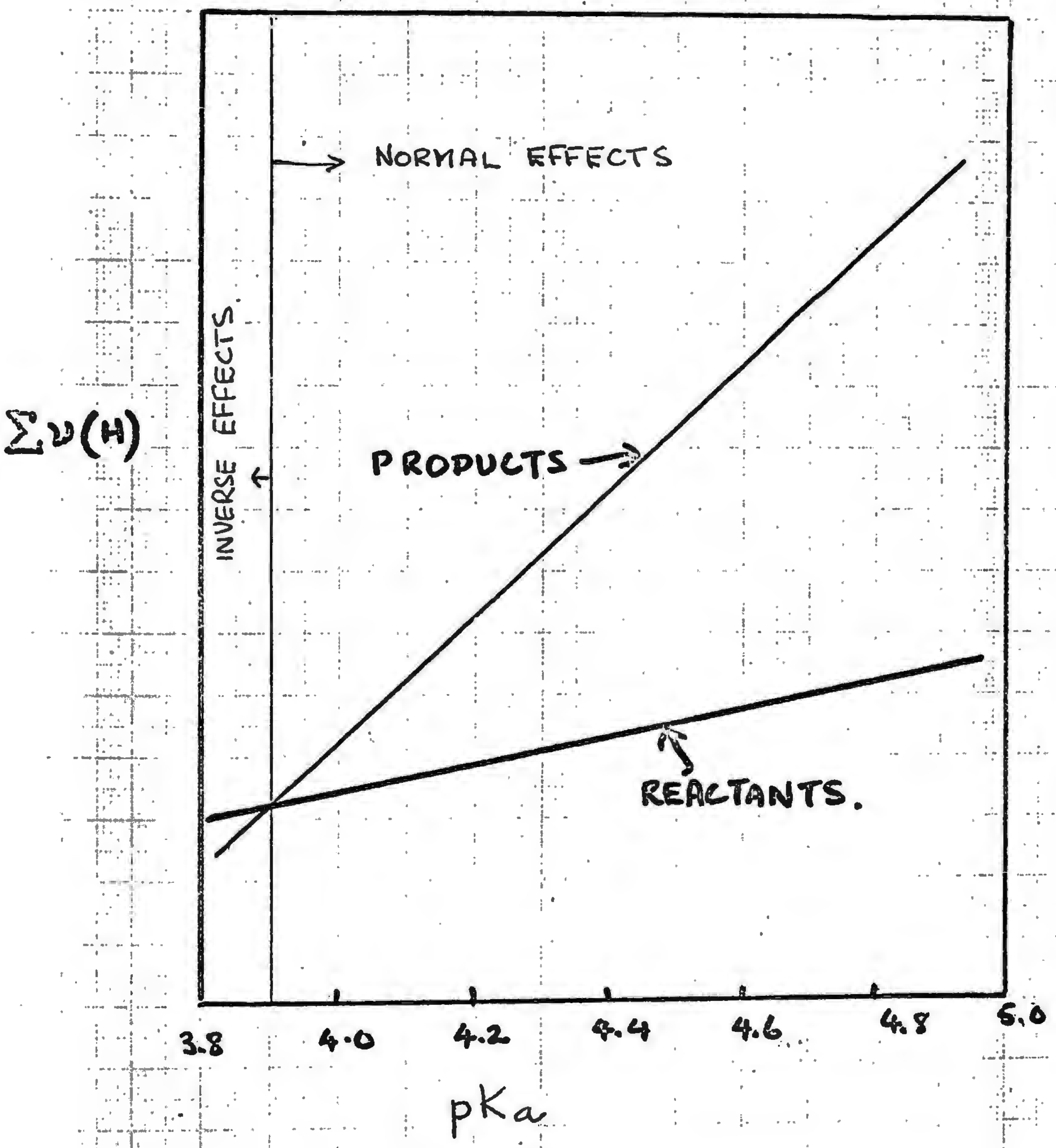
(b) Increased electron withdrawal will reduce the charge density at the methylene carbon-hydrogen bonds leading to a reduction of the frequency sum for the frequencies which involve the motion of these hydrogens in an important way.

The effect noted in item (b) will presumably occur both in the acid and the anion but the sensitivity of the frequency sum decrease with increasing electron withdrawal may be different in the acids and the related anions. This postulate is required by the data in the present thesis if the isotope effect is purely a consequence of zero point energy changes. The difference in sensitivity vity of the vibrational sum to the pK_a parameters for anion and acid is implied in Fig. XXXII by making the slopes of the assumed correlation different for these species. The curve for the anions is lower than that for the acids at $pK_a \simeq 5$ since it is experimentally established that this is the case for the acetic acid-acetate ion system. If the curves for acids and related anions have different slopes than they must theoretically intersect. The point of intersection will correspond to the condition $\sum_r \nu (H) = \sum_p' \nu(H)$ i.e. $K(H)/K(D) = 1$. To the right of the intersection isotope effects will be normal and to the left they will be inverse.

Fig. XXXII Schematic Correlation of $\sum\nu(H)$

- vs -

pKa



To definitely establish the trend between the pK_a and isotope effect evidently requires further measurements particularly on acids with a $pK_a < 4$. In this respect the halogenacetic acids and cyanoacetic acid represent suitable structures to test these predictions and the relative simplicity of these molecules might also allow of a detailed spectroscopic examination of both the acid and the related anion. If the trend from normal to inverse as the pK_a decreases can be established with greater certainty, it would appear that the inductive theory of secondary hydrogen-deuterium isotope effects will require considerable revision.

LEAST SQUARES FROM CONC. AND EQ. COND.

```
      DIMENSIONC(100),EC(100),AC(100),X(100),CALCY(100),DIF(100),R(100),
     1AIF(100)
21    L=0
20    L=L+1
      READ 1,C(L),EC(L),R(L),LAST
1     FORMAT(E11.4,F9.4,F7.1,I1)
      IF(LAST)20,20,30
30    K=L
       PUNCH 35
35     FORMAT(13HCONCENTRATION,3X,10HRESISTANCE,3X,10HLAMBDA X C,4X,11HR
     1EC. LAMBDA)
      SUMX=0.0
      SUMXX=0.0
      SUMY=0.0
      SUMXY=0.0
      DO 3 L=1,K
      AC(L)=EC(L)*C(L)
      X(L)=1.0/EC(L)
      PUNCH 14,C(L),R(L),AC(L),X(L)
14    FORMAT(E11.4,5X,F7.1,5X,E11.4,3X,E11.4)
      SUMX=SUMX+AC(L)
      SUMY=SUMY+X(L)
       SUMXX=SUMXX+AC(L)**2
3     SUMXY=SUMXY+X(L)*AC(L)
      OK=K
      DENOM=SUMX**2-OK*SUMXX
      SLOPE=(SUMX*SUMY-OK*SUMXY)/DENOM
      B=(SUMX*SUMXY-SUMY*SUMXX)/DENOM
      F=1.0/B
       PUNCH 6, SLOPE,F
6     FORMAT(10HSLOPE IS  ,E11.4,3X,16H1/INTERCEPT IS  ,F7.2)
15    SAKA=1./(SLOPE*F**2)
       PUNCH 23,SAKA
23    FORMAT (19H KA FROM SLOPE IS  ,E11.4)
       PUNCH 33
33     FORMAT(10H CALC. 1/L,5X,10HDIFFERENCE)
      SUMD=0.0
       DO 5 L=1,K
      CALCY(L)=SLOPE*AC(L)+B
      DIF(L)=X(L)-CALCY(L)
      AIF(L)=DIF(L)**2
      SUMD=SUMD+AIF(L)
       PUNCH 7,CALCY(L),DIF(L)
7      FORMAT(E11.4,3X,E11.4)
5     CONTINUE
      RE=0.6745*SQRTF(SUMD/(OK-2.))
      ERROR=RE*SQRTF(SUMXX/(-DENOM))
      ERB=SQRTF(OK/(-DENOM))*RE
      PUNCH 91,ERROR
91    FORMAT(23HERROR IN INTERCEPT IS  ,E11.4)
      PUNCH 92,ERB
92    FORMAT(19HERROR IN SLOPE IS  ,E11.4)
      GO TO 21
        END
```

APPENDIX

ROBINSON AND STOKES

```
      DIMENSION C(100),EC(100),ALF(100),Y(100),DENOM(100),ALI(100),BLF(1
     100),YY(100),DENON(100),GOLE(100),Z(100),EP(100),S(100),AKA(100),R(
     2100),DEV(100),ADEV(100)
5      PUNCH 3
3     FORMAT(26HMC INNES-SHEDLOVSKY METHOD)
      READ 2,ALO,BETA,BA,B1,B2
2     FORMAT (F6.1,F7.4,F8.5,F9.6,F8.4)
      L=0
20    L=L+1
      READ 1,C(L),EC(L),R(L),LAST
1     FORMAT (E11.4,F9.4,F7.1,I1)
      IF(LAST)20,20,30
30    K=L
      EL=L
       PUNCH 18
18    FORMAT (13HCONCENTRATION,3X,10HRESISTANCE,3X,8HEQUIVCON,3X,8HLAMBD
     1A I,5X,11HEQUIL.CONST,3X,9HDEVIATION)
      SUMK=0.0
      DO 9 L=1,K
13    ALF(L)=EC(L)/ALO
      X=B1*ALO+B2
      Y(L)=SQRTF(ALF(L)*C(L))
      DENOM(L)=1.+BA*Y(L)
21    ALI(L)=ALO-(X*Y(L))/DENOM(L)
      BLF(L)=EC(L)/ALI(L)
      YY(L)=SQRTF(BLF(L)*C(L))
      DENON(L)=1.+BA*YY(L)
       GOLE(L)=-BETA*YY(L)/DENON(L)
      Z(L)=2.30259*GOLE(L)
      EP(L)=EXPF(Z(L))
      S(L)=(BLF(L)**2)*EP(L)**2*C(L)
      AKA(L)=S(L)/(1.0-BLF(L))
      SUMK=SUMK+AKA(L)
9     CONTINUE
      AVKA=SUMK/EL
      SUMD=0.0
      DO 4 L=1,K
      ADEV(L)=(AVKA-AKA(L))**2
      SUMD=SUMD+ADEV(L)
      DEV(L)=((AVKA-AKA(L))/AVKA)*100.
       PUNCH 14,C(L),R(L),EC(L),ALI(L),AKA(L),DEV(L)
14    FORMAT (E11.4,7X,F7.1,5X,F9.4,4X,F7.2,3X,E11.4,3X,E11.4)
4     CONTINUE
      EDEV=SQRTF(SUMD/(EL-2.))
      PUNCH 92,EDEV
92    FORMAT(22HAVERAGE DEVIATION IS  ,E11.4)
      PUNCH 91,AVKA
91    FORMAT(15HAVERAGE KA IS  ,E11.4)
      PRINT 91,AVKA
      GO TO 5
      END
```

```
          FUOSS ITERATION METHOD FROM CONC. + EQ. CONST.
      DIMENSION C(100),EC(100),AC(100),ALF(100),Z(100),F1(100),F2(100),F
     13(100),GOLE(100),Q(100),EP(100),        Y(100),XX(100),S(100),AKA(
     2100),R(100),CALCY(100),DIB(100),DEV(100),ADEV(100)
5      PUNCH 4
4     FORMAT (22HFUOSS ITERATION METHOD)
      READ 2,ALO,BETA,BA,B1,B2
2     FORMAT (F6.1,F7.4,F8.5,F9.6,F8.4)
      PUNCH 31,ALO
31    FORMAT(12HLAMBDA(0) = ,F6.1)
21    L=0
20    L=L+1
      READ 1,C(L),EC(L),LAST
1     FORMAT(E11.4,F9.4,7X,I1)
      IF(LAST)20,20,30
30    K=L
       EL=L
       PUNCH 88
      PRINT 88
88    FORMAT (8H   SLOPE,6X,11H1/INTERCEPT,3X,10HERROR IN B,3X,14HERROR
     1IN SLOPE)
60    CONTINUE
      SUMX=0.0
      SUMY=0.0
      SUMXY=0.0
      SUMXX=0.0
      DO 9 L=1,K
      AC(L)=EC(L)*C(L)
      X=B1*ALO+B2
      Z(L)=X*SQRTF(AC(L)/ALO**3)
      F1(L)=1.-Z(L)
      F2(L)=1.-Z(L)*SQRTF(1./F1(L))
      F3(L)=1.-Z(L)*SQRTF(1./F2(L))
      ALF(L)=EC(L)/(ALO*F3(L))
      GOLE(L)=-BETA*SQRTF(ALF(L)*C(L))
      Q(L)=2.30259*GOLE(L)
      EP(L)=EXPF(Q(L))
      Y(L)=F3(L)/EC(L)
      XX(L)=C(L)*EC(L)*EP(L)**2/F3(L)
      SUMX=SUMX+XX(L)
      SUMY=SUMY+Y(L)
      SUMXX=SUMXX+XX(L)**2
9     SUMXY=SUMXY+XX(L)*Y(L)
      OK=K
      DENOM=SUMX**2-OK*SUMXX
      SLOPE=(SUMX*SUMY-OK*SUMXY)/DENOM
      B=(SUMX*SUMXY-SUMY*SUMXX)/DENOM
      F=1.0/B
      SUMD=0.0
      DO 91 L=1,K
      CALCY(L)=SLOPE*XX(L)+B
      DIB(L)=(Y(L)-CALCY(L))**2
91    SUMD=SUMD+DIB(L)
22     RE=0.6745*SQRTF(SUMD   /(EL-2.))
       ERROR=RE*SQRTF(SUMXX/(-DENOM))
      ERB=RE*SQRTF(OK/(-DENOM))
       PUNCH 6, SLOPE,F,ERROR,ERB
6     FORMAT (E11.4,3X,F9.4,3X,E11.4,5X,E11.4)
      PRINT 41,F
41    FORMAT(14X,F9.4)
```

```
      DIF=ABSF(ALO-F)
      IF(DIF-0.01)15,15,17
17    IF(SENSE SWITCH 2)49,16
49    IF(DIF-20.) 16,16,18
16    ALO=F
      GO TO 60
15    SAKA=1./(SLOPE*F**2)
      PRINT 43,SLOPE,ERROR,ERB
43    FORMAT(E11.4,15X,E11.4,5X,E11.4)
       PUNCH 23,SAKA
      PRINT 23,SAKA
23    FORMAT (19H KA FROM SLOPE IS  ,E11.4)
      PUNCH 33
33    FORMAT(13HCONCENTRATION,3X,11HEQUIL.CONST,3X,13H    DEVIATION)
      SUMK=0.0
      DO 29 L=1,K
      S(L)=(ALF(L)**2)*(EP(L)**2)*C(L)
      AKA(L)=S(L)/(1.0-ALF(L))
29    SUMK=SUMK+AKA(L)
      AVKA=SUMK/OK
      SUMB=0.0
      DO 45 L=1,K
      DEV(L)=AVKA-AKA(L)
      ADEV(L)=(AVKA-AKA(L))**2
      SUMB=SUMB+ADEV(L)
      PUNCH 42 ,C(L),AKA(L),DEV(L)
42    FORMAT(E11.4,5X,E11.4,4X,E11.4)
45    CONTINUE
      PUNCH 93,AVKA
93    FORMAT(15HAVERAGE KA IS  ,E11.4)
      EDEV=SQRTF(SUMB/(EL-2.))
      PUNCH 92,EDEV
92    FORMAT(22HAVERAGE DEVIATION IS  ,E11.4)
18     PUNCH 50,DIF
      PRINT 50,DIF
50    FORMAT(37HDIFFERENCE,LAMBDA(0)-1/INTERCEPT IS  ,F7.2)
      GO TO 5
      END
```

SHEDLOVSKY METHOD FROM CONC. AND EQ. COND.

```
      DIMENSION C(100),AC(100),EC(100),Z(100),F1(100),
     1F3(100),ALF(100),GOLE(100),Q(100),EP(100),Y(100),XX(100),S(100),AK
     2A(100),DEV(100),R(100),CALCY(100),DIB(100)
100    PUNCH 26
26    FORMAT(17HSHEDLOVSKY METHOD)
      READ 2,ALO,BETA,BA,B1,B2
2     FORMAT (F6.1,F7.4,F8.5,F9.6,F8.4)
      L=0
20    L=L+1
      READ 1,C(L),EC(L),R(L),LAST
1     FORMAT (E11.4,F9.4,F7.1,I1)
      IF (LAST) 20,20,30
30    K=L
      EL=L
       PUNCH 88
      PRINT 88
88    FORMAT (8H   SLOPE,6X,11H1/INTERCEPT,3X,10HERROR IN B,3X,14HERROR
     1IN SLOPE)
60    CONTINUE
      SUMX=0.0
      SUMXX=0.0
      SUMY=0.0
      SUMXY=0.0
      DO 40 L=1,K
      AC(L)=EC(L)*C(L)
      X=B1*ALO+B2
      Z(L)=X*SQRT(AC(L)/(ALO**3))
      F1(L)=.5*Z(L)
      F3(L)=(F1(L)+SQRTF(1.+F1(L)**2))**2
      ALF(L)=EC(L)*F3(L)/ALO
      GOLE(L)=-BETA*SQRTF(ALF(L)*C(L))
      Q(L)=2.30259*GOLE(L)
      EP(L)=EXPF(Q(L))
      Y(L)=1./(F3(L)*EC(L))
      XX(L)=C(L)*EC(L)*EP(L)**2*F3(L)
      SUMX=SUMX+XX(L)
      SUMY=SUMY+Y(L)
      SUMXX=SUMXX+XX(L)**2
3     SUMXY=SUMXY+Y(L)*XX(L)
40    CONTINUE
      OK=K
      DENOM=SUMX**2-OK*SUMXX
      SLOPE=(SUMX*SUMY-OK*SUMXY)/DENOM
      B=(SUMX*SUMXY-SUMY*SUMXX)/DENOM
      F=1.0/B
      DIF=ABSF(ALO-F)
      SUMD=0.0
      DO 91 L=1,K
      CALCY(L)=SLOPE*XX(L)+B
      DIB(L)=(Y(L)-CALCY(L))**2
91    SUMD=SUMD+DIB(L)
22     RE=0.6745*SQRTF(SUMD   /(EL-2.))
       ERROR=RE*SQRTF(SUMXX/(-DENOM))
      ERB=RE*SQRTF(OK/(-DENOM))
       PUNCH 6, SLOPE,F,ERROR,ERB
6     FORMAT (E11.4,3X,F9.4,3X,E11.4,5X,E11.4)
      PRINT 41,F
41    FORMAT(14X,F9.4)
      IF (DIF-0.01) 15,15,17
```

```
17     IF(SENSE SWITCH 2)51,16
51     IF (DIF-20.) 16,16,18
16     ALO=F
       GO TO 60
15     SAKA=1./(SLOPE*F**2)
       PRINT 43,SLOPE,ERROR,ERB
43     FORMAT(E11.4,15X,E11.4,5X,E11.4)
       PRINT 23,SAKA
        PUNCH 23,SAKA
23     FORMAT (19H KA FROM SLOPE IS  ,E14.4)
24      PUNCH 5
5      FORMAT(13HCONCENTRATION,3X,11HEQUIL.CONST,3X,13H0/0 DEVIATION)
       SUMK=0.0
70     TDEV=0.0
       DO 29 L=1,K
       S(L)=(ALF(L)**2)*(EP(L)**2)*C(L)
       AKA(L)=S(L)/(1.0-ALF(L))
29     SUMK=SUMK+AKA(L)
       AVKA=SUMK/OK
       DO 45 L=1,K
       DEV(L)=(AVKA-AKA(L))*100./AVKA
       PUNCH 42 ,C(L),AKA(L),DEV(L)
42     FORMAT(E11.4,5X,E11.4,4X,F6.2)
45     TDEV=TDEV+(AVKA-AKA(L))**2
       ADEV=SQRTF(TDEV/(OK-2.))
        PUNCH 46,ADEV
46     FORMAT(23H AVERAGE DEVIATION IS  ,E14.4)
18      PUNCH 50,DIF
       PRINT 50,DIF
50     FORMAT(37HDIFFERENCE,LAMBDA(0)-1/INTERCEPT IS  ,F7.2)
       GO TO 100
       END
```

```
          SHEDLOVSKY 2

      DIMENSION C(100),EC(100),AC(100),R(100),Z(100),F1(100),F3(100),ALF
     1(100),GOLE(100),Q(100),EP(100),S(100),AKA(100),DEV(100),ADEV(100)
100    PUNCH 26
26    FORMAT(12HSHEDLOVSKY 2)
      READ 2,ALO,BETA,BA,B1,B2
2     FORMAT (F6.1,F7.4,F8.5,F9.6,F8.4)
      IF(SENSE SWITCH 1)7,8
7     L=0
20    L=L+1
      READ 1,C(L),EC(L),R(L),LAST
1     FORMAT (E11.4,F9.4,F7.1,I1)
      IF (LAST) 20,20,30
30    K=L
      OK=K
      EL=L
      SUMK=0.0
      DO 40 L=1,K
      AC(L)=EC(L)*C(L)
      X=B1*ALO+B2
      Z(L)=X*SQRT(AC(L)/(ALO**3))
      F1(L)=.5*Z(L)
      F3(L)=(F1(L)+SQRTF(1.+F1(L)**2))**2
      ALF(L)=EC(L)*F3(L)/ALO
      GOLE(L)=-BETA*SQRTF(ALF(L)*C(L))
      Q(L)=2.30259*GOLE(L)
      EP(L)=EXPF(Q(L))
      S(L)=(ALF(L)**2)*(EP(L)**2)*C(L)
      AKA(L)=S(L)/(1.0-ALF(L))
      SUMK=SUMK+AKA(L)
40    CONTINUE
      AVKA=SUMK/OK
      SUMD=0.0
      DO 45 L=1,K
      DEV(L)=(AVKA-AKA(L))*100./AVKA
      ADEV(L)=(AVKA-AKA(L))**2
45    SUMD=SUMD+ADEV(L)
      EDEV=SQRTF(SUMD/(EL-2.))
      PUNCH 92,EDEV
92    FORMAT(22HAVERAGE DEVIATION IS  ,E11.4)
      PUNCH 91,AVKA
91    FORMAT(15HAVERAGE KA IS  ,E11.4)
8     IF(SENSE SWITCH 2)10,11
10    READ 9,SLOPE
9     FORMAT(E11.4)
      SAKA=1./(SLOPE*ALO**2)
       PUNCH 23,SAKA
23    FORMAT (19H KA FROM SLOPE IS  ,E14.4)
11    GO TO 100
      END
```

```
              SHEDLOVSKY 3
        DIMENSION C(100),AC(100),EC(100),Z(100),F1(100),
       1F3(100),ALF(100),GOLE(100),Q(100),EP(100),Y(100),XX(100),S(100),AK
       2A(100),DEV(100),R(100),CALCY(100),DIB(100)
100     READ43,T1,T2,T3,T4,T5
43      FORMAT(5A4)
        READ 42,ALO,BLO,CLO
42      FORMAT(F7.2,F6.2,F7.2)
        READ 2, BETA,BA,B1,B2
2       FORMAT(F7.4,F8.5,F9.6,F8.4)
        L=0
20      L=L+1
        READ 1,C(L),EC(L),R(L),LAST
1       FORMAT (E11.4,F9.4,F7.1,I1)
        IF (LAST) 20,20,30
30      K=L
        OK=K
 31     EL=L
        DO 40 L=1,K
        AC(L)=EC(L)*C(L)
        X=B1*ALO+B2
        Z(L)=X*SQRT(AC(L)/(ALO**3))
        F1(L)=.5*Z(L)
        F3(L)=(F1(L)+SQRTF(1.+F1(L)**2))**2
        ALF(L)=EC(L)*F3(L)/ALO
        GOLE(L)=-BETA*SQRTF(ALF(L)*C(L))
        Q(L)=2.30259*GOLE(L)
        EP(L)=EXPF(Q(L))
        Y(L)=1./(F3(L)*EC(L))
        XX(L)=C(L)*EC(L)*EP(L)**2*F3(L)
40      CONTINUE
12      SUMX=0.0
        SUMXX=0.0
        SUMY=0.0
        SUMXY=0.0
        DO 3 L=1,K
        SUMX=SUMX+XX(L)
        SUMY=SUMY+Y(L)
        SUMXX=SUMXX+XX(L)**2
3       SUMXY=SUMXY+Y(L)*XX(L)
        DENOM=SUMX**2-OK*SUMXX
        SLOPE=(SUMX*SUMY-OK*SUMXY)/DENOM
        B=(SUMX*SUMXY-SUMY*SUMXX)/DENOM
        F=1.0/B
        SUMD=0.0
        DO 91 L=1,K
        CALCY(L)=SLOPE*XX(L)+B
        DIB(L)=(Y(L)-CALCY(L))**2
91      SUMD=SUMD+DIB(L)
        ADEV=SQRTF(SUMD/(OK-2.))
        IF(SENSE SWITCH 1)22,13
13      M=0
        DO 18 L=1,K
        DEV(L)=CALCY(L)-Y(L)
        IF(DEV(L)-4.*ADEV)45,45,46
46      PUNCH 65,C(L),EC(L),DEV(L)
65      FORMAT(E11.4,3X,F9.4,3X,E11.4)
        XX(L)=0.0
        Y(L)=0.0
        OK=OK-1.
```

```
      M=M+1
45    CONTINUE
18    CONTINUE
      IF(M)22,22,12
22     RE=0.6745*SQRTF(SUMD    /(OK-2.))
       ERROR=RE*SQRTF(SUMXX/(-DENOM))
      ERB=RE*SQRTF(OK/(-DENOM))
       PUNCH 6, SLOPE,F,ERROR,ERB
6     FORMAT (E11.4,3X,F9.4,3X,E11.4,5X,E11.4)
      IF(CLO-ALO)8,8,5
5     ALO=ALO+BLO
      GO TO 31
8     GO TO 100
      END
```

SHEDLOVSKY 4

```
      DIMENSION C(100),EC(100),AC(100),R(100),Z(100),F1(100),F3(100),ALF
     1(100),GOLE(100),Q(100),EP(100),S(100),AKA(100),DEV(100),ADEV(100)
100   READ43,T1,T2,T3,T4,T5
43    FORMAT(5A4)
      READ 42,ALO,BLO,CLO
42    FORMAT(F7.2,F6.2,F7.2)
      READ 2, BETA,BA,B1,B2
2     FORMAT(F7.4,F8.5,F9.6,F8.4)
      IF(SENSE SWITCH 1)7,8
7     L=0
20    L=L+1
      READ 1,C(L),EC(L),R(L),LAST
1     FORMAT (E11.4,F9.4,F7.1,I1)
      IF (LAST) 20,20,30
30    K=L
      OK=K
      EL=L
31    PUNCH 26,T1,T2,T3,T4,T5,ALO
26    FORMAT(12HSHEDLOVSKY 4,3X,5A4,3X,12HLAMBDA(0) = ,F7.2)
      SUMK=0.0
      DO 40 L=1,K
      AC(L)=EC(L)*C(L)
      X=B1*ALO+B2
      Z(L)=X*SQRT(AC(L)/(ALO**3))
      F1(L)=.5*Z(L)
      F3(L)=(F1(L)+SQRTF(1.+F1(L)**2))**2
      ALF(L)=EC(L)*F3(L)/ALO
      GOLE(L)=-BETA*SQRTF(ALF(L)*C(L))
      Q(L)=2.30259*GOLE(L)
      EP(L)=EXPF(Q(L))
      S(L)=(ALF(L)**2)*(EP(L)**2)*C(L)
      AKA(L)=S(L)/(1.0-ALF(L))
      SUMK=SUMK+AKA(L)
40    CONTINUE
      AVKA=SUMK/OK
      SUMD=0.0
      DO 45 L=1,K
      DEV(L)=(AVKA-AKA(L))*100./AVKA
      ADEV(L)=(AVKA-AKA(L))**2
45    SUMD=SUMD+ADEV(L)
      EDEV=SQRTF(SUMD/(EL-2.))
      PUNCH 92,EDEV
92    FORMAT(22HAVERAGE DEVIATION IS  ,E11.4)
      PUNCH 91,AVKA
91    FORMAT(15HAVERAGE KA IS  ,E11.4)
      IF(CLO-ALO)8,8,5
5     ALO=ALO+BLO
      GO TO 31
8     IF(SENSE SWITCH 2)10,11
10    READ 9,SLOPE
9     FORMAT(E11.4)
      SAKA=1./(SLOPE*ALO**2)
       PUNCH 23,SAKA
23    FORMAT (19H KA FROM SLOPE IS  ,E14.4)
11    GO TO 100
      END
```

IVES METHOD

```
       DIMENSION C(100),EC(100),ALF(100),CI(100),Y(100),X(100),CALCY(100)
      1,DIB(100),AKA(100),DEV(100),ADEV(100) ,Z(100),ZZ(100)
5       PUNCH 4
       READ 2,ALO,BETA,BA,B1,B2
       PUNCH 31,ALO
       L=0
20     L=L+1
       READ 1,C(L),EC(L),LAST
       IF(LAST)20,20,30
30     K=L
       OK=K
       EL=L
        PUNCH 88
60     SUMK=0.0
       SUMX=0.0
       SUMY=0.0
       SUMXY=0.0
       SUMXX=0.0
       DO 25 L=1,K
       ALF(L)=EC(L)/ALO
       A=B1*ALO+B2
       CI(L)=SQRTF(ALF(L)*C(L))
       Y(L)=EC(L)+A*CI(L)
       Z(L)=2.*BETA*CI(L)
       ZZ(L)=10.**Z(L)
       X(L)=(C(L)*EC(L)**2)/(ZZ(L)*(ALO-A*CI(L)))
       SUMX=SUMX+X(L)
       SUMY=SUMY+Y(L)
       SUMXY=SUMXY+X(L)*Y(L)
25     SUMXX=SUMXX+X(L)**2
       DENOM=SUMX**2-OK*SUMXX
       SLOPE=(SUMX*SUMY-OK*SUMXY)/DENOM
       B=(SUMX*SUMXY-SUMY*SUMXX)/DENOM
       SUMD=0.0
       DO 3  L=1,K
       CALCY(L)=SLOPE* X(L)+B
       DIB(L)=(Y(L)-CALCY(L))**2
3      SUMD=SUMD+DIB(L)
        RE=0.6745*SQRTF(SUMD   /(EL-2.))
        ERROR=RE*SQRTF(SUMXX/(-DENOM))
       ERB=RE*SQRTF(OK/(-DENOM))
        PUNCH 6, SLOPE,B,ERROR,ERB
       PRINT 7 ,B
       DIF=ABSF(ALO-B)
       IF(DIF-0.01)15,15,17
17     IF(SENSE SWITCH 2)49,16
49     IF(DIF-20.) 16,16,18
16     ALO=B
       GO TO 60
15     SAKA=-1./SLOPE
        PUNCH 23,SAKA
       PUNCH 33
       DO 29 L=1,K
       AKA(L)=X(L)/(B-Y(L))
29     SUMK=SUMK+AKA(L)
       AVKA=SUMK/OK
       PUNCH 93,AVKA
       SUMB=0.0
       DO 45 L=1,K
```

```
      DEV(L)=AVKA-AKA(L)
      ADEV(L)=(AVKA-AKA(L))**2
      SUMB=SUMB+ADEV(L)
      PUNCH 42 ,C(L),AKA(L),DEV(L)
45    CONTINUE
      EDEV=SQRTF(SUMB/(EL-2.))
      PUNCH 92,EDEV
      GO TO 5
18     PUNCH 50,DIF
      GO TO 5
1     FORMAT(E11.4,F9.4,7X,I1)
2     FORMAT (F6.1,F7.4,F8.5,F9.6,F8.4)
4     FORMAT(11HIVES METHOD)
6     FORMAT (E11.4,3X,F9.4,3X,E11.4,5X,E11.4)
7     FORMAT(F9.4)
23    FORMAT (19H KA FROM SLOPE IS  ,E11.4)
31    FORMAT(12HLAMBDA(0) = ,F6.1)
33    FORMAT(13HCONCENTRATION,3X,11HEQUIL.CONST,3X,13H    DEVIATION)
42    FORMAT(E11.4,5X,E11.4,4X,E11.4)
50    FORMAT(37HDIFFERENCE,LAMBDA(0)-1/INTERCEPT IS  ,F7.2)
88    FORMAT (8H   SLOPE,6X,11H  INTERCEPT,3X,10HERROR IN B,3X,14HERROR
     1IN SLOPE)
92    FORMAT(22HAVERAGE DEVIATION IS  ,E11.4)
93    FORMAT(15HAVERAGE KA IS  ,E11.4)
      END
```

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