THE LIMITING EQUIVALENT CONDUCTANCES OF ACID ANIONS AT 25°C.

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ABSTRACT

The methods for determining the limiting equivalent conductance of acid anions ($\lambda^{o}_{HA^-}$) are discussed. The literature conductances of the appropriate acid salts and of the parent acids are critically analysed to obtain values for $\lambda^{o}_{HA^-}$. A new method, having some advantages over the Fuoss-Shedlovsky extrapolation, is given for simultaneously determining $\lambda^{o}_{HA^-}$ and the dissociation constant from conductance data on the acid alone. It is shown that this method does not suffer, even for very weak electrolytes, from the disadvantage of a long extrapolation and that it is particularly suitable for evaluating $\lambda^{o}_{HA^-}$ when independent values for the dissociation constant are available. Anion transference number measurements for phosphoric and tartaric acids have been carried out by the author. The transference results are shown to disagree with the Debye-Hückel-Onsager theory and can be explained only by assuming the presence of complex anions in solution. Complex ion formation is quantitatively allowed for in the case of H_3PO_4 and $\lambda^{o}_{H_2PO_4^-}$ is then obtained as 32.3 ± 0.1 $cm^2 ohm^{-1} equiv.^{-1}$. The limiting conductance of the bitartrate ion is shown to be 29.4 ± 0.2 $cm^2 ohm^{-1} equiv.^{-1}$. The $\lambda^{o}_{HA^-}$ values from all sources are compared with each other and with values of $\lambda^{o}_{A^{--}}$ and the applicability of the Stokes equation is tested.

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LIST OF SYMBOLS

a	:	Leading solution.
$\overset{o}{a}$	:	Distance of closest approach of ions in an electrolyte, in Angstrom units.
$\overset{o}{A}$	:	One Angstrom unit $= 10^{-8}$ cm.
b	:	Following solution.
B_i	:	Molar contribution to the viscosity due to the ions.
B_u	:	Molar contribution to the viscosity due to the neutral molecules.
C_i	:	Equivalent concentration of species i.
$\overline{C}_R^a$	:	Equivalent concentration of ion-constituent R in solution a.
f_i	:	Molar activity coefficient of species i.
$f_{\pm}$	:	Mean ionic activity coefficient.
F	:	One Faraday, i.e. 96,494 coulombs gram-equiv.$^{-1}$.
I	:	Current.
K_1, K_2, K_3,	:	1st, 2nd and 3rd dissociation constants of an acid.
K_{AHA^-}	:	Stability constant of the complex ion AHA^-.
$k_{soln.}$	:	Specific conductance of the solution.
k_i	:	Specific conductance due to species i.
m	:	Concentration in molarity.
M	:	Abbreviation for molar.
$N_{R,i}$	:	Number of gram-formula-weights of ion constituent R in 1 gram-ion of species i.
R	:	Leading ion-constituent.
S	:	Following ion-constituent.
t	:	Time taken for boundary movement.
T_R^a	:	Transference number of ion constituent R in solution a.

u_i^a : Mobility of species i in solution a (velocity in cm.sec.$^{-1}$ under a potential gradient of one volt cm.$^{-1}$).

$\bar{u}_R^a$: Mobility of ion-constituent R in solution a.

V_F : Volume swept out by the moving boundary on the passage of one Faraday of electricity.

$\bar{V}$: Partial molal volume.

z_i : Charge number of the species i.

$|z_i|$: Positive numerical value of z_i.

Z_R : Charge number of the ion-constituent R.

λ_i , λ_i^o : Equivalent conductance, limiting equivalent conductance of ion i in cm^2 ohm^{-1} equiv.$^{-1}$.

Λ , Λ^o : Equivalent conductance, limiting equivalent conductance of the whole solution.

η : Viscosity of the solution.

$S_{(\lambda)}$, $S_{(\Lambda)}$, $S_{(\eta)}$: Limiting theoretical slopes of the quantities indicated in the subscript.

μ : Ionic strength of the solution, $\mu = \frac{1}{2} \sum m_i z_i^2$.

ρ : Density of the solution.

$\doteq$: Approximately equal to.

(X) : Molar concentration of X.

THE LIMITING EQUIVALENT CONDUCTANCES OF ACID ANIONS AT 25°C.

INTRODUCTION

The term acid anion refers to any negatively charged ion that is capable of producing H^+ ions by dissociation. A diprotic acid, H_2A, on partial dissociation gives one acid anion HA^- ; a triprotic acid H_3A can give two acid anions, H_2A^- and HA^{--}.

Values for the limiting equivalent conductances of these acid anions ($\lambda^o_{HA^-}$) have been obtained in the past[1] by conductance measurements on either the parent acid or its sodium, potassium or ammonium salt. In the case of the acid the method involves determining the equivalent conductance of the acid at various low concentrations and extrapolating the results, after any corrections for secondary dissociation, to infinite dilution by a suitable extrapolation function. This gives the limiting equivalent conductance of the acid, Λ^o, from which $\lambda^o_{HA^-}$ may be obtained by subtracting $\lambda^o_{H^+}$ since

$$\Lambda^o_{H_2A} = \lambda^o_{H^+} + \lambda^o_{HA^-} \qquad (1)$$

The contribution of $\lambda^o_{HA^-}$ to the total conductance is usually less than 10% and this leads to a loss in accuracy in evaluating $\lambda^o_{HA^-}$ since, as can be seen from equation (1), it involves taking the small difference between two large quantities ($\lambda^o_{H^+} = 349.8$[a], $\lambda^o_{HA^-} \doteqdot 30$). Another difficulty of the method has been the long extrapolation to infinite dilution; the extrapolation is longer the weaker the electrolyte. This difficulty is overcome in a method suggested by the author and is discussed in Part I of this thesis.

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a. Conductance units are always given in $cm^2 ohm^{-1} equiv.^{-1}$ in this thesis.

Many workers have therefore preferred to evaluate $\lambda^{o}_{HA^-}$ by measuring the conductances of acid salts of the type MHA, where M refers to Na, K or NH_4. In solutions of these salts in water M^+, HA^-, H^+, A^{--} and H_2A species are present. As in the case of an acid where both primary and secondary dissociation occurs, $\lambda^{o}_{HA^-}$ can be calculated only if the concentrations and conductances of all the other ions in solution are known and corrected for.

The values of $\lambda^{o}_{HA^-}$ determined from conductance measurements on the acids or their salts are fairly sensitive to changes in the values chosen for the dissociation constants. Also, as the contribution of the HA^- ion to the total conductance of the solution is not large, it is evident that small errors in (a) the conductance measurements (b) the calculation of the contribution to the conductance due to the other ions, and (c) the principle of additivity of specific conductances would lead to large errors in $\lambda^{o}_{HA^-}$. Quantitative calculations showing the sensitivity of the calculated value of $\lambda^{o}_{HA^-}$ to changes in dissociation constants, $\lambda^{o}_{A^{--}}$ etc. are tabulated in Part I of this thesis.

It will be shown that anion transference number (T_-) measurements on the weak acid at a series of low concentrations provide the most accurate method for the determination of $\lambda^{o}_{HA^-}$. The results are not very sensitive to values for the dissociation constants; the extrapolation to infinite dilution is quite small since the solutions have low ionic strengths, and the quantity sought (λ_{HA^-}) is almost directly proportional to the quantity measured (T_-). The experimental measurements of the author to determine $\lambda^{o}_{HA^-}$ are given in Part II of this thesis.

PART 1

In this section the determination of the limiting equivalent conductances of acid anions from conductance measurements on the acid or salts are critically discussed. In almost all instances re-calculations were carried out either to take into account recent more accurate values for the dissociation constants or to interpret the results according to modern views.

1. $\lambda^{o}_{HA^-}$ FROM CONDUCTANCE MEASUREMENTS ON ACID SALTS.

1.1. Introduction.

The method for calculating $\lambda^{o}_{HA^-}$ from conductances of acid salts, taking activity coefficients into account, was first employed by C.W. Davies[2] in 1939 using some of the conductance data tabulated four years earlier by Jeffery and Vogel.[3] Later Topp and Davies,[4] from their own conductance measurements on the neutral and acid ammonium salts of some dicarboxylic acids, calculated $\lambda^{o}_{HA^-}$ using the same method. Their results are compared with those obtained by the present re-calculations in Tables III, V, VIII, IX, X, XI and XII.

1.2. Theory.

The method of calculation used by the author was the same as that of Davies except that a different equation (eqn. 7) was used for the activity coefficient. In solutions of the acid salts in water the following equilibria exist:

$$MHA \rightleftharpoons M^+ + HA^-$$

$$HA^- \rightleftharpoons H^+ + A^{--}$$

$$HA^- + H^+ \rightleftharpoons H_2A$$

If m is the original molar concentration of the salt, and α and β the degrees of formation of A^{--} and H_2A respectively, it follows that the molar concentrations of the different species at equilibrium are given by $(HA^-) = m(1-\alpha-\beta)$, $(H^+) = m(\alpha-\beta)$, $(A^{--}) = m\alpha$, $(H_2A) = m\beta$. Substitution of these expressions for the concentrations in the equations for the first and second dissociation constants K_1 and K_2 of the acid gives

$$K_1 = \frac{(H^+)(HA^-)\ f_{H^+}\ f_{HA^-}}{(H_2A)} = \frac{m(\alpha-\beta)(1-\alpha-\beta)\ f_{H^+}\ f_{HA^-}}{\beta} \qquad (2)$$

$$K_2 = \frac{(H^+)(A^{--})\ f_{H^+}\ f_{A^{--}}}{(HA^-)\ f_{HA^-}} = \frac{m(\alpha-\beta)\alpha\ f_{H^+}\ f_{A^{--}}}{(1-\alpha-\beta)\ f_{HA^-}} \qquad (3)$$

where f_i is the activity coefficient of the ion i.

According to the full Debye-Hückel equation[5] f_i, in aqueous solution at 25°C, is given by

$$\log f_i = - \frac{0.5098\ Z_i^2\ \sqrt{\mu}}{1 + 0.3286\ \mathring{a}\ \sqrt{\mu}} \qquad (4)$$

where μ is the ionic strength of the solution and $\mathring{a}$ a parameter denoting the distance of closest approach of the ions in Angstrom units. The ionic strength μ is defined as

$$\mu = \frac{1}{2} \sum m_i\ Z_i^2$$

where Z_i is the charge on the ion i. It is clear from eqn. (4) that the magnitude of the activity coefficient does not depend on the sign of the charge on the ion and therefore f_{H^+} and f_{HA^-} are equal and may be cancelled out in eqn. (3).

Rearrangement of eqns. (2) and (3) leads to

$$\frac{\alpha}{\beta} = \frac{K_1}{m(1-\alpha-\beta) f_{H^+} f_{HA^-}} + 1 \qquad (5)$$

and

$$\alpha\beta = \frac{K_2(1-\alpha-\beta)^2 f_{H^+} f_{HA^-}}{K_1 f_{A^{--}}} \qquad (6)$$

from which α and β, and thereby the molar concentrations of the various species, were calculated by successive approximations. The Güntelberg expression[6],

$$\log f_i = - \frac{0.5098\, Z_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}} , \qquad (7)$$

in which $\overset{o}{a}$ is assumed to be approximately 3 (see eqn. (4)), has been widely used for calculating the activity coefficient of a species i and was employed in the present calculation. The ionic strength of the solution is $m(1+2\alpha-\beta)$. Davies evaluated the mean ionic activity coefficient $f_{\pm}$ using the equation

$$- \log f_{\pm} = 0.50\, Z_+ Z_- \left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.20\mu \right)$$

The mean ionic activity coefficient is related to the activity coefficient of the positive (f_+) and negative (f_-) ions by $(f_{\pm})^{\nu} = f_+^{\nu_+} f_-^{\nu_-}$ where ν, ν_+ and ν_- refer to the total number, the number of positive and the number of negative ions formed by the dissociation of 1 molecule of the electrolyte.

The equivalent conductances of the H^+, M^+ and A^{---} ions at the ionic strength μ were calculated from known λ^o values with the help of

the Robinson and Stokes conductance equation[7] in the modified form

$$\lambda_i = \lambda_i^o - S_{(\lambda_i)} \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \qquad (8)$$

where $S_{(\lambda_i)}$[8] is equal to $0.2292\ \lambda_i^o + 30.3$ for single univalent ions and

$(\theta\wedge_{M_2A} + 90.9) - (0.2292\ \lambda_{M^+}^o + 30.3)$ for the A^{--} ion in aqueous solutions at 25°C .

$\theta = 1.5654 \dfrac{q^{\ast}}{1 + \sqrt{q^{\ast}}}$ for uni-bi valent electrolytes in water at 25°C and $q^{\ast}$ is given by

$$q^{\ast} = \frac{|Z_+ Z_-| \cdot (\lambda_+^o + \lambda_-^o)}{(|Z_+| + |Z_-|)(|Z_-|\lambda_+^o + |Z_+|\lambda_-^o)}$$

The conductance equation (8) is consistent with equation (7) for the activity coefficient since both assume the distance of closest approach to be 3 angstroms.

As shown earlier, in solutions of the acid salt H^+, M^+, A^{--} and HA^- ions are present. The experimental specific conductance of the solution (k_{soln}) was assumed to be equal to the sum of the specific conductances of all the ions (k_i) in solution. The contributions of the H^+, M^+ and A^{--} ions to the experimental or total specific conductance of the solution (k_{soln}) were then calculated using the relationship

$$1000\ k_i = \lambda_i\ C_i \qquad (9)$$

where C_i is the <u>equivalent</u> concentration of the ionic species i. The difference between the experimental specific conductance and the sum due

to the contributions from H^+, M^+ and A^{--} ions gave the specific conductance due to the HA^- ions (k_{HA^-}) . From k_{HA^-} , $\lambda^o_{HA^-}$ was calculated by first obtaining λ_{HA^-} using equation (9) and then correcting for interionic attractions by equation (8).

The calculation of $\lambda^o_{HA^-}$ as outlined above would have been very laborious even with a calculating machine and so the University of London "Mercury" oomputer was used to do the calculations. The computer programme that was used is given in Appendix 1.

1.3. Results.

Conductance measurements have been published for the acid salts of the following acids:- Malonic[3], Succinic[3,4], glutaric[3], adipic[3,4], pimelic[3], suberic[3], Malic[4], Maleic[4], fumaric[4], O-phthalic[4], tartaric[4] and phosphoric acids[1]. The calculation of the limiting conductance of the acid anions depends on the values chosen for the dissociation constants and $\lambda^o_{A^{--}}$; the published results for these quantities, together with the method used for obtaining them and the values selected for the present calculation are summarised in Table I. The results obtained by the calculation are given in Tables II to XIII. Columns 2, 3 and 4 in the tables give the molar concentrations of the ionic species present in an acid salt solution of molarity given in column 1; column 5 gives the experimental specific conductance of the solution, from which the specific conductivity due to the HA^- ions (column 9) was obtained by subtracting the contribution due to the H^+ (column 6), M^+ (column 7) and A^{--} ions (column 8). It should be noted that column 3 gives the molar concentration of A^{--} and it is necessary to multiply it by two before

substituting in equation (9) to obtain k_{HA^-}. The required quantity $\lambda^o_{HA^-}$ is given in the last column and was obtained from k_{HA^-} first using equation (9) and then (8).

1.4. Discussion

Tables II to XIII show that the results obtained for $\lambda^o_{HA^-}$, at the different concentrations, are widely scattered. This is clearly shown in Figures 1, 2, 3 and 4, where the $\lambda^o_{HA^-}$ values are plotted against the molar concentration. In nearly all cases the scatter can be seen to be very severe at concentrations below 2×10^{-3} molar and these results may therefore be considered unreliable. At these low concentrations, in addition to the experimental technique being more difficult, uncertainty in the solvent correction would make the conductance data less accurate. Also, the percentage contribution of the HA^- ion to the total conductance decreases as the concentration decreases (see Tables II to XIII) and so increases the error in evaluating $\lambda^o_{HA^-}$. It is unfortunate that the conductance data of Topp and Davies[4], from which they calculated $\lambda^o_{HA^-}$, always refer to concentrations less than 2.4×10^{-3} molar. Recalculation, using their data, is therefore relatively unreliable.

The graphs show that the results obtained for $\lambda^o_{HA^-}$ are scattered even above 2×10^{-3} molar. These random errors are presumably due partly to experimental errors and partly to the method used to determine $\lambda^o_{HA^-}$. A number of implicit assumptions have been made in the above calculations. Ion-pair formation between the metal and the acid anion has been presumed absent and the specific conductivities have been assumed to be additive. These assumptions might not be strictly true at concentrations above about 0.01 M. Davies[9] has pointed out that the assumption of

additivities of specific conductances would be expected to lead to higher and higher values for $\lambda^{o}_{HA^-}$ as the concentration is increased. However, no such trend is observed except for the $\lambda^{o}_{H_2PO_4^-}$ results. In the more concentrated solutions error may also be introduced, by inadequacies in the equations used for f_i and λ_i.

The tables show that the percentage contribution of the HA^- ion to the total specific conductance in, say, an approximately 0.002 M solution is:- 36% for malonic, 27% for succinic, 19% for glutaric adipic and pimelic, 17% for suberic, 18% for Malic, 36% for maleic, 19% for fumaric, 22% for O-phthalic, 11% for tartaric and 38% for phosphoric acids. It is significant that the scatter in $\lambda^{o}_{HA^-}$ increases as its percentage contribution to the total specific conductance decreases. The relative percentage contribution depends on the values of the dissociation constants. As K_1 becomes larger and K_2 smaller the proportion of HA^- ions in solution increases thereby increasing their contribution to the total specific conductance.

In addition to the random errors which result in scatter, constant errors can be introduced due to lack of accurate values for K_1, K_2 or $\lambda^{o}_{A^{--}}$. These errors become more and more important as K_1 becomes smaller and K_2 larger, since the concentrations of A^{--} and H_2A become greater under these conditions. The effect of an increase of 10% in K_1, of 10% in K_2, and one conductance unit in $\lambda^{o}_{A^{--}}$ at one of the higher and one of the lower concentrations is also shown in tables II to XIII, (results superscripted a, b and c respectively). For phosphoric acid (Table XIII) K_1 is relatively large (7.516×10^{-3}) and K_2 is quite small (6.339×10^{-8}) and, as is to be expected, the $\lambda^{o}_{H_2PO_4^-}$ results can be seen

to be not significantly affected by the increase in K_1 , K_2 or $\lambda^o_{A^{--}}$ — the change in $\lambda^o_{H_2PO_4^-}$ being less than 0.1 of a conductance unit. For suberic acid, (Table VII), on the other hand, ($K_1 = 3.04 \times 10^{-5}$, $K_2 = 3.96 \times 10^{-6}$) the said increase in K_1, K_2 and $\lambda^o_{A^{--}}$ results in $\lambda^o_{HA^-}$ being increased by +0.2, -0.5 and -0.8 conductance unit respectively. Tartaric acid (Table XII) shows the most sensitive behaviour; a 10% increase in K_2 decreasing $\lambda^o_{HA^-}$ by 2.9 units. K_1 and K_2 are known accurately for many of the acids[10] but reliable values for $\lambda^o_{A^{--}}$ are generally lacking.

The results given in the tables and the discussion makes it clear that, even when reliable values are available for K_1 and K_2, the method does not give $\lambda^o_{HA^-}$ with an accuracy greater than two or three per cent. The results become less and less reliable as K_1 becomes smaller and K_2 larger. If in addition K_1 , K_2 or $\lambda^o_{A^{--}}$ are uncertain the method, in general, can give only an approximate value for the limiting conductance of the acid anion.

Table I

DISSOCIATION CONSTANTS OF ACIDS AND λ_A^o — VALUES.

Acid	10^4K_1	10^6K_2	Method	Reference	Values selected	λ_A^o —	Values Selected.
Malonic	13.97	-	Conductivity	Jeffery & Vogel (1935)	10^4K_1 = 14.24	64.7[15]	
	-	2.014	e.m.f.	Hamer etal (1940)[11]	10^6K_2 = 2.013	63.5[16]	64
	14.236	2.0130	e.m.f.	Das & Ives (1961)		64.8[17]	
Succinic	0.621	2.31	e.m.f.	Pinching & Bates (1950)	10^5K_1 = 6.21	57.3[18]	
	0.663	-	Conductivity	Jeffery & Vogel (1935)	10^6K_2 = 2.31	60.9[15]	
						58.8[16]	60
						64.7[17]	
Glutaric	0.453	3.80	pH titration	Gane & Ingold (1931)	10^5K_1 = 4.53	56.9[15]	
	0.446	3.77	pH titration	German & Vogel (1936)	10^6K_2 = 3.80	55.2[17]	55.2
	0.458	3.89	e.m.f.	Jones & Soper (1936)			
	0.454	-	Conductivity	Jeffery & Vogel (1935)			
Adipic	0.382	3.87	pH titration	Gane & Ingold (1931)	10^5K_1 = 3.82	52.6[18]	
	0.370	3.86	e.m.f.	Jones & Soper (1936)	10^6K_2 = 3.87	52.9[15]	52
	0.372	-	Conductivity	Jeffery & Vogel (1935)		51.1[17]	
Pimelic	0.328	3.77	pH titration	Gane & Ingold (1931)	10^5K_1 = 3.28	50.1[15]	
	0.310	-	Conductivity	Jeffery & Vogel (1935)	10^6K_1 = 3.77	48.5[17]	48.5
Suberic	0.304	3.95	pH titration	Gane & Ingold (1931)	10^5K_1 = 3.04	47.4[15]	
	0.299	-	Conductivity	Jeffery & Vogel (1935)	10^6K_2 = 3.95	47.2[17]	47.2
Malic	3.48	7.99	e.m.f.	Eden & Bates (1959)[12]	10^4K_1 = 3.48 10^6K_2 = 7.99	58.8[18]	58.8

Acid	10^4K_1	10^6K_2	Method	Reference	Values selected	λ_A^o	Value Selected
Maleic	123.0	~~0.15656~~ 0.4656	e.m.f.	Dalgren & Long (1960)[13]	10^2K_1 = 1.230 10^7K_2 = 4.656	61.9[18]	61.9
	120	0.595	pH titration	German etal (1936)			
Fumaric	8.035	25.00	e.m.f.	Dalgren & Long (1960)[14]	10^4K_1 = 8.035 10^5K_2 = 2.500	61.8[18]	61.8
	9.57	41.3	pH titration	German etal (1936)			
O-Phthalic	11.23	3.906	e.m.f.	Hamer etal (1945)	10^3K_1 = 1.123 10^6K_2 = 3.906	52.3[18]	52.3
Tartaric	9.17	43.0	e.m.f.	Bates & Canham (1951)	10^4K_1 = 9.17 10^5K_2 = 4.30	59.6[18] 63.2[19]	60
Phosphoric	7.11	-	e.m.f.	Bates (1951)	10^3K_1 = 7.516 10^8K_2 = 6.339	55[20]	55
	7.516	0.06226	e.m.f.	Nims (1934)			
	-	0.06339	e.m.f.	Bates & Acree (1945)			
		0.06304	e.m.f.	Grzybowski (1958)[14]			

Note: References are only given for those cases which are not listed in Appendix 12.1 of Ref. 6.

Table II

ANALYSIS OF CONDUCTANCES OF SODIUM HYDROGEN MALONATE .[3]

$K_1 = 1.424 \times 10^{-3}$; $K_2 = 2.013 \times 10^{-6}$; $\lambda^o_{A^{--}} = 64$

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^6 k_{soln.}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$\therefore 10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^o_{HA^-}$
0.1064	0.1350	0.1435	0.9121	15.343	4.707	5.281	1.804	3.551	38.93	39.38
0.2811	0.2172	0.2540	2.5202	34.036	7.553	13.878	3.162	9.443	37.47	38.17
0.3654	0.2446	0.2986	3.3014	43.366	8.501	18.003	3.705	13.157	39.85	40.65
0.5801	0.2978	0.4022	5.2944	62.906	10.336	28.466	4.952	19.152	36.17	37.13
0.6124	0.3044	0.4170	5.5944	67.101	10.563	30.032	5.128	21.378	38.21	39.21
0.9473	0.3598	0.5640	8.7048	99.230	12.461	46.228	6.873	33.668	38.68	39.92
0.9847	0.3648	0.5799	9.0520	101.35	12.634	48.034	7.060	33.622	37.14	38.38
1.101	0.3795	0.6289	10.132	112.85	13.136	53.630	7.635	38.452	37.95	39.27
1.812	0.4462	0.9203	16.726	178.05	15.399	87.592	11.015	64.044	38.29	39.96
1.885	0.4515	0.9498	17.402	182.81	15.578	91.064	11.354	64.814	37.25	38.93
2.290	0.4775	1.1124	21.152	218.79	16.456	110.24	13.206	78.880	37.29	39.14
3.264	0.5252	1.5009	30.163	303.03	18.051	155.99	17.570	111.42	36.94	39.12
3.334	0.5281	1.5288	30.810	311.36	18.145	159.23	17.881	116.10	37.68	39.89
4.368	0.5644	1.9410	40.362	396.70	19.345	207.26	22.419	147.67	36.59	39.09
5.353	0.5919	2.3351	49.452	476.42	20.248	252.61	26.681	176.88	35.77	38.51
6.020	0.6080	2.6030	55.602	532.41	20.772	283.12	29.544	198.96	35.78	38.66
6.347	0.6153	2.7346	58.616	562.34	21.009	297.99	30.939	212.40	36.24	39.21
6.867	0.6262	2.9445	63.407	602.99	21.363	321.65	33.155	226.82	35.77	38.84
8.550	0.6574	3.6278	78.902	741.20	22.366	397.49	40.261	281.08	35.62	39.01
9.254	0.6689	3.9154	85.378	800.47	22.736	429.02	43.210	305.50	35.78	39.31
10.02	0.6804	4.2296	92.422	859.11	23.103	463.12	46.399	326.48	35.32	38.97
2.290	0.4775	1.1124	21.152	218.79	16.456	110.24	13.206	78.880	37.29	39.14
2.290[a]	0.4909	1.0857	21.220	218.79	16.916	110.24	12.890	78.740	37.11	38.96[a]
2.290[b]	0.5006	1.1633	21.074	218.79	17.250	110.23	13.810	77.494	36.77	38.62[b]

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^6 k_{soln}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^o_{HA^-}$
2.290[c]	0.4775	1.1124	21.152	218.79	16.456	110.24	13.426	78.665	37.19	39.04[c]
10.02	0.6804	4.2296	92.422	859.11	23.103	463.12	46.399	326.48	35.32	38.97
10.02[a]	0.7084	4.0775	92.753	859.11	24.052	463.19	44.737	327.14	35.27	38.91[a]
10.02[b]	0.7138	4.4207	92.072	859.11	24.235	463.13	48.492	323.26	35.11	38.76[b]
10.02[c]	0.6804	4.2296	92.422	859.11	23.103	463.12	47.218	325.63	35.23	38.88[c]

a : This refers to results obtained when K_1 is increased by 10%

b : " " " " " " K_2 " " " "

c : " " "" " " " $\lambda^o_{A^{--}}$ is increased by one conductance unit

This designation is also used in all the following tables.

Table III

CONDUCTANCES OF SODIUM HYDROGEN SUCCINATE [3]

$K_1 = 6.21 \times 10^{-5}$, $K_2 = 2.31 \times 10^{-6}$, $\lambda^{o}_{A^{--}} = 60$

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^6 k_{soln.}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$\therefore 10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^{o}_{HA^-}$
0.1306	0.0964	0.2364	0.9295	16.043	3.358	6.475	2.779	3.430	36.90	37.38
0.1706	0.1019	0.2952	1.2176	20.165	3.549	8.446	3.461	4.159	42.37	42.95
0.6001	0.1221	0.9163	4.2906	59.614	4.237	29.423	10.539	15.416	35.93	36.93
0.9570	0.1281	1.4338	6.8305	91.671	4.434	46.663	16.314	24.261	35.52	36.77
1.074	0.1295	1.6041	7.6613	101.90	4.481	52.282	18.196	26.940	35.16	36.48
1.626	0.1347	2.4117	11.571	150.91	4.651	78.650	27.011	40.595	35.08	36.69
1.945	0.1371	2.8812	13.825	178.43	4.727	93.788	32.065	47.860	34.62	36.37
3.301	0.1448	4.8967	23.362	295.57	4.972	157.39	53.284	79.923	34.21	36.46
4.539	0.1502	6.7600	32.020	401.07	5.142	214.65	72.346	108.93	34.02	36.63
5.214	0.1528	7.7839	36.725	457.06	5.223	245.58	82.632	123.61	33.66	36.44
6.137	0.1561	9.1923	43.142	534.04	5.325	287.64	96.585	144.51	33.50	36.49
7.062	0.1591	10.612	49.554	609.10	5.420	329.44	110.45	163.78	33.05	36.25
8.832	0.1644	13.352	61.781	754.87	5.584	408.75	136.67	203.88	33.00	36.55
11.37	0.1712	17.324	79.222	958.38	5.793	520.97	173.63	258.04	32.57	36.55
0.5950*	0.122	0.909	4.254	70.5	4.23	42.95	9.963	13.35	31.38	32.4*(30.8)
0.7730*	0.125	1.167	5.522	90.0	4.35	55.68	12.71	17.26	31.26	32.4*(29.9)
1.368*	0.133	2.033	9.746	157.0	4.58	97.95	21.80	32.67	33.52	35.0*(34.7)
1.945	0.1371	2.8812	13.825	178.43	4.727	93.788	32.065	47.860	34.62	36.37
1.945 a	0.1434	2.7901	14.013	178.43	4.943	93.793	31.056	48.643	34.713	36.46 a
1.945 b	0.1437	2.9806	13.633	178.43	4.953	93.778	33.166	46.538	34.14	35.88 b
1.945 c	0.1370	2.8812	13.825	178.43	4.724	93.786	32.627	47.297	34.21	35.96 c
11.37	0.1712	17.324	79.222	958.38	5.793	520.97	173.63	258.04	32.57	36.55
11.37 a	0.1790	16.7594	80.360	958.38	6.061	521.02	168.04	263.26	32.76	36.73 a
11.37 b	0.1791	17.9065	78.066	958.38	6.062	520.83	179.40	252.09	32.29	36.27 b
11.37 c	0.1709	17.324	79.223	958.38	5.785	520.93	176.91	254.76	32.16	36.12 c

* Results on ammonium hydrogen succinate [4]; the values obtained by Topp and Davies are given within the brackets.

Table IV

CONDUCTANCES OF SODIUM HYDROGEN GLUTARATE[3]

$K_1 = 4.53 \times 10^{-5}$, $K_2 = 3.80 \times 10^{-6}$, $\lambda^{o}_{A^{--}} = 55.2$

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^6 k_{soln}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$\therefore 10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^{o}_{HA^-}$
0.0970	0.1025	0.2353	0.6020	12.973	3.574	4.815	2.547	2.037	33.84	34.27
0.3608	0.1283	0.7380	2.2603	37.285	4.458	17.766	7.861	7.200	31.85	32.64
0.6031	0.1356	1.1969	3.7727	57.469	4.703	29.558	12.623	10.585	28.06	29.04
1.013	0.1424	1.9768	6.3189	93.034	4.927	49.333	20.575	18.199	28.80	30.05
1.040	0.1427	2.0283	6.4861	95.888	4.939	50.627	21.090	19.232	29.65	30.93
1.846	0.1505	3.5752	11.460	163.19	5.188	89.033	36.460	32.510	28.37	30.04
2.018	0.1516	3.9072	12.517	176.78	5.229	97.167	39.701	34.686	27.70	29.45
3.669	0.1615	7.124	22.604	310.03	5.537	174.31	70.355	59.82	26.46	28.75
4.205	0.1640	8.177	25.859	354.27	5.618	199.07	80.126	69.46	26.86	29.32
5.566	0.1698	10.872	34.085	462.26	5.799	261.32	104.65	90.49	26.55	29.36
7.184	0.1758	14.105	43.805	587.72	5.986	334.49	133.29	113.95	26.01	29.15
7.291	0.1762	14.320	44.446	595.97	5.998	339.32	135.15	115.50	25.99	29.15
8.623	0.1806	17.005	52.402	697.51	6.134	398.81	158.35	134.22	25.61	29.02
8.776	0.1811	17.314	53.313	709.45	6.150	405.63	160.99	136.68	25.64	29.08
10.78	0.1862	21.387	65.213	858.41	6.336	494.16	195.20	162.72	24.95	28.72
2.018	0.1516	3.9072	12.517	176.78	5.229	97.167	39.701	34.686	27.71	29.45
2.018[a]	0.1586	3.7986	12.741	176.78	5.467	97.173	38.605	35.532	27.89	29.62[a]
2.018[b]	0.1590	4.0251	12.289	176.78	5.478	97.156	40.891	33.252	27.06	28.79[b]
2.018[c]	0.1516	3.9072	12.517	176.78	5.229	97.167	40.463	33.925	27.10	28.41[c]
10.78	0.1862	21.387	65.213	858.41	6.336	494.16	195.20	162.72	24.95	28.72
10.78[a]	0.1950	20.7810	66.433	858.41	6.602	494.28	189.75	167.78	25.26	29.02[a]
10.78[b]	0.1954	22.0115	63.973	858.41	6.615	494.08	200.81	156.90	24.53	28.29[b]
10.78[c]	0.1862	21.387	65.213	858.41	6.336	494.16	199.24	158.67	24.33	28.08[c]

Table V

CONDUCTANCES OF SODIUM HYDROGEN ADIPATE[3]

$K_1 = 3.82 \times 10^{-5}$, $K_2 = 3.87 \times 10^{-6}$, $\lambda^o_{A^{--}} = 52$.

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^6 k_{soln.}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^o_{HA^-}$
0.1544	0.1070	0.3597	0.9317	19.337	3.728	7.647	3.648	4.314	46.30	46.87
0.1545	0.1071	0.3599	0.9323	19.228	3.728	7.647	3.650	4.203	45.08	45.65
0.4629	0.1234	0.9784	2.7957	46.929	4.285	22.742	9.754	10.148	36.30	37.21
0.7369	0.1289	1.5286	4.4408	70.234	4.469	36.027	15.078	14.660	33.01	34.12
1.348	0.1360	2.7637	8.0887	120.27	4.698	65.351	26.764	23.457	29.00	30.45
1.459	0.1369	2.9891	8.7487	129.34	4.729	70.645	28.869	25.101	28.69	30.19
2.420	0.1434	4.9530	14.437	206.89	4.935	116.06	46.834	39.043	27.05	28.94
2.574	0.1444	5.2697	15.345	220.90	4.969	123.29	49.684	42.96	28.00	29.96
4.799	0.1548	9.8890	28.367	396.73	5.293	226.27	89.97	75.20	26.51	29.12
5.279	0.1566	10.895	31.156	433.78	5.352	248.22	98.49	81.72	26.23	28.96
7.054	01629	14.641	41.420	571.23	5.545	328.58	129.48	107.63	25.99	29.11
7.193	0.1633	14.936	42.221	581.84	5.559	334.76	131.88	109.64	25.97	29.13
9.235	0.1695	19.292	53.936	733.07	5.751	425.83	166.72	134.77	24.99	28.52
10.63	0.1734	22.290	61.893	840.20	5.870	487.39	190.04	156.90	25.35	29.12
11.39	0.1744	23.931	66.214	899.13	5.902	520.72	202.61	169.89	25.65	29.55
0.6710*	0.128	1.396	4.046	78.0	4.43	48.37	13.79	11.41	28.20	29.2* (29.3)
1.019*	0.133	2.097	6.128	114.0	4.59	73.16	20.48	15.77	25.73	27.0* (27.7)
1.151*	0.134	2.364	6.915	129.0	4.64	82.52	22.99	18.85	27.26	28.6* (29.7)
2.420	0.1434	4.9530	14.437	206.89	4.935	116.06	46.834	39.043	27.04	28.94
2.420[a]	0.1501	4.8186	14.713	206.89	5.166	116.09	45.573	40.061	27.23	29.12[a]
2.420[b]	0.1505	5.0974	14.156	206.89	5.178	116.06	48.188	37.459	26.46	28.36[b]
2.420[c]	0.4134	4.9530	14.437	206.89	4.935	116.06	47.798	38.079	26.38	28.26[c]
11.39	0.1744	23.931	66.214	899.13	5.902	520.72	202.61	169.89	25.66	29.55
11.39[a]	0.1828	23.276	67.530	899.13	6.182	520.83	197.17	174.95	25.91	29.80[a]
11.39[b]	0.1832	24.606	64.870	899.13	6.196	520.61	208.23	164.09	25.30	29.19[b]
11.39[c]	0.1744	23.931	66.214	899.13	5.902	520.72	207.14	165.37	24.98	28.85[c]

* Results on ammonium hydrogen adipate[4]; the values obtained by Topp & Davies are given in brackets.

Table VI

CONDUCTANCES OF SODIUM HYDROGEN PIMELATE[3]

$K_1 = 3.28 \times 10^{-5}$, $K_2 = 3.77 \times 10^{-6}$, $\lambda^o_{A^{--}} = 48.5$

$\cdot 10^3 m$	$\cdot 10^4 H^+$	$\cdot 10^4 A^{--}$	$\cdot 10^4 HA^-$	$\cdot 10^6 k_{soln.}$	$10^6 k_{H^+}$	$\cdot 10^6 k_{M^+}$	$\cdot 10^6 k_{A^{--}}$	$\cdot 10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^o_{HA^-}$
0.1280	0.0966	0.3119	0.7528	18.848	3.367	6.345	3.953	6.183	82.13	82.76
0.2510	0.1066	0.5682	1.4800	31.119	3.709	12.394	5.333	9.683	65.42	66.22
0.6244	0.1169	1.3446	3.6716	59.842	4.053	30.583	12.389	12.817	34.91	35.95
0.7102	0.1182	1.5236	4.1730	65.921	4.096	34.736	13.990	13.099	31.39	32.47
1.101	0.1226	2.3415	6.4496	98.914	4.242	53.542	21.219	19.911	30.87	32.20
1.304	0.1244	2.7682	7.6280	115.59	4.299	63.257	24.936	23.098	30.28	31.72
2.015	0.1293	4.27119	11.737	173.65	4.456	97.002	37.799	34.391	29.30	31.07
2.682	0.1326	5.6914	15.570	227.46	4.560	128.33	49.662	44.900	28.83	30.86
3.986	0.1387	8.4920	23.015	329.84	4.752	188.90	72.403	63.79	27.72	30.14
5.936	0.1457	12.728	34.049	477.91	4.970	278.04	105.49	89.41	26.26	29.15
6.178	0.1465	13.258	35.411	496.16	4.994	289.01	109.56	92.60	26.15	29.10
7.828	0.1514	16.884	44.663	619.90	5.148	363.14	136.73	114.88	25.72	29.01
8.510	0.1533	18.392	48.470	668.72	5.207	393.59	147.80	122.12	25.19	28.60
9.461	0.1559	20.502	53.762	739.38	5.285	435.77	163.07	135.26	25.16	28.74
11.36	0.1598	24.740	64.280	878.58	5.403	519.27	193.04	160.88	25.02	28.91
2.682	0.1326	5.6914	15.570	227.46	4.560	128.33	49.662	44.900	28.84	30.86
2.682[a]	0.1390	5.5381	15.883	227.46	4.778	128.35	48.337	45.994	28.96	30.98[a]
2.682[b]	0.1392	5.8524	15.255	227.46	4.785	128.32	51.054	43.297	28.38	30.40[b]
2.682[c]	0.1326	5.6912	15.570	227.46	4.560	128.34	49.662	44.900	28.84	30.86[c]
11.36	0.1598	24.740	64.280	878.58	5.403	519.27	193.04	160.88	25.03	28.91
11.36[a]	0.1674	24.073	65.621	878.58	5.662	519.38	187.93	165.61	25.24	29.12[a]
11.36[b]	0.1677	25.419	62.928	878.58	5.672	519.16	198.23	155.52	24.71	28.60[b]
11.36[c]	0.1598	24.739.	64.280	878.58	5.403	519.27	193.04	160.88	25.03	28.92[c]

Table VII

CONDUCTANCES OF SODIUM HYDROGEN SUBERATE[3]

$K_1 = 3.04 \times 10^{-5}$, $K_2 = 3.95 \times 10^{-6}$, $\lambda^o_{A^{--}} = 47.2$

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^6 k_{soln}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^o_{HA^-}$
0.1352	0.0969	0.3365	0.7758	21.015	3.374	6.701	3.098	7.842	101.1	101.8
0.2501	0.1055	0.5844	1.4377	34.349	3.671	12.350	5.333	12.995	90.39	91.29
0.3331	0.1089	0.7629	1.9140	44.059	3.785	16.412	6.927	16.935	88.48	89.50
0.6138	0.1153	1.3676	3.5180	60.772	3.998	30.070	12.254	14.450	41.07	42.14
0.7352	0.1170	1.6299	4.2092	70.587	4.056	35.944	14.630	15.957	37.91	39.06
0.8934	0.1190	1.9725	5.1081	81.246	4.119	43.571	17.488	16.068	31.46	32.67
1.009	0.1202	2.2233	5.7636	98.024	4.158	49.128	19.632	25.106	43.56	44.94
1.212	0.1220	2.6647	6.9127	105.01	4.218	58.855	23.385	18.554	26.84	28.81
1.314	0.1229	2.8869	7.4891	113.00	4.245	63.729	25.255	19.775	26.41	27.83
2.112	0.1281	4.6348	11.979	175.17	4.414	101.57	39.739	29.451	24.59	26.35
2.807	0.1315	6.1688	15.864	228.52	4.518	134.17	52.123	37.714	23.76	25.78
3.551	0.1351	7.8212	20.003	286.10	4.633	168.78	65.338	47.349	23.67	25.91
4.987	0.1405	11.036	27.939	396.77	4.804	234.79	89.877	67.299	24.09	26.73
5.498	0.1423	12.187	30.749	434.62	4.858	258.08	98.520	73.162	23.79	26.55
6.572	0.1457	14.617	36.631	515.31	4.964	306.72	116.47	87.156	23.79	26.79
6.613	0.1458	14.710	36.855	517.47	4.968	308.56	117.15	86.792	23.55	26.55
7.761	0.1492	17.323	43.112	601.63	5.072	360.11	135.99	100.46	23.30	26.53
8.638	0.1516	19.330	47.873	663.57	5.147	399.16	150.23	109.03	22.77	26.16
9.992	0.1551	22.442	55.192	718.22	5.255	459.13	171.86	81.97	14.85	18.29
11.08	0.1570	24.954	61.049	831.44	5.309	506.91	188.97	130.28	21.33	25.10

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^4 k_{soln.}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^o_{HA^-}$
2.807	0.1315	6.1688	15.864	228.52	4.518	134.17	52.123	37.714	23.77	25.78
2.807[a]	0.1376	6.0095	16.189	228.52	4.730	134.18	50.791	38.821	23.98	25.98[a]
2.807[b]	0.3800	6.3393	15.529	228.52	4.742	134.15	53.550	36.079	23.23	25.24[b]
2.807[c]	0.1315	6.1688	15.864	228.52	4.518	134.17	53.321	36.517	23.02	25.01[c]
11.08	0.1570	24.945	61.049	831.44	5.309	506.91	188.97	130.28	21.34	25.10
11.08[a]	0.1644	24.311	62.343	831.44	5.560	506.98	184.20	134.70	21.61	25.37[a]
11.08[b]	0.1648	25.624	59.716	831.44	5.576	506.77	193.94	125.15	20.96	24.72[b]
11.08[c]	0.1570	24.945	61.049	831.44	5.309	506.91	193.69	125.56	20.57	24.31[c]

Table VIII

CONDUCTANCES OF AMMONIUM HYDROGEN MALATE[4]

$K_1 = 3.48 \times 10^{-4}$, $K_2 = 7.99 \times 10^{-6}$, $\lambda^{\circ}_{A^{--}} = 58.8$

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^6 k_{soln}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^{\circ}_{HA^-}$
1.143	0.4985	1.638	8.651	140.0	17.24	81.99	18.14	22.64	26.17	27.5 (41.0)
1.512	0.5263	2.100	11.445	184.5	18.18	108.11	23.05	35.17	30.73	32.3 (41.2)
2.250	0.5644	3.026	17.013	259.0	19.44	160.00	32.72	46.84	27.53	29.3 (37.5)
2.301	0.5665	3.090	17.397	266.0	19.51	163.58	33.38	49.53	28.47	30.3 (37.8)
1.561	0.5294	2.162	11.816	186.0	18.28	111.56	23.70	32.46	27.47	29.0 (38.0)
1.561[c]	0.5294	2.162	11.816	186.0	18.28	111.56	24.12	32.04		28.6[c]
1.987	0.5526	2.696	15.031	233.0	19.05	141.55	29.29	43.11	28.68	30.4 (38.3)
1.987[a]	0.5744	2.622	15.200	233.0	19.80	141.55	28.49	43.23	28.44	30.1a
1.987[b]	0.5790	2.798	14.853	233.0	19.96	141.54	30.39	41.18	27.73	29.4[b]
									Mean =	29.8 ± 3

Results obtained by Topp and Davies are given within the brackets.

Table IX

CONDUCTANCES OF AMMONIUM HYDROGEN MALEATE[4]

$K_1 = 1.230 \times 10^{-2}$, $K_2 = 4.656 \times 10^{-7}$, $\lambda^o_{A^{--}} = 61.9$

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^6 k_{soln}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$\therefore 10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^o_{HA^-}$
0.0230	0.2125	0.2269	8.988	115.0	7.36	66.44	2.67	38.53	42.78	44.1 (43.5)
1.803	0.2972	0.3359	17.655	220.0	10.26	128.82	3.88	77.04	43.64	45.3 (45.0)
1.867	0.3024	0.3431	18.286	228.0	10.44	133.34	3.96	80.26	43.92	45.6 (44.8)
2.179	0.3262	0.3771	21.362	267.0	11.25	155.30	4.33	96.12	45.00	46.9 (46.6)
1.697	0.2884	0.3239	16.611	202.5	9.96	121.34	3.75	67.45	40.61	42.2 (41.8)
0.1697[a]	0.2899	0.3223	16.615	202.5	10.01	121.34	3.73	67.37	40.55	42.2[a]
0.1697[b]	0.3024	0.3394	16.593	202.5	10.44	121.34	3.93	66.74	40.22	41.8[b]
0.1697[c]	0.2884	0.3239	16.611	202.5	9.96	121.34	3.82	67.39	40.57	42.2[c]
									Mean =	44.8 ± 3

Table X

CONDUCTANCES OF AMMONIUM HYDROGEN FUMARATE[4]

$K_1 = 8.035 \times 10^{-4}$, $K_2 = 2.500 \times 10^{-5}$, $\lambda^o_{A^{--}} = 61.8$.

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^6 k_{soln}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$\therefore 10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^o_{HA^-}$
0.8510	1.0194	1.7323	6.0647	142.5	35.29	61.16	20.33	25.71	42.39	43.7 (29.3)
0.8670	1.0259	1.7569	6.1822	144.3	35.52	62.30	20.61	25.87	41.85	43.2 (29.6)
0.9360	1.0527	1.8621	6.6886	154.3	36.43	67.21	21.81	28.85	43.13	44.5 (31.1)
0.9360[c]	1.0527	1.8621	6.6886	154.3	36.43	67.21	22.18	28.48		44.0[c]
2.069	1.3267	3.5319	14.953	288.0	45.70	147.17	40.36	54.76	36.62	38.5 (32.1)
1.022	1.0835	1.9922	7.3191	163.5	37.48	73.32	23.28	29.42	40.20	41.6 (29.7)
1.022[a]	0.1110	1.9655	7.3990	163.5	38.40	73.32	22.93	28.87	39.02	40.4[a]
1.022[b]	0.1132	2.0684	7.2156	163.5	39.17	73.31	24.12	26.92	37.31	38.7[b]
									Mean =	42.3 ± 3

Table XI

CONDUCTANCES OF AMMONIUM HYDROGEN O-PHTHALATE[4]

$K_1 = 1.123 \times 10^{-3}$, $K_2 = 3.906 \times 10^{-6}$, $\lambda^{o}_{A^{--}} = 52.3$

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^6 k_{soln}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$\therefore 10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^{o}_{HA^-}$
0.8220	0.4504	0.7208	7.2288	105.7	15.61	59.18	7.14	23.77	32.88	34.0 (40.0)
0.9310	0.4704	0.7895	8.2014	117.0	16.29	66.96	7.79	25.96	31.65	32.8 (37.1)
1.819	0.5789	1.330	16.110	209.7	19.98	129.84	12.84	47.05	29.21	30.8 (35.0)
1.819[a]	0.5948	1.2998	16.185	209.7	20.53	129.84	12.55	46.82	28.93	30.5[a]
1.819[b]	0.6067	1.3891	16.019	2209.7	20.93	129.83	13.41	45.56	28.44	30.0[b]
									Mean =	32.5 ± 3

Table XII

CONDUCTANCES OF AMMONIUM HYDROGEN TARTRATE[4]

$K_1 = 9.17 \times 10^{-4}$, $K_2 = 4.30 \times 10^{-5}$, $\lambda^{o}_{A^{--}} = 60$

$10^3 m$	$10^4 H^+$	$10^4 A^{--}$	$10^4 HA^-$	$10^6 k_{soln}$	$10^6 k_{H^+}$	$10^6 k_{M^+}$	$10^6 k_{A^{--}}$	$\therefore 10^6 k_{HA^-}$	λ_{HA^-}	$\lambda^{o}_{HA^-}$
1.024	1.438	2.422	6.834	166.5	49.72	73.41	27.35	15.87	23.22	24.5 (45.9)
1.393	1.594	3.073	9.378	213.7	55.02	-	-	24.56	26.19	27.7 (45.4)
1.714	1.698	3.627	11.584	249.5	58.56	-	-	28.22	24.36	26.0 (43.0)
1.520	1.638	3.293	10.252	231.0	56.51	-	-	29.02	28.31	29.9 (47.2)
1.520[a]	0.1682	3.2478	10.386	231.0	58.04	108.49	36.24	28.26	27.21	28.8[a]
1.520[b]	0.1707	3.4048	10.097	231.0	58.88	108.48	37.98	25.70	25.45	27.0[b]
									Mean =	32.5 ± 3

Table XIII

CONDUCTANCES OF SODIUM DIHYDROGEN PHOSPHATE[1]

$K_1 = 7.50 \times 10^{-3}$, $K_2 = 6.339 \times 10^{-8}$, $\lambda^{o}_{A^{--}} = 55$

$10^3 m$	$10^3 H^+$	$10^3 A^{--}$	$10^3 HA^-$	$10^5 k_{soln.}$	$10^5 k_{H^+}$	$10^5 k_{M^+}$	$10^5 k_{A^{--}}$	$\therefore 10^5 k_{HA^-}$	λ_{HA^-}	$\lambda^{o}_{HA^-}$
1.020	0.0081	0.0092	1.0098	8.632	0.280	4.979	0.095	3.278	32.47	33.65
2.064	0.0112	0.0142	2.0469	16.888	0.388	9.970	0.147	6.383	31.18	32.84
4.007	0.0150	0.0223	3.9774	32.054	0.514	19.077	0.220	12.243	30.77	33.03
6.859	0.0185	0.0334	6.8108	53.448	0.633	32.169	0.319	20.327	29.85	32.75
8.265	0.0199	0.0387	8.2074	64.084	0.677	38.531	0.366	24.510	29.86	33.03
10.30	0.0215	0.0465	10.229	79.113	0.731	47.638	0.431	30.314	29.64	33.14
13.72	0.0238	0.0594	13.625	103.33	0.805	62.728	0.544	39.249	28.81	32.78
20.00	0.0270	0.0834	19.860	148.16	0.909	89.640	0.750	56.660	28.53	33.24
25.66	0.0294	0.1054	25.479	186.99	0.982	113.75	0.886	71.373	28.01	33.26
27.51	0.0300	0.1126	27.315	197.02	1.004	121.46	0.938	73.626	26.95	32.33
38.78	0.0336	0.1573	38.499	273.40	1.116	167.61	1.245	103.43	26.87	33.11
51.52	0.0370	0.2092	51.139	354.87	1.219	218.29	1.576	133.79	26.16	33.19
68.64	0.0408	0.2808	68.119	460.01	1.335	284.31	1.996	172.37	25.30	33.19
77.78	0.0427	0.3199	77.183	514.42	1.389	318.74	2.211	192.08	24.89	33.17
92.74	0.0454	0.3849	92.016	604.06	1.472	374.11	2.550	225.93	24.55	33.43
103.0	0.0472	0.4303	102.19	663.42	1.524	411.38	2.687	247.73	24.25	33.50
137.4	0.0526	0.5861	136.28	851.01	1.682	532.98	3.477	312.88	22.96	33.23
193.5	0.0601	0.8510	191.86	1147.3	1.900	722.14	4.490	418.85	21.83	33.44
275.4	0.0695	1.2566	272.96	1537.0	2.166	983.45	5.720	545.67	19.99	33.05

CONDUCTANCES OF POTASSIUM DIHYDROGEN PHOSPHATE[1]

1.000	0.0080	0.0091	0.0990	10.709	0.278	7.206	0.094	3.131	31.63	32.80
1.401	0.0094	0.0111	1.3882	14.972	0.325	10.061	0.114	4.472	32.21	33.59
2.000	0.0111	0.0139	1.9833	20.913	0.383	14.298	0.141	6.091	30.71	32.34
2.564	0.0124	0.0163	2.5437	26.359	0.427	18.266	0.165	7.502	29.49	31.31
4.000	0.0150	0.0222	3.9705	40.634	0.514	28.280	0.219	11.621	29.27	31.51

$10^3 m$	$10^3 H^+$	$10^3 A^{--}$	$10^3 HA^-$	$10^5 k_{soln.}$	$10^5 k_{H^+}$	$10^5 k_{M^+}$	$10^5 k_{A^{--}}$	$\therefore 10^5 k_{HA^-}$	λ_{HA^-}	$\lambda^o_{HA^-}$
5.000	0.0164	0.0262	4.9640	50.394	0.562	35.195	0.255	14.382	28.97	31.46
6.000	0.0176	0.0301	5.9575	59.941	0.602	42.072	0.289	16.978	28.50	31.20
7.000	0.0187	0.0339	6.9509	69.504	0.638	48.909	0.323	19.634	28.25	31.15
8.000	0.0196	0.0377	7.9442	79.131	0.669	55.712	0.356	22.394	28.19	31.28
9.000	0.0205	0.0415	8.9374	88.526	0.698	62.478	0.388	24.962	27.93	31.18
10.00	0.0213	0.0453	9.9307	98.003	0.724	69.220	0.420	27.639	27.83	31.25
20.00	0.0270	0.0834	19.860	189.81	0.909	135.32	0.720	52.857	26.62	31.27
30.00	0.0309	0.1224	29.786	278.05	1.030	199.62	1.001	76.395	25.65	31.19
40.00	0.0339	0.1622	39.710	364.43	1.126	262.60	1.267	99.434	25.04	31.30
50.00	0.0366	0.2029	49.631	453.52	1.207	324.45	1.523	126.34	25.46	32.36
60.00	0.0390	0.2444	59.550	530.89	1.278	385.38	1.769	142.47	23.92	31.31
70.00	0.0411	0.2866	69.468	618.77	1.343	445.48	2.006	169.94	24.46	32.37
80.00	0.0431	0.3295	79.384	691.84	1.402	504.88	2.235	183.32	23.09	31.37
90.00	0.0449	0.3729	89.299	777.32	1.458	563.58	2.457	209.83	23.50	32.21
100.0	0.0467	0.4169	99.213	856.41	1.509	621.70	2.671	230.53	23.24	32.31
200.0	0.0609	0.8824	198.30	1585.6	1.923	1178.6	4.495	400.56	20.20	31.84
4.007	0.0150	0.0223	3.9774	32.054	0.514	19.077	0.220	12.243	30.77	33.03
4.007[a]	0.0153	0.0218	3.979	32.054	0.527	19.078	0.215	12.235	30.75	33.01[a]
4.007[b]	0.0159	0.0232	3.977	32.054	0.545	19.078	0.229	12.203	30.68	32.95[b]
4.007[c]	0.0550	0.0223	3.9774	32.054	0.514	19.077	0.229	12.240	30.77	33.04[c]

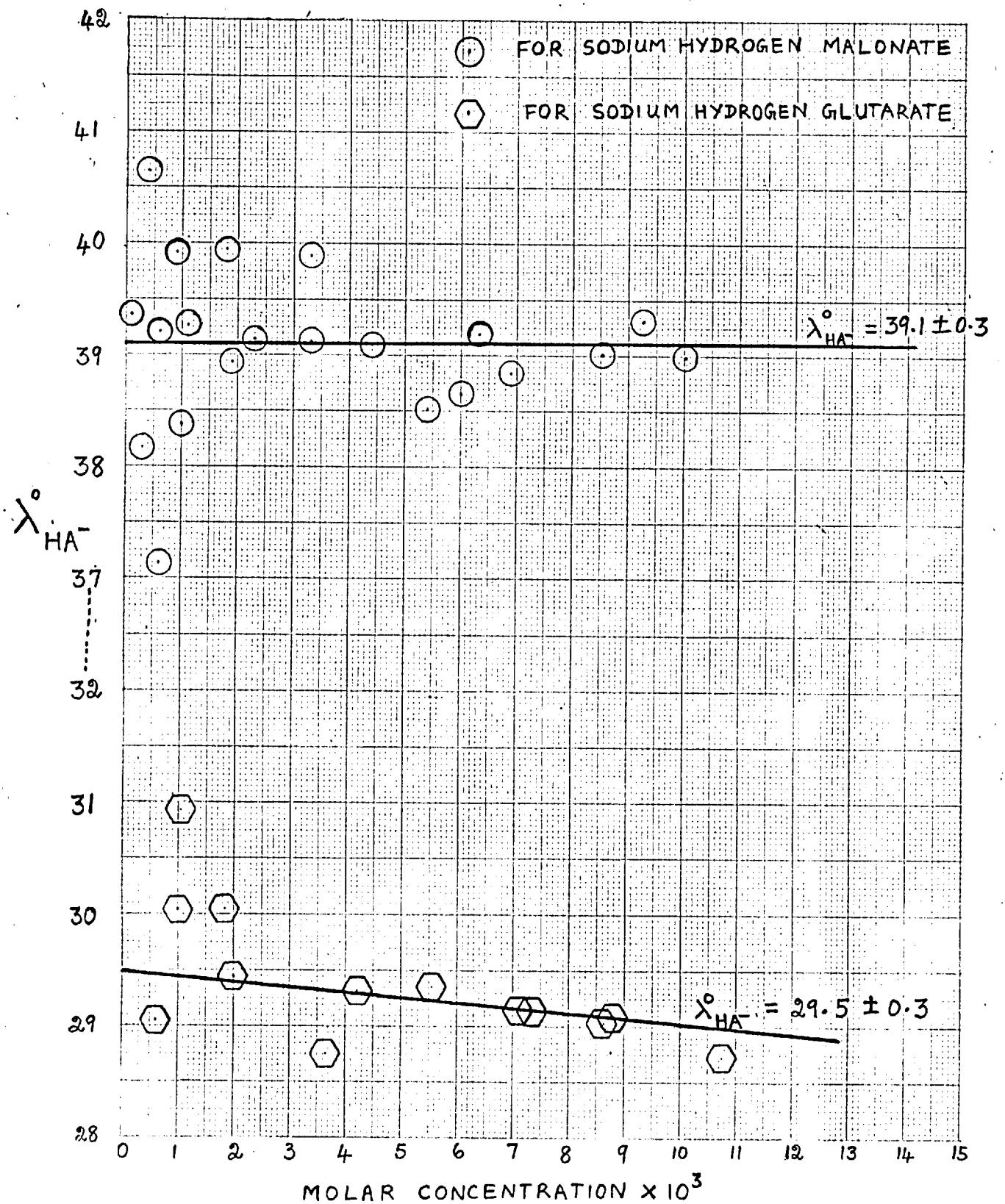

FOR SODIUM HYDROGEN MALONATE
FOR SODIUM HYDROGEN GLUTARATE
$\lambda^{\circ}_{HA^-} = 39.1 \pm 0.3$
$\lambda^{\circ}_{HA^-} = 29.5 \pm 0.3$
$\lambda^{\circ}_{HA^-}$
42
41
40
39
38
37
32
31
30
29
28
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
MOLAR CONCENTRATION X 10^3

FIG. 1

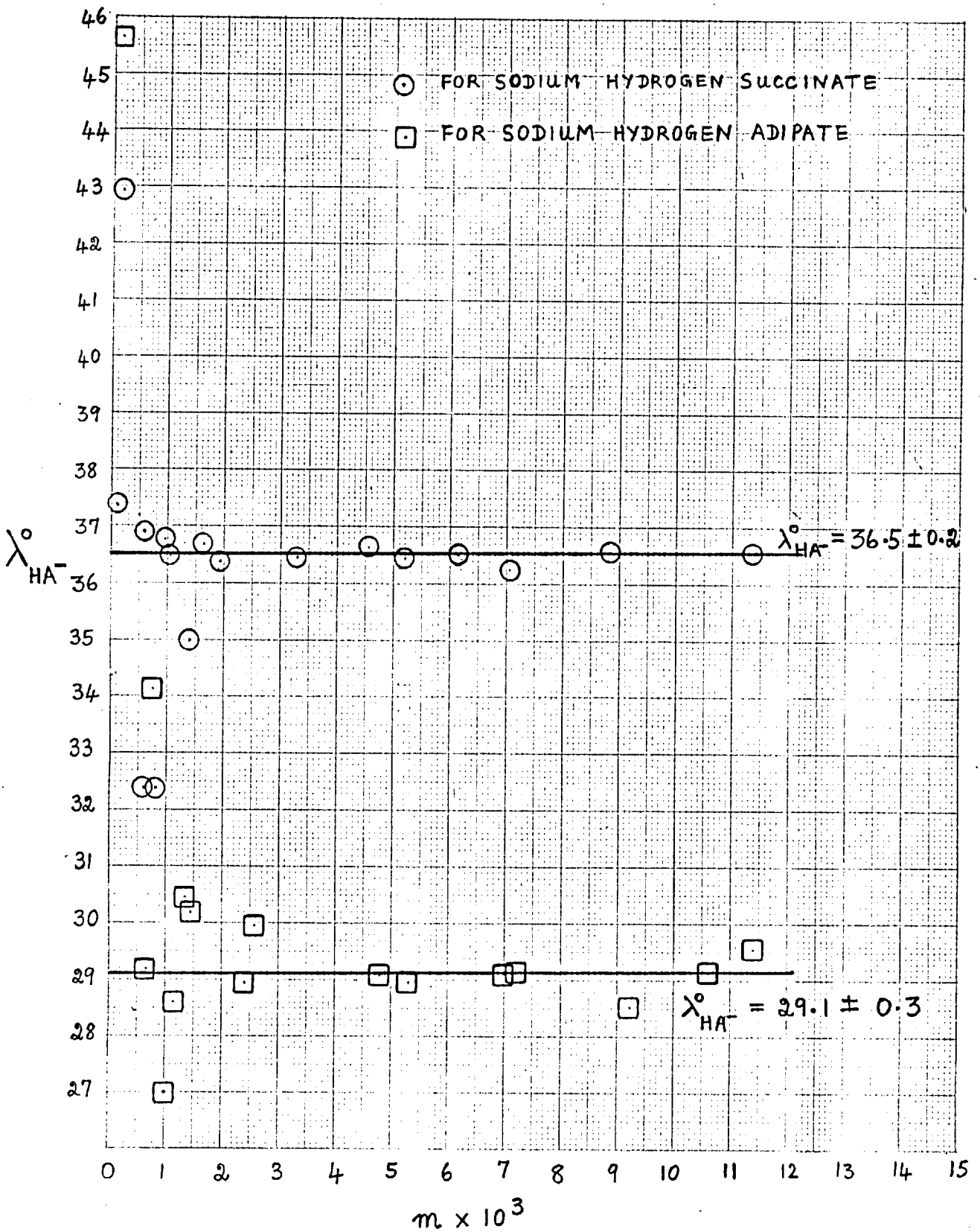

FOR SODIUM HYDROGEN SUCCINATE
FOR SODIUM-HYDROGEN ADIPATE
$\lambda^\circ_{HA^-}$
$\lambda^\circ_{HA^-} = 36.5 \pm 0.2$
$\lambda^\circ_{HA^-} = 29.1 \pm 0.3$
46
45
44
43
42
41
40
39
38
37
36
35
34
33
32
31
30
29
28
27
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
$m \times 10^3$

FIG. 2

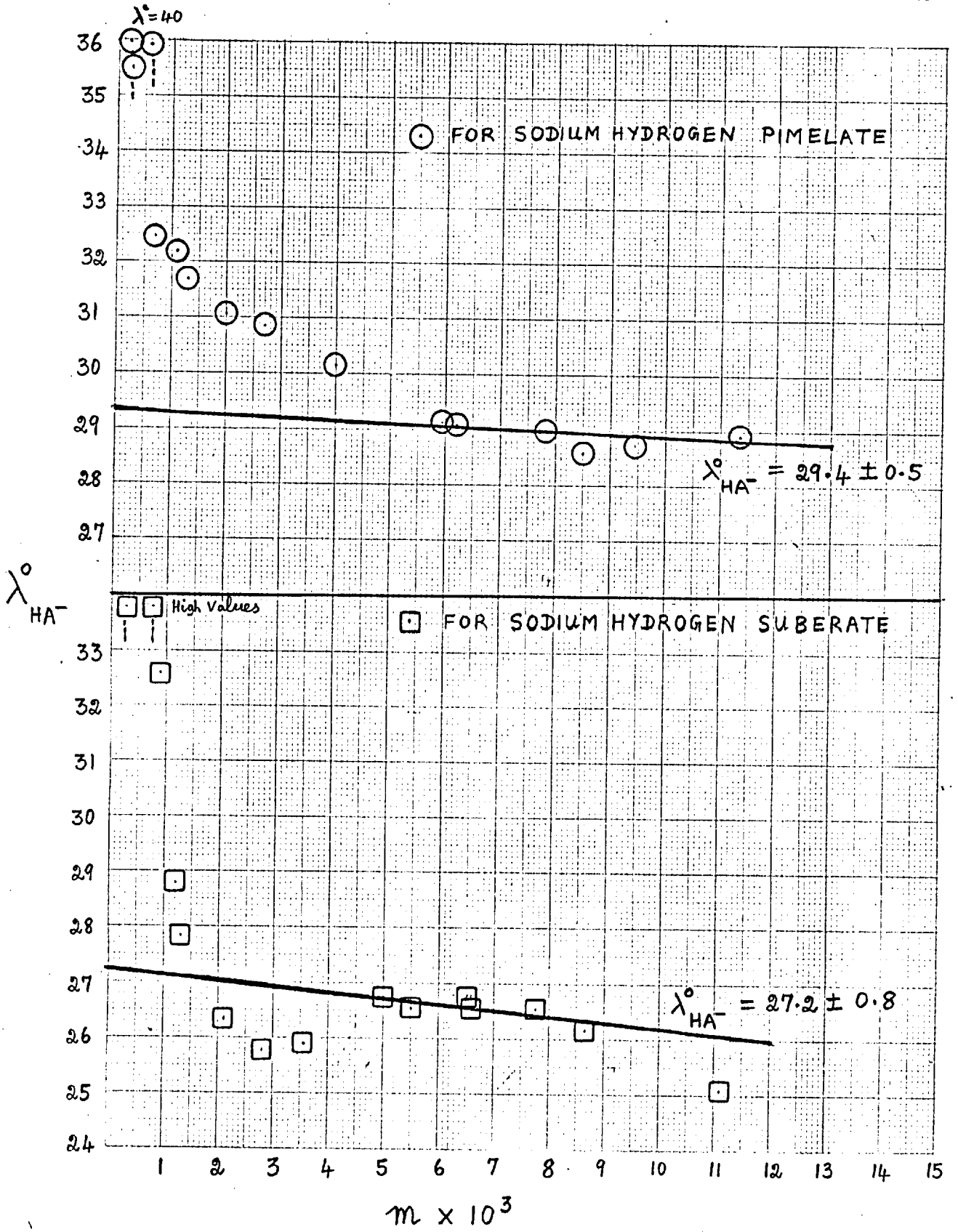

λ°=40
36
35
34
33
32
31
30
29
28
27
FOR SODIUM HYDROGEN PIMELATE
λ°HA⁻ = 29.4 ± 0.5
λ°HA⁻
High Values
FOR SODIUM HYDROGEN SUBERATE
33
32
31
30
29
28
27
26
25
24
λ°HA⁻ = 27.2 ± 0.8
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
m x 10³

FIG. 3

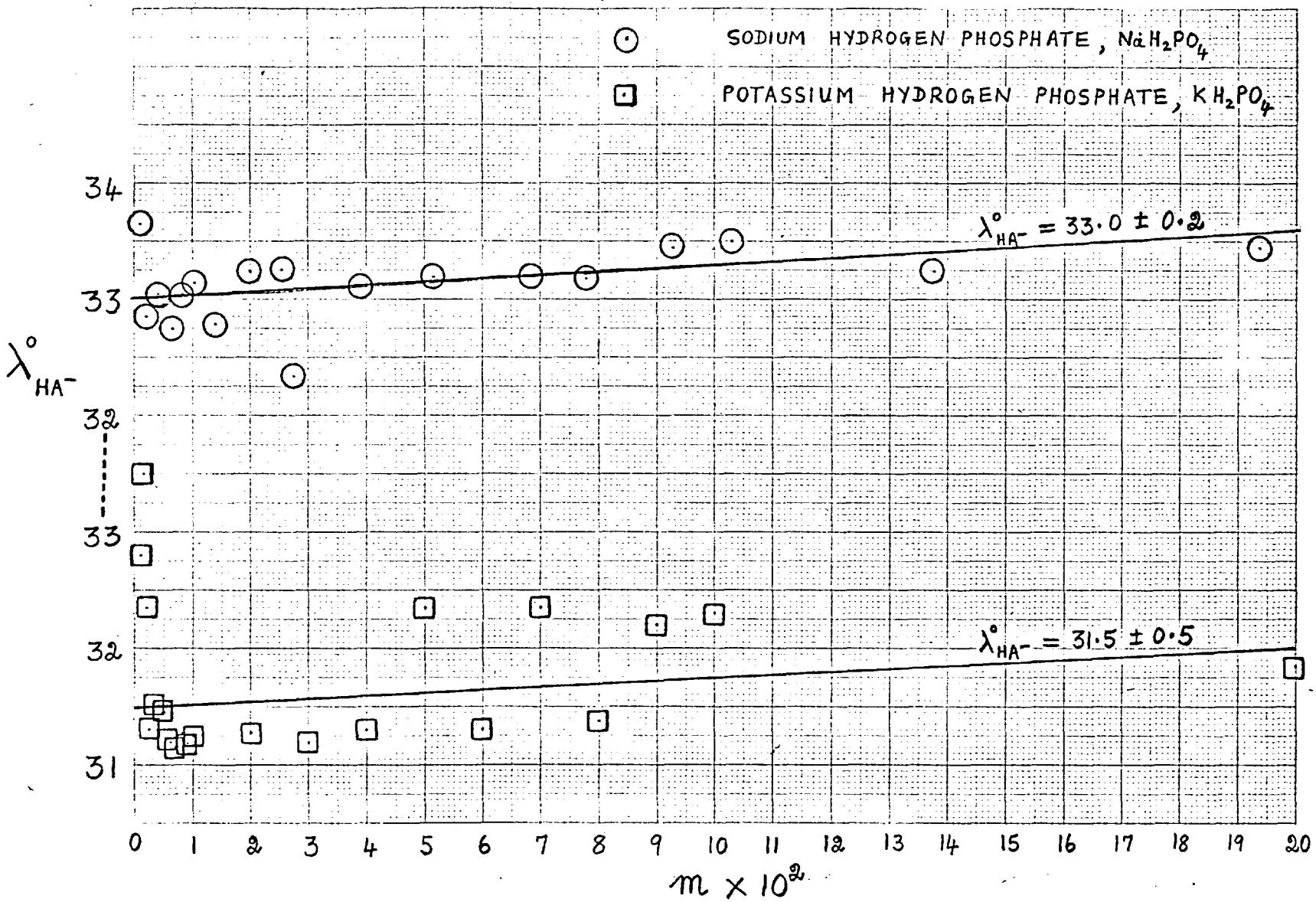

SODIUM HYDROGEN PHOSPHATE, NaH_2PO_4
POTASSIUM HYDROGEN PHOSPHATE, KH_2PO_4
$\lambda^\circ_{HA^-} = 33.0 \pm 0.2$
$\lambda^\circ_{HA^-} = 31.5 \pm 0.5$
$\lambda^\circ_{HA^-}$
$m \times 10^2$
34
33
32
33
32
31
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

FIG. 4

2. $\lambda^{o}_{HA^-}$ FROM CONDUCTANCE MEASUREMENTS ON THE ACID.

2.1. Introduction.

To obtain $\lambda^{o}_{HA^-}$ from conductance measurements on an acid (H_2A) it is necessary first to correct for any secondary dissociation and then to extrapolate the results to infinite dilution. For correcting the conductance due to secondary dissociation, values for the second dissociation constant and $\lambda^{o}_{A^{--}}$ are necessary. Obtaining $\lambda^{o}_{A^{--}}$ from conductance data on the disodium salts presents a difficulty in that $\lambda^{o}_{HA^-}$ values should be known so as to allow for the hydrolysis reaction $A^{--} + H_2O \rightleftharpoons HA^- + OH^-$. It is therefore necessary either to make some fairly arbitrary assumptions regarding their magnitude or to have accurate conductance data on both the salt and the acid in which case self-consistent values for $\lambda^{o}_{HA^-}$ and $\lambda^{o}_{A^{--}}$ may be obtained by successive approximations.

2.2. The Fuoss - Shedlovsky extrapolation.

The usual method of extrapolating conductance data, after correcting for any secondary dissociation, has been to use the Fuoss and Kraus[21] or Shedlovsky[22] graphical extrapolation procedure. Both these methods are based on the Ostwald dilution equation

$$K = \Lambda^2 m / \Lambda^{o}(\Lambda^{o} - \Lambda)$$

but take into account the effect of interionic attraction upon the conductances and activities of the ions. In these methods both K and Λ^{o} are obtained from a suitable plot based on the acid conductance data. For example, the Shedlovsky extrapolation function is given by[23]

$$\Lambda S(Z) = \Lambda^{o} - m\Lambda^{2}S(Z)^{2}f_{\pm}^{2}/K\Lambda^{o} \qquad (10)$$

where $S(Z) = \left[\frac{Z}{2} + \sqrt{1 + (\frac{Z}{2})^{2}}\right]^{2}$ and $Z = S_{(\Lambda)}\sqrt{\Lambda m}/(\Lambda^{o})^{3/2}$.

From the final plot of $\Lambda S(Z)$ against $m\Lambda^{2} S(Z)^{2}f_{\pm}^{2}$, K and Λ^{o} can be obtained from the gradient and the intercept. These methods, though widely used, have a number of disadvantages:-

(i) The derivation of the Fuoss and Kraus equation assumes that the Debye-Hückel-Onsager limiting law applies to the ions in solution. The Shedlovsky procedure is based on the equation

$$\Lambda = \alpha\Lambda^{o} - \frac{\Lambda}{\Lambda^{o}} S_{(\Lambda)}\sqrt{\alpha m} \qquad (11)$$

which is the limiting law worked out in terms of the resistance of the solution. Shedlovsky[22] has observed that equation (11) reproduces conductance data to somewhat higher concentrations than does the limiting law. These equations would be expected to apply only to very dilute solutions and conductance measurements are therefore needed at very low concentrations where the experimental technique is more difficult and the results are less reliable.

(ii) The method is not applicable for all electrolytes. It has been shown[24] that when K is less than about 10^{-5} the method breaks down because of the long extrapolations involved. There is also reason to believe that the method becomes unreliable for slightly associated electrolytes,[25] e.g. when K is greater than about 0.1, because it then becomes very sensitive to the form of the conductance equation employed.

(iii) The plot of $S(Z)$ against $m\Lambda^{2}S(Z)^{2}f_{\pm}^{2}$ does not, in general, give Λ^{o} to better than one conductance unit.

In spite of these limitations the Fuoss-Shedlovsky type of extrapolation has been widely used since it provided the only method for simultaneously determining Λ^{o} and K from the same conductance data on the weak electrolyte. It is moreover the only method for determining these quantities for electrolytes in solvents of low dielectric constant since the alternative procedure, the external method[25], which also requires conductance data on fully dissociated salts, is not applicable.

2.3. A new procedure for simultaneously obtaining K and Λ^{o}.

(a) The method

A new method for simultaneously getting K and Λ^{o} is suggested by the author which has some advantages over the Fuoss and Kraus or the Shedlovsky procedures. This method which at the same time corrects for secondary dissocation is as follows. A diprotic acid (H_2A) can undergo both primary and secondary dissociation to give the following equilibria:-

$$H_2A \rightleftharpoons H^+ + HA^- \qquad (12)$$

$$HA^- \rightleftharpoons H^+ + A^{--} \qquad (13)$$

If m is the molar concentration of the acid started with, and α and β the degrees of first and second dissociations respectively, the molar concentrations of the different species at equilibrium are given by $(H_2A) = m(1-\alpha)$, $(H^+) = m(\alpha+\beta)$, $(HA^-) = m(\alpha-\beta)$, and $(A^{--}) = m\beta$. The equations for the first and second dissociation constants then become

$$K_1 = \frac{(H^+)\,(HA^-)\,f_{\pm}^{2}}{(H_2A)} = \frac{m(\alpha+\beta)\,(\alpha-\beta)\,f_{\pm}^{2}}{(1-\alpha)} \qquad (14)$$

$$K_2 = \frac{(H^+)\ (A^{--})\ f_{H^+}\ f_{A^{--}}}{(HA^-)\ f_{HA^-}} = \frac{m(\alpha+\beta)\beta\ f_{A^{--}}}{(\alpha-\beta)} \qquad (15)$$

Rearrangement of equations (14) and (15) and putting $\frac{K_1}{mf_{\pm}^2} = K'$ gives

$$\alpha^2 + K'\alpha - (K' + \beta^2) = 0 \qquad (16)$$

and

$$\beta = \frac{K_2(\alpha-\beta)}{mf_{A^{--}}(\alpha+\beta)} \qquad (17)$$

f_i is given by equation (4) and therefore at any given concentration m self-consistent values for α, β and f_i may be obtained from equations (16), (17) and (4) provided K_2 is known and a value for K_1 has been provisionally assumed. The method of solving involves iteration and is carried out by the same procedure as for the salt.

The next step is to consider the conductances of the ions concerned. The equivalent conductances of the H^+ and A^{--} ions in any particular solution may be estimated from known $\lambda^o_{H^+}$ and $\lambda^o_{A^{--}}$ values by correcting for interionic attraction. Any desired equation (e.g. equation (8)) may be used for this purpose and an appropriate one may be obtained by taking into consideration the concentration range of the experimental conductance data and the size of the ions constituting the electrolyte. The specific conductances due to the H^+ and A^{--} ions can then be calculated using equation (9).

The experimental specific conductance of the solution can be assumed to be additively composed of the specific conductivities due to the H^+, A^{--} and HA^- ions and subtraction of the contributions due to the H^+ and A^{--} ions from the experimental conductance will therefore give the

specific conductance due to the HA^- ions. $\lambda^o_{HA^-}$ may then be obtained using equation (9) and then (8). The University of London "Mercury" computer was used to determine the $\lambda^o_{HA^-}$ values at the various concentrations. The computer programme used is given in Appendix II.

Within the concentration range for which the equations for λ_i and f_i are applicable, tho $\lambda^o_{HA^-}$ values so obtained should be independent of concentration provided that the correct K_1 value has been used for calculating the ionic concentrations of the different species. Had a smaller K_1 been used, lower values would have been predicted, in any given solution, for (H^+) and (A^{--}) and therefore for k_{H^+} and $k_{A^{--}}$. Subtraction of k_{H^+} and $k_{A^{--}}$ from the experimental specific conductance would therefore lead to a higher result for $\lambda^o_{HA^-}$. The significant fact, however, is that this effect becomes more and more important as the concentration of the solution is increased provided α is not too small compared with 1. In cases when α is negligible compared with unity,

$$K_1 = \frac{\alpha^2 m f_\pm^2}{1-\alpha} \doteq \alpha^2 m \; ; \quad \therefore \alpha = \sqrt{\frac{K_1}{m}}$$

$$\Lambda^o \doteq \frac{\Delta}{\alpha} \doteq \frac{\Lambda\sqrt{m}}{\sqrt{K_1}} \qquad (18)$$

Therefore Λ^o is uniformly high, with very little trend, if K_1 is low. On the other hand when α approaches unity

$$K_1 \doteq \frac{m}{1-\alpha} \; , \quad \therefore \alpha = 1 - \frac{m}{K}$$

$$\Lambda^o \doteq \frac{\Delta}{\alpha} \doteq \Lambda\left(1 + \frac{m}{K_1}\right) \qquad (19)$$

Too low a value for K_1 therefore gives Λ^o rising linearly with increasing

concentration. A plot of $\lambda^{o}_{HA^-}$ against μ would therefore show a positive gradient. On the other hand had too high a K_1 value been used the specific conductance of the solution would have been "overcorrected" for H^+ and A^{--} ions and $\lambda^{o}_{HA^-}$ would decrease with increasing ionic strength.

Determination of the values for K_1 and $\lambda^{o}_{HA^-}$ therefore depends on choosing a value for K_1 which gives $\lambda^{o}_{HA^-}$ values which do not show a trend with concentration.

(b) Comparison with the Fuoss-Shedlovsky extrapolation.

The main improvements of this method over the Fuoss-Shedlovsky type of extrapolation are that

(i) any chosen equations may be used to correct for the influence of the ionic strength on the activities and on the conductances of the ions, and

(ii) unlike in the Shedlovsky plot where essentially the experimental conductivity values are extrapolated graphically to infinite dilution, the suggested method treats each conductance point independently.

The method will be illustrated and compared with the Shedlovsky extrapolation procedure using malonic acid as an example. Malonic acid was selected because

(a) conductance data are available[26] over the concentration range 0.0001 to 0.01M ,

(b) its dissociation constants ($K_1 = 1.424 \times 10^{-3}$, $K_2 = 2.013 \times 10^{-6}$) have recently been determined[11] by an independent method (e.m.f.) so that K from conductance can be compared,

(c) the second dissociation constant is relatively small and any uncertainties in K_2 or $\lambda^{o}_{A^{--}}$ will not significantly affect the results,

(d) its K_1 value is within the range in which the extrapolation procedure is considered to be reliable.

The results obtained by the present method are given in Fig. (7) where $\lambda^o_{HA^-}$ is plotted against μ for 10^3K_1 values of 1.42, 1.36 and 1.30. The Güntelberg expression for activity coefficients (equation (7)) and the modified Robinson and Stokes equation for conductance (equation (8)), in both of which $\overset{o}{a}$ is assumed to be about 3 angstroms, were used during the calculations. The graphs show that a K_1 value of 1.36×10^{-3} and $\lambda^o_{HA^-}$ of 40.4 are indicated by this method. The Shedlovsky plot for the same data is given in Fig. (8) and gives $K_1 = 1.28 \times 10^{-3}$ and $\lambda^o_{HA^-} = 48$. The K_1 values obtained by both methods are different to those determined from e.m.f.. The experimental errors in the conductances are clearly brought out in Fig. (7) which also shows that the results are relatively unreliable below an ionic strength (μ) of 0.001. The Shedlovsky plot, in addition to being very insensitive, has the limitation of relying mainly on the relatively inaccurate results at the lower concentrations. It is, however, difficult quantitatively to compare the two methods in this particular case, because of the relatively large errors in the conductances causing scatter in the $\lambda^o_{HA^-}$ values.

Another advantage of the present method is that it should be applicable to all weak electrolytes. Belcher[27] has shown that the Fuoss extrapolation method may give figures for Λ^o and K that are seriously in error if $K < 10^{-5}$. This conclusion was also reached on theoretical grounds by Kilpatrick[28] by examining the accuracy necessary for the experimental conductance data in order to get a reliable value for K. This

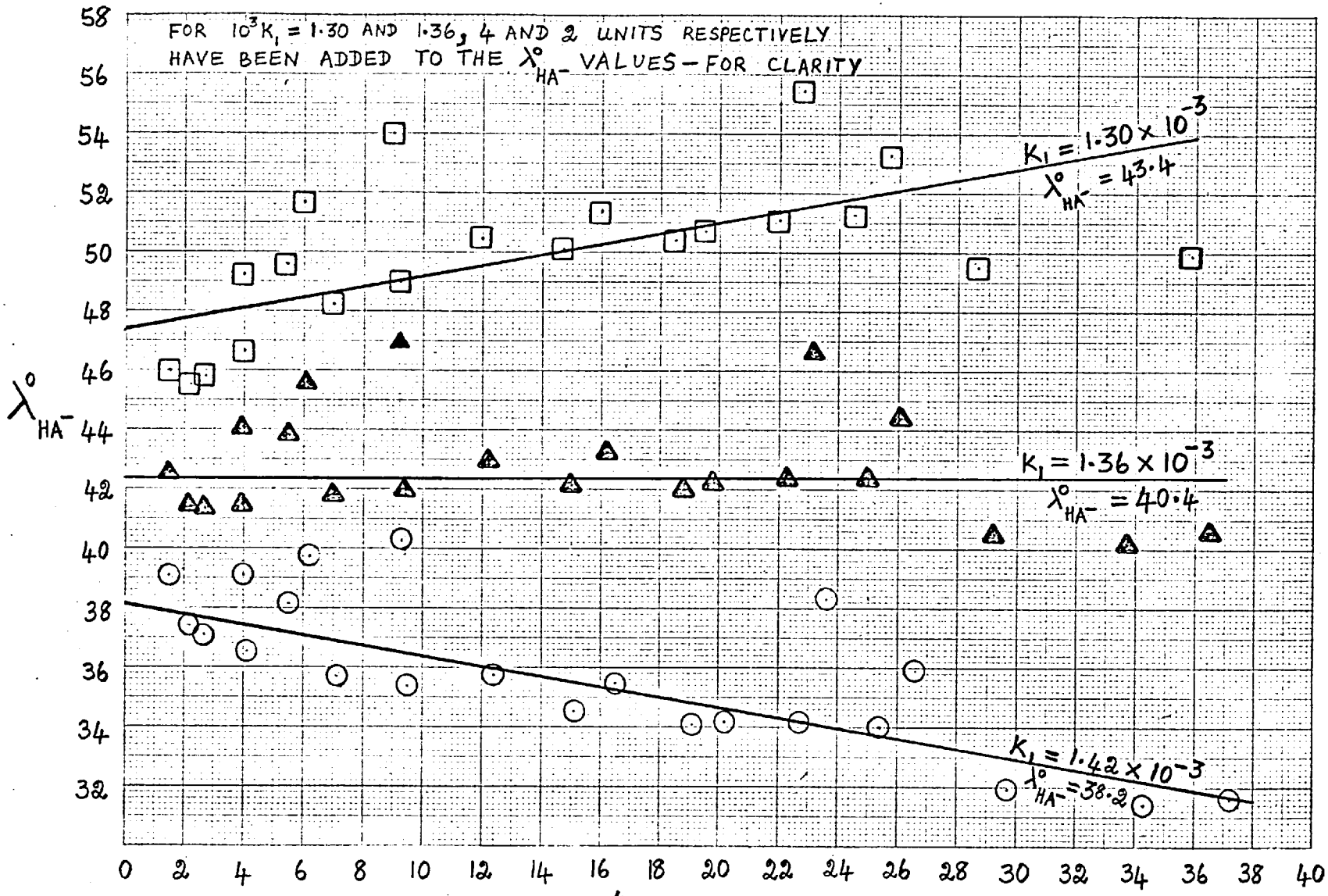


FIG. 7 – MALONIC ACID

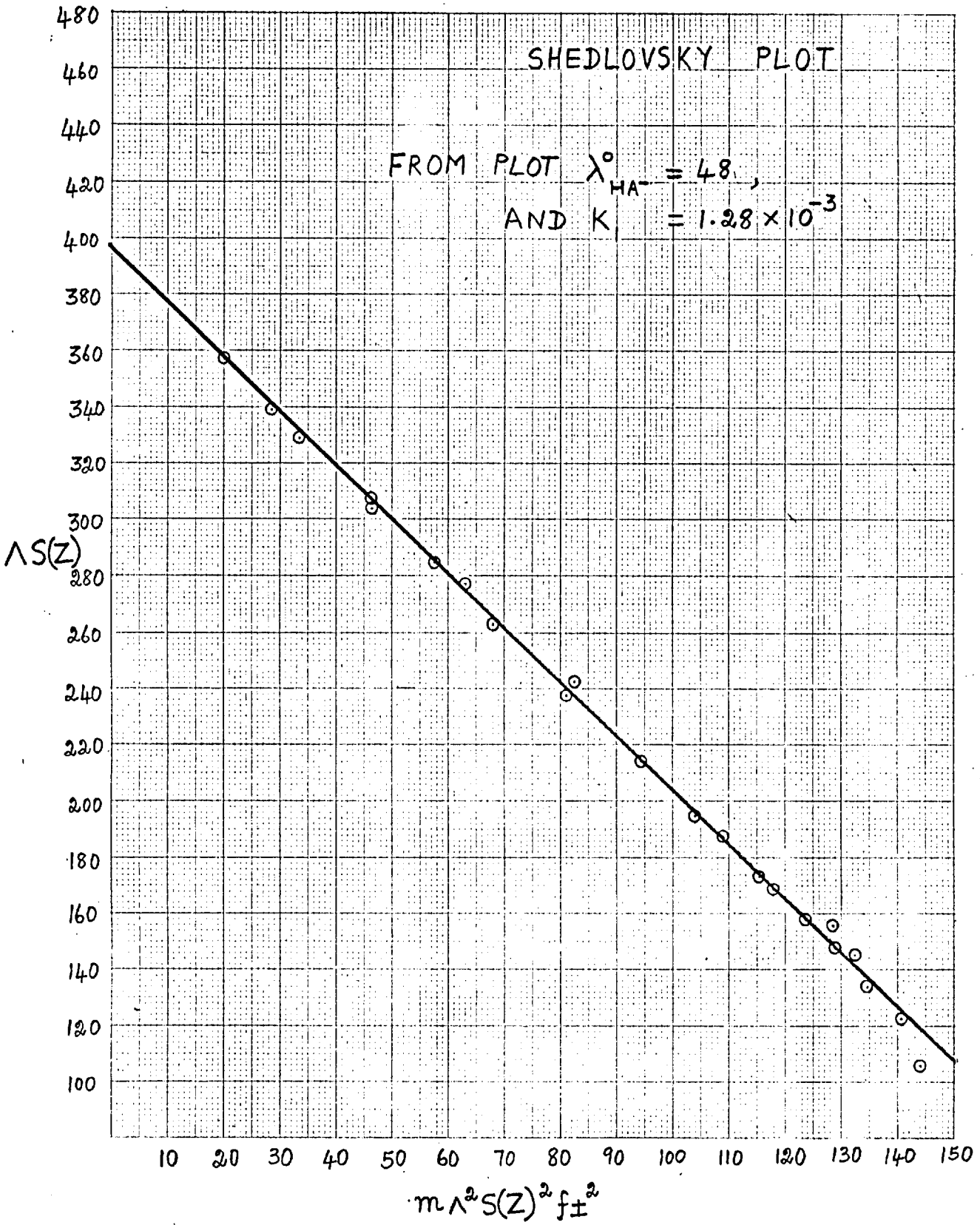


FIG. 8 — MALONIC ACID

limitation arises from the necessity for long extrapolation. The values obtained by Belcher using the extrapolation method are compared with those determined by other methods for some weak acids in the following table.

Acid	Fuoss extrapolation method[27]		External method		e.m.f.	
	K	λ^{o}_{HA}-(or λ^{o}_{A}-)	K	λ^{o}_{HA}-	K	
Acetic acid	1.705×10^{-5}	45.5	1.753×10^{-5}	40.91[29]	1.75×10^{-5}	[30]
Propionic acid	1.337×10^{-5}	36.5	1.343×10^{-5}	35.7[27]	-	
Carbonic acid	3.65×10^{-7}	74.2	4.31×10^{-7}	44.5[31]	4.5×10^{-7}	[32]

Taking, say, acetic acid as an example there seems to be very strong evidence for a value of K of 1.75×10^{-5} and $\lambda^{o}_{A^-}$ of 40.9 and the Fuoss extrapolation method therefore gives values for K and $\lambda^{o}_{OAc^-}$ that are out by about 3% and 10% respectively. The present method, however, does not suffer from the disadvantage of a long extrapolation and in fact the extrapolation becomes shorter the weaker the electrolyte. This is illustrated in the plot for acetic acid in Fig. (9) and it can be seen that the K and $\lambda^{o}_{OAc^-}$ values are in good agreement with those obtained by the e.m.f. and external methods.

2.4. Determination of λ^{o}_{HA}- when K is known from independent data.

(a) Results

Even when reliable K values are available from e.m.f. data the usual procedure has been to evaluate Λ^{o} using the Shedlovsky plot. The

new procedure suggested would, however, give this quantity with far greater accuracy. Using the e.m.f. value for K_1, $\lambda^{o}_{HA^-}$ may be calculated at the various concentrations. If these show a trend with concentration it indicates the necessity for some type of correction (see later) and extrapolating a plot of $\lambda^{o}_{HA^-}$ against μ would do this, at least partially, and give a better value for the required ion conductance at infinite dilution.

It is instructive to apply the method, in the first instance, to monocarboxylic acids and this has been done for acetic and benzoic acids. The results are given in Figures (9) and (10). Acetic acid was selected because it furnishes a classic example of conductance measurements of very high accuracy, and benzoic acid because several independent measurements are available.

The falling off of $\lambda^{o}_{OAc^-}$ in Figure (9) with increasing μ can be quantitatively accounted for by correcting for the effect of viscosity and the presence of $(HOAc)_2$ dimers in solution[33]. The necessity or otherwise of viscosity corrections has been a problem since they have been helpful in certain cases and superfluous in others[34]. The correction has been generally avoided because independent viscosity data are necessary and have not always been available. However, it appears probable that viscosity changes should be allowed for in treating all conductance data and where the correction does not seem to be required complex ions may be present. The theory of viscosity corrections will now be considered in outline since it will be necessary later for a quantitative correction in the case of H_3PO_4.

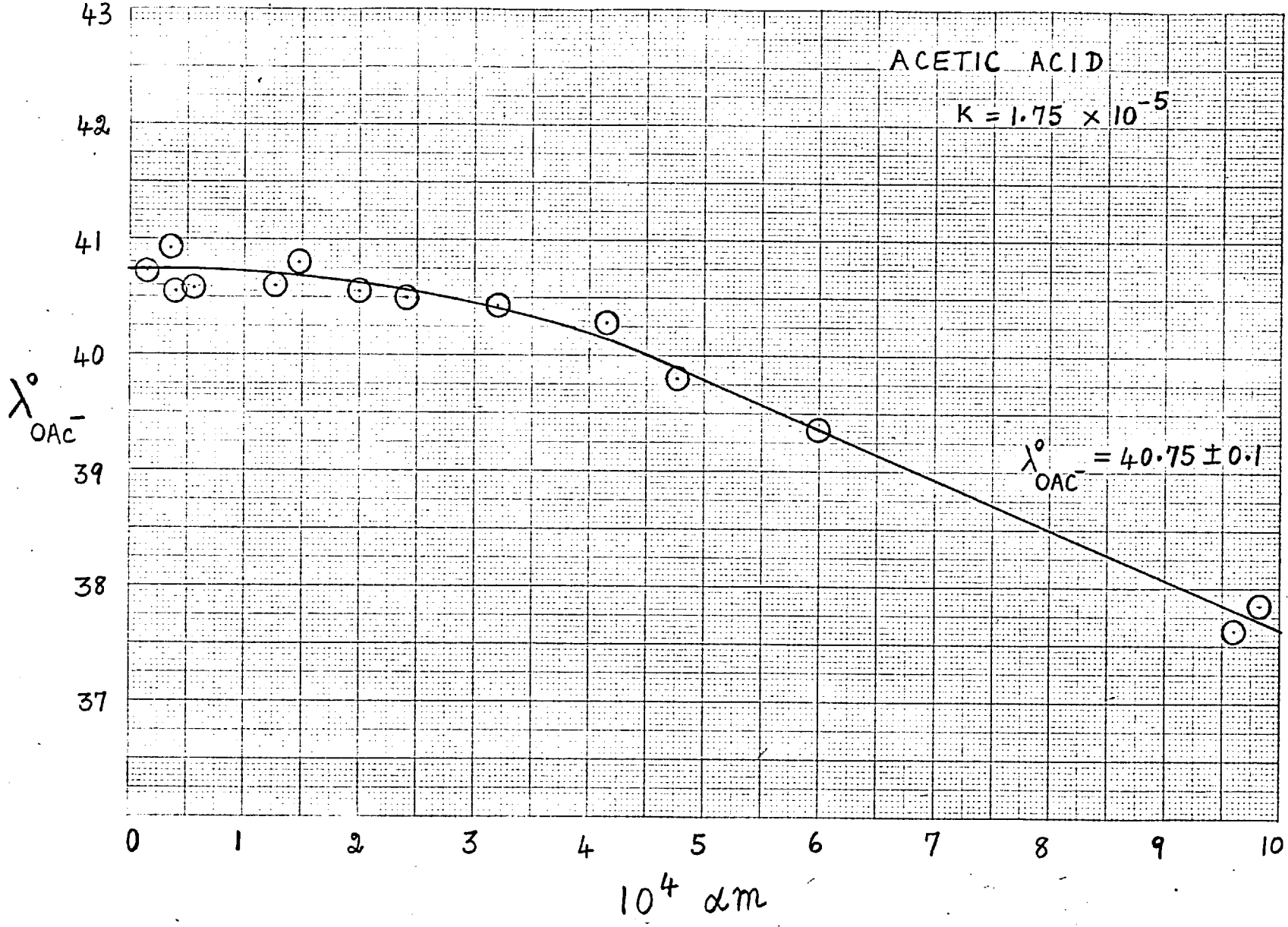

ACETIC ACID
K = 1.75 × 10⁻⁵
λ°OAc⁻ = 40.75 ± 0.1
λ°OAc⁻
43
42
41
40
39
38
37
0
1
2
3
4
5
6
7
8
9
10
10⁴ αm

FIG. 9

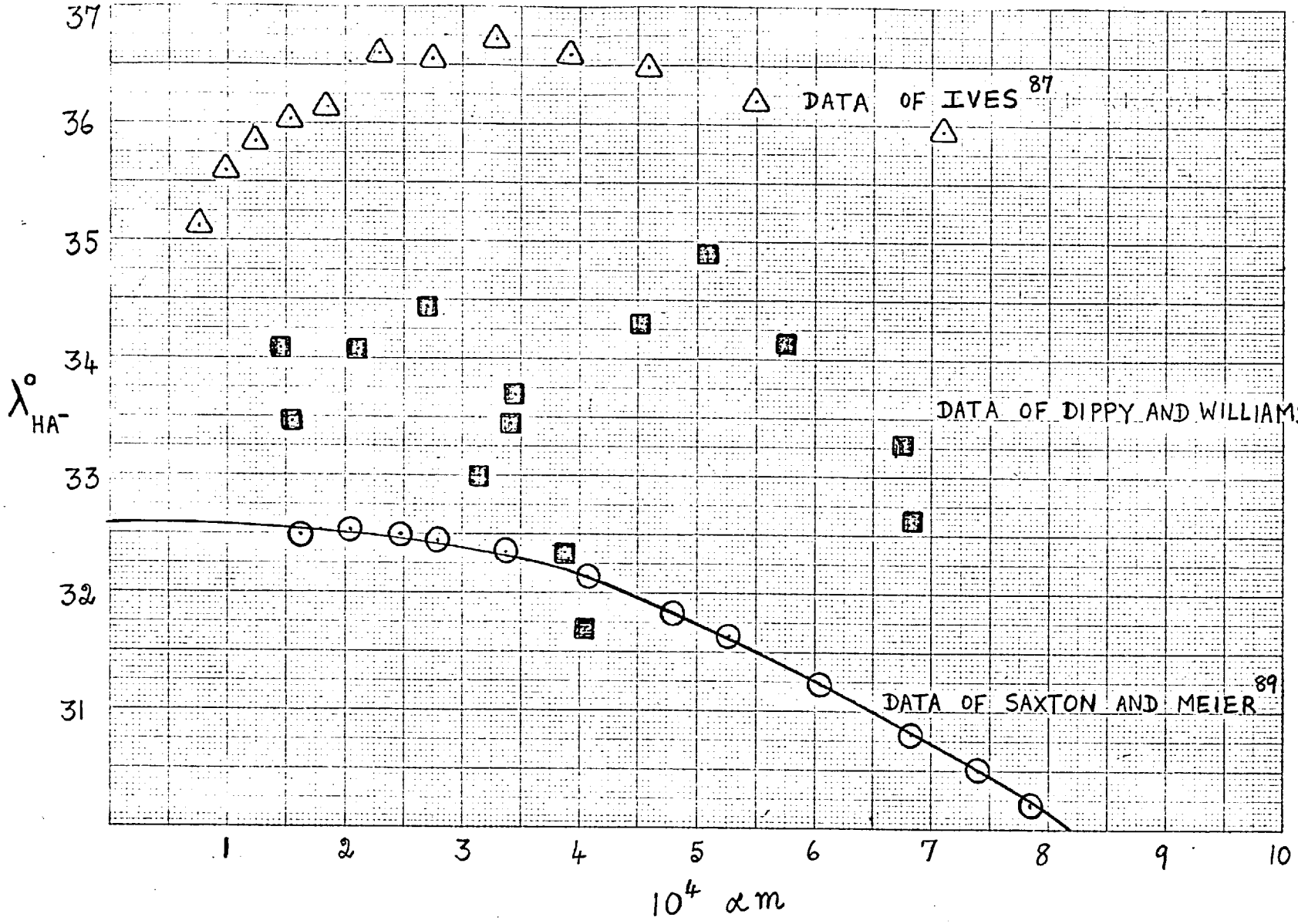


FIG. 10 – BENZOIC ACID 90
$K = 6.28 \times 10^{-5}$

The general equation for viscosity is given by[35]

$$\frac{\eta}{\eta^0} = 1 + S_{(\eta)} \sqrt{\alpha m} + B_i \alpha m + B_u(1-\alpha)m \qquad (20)$$

where η is the viscosity of the solution and η^0 that of the solvent. $S_{(\eta)}$ is the theoretical limiting slope which for aqueous solutions of binary electrolytes at 25°C is equal to

$$S_{(\eta)} = \frac{60.6\,\Lambda^0}{320\,\lambda_+^0\,\lambda_-^0}\left[1 - 0.6863\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2\right] \qquad (21)$$

and B_i and B_u are the molar contributions to the relative viscosity due to the ionic species and neutral molecules respectively. B_i is additive for the ions of an electrolyte[40] and may therefore be obtained from viscosity data on fully dissociated salts. B_u can be determined using equation (20) provided viscosity data on the acid are available. According to Walden's rule[36] the conductivity of a solution is inversely proportional to the viscosity of the medium and therefore to correct for the effect of viscosity, conductance data should be multiplied by η/η_0. The interionic forces represented by the term $S_{(\eta)} \sqrt{\alpha m}$ are, however, taken care of in the Debye-Hückel-Onsager conductance equations and therefore the equivalent conductance should be multiplied only by $(1 + B_i \alpha m + B_u(1-\alpha)\, m)$.

The results for benzoic acid given in Fig. (10) are interesting and show the disagreement between the various workers quite clearly. The values obtained from Saxton and Meier's data do not show any scatter and the falling off of λ_A^0 with increasing ionic strength may be accounted for by the correction for viscosity. Since viscosity data are not

available a quantitative correction cannot be made but, by using equation (20) and neglecting the small ionic contributions to the viscosity, a rough estimate may be made of the value of B_u which would account for the decreasing trend. This value is about 0.5 which, though high, seems not unreasonable.

Conductance data have been published only for a few dicarboxylic acids. These have now been used to estimate $\lambda^o_{HA^-}$ using literature values for the dissociation constants. The results for malonic[37], succinic[37], glutaric[37], adipic[37], pimelic[37], suberic[37], tartaric[38] and phosphoric[1] acids are given in Figs. (7), (11), (12), (13), (14), (15), (16) and (17) respectively where $\lambda^o_{HA^-}$ is plotted against $\sqrt{m}$. The scatter in the points give an indication of the accuracy of the conductance data and these seem reasonably reliable only for malonic, succinic, tartaric and phosphoric acids. The full results are therefore given only for these acids (Tables XIV, XV, XVI and XVII.) In all cases the scatter can be seen to be very severe at ionic strengths below 0.002μ.

It can be seen from the Figures that with increasing concentration $\lambda^o_{HA^-}$ values increase for succinic and phosphoric acids, decrease for malonic acid and are virtually constant for tartaric acid. A constant value for $\lambda^o_{HA^-}$ should, however, have been obtained in all cases. This discrepancy must clearly be due to one or more incorrect assumptions which are implicit in the method. These assumptions are:

(i) the K_1 value used is correct,

(ii) no viscosity or other corrections are necessary to the conductance data,

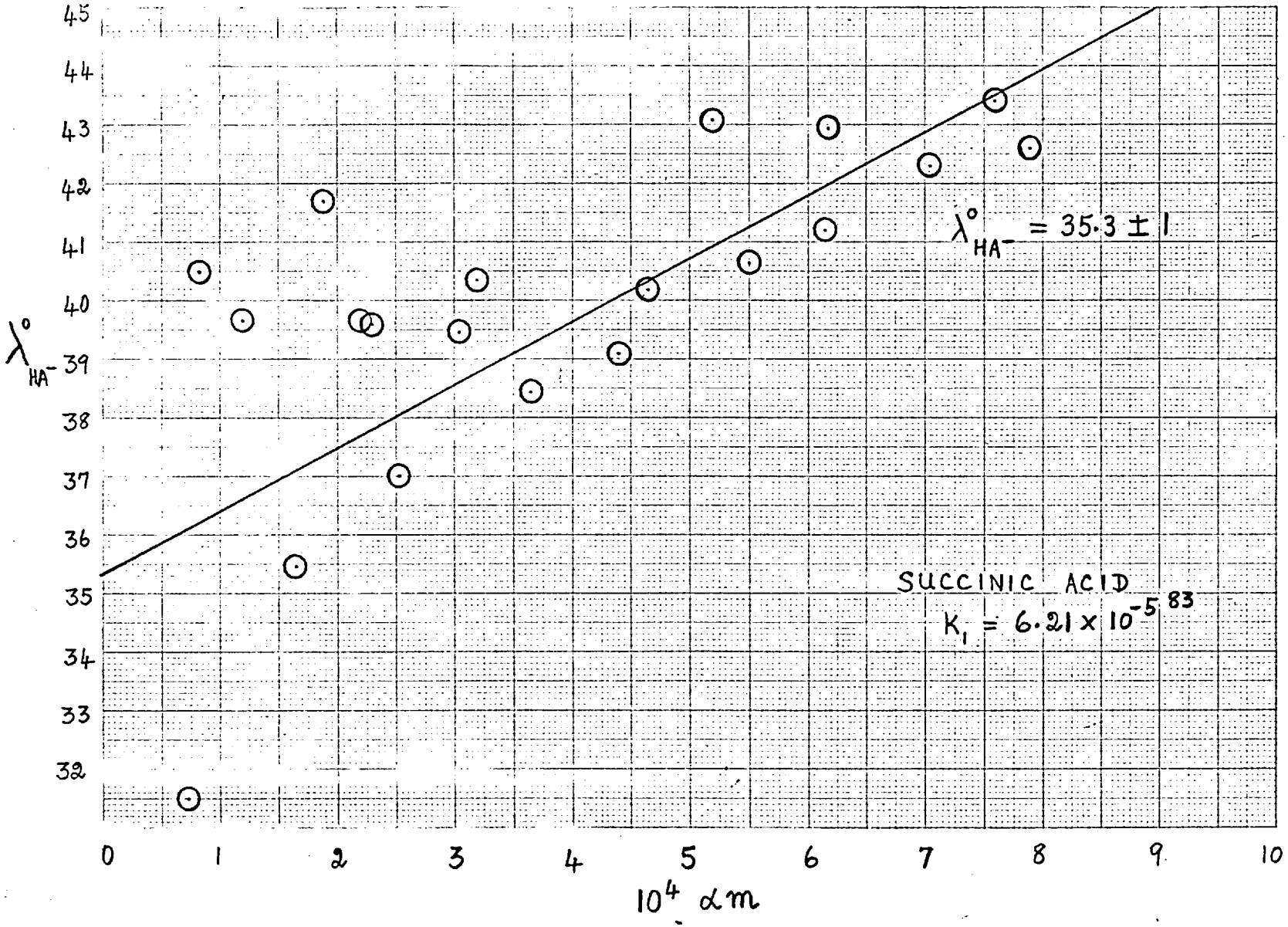
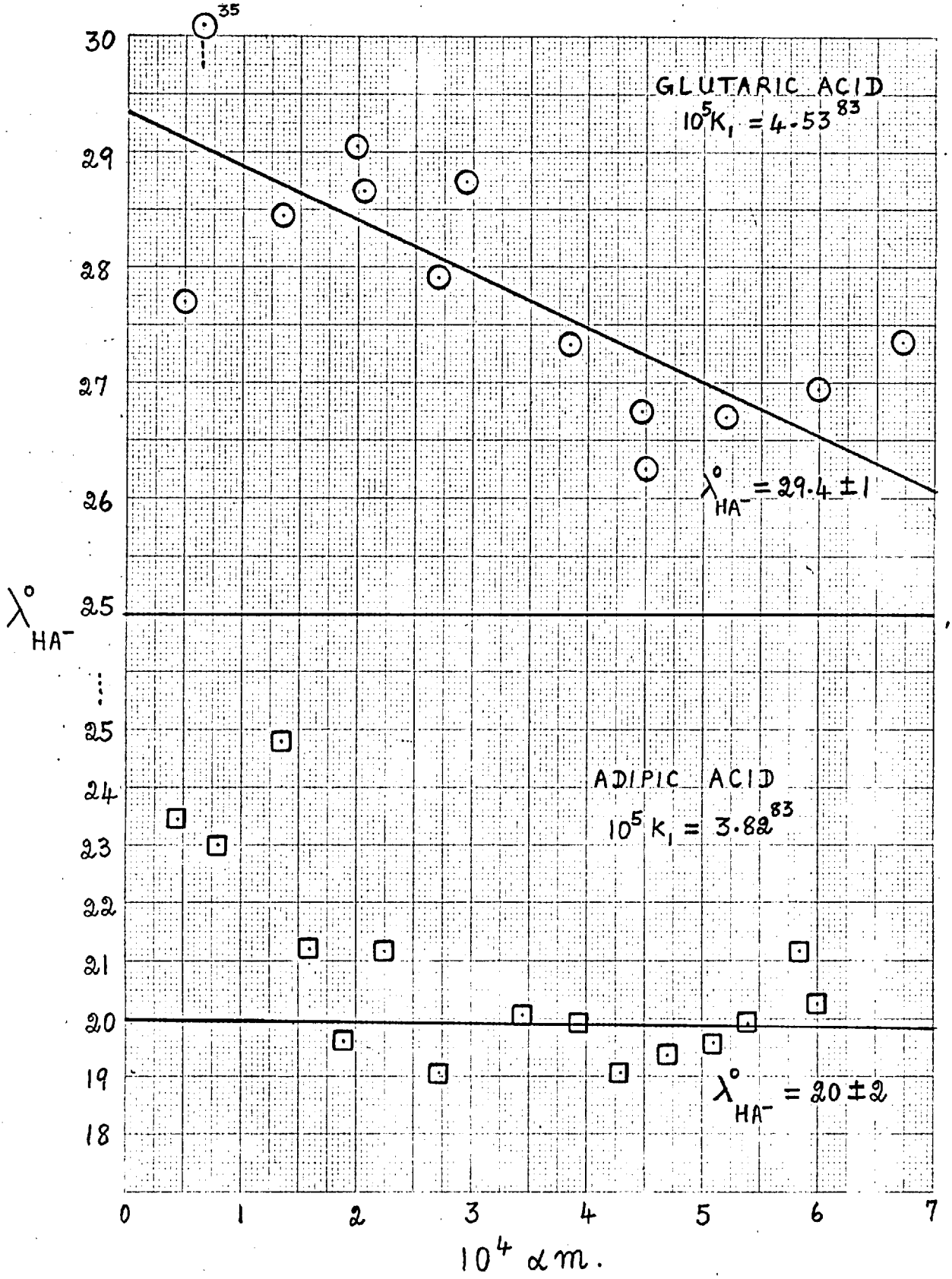
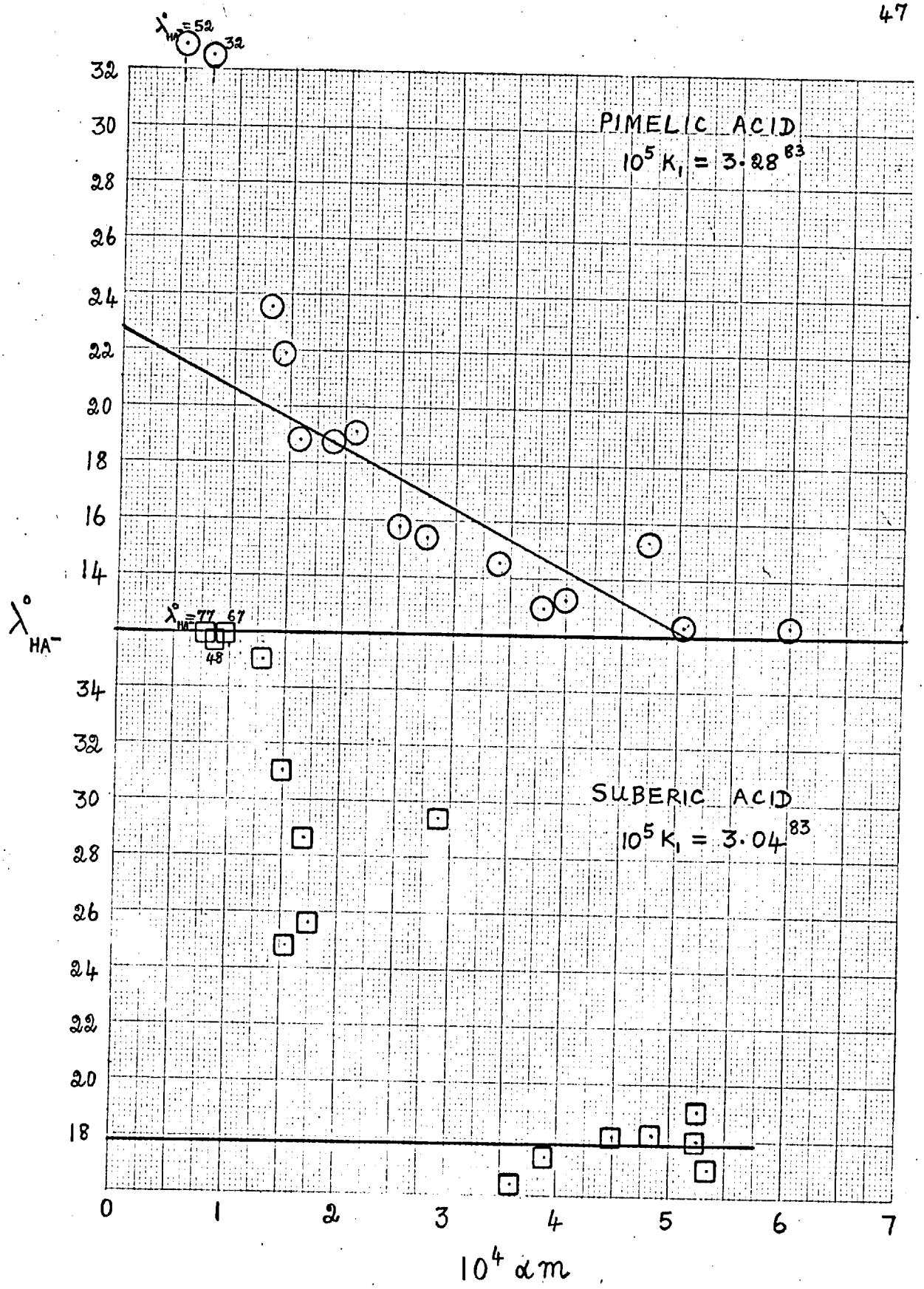

45
44
43
42
41
40
39
38
37
36
35
34
33
32
$\lambda^\circ_{HA^-}$
$\lambda^\circ_{HA^-} = 35.3 \pm 1$
SUCCINIC ACID
$K_1 = 6.21 \times 10^{-5}$ 83
0
1
2
3
4
5
6
7
8
9
10
10^4 αm

FIG. 11


GLUTARIC ACID
$10^5 K_1 = 4.53^{83}$
$\lambda^\circ_{HA^-} = 29.4 \pm 1$
ADIPIC ACID
$10^5 K_1 = 3.88^{83}$
$\lambda^\circ_{HA^-} = 20 \pm 2$
$\lambda^\circ_{HA^-}$
$10^4 \alpha m.$
30
29
28
27
26
25
24
23
22
21
20
19
18
0
1
2
3
4
5
6
7
35

FIGS. 12 & 13.


PIMELIC ACID
$10^5 K_1 = 3.28^{83}$
SUBERIC ACID
$10^5 K_1 = 3.04^{83}$
$\lambda^\circ_{HA^-}$
λ°_{HA}=52
32
λ°_{HA}=77
67
48
$10^4 \alpha m$

FIGS. 14 & 15

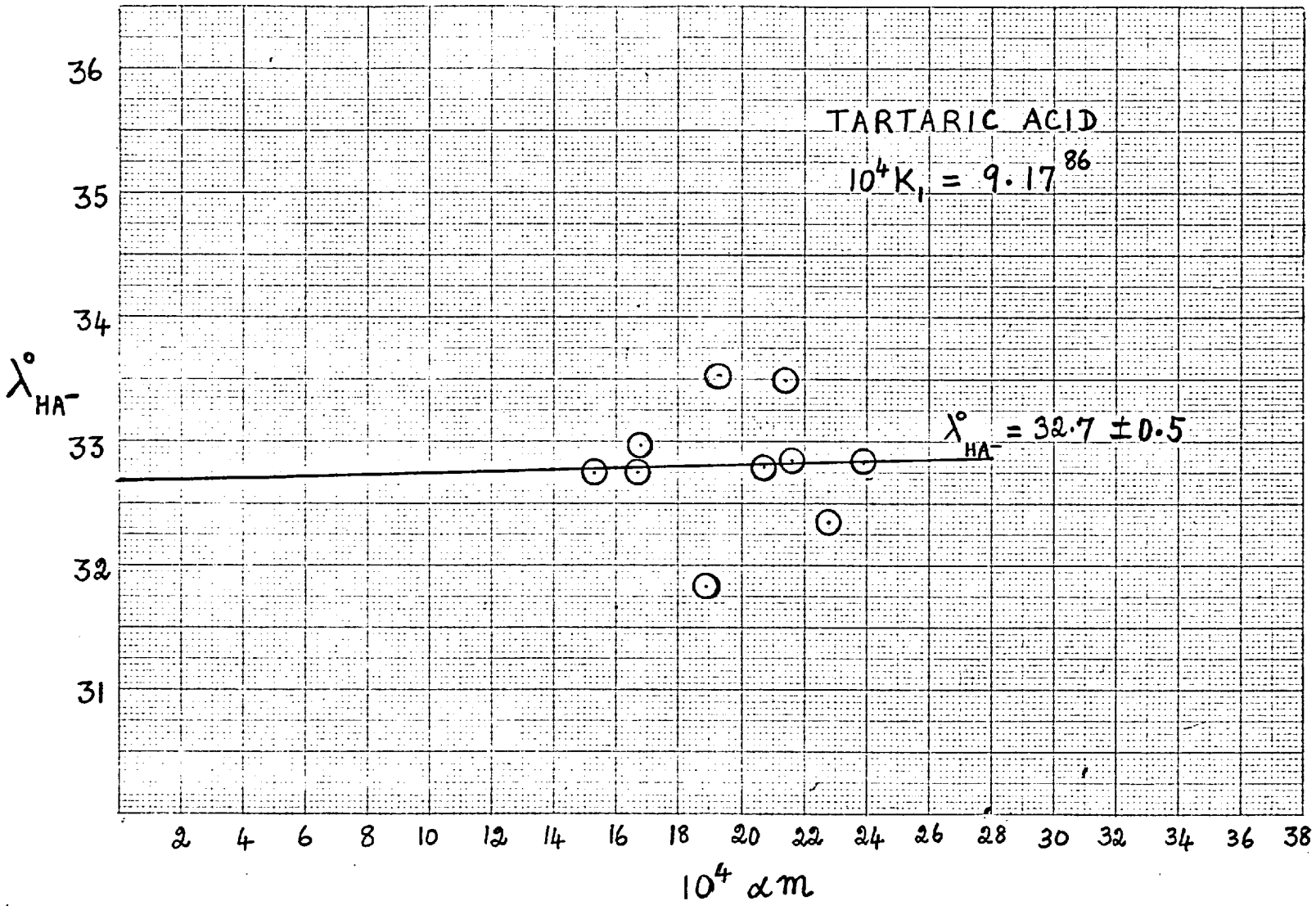

TARTARIC ACID
$10^4 K_1 = 9.17^{86}$
$\lambda^\circ_{HA^-} = 32.7 \pm 0.5$
$\lambda^\circ_{HA^-}$
36
35
34
33
32
31
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38
$10^4 \alpha m$

FIG. 16

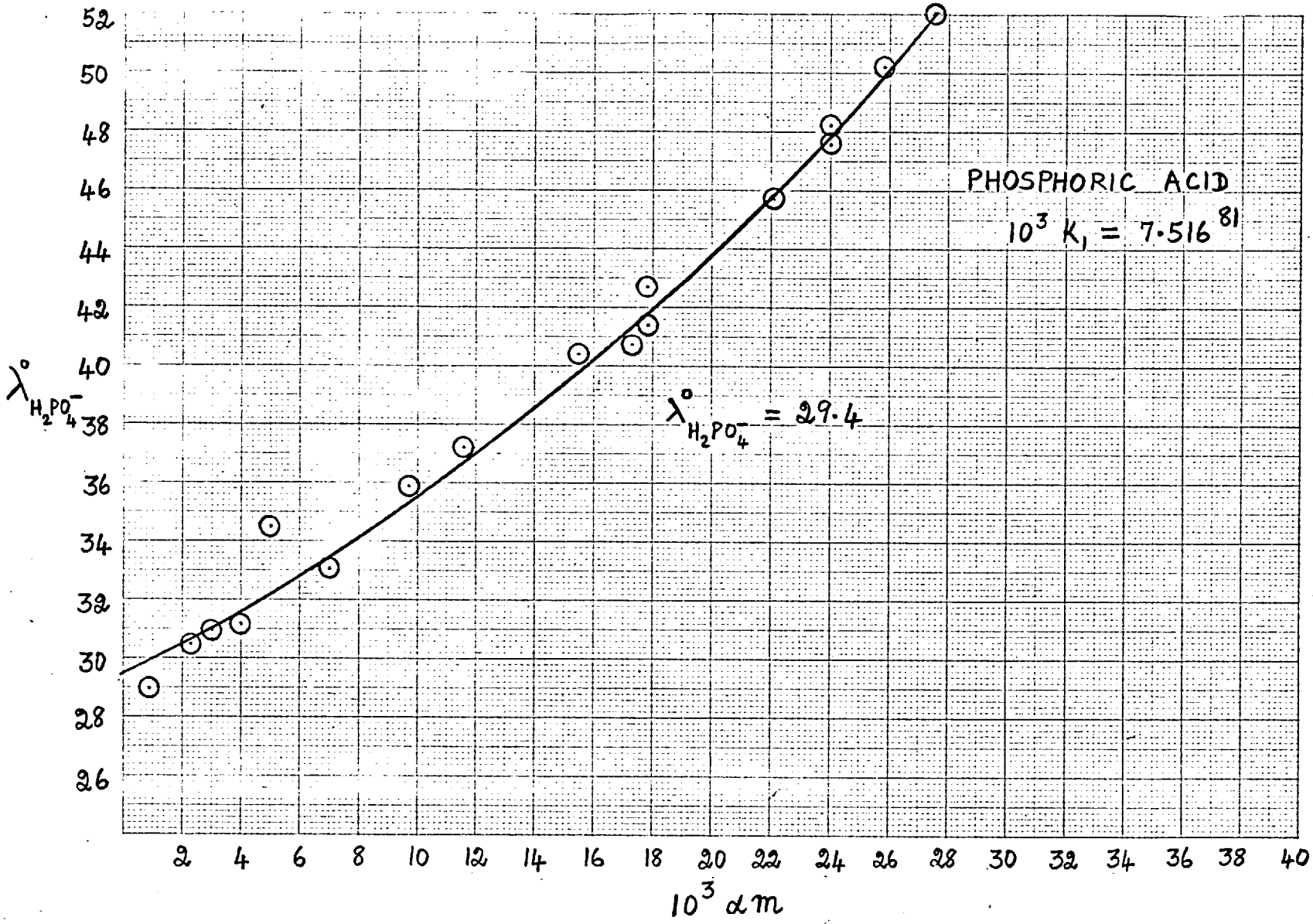

PHOSPHORIC ACID
$10^3 K_1 = 7.516^{81}$
$\lambda^\circ_{H_2PO_4^-} = 29.4$
$\lambda^\circ_{H_2PO_4^-}$
$10^3 \alpha m$
52
50
48
46
44
42
40
38
36
34
32
30
28
26
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40

FIG. 17

Table XIV

Malonic Acid

$10^3K_1 = 1.424^{11}x\ 0.99707^a$, $10^6K_2 = 2.013^{11}x\ 0.99707^a$,

$\lambda^o_{A^{--}} = 64^b$

10^3m	α	$10^3\beta$	$10^6k_{soln.}$	$10^6k_{HA^-}$	$\lambda^o_{HA^-}$
0.1626	0.9082	12.71	58.056	5.618	39.06
0.2550	0.8690	8.278	86.24	8.089	37.43
0.3206	0.8449	6.653	105.05	9.783	37.04
0.5163	0.7857	4.222	157.52	15.45	39.08
0.5262	0.7831	4.146	158.89	14.63	36.46
0.7541	0.7311	2.942	212.93	20.45	38.14
0.8702	0.7090	2.567	239.01	23.84	39.75
0.043	0.6802	2.161	271.74	24.57	35.74
0.503	0.6202	1.528	360.42	36.34	40.26
1.540	0.6162	1.493	362.22	32.37	35.34
2.228	0.5545	1.053	471.05	42.47	35.75
2.994	0.5059	0.7970	574.65	50.07	34.55
3.393	0.4857	0.7086	626.45	55.97	35.51
4.250	0.4502	0.5736	723.58	62.00	34.05
4.603	0.4379	0.5324	762.15	65.47	34.16
5.519	0.4107	0.4493	856.02	73.34	34.12
5.879	0.4015	0.4236	900.74	86.06	38.31
6.586	0.3852	0.3810	956.55	81.50	33.99
7.096	0.3747	0.3555	1006.98	90.19	35.84
8.472	0.3506	0.3015	1112.87	88.78	31.86
10.70	0.3205	0.2429	1280.00	100.40	31.39
12.24	0.3040	0.2145	1388.59	109.50	31.61

[a] The 0.99707 term is to convert $K_{e.m.f.}$ to $K_{conductance}$.

[b] See Table I.

Table XV

Succinic Acid

$10^5K_1 = 6.21^{83} \times 0.99707$, $10^6K_2 = 2.31^{83} \times 0.99707$, $\lambda^o_{A^{--}} = 60$.[b]

10^3m	α	$10^3\beta$	10^6k_{soln}	$10^6k_{HA^-}$	$\lambda^o_{HA^-}$
0.1375	0.4861	16.29	26.38	2.016	31.52
0.1890	0.4351	12.04	32.95	3.212	40.54
0.3443	0.3472	6.775	47.35	4.599	39.67
0.6019	0.2769	3.952	64.92	5.741	35.44
0.7440	0.2533	3.219	74.43	7.655	41.68
0.9942	0.2236	2.431	87.17	8.599	39.67
1.034	0.2236	2.340	89.09	8.779	39.60
1.238	0.2034	1.965	97.84	9.088	37.07
1.771	0.1735	1.389	119.84	11.81	39.44
1.895	0.1683	1.300	124.63	12.55	40.35
2.409	0.1510	1.030	141.29	13.63	38.46
3.445	0.1283	0.7285	171.51	16.82	39.11
3.790	0.1227	0.6642	181.01	18.22	40.22
4.649	0.1117	0.5450	203.30	21.82	43.13
5.195	0.1061	0.4895	214.29	21.80	40.67
6.381	0.09635	0.4012	239.22	24.63	41.20
6.448	0.09588	0.3972	241.61	25.83	42.93
7.727	0.08808	0.3335	266.27	28.92	43.69
8.239	0.08547	0.3135	274.43	28.95	42.31
9.576	0.07962	0.2711	297.81	32.17	43.43
10.21	0.07725	0.2549	307.32	32.61	42.58

Table XVI

Tartaric Acid

$10^4K_1 = 9.17^{86} \times 0.99707$, $10^5K_2 = 4.30^{86} \times 0.99707$, $\lambda^o_{A^{--}} = 60$.[b]

10^3m	α	$10^3\beta$	10^6k_{soln}	$10^6k_{HA^-}$	$\lambda^o_{HA^-}$
3.869	0.3957	12.48	597.36	46.40	32.76
4.437	0.3761	11.01	649.14	50.59	32.75
4.497	0.3742	10.88	654.76	51.39	32.97
5.413	0.3488	9.182	729.67	55.53	31.81
5.593	0.3445	8.911	747.22	59.85	33.53
6.306	0.3288	7.984	800.86	62.94	32.79
6.634	0.3224	7.621	826.59	66.32	33.48
6.766	0.3199	7.485	834.92	65.79	32.85
7.441	0.3081	6.860	881.76	68.58	32.36
7.970	0.2998	6.442	918.94	72.54	32.83

[b] see Table I.

Table XVII

Phosphoric Acid

$10^3K_1 = 7.516^{81} \times 0.99707^a$, $10^8K_2 = 6.339^{82} \times 0.99707^a$,

$\lambda^o_{A^{--}} = 55$

10^2m	α	$\Lambda_{soln.}$	$\lambda^o_{H_2PO_4^-}$
0.1	0.8995	336.38	28.95
0.3	0.7814	291.82	30.47
0.4	0.7411	276.21	30.97
0.6	0.6798	253.71	31.16
0.8	0.6341	236.99	34.50
1.2471	0.5623	208.3	33.05
2.0	0.4877	180.95	35.87
2.593	0.4483	166.34	37.22
4.0	0.3866	143.73	40.41
4.777	0.3629	134.63	40.70
5.0	0.3570	132.6	41.41
5.0	0.3570	133.05	42.67
7.0	0.3156	117.89	45.77
8.0	0.3002	112.4	47.61
8.0	0.3002	112.59	48.22
9.0	0.2871	108.00	50.20
9.927	0.2765	104.43	52.45
10.0	0.2758	104.05	52.08

[a] The 0.99707 term is to convert $K_{e.m.f.}$ to $K_{conductance}$.

(iii) the equations used for λ_i and f_i are adequate,

(iv) the only species present in solution are those formed by primary and secondary dissociation.

The magnitude of the trends is such that they cannot be accounted for by any uncertainty in K_1 or by using any physically meaningful value for $\overset{o}{a}$ in the equations for the conductivity and activity coefficient. For example, to eliminate the slope in the case of succinic acid either K_1 should be increased by over 20% or an $\overset{o}{a}$ value of over 200 $\overset{o}{A}$ should be used since the slope of the plots can be shown[25] to be approximately equal to $S_{(\Lambda)}$ $(B\overset{o}{a} - 1)$. The viscosity correction would always increase the slope and therefore it appears probable that some unsuspected ionic species is present in all solutions which show a marked positive gradient in the plot of $\lambda^o_{HA^-}$ vs αm. This is supported in the case of H_3PO_4 by the author's transference number measurements which will be discussed in Part II. Recent investigations[39] have also shown that in electrolyte solutions complex ions are more common than was previously supposed. The decreasing trend of $\lambda^o_{HA^-}$ with αm (e.g. malonic acid) seems to indicate the necessity for viscosity correction and/or the presence of associated neutral molecules in solution. This aspect is treated quantitatively in the following section.

(b) Quantitative treatment of the effect of complex formation on conductance of the acid.

For this discussion all the acids are assumed to be effectively monoprotic since the small amount of secondary dissociation would not significantly affect the argument. The dissociation of the acid can be represented by

$$HA \rightleftharpoons H^+ + A^- \qquad (22)$$

and further species may be formed in solution by the following combinations

$$HA + A^- \rightleftharpoons AHA^- \qquad (23)$$

$$HA + H^+ \rightleftharpoons HAH^+ \qquad (24)$$

$$HA + HA \rightleftharpoons (HA)_2 \qquad (25)$$

The effect of the formation of these species on the conductance of the solution will now be considered quantitatively.

(i) Effect of A^- HA formation on the conductance of the acid.

If only equilibria (22) and (23) exist in solution and if the degree of dissociation of the acid and the degree of formation of $HA.A^-$ are represented by α and β respectively, the molar concentrations of the different species will be given by

$$(H^+) = m\alpha \ , \ (A^-) = m(\alpha-\beta) \ , \ (HA) = m(1-\alpha-\beta)$$

$$(AHA^-) = m\beta \ .$$

The molar conductance of the solution Λ will therefore be given by

$$1000\kappa = \Lambda m = m(\alpha \lambda_{H^+} + (\alpha-\beta) \lambda_{A^-} + \beta \lambda_{AHA^-})$$

$$\therefore \Lambda = \alpha(\lambda_{H^+} + \lambda_{A^-}) - \beta(\lambda_{A^-} - \lambda_{AHA^-})$$

$$\therefore (\lambda_{H^+} + \lambda_{A^-}) = \frac{\Lambda}{\alpha} + \frac{\beta}{\alpha} (\lambda_{A^-} - \lambda_{AHA^-})$$

$$\Lambda^\circ_{HA} = (\lambda_{H^+} + \lambda_{A^-}) + S_{(\Lambda)} \frac{\sqrt{\mu}}{1+\sqrt{\mu}} = \frac{\Lambda}{\alpha} + \frac{\beta}{\alpha} (\lambda_{A^-} - \lambda_{AHA^-}) + S_{(\Lambda)} \frac{\sqrt{\mu}}{1+\sqrt{\mu}}$$

...(26)

If the presence of complex ions had not been known and taken into account, a figure $\Lambda^{\circ\prime}_{HA}$ would have been calculated using the incorrect

equation

$$\Lambda^{o'}_{HA} = \hat{\Lambda}_{\alpha'} + S_{(\Lambda)} \frac{\sqrt{\mu}}{1+\sqrt{\mu}} \qquad (27)$$

where α' represents the hypothetical degree of dissociation of the acid assuming the absence of complex ion formation. The relationship between α and α' may be obtained as follows.

$$K = \frac{m\alpha(\alpha-\beta)\, f_{\pm}^2}{(1-\alpha-\beta)}$$

$$= \frac{m\alpha^2 f_{\pm}^2}{1-\alpha} - \frac{m\alpha\beta\, f_{\pm}^2}{1-\alpha} + \frac{K\beta}{1-\alpha}$$

$$\therefore \frac{m\alpha^2 f_{\pm}^2}{1-\alpha} = K + \frac{m\alpha\beta\, f_{\pm}^2}{1-\alpha} - \frac{K\beta}{1-\alpha} \qquad (28)$$

$$\text{But } \frac{m\alpha'^2 f_{\pm}'^2}{(1-\alpha')} = K \qquad (29)$$

Comparison of equations (28) and (29), after assuming that $f_{\pm}^2 = f_{\pm}'^2$, shows that

$$\alpha > \alpha' \quad \text{when} \quad \frac{m\alpha\beta\, f_{\pm}^2}{1-\alpha} > \frac{K\beta}{1-\alpha}$$

$$\text{i.e. when } m\alpha\, f_{\pm}^2 > K \qquad (30)$$

This is usually the case except when m is very small or K quite large. When $m\alpha\, f_{\pm}^2 = K$, $\alpha = \alpha'$. For phosphoric acid ($K_1 = 7.516 \times 10^{-3}$) this occurs at a concentration of about 0.02M.

Suppose that the complex ion $A^-.HA$ is present in the solution but has not been suspected. The correct equation for the determination

of Λ^{o}_{HA} is given by equation (26) but out of ignorance the incorrect equation (27) would be used. The effect of this error can be seen by subtracting equation (26) from (27)

$$\Lambda^{o'}_{HA} - \Lambda^{o}_{HA} = \left(\frac{\Delta}{\alpha'} - \frac{\Delta}{\alpha}\right) - \frac{\beta}{\alpha}\left(\lambda_{A^-} - \lambda_{AHA^-}\right) \qquad (31)$$

The second term on the right hand side of the equation is comparatively small since λ_{AHA^-} is not much smaller than λ_{A^-} and β/α is usually less than 0.2. The first term is important since, except in very dilute solutions, $\alpha > \alpha'$ and therefore $\Lambda^{o'}_{HA} > \Lambda^{o}_{HA}$. That is, a higher value is predicted for the limiting equivalent conductance of HA (and therefore of $\lambda^{o}_{A^-}$) if complex ion formation is ignored. As the concentration is increased a higher and higher value will be predicted for Λ^{o}_{HA} as can be seen from equations (30) and (31).

The observed increase of $\lambda^{o}_{A^-}$ (or $\lambda^{o}_{HA^-}$) with increasing concentration for phosphoric and succinic acids can therefore be explained by postulating the presence of a complex anionic species.

(ii) Effect of $HA.H^+$ formation on the conductance of the acid.

If the equilibria existing are those represented by equation (22) and (24) then H^+, A^- and $HA.H^+$ ions would be present in solution. The mathematical treatment is the same as that in case (i) the only differences being that βm now stands for (HAH^+) and that $(\lambda_{A^-} - \lambda_{AHA^-})$ should be replaced wherever it occurs by $(\lambda_{H^+} - \lambda_{HAH^+})$. Equation (31) therefore becomes

$$\Lambda^{o'}_{HA} - \Lambda^{o}_{HA} = \left(\frac{\Delta}{\alpha'} - \frac{\Delta}{\alpha}\right) - \beta/\alpha\left(\lambda_{H^+} - \lambda_{HAH^+}\right) \qquad (32)$$

The last term in the above equation, unlike that in case (i), is now very important since $(\lambda_{H^+} - \lambda_{HAH^+})$ should be of the order of 300. This is because the HAH^+ ion would not be expected to conduct by the 'proton jump' mechanism and its λ^o value should therefore be less than about 50 conductance units. Rough numerical calculations show that the $\beta/\alpha\ (\lambda_{H^+} - \lambda_{HAH^+})$ term would usually be greater than $(\hat{\Lambda}_{\alpha'} - \hat{\Lambda}_{\alpha})$. For example in a 0.1M solution of phosphoric acid ($K_1 = 7.516 \times 10^{-3}$)

$$\hat{\Lambda}_{\alpha'} \doteqdot 377 \text{ and } \hat{\Lambda}_{\alpha} \doteqdot 360 \text{ if } \beta/\alpha = 0.15$$

$$\therefore \quad \Lambda^{o'}_{HA} - \Lambda^{o}_{HA} = (377 - 360) - 0.15 \times 300$$

$$= -28 \text{ cm}^2\text{ohm}^{-1}\text{equiv}^{-1} .$$

The formation of a complex species of the type $HA.H^+$ would therefore lead to a decrease of $\lambda^o_{A^-}$ with increase in concentration. It is possible that this type of species is present in malonic acid solutions.

(iii) Effect of dimer formation on the conductance of the acid:

If the only equilibria existing in solution are those represented by equations (22) and (25) and if β is the degree of formation of the dimer, the molar concentrations of the different species will be given by

$$(H^+) = \alpha m\ ,\ (A^-) = \alpha m\ ,\ (HA) = (1-\alpha-2\beta)\ ,$$

$$(HA_{\beta})_2 = \beta m$$

As before

$$1000k = \Lambda m = m(\alpha\lambda_{H^+} + \alpha\lambda_{A^-})$$

$$\therefore \Lambda^{o}_{HA} = \hat{\Lambda}_{\alpha} + S_{(\Lambda)} \frac{\sqrt{\mu}}{1+\sqrt{\mu}} \qquad (33)$$

Had dimer formation not been suspected, $\Lambda^{o'}_{HA}$ would be calculated using the incorrect equation

$$\Lambda^{o'}_{HA} = \frac{\Lambda}{\alpha'} + S_{(\Lambda)}\frac{\sqrt{\mu}}{1+\sqrt{\mu}} \qquad (34)$$

where α' represents the hypothetical degree of dissociation of the acid assuming the absence of complex ion formation. The relationship between α and α' may be obtained as follows

$$K = \frac{\alpha^2 m f_{\pm}^2}{1-\alpha-2\beta}$$

On rearranging this gives

$$\frac{\alpha^2 m f_{\pm}^2}{1-\alpha} = K - \frac{2K\beta}{1-\alpha} \qquad (35)$$

But

$$\frac{\alpha'^2 m f_{\pm}^2}{1-\alpha} = K \qquad (29)$$

Comparison of equations (35) and (29) shows that α' is always greater than α .

$$\therefore \frac{\Lambda}{\alpha'} < \frac{\Lambda}{\alpha} \quad \text{and} \quad \Lambda^{o'}_{HA} < \Lambda^{o}_{HA}$$

Thus if dimers are formed in solution and if they had not been suspected, Λ^{o}_{HA} will decrease with increasing concentration. This type of behaviour is found, as has been shown earlier, with acetic and malonic acids.

PART II

3. DETERMINATION OF λ^{o}_{HA} - FROM TRANSFERENCE NUMBER MEASUREMENTS BY THE MOVING BOUNDARY METHOD

3.1. Theoretical

3.1.1. Definition of Transference Number and Fundamental Relationships.

Early experimental studies were carried out nearly always on strong electrolytes, and this led to the transference number of an ionic species being defined as the fraction of the total electric current carried by that species. This definition, which has been referred to [42] as the electrical transport number, is not of general utility since a detailed knowledge of the composition of the solution is required to determine the electrical transport number from Hittorf or moving boundary experiments. It is therefore more convenient to define transference number so as to make it obtainable directly from experiments, without the necessity of knowing the composition of the solution. To do this it is necessary to distinguish between an ion and an ion-constituent, as was first done by Noyes and Falk [43]. An ion-constituent can be defined as "the ion-forming portion of an electrolyte without reference to the extent to which it may actually exist in the dissociated state". For example, though the concentration of the hydrogen ion constituent in a one-molar solution of acetic acid is 1M, the concentration of hydrogen ions is only α molar, if α denotes the degree of dissociation in the 1M solution. In a moving boundary experiment the rate of movement of the boundary is that of the ion-constituent and not that of the ion; similarly, in the Hittorf method analysis gives the change in the concentration of the ion-constituent and not that of the ion.

It is clear, therefore, that to obtain $\overset{a}{\Lambda}$ transference numbers directly from experimental data it is necessary to define it in terms of ion-constituents. The transference number, T_R, of a cation or anion constituent may be defined as the net number of faradays carried by that ion-constituent across an imaginary plane in the solution, in the direction of the cathode or anode respectively, when one faraday of electricity passes across that plane. The plane is usually taken as fixed with respect to the solvent. The ion-constituent should be so chosen that it does not dissociate into smaller particles under the experimental conditions.

To determine λ_i for any ion i it is necessary to know the relationship between the experimentally determined transference number and the conductances of the ions present in solution. It can be shown[42] by a detailed consideration of the flux of matter through any plane in the solution that

$$T_R = Z_R \frac{\sum_i \lambda_i m_i N_{R,i} \frac{Z_i}{|Z_i|}}{\sum_i \lambda_i m_i |Z_i|} \qquad (36)$$

where Z_i and Z_R are the charge numbers of the species i and of the ion-constituent R respectively; $|Z_i|$ is the positive numerical value of Z_i and $N_{R,i}$ is the number of gram-formula-weights of R in 1 gram-ion of species i.

3.1.2. Determination of Transference Numbers.[44]

Three main methods have been used for the determination of transference numbers. In the Hittorf method the transference number is calculated from the concentration changes around the cathode and anode

when a known amount of electricity is passed through a suitably devised cell filled with solution. On the passage of one faraday of electricity T_- and T_+ gram-equivalents of the anion and cation constituents would migrate into the anode and cathode compartments respectively. In spite of its simplicity it is hard to obtain accurate results by the Hittorf method because of the difficulty of measuring precisely the relatively small concentration changes around the electrodes. For example if the concentration change is 10% of the initial concentration an error of, say, 0.1% in the analytical determination of concentration would lead to an error of 1% in the evaluation of the concentration change and consequently in the transference number. Accurate results, comparable with those usually obtained using the moving boundary method, have been obtained only in a few cases.

Transference numbers have also been determined by measuring the e.m.f. of concentration cells with transference (E_t). A knowledge of the activity coefficients of the cell solutions is necessary for the calculation and this has usually been obtained by determining the e.m.f. of the same cell without transference (E). The transference number of the ion-constituent (T_R), to which the electrode in the cell with transference is not reversible, is related to E_t and E, provided the electrodes are simple,[45] by the expression

$$T_R = \frac{dE_t}{dE} \quad .$$

Since T_R is related to the small rate of change of E_t and E it is very sensitive to even small experimental errors. For example, an error of $\pm$0.01 mV. in E_t or E leads to an error of $\pm$ 0.001 in T_R in the case of

HC ℓ [46]. The e.m.f. method, in general, cannot be used when very accurate results are required but it is useful, because of its ease and rapidity, for a survey over a wide concentration and temperature range. In a few cases[47] transference numbers have also been obtained from the e.m.f. of a cell subjected to a centrifugal or gravitational force field. This method, though capable of an accuracy of 0.1%, has not been widely used; presumably because of the complex apparatus required.

The moving boundary method[48] is capable of high accuracy and has been very widely used. The transference number is directly proportional to the experimentally measured quantity - the rate of movement of the boundary - and no computational errors are involved. However, only strong or moderately strong[49] electrolytes have been studied by this method. Since the moving boundary method is capable of giving the most accurate results, it was decided to extend the applicability of this method to the weak acids under study.

3.1.3. The Moving Boundary Equation

In the moving boundary (m.b.) method the transference number is calculated from the volume swept out by a boundary between two solutions when a known amount of electricity is passed through the solutions. The solutions in front and behind the boundary are called the leading and following (or indicator) solutions respectively. In this discussion the leading and following solutions will be designated by superscripts a and b respectively. The volume swept out by the boundary is related to the equivalent concentration (C) and transference numbers (T) of an ion-constituent (R) in the leading and indicator solutions by the

expression[50]

$$T_R^a - T_R^b = V_F (\bar{C}_R^a - \bar{C}_R^b) \qquad (37)$$

where V_F is the volume swept out by the boundary in litres per faraday of electricity.

Equation (37) is the fundamental equation for the determination of transference numbers and is usually known as the moving boundary equation. The conditions under which this equation may be applied have been critically discussed by Svensson[51] with particular reference to the proper choice of the ion-constituent and concentration scales.

It can be easily shown[50] that the m.b. equation follows directly from the definition of transference number by a conservation of mass argument.

In cases where the R ion-constituent is present only in the leading solution $\bar{C}_R^b$ and T_R^b are zero and the moving boundary equation simplifies to

$$T_R = V_F \bar{C}_R \qquad (38)$$

In the derivation of the m.b. equation it has been tacitly assumed that there are no disturbing effects due to diffusion and that the boundary velocity is not influenced by the nature or concentration of the indicator solution. The effect of diffusion has been studied by MacInnes and Longsworth[48] and they have shown both theoretically and experimentally that diffusion affects only the thickness of the boundary but not its speed.

3.1.4. The Indicator Solution.

The indicator solution should be selected so as not to introduce gravitational instability in the experimental set up. In a falling boundary cell the indicator solution of the appropriate concentration should be less dense than the leading solution and vice-versa for a rising boundary cell. The indicator solution should also not react chemically with the leading solution or the electrode. The indicator ion-constituent should satisfy certain mobility conditions if it is to form a stable boundary with a leading solution and since this subject has not been reviewed for weak electrolyte systems it will be discussed in some detail.

(a) Mobility of indicator ion constituent.

To obtain a stable steady-state moving boundary between two solutions, say, a and b, it is necessary for the leading ion-constituent (say R) to have a higher velocity (V) in the following solution than in the leading solution, and for the following ion-constituent (say S) to have a lower velocity in the leading solution than in the following solution. If this were not so, diffusion of the leading and following solutions into each other would eventually destroy the boundary. Mathematically, these conditions may be expressed as

$$V_R^b > V_R^a \qquad (39)$$

$$V_S^b > V_S^a \qquad (40)$$

where V stands for the velocity of the ion-constituent subscripted in the solution superscripted. When the boundary moves in a steady state $V_R^a = V_S^b = V_{m.b.}$ and therefore the stability conditions (39) and (40) may be expressed as

$$V_R^b > V_{m.b.} > V_S^a \qquad (41)$$

Equations (39), (40) and (41) are of general applicability and are true for both strong and weak electrolyte systems.

For strong electrolytes the velocity of an ion R^- , V_{R^-} , is by definition equal to $u_{R^-}E$; u_{R^-} referring to the mobility of the ion R^- and E to the electric field strength to which it is subjected. Equations (39) and (40) may consequently be written as

$$u^b_{R^-} E^b \quad > \quad u^a_{R^-} E^a \qquad (42)$$

$$u^b_{S^-} E^b \quad > \quad u^a_{S^-} E^a \qquad (43)$$

Equations (42) and (43) necessarily follow if $u_{R^-} > u_{S^-}$; that this is so is easily seen from the following considerations by making the reasonable assumption that $u^a_{X^-} = u^b_{X^-}$ (X = R or S). When the boundary moves in a steady state the S^- ion must move at the same velocity as the R^- ion, that is $u_{R^-} E^a = u_{S^-} E^b$, and if $u_{R^-} > u_{S^-}$ it follows that $E^b > E^a$ and therefore equations (42) and (43) follow. Thus $u_{R^-} > u_{S^-}$ is a necessary and sufficient condition for boundary stability in strong electrolyte systems and this was realised as early as 1899 by Masson.[52]

The conditions necessary for boundary stability in weak electrolyte systems have been studied particularly by Hartley and Moilliet[53], Svensson[51], and Alberty[54]. For weak electrolyte systems conditions (42) and (43) for boundary stability have to be modified, since the mobility of an ion-constituent usually changes across the boundary, and should be expressed as

$$\bar{u}^b_{R^-} E^b \quad > \quad \bar{u}^a_{R^-} E^a \qquad (44)$$

$$\bar{u}^b_{S^-} E^b \quad > \quad \bar{u}^a_{S^-} E^a \qquad (45)$$

When the boundary moves in a steady state

$$V_{m.b.} = \bar{u}_R^a E^a = \bar{u}_S^b E^b \qquad (46)$$

The mobility of an ion-constituent R, $\bar{u}_R$, depends on the concentrations and mobilities of the various species in the solution, which in turn depends on the pH for acid systems. Tiselius in 1930 pointed out that the mobility of an ion-constituent is related to the mobility of the various species in equilibrium with it by the relationship.[55]

$$\bar{u}_R = \sum_i a_i u_i \qquad (47)$$

where a_i is the fraction of the substance with mobility u_i. For the general case a_i is given by[56] $a_i = (\frac{C_i}{C})\ N_{R,i}\ (\frac{Z_R}{Z_i})$ where C_i and C are the equivalent concentrations of the species i and the solution respectively.

To predict whether an indicator solution would give a stable boundary with a particular leading solution, equations (44) and (45) are inconvenient to use since a knowledge of the potential gradient in the two solutions is necessary. This disadvantage has been overcome by substituting equation (46) in equations (44) and (45) and expressing the stability condition as[57] :-

$$\bar{u}_R^a > \bar{u}_S^a \qquad (48)$$

and

$$\bar{u}_R^b > \bar{u}_S^b \qquad (49)$$

Equations (48) and (49) show that for boundary stability the indicator ion-constituent should have a mobility lower than that of the leading ion-constituent in both the leading and following solutions. Introduction

of equation (47) into equations (48) and (49) for the special case where the leading and indicator electrolytes are both weak 1:1 electrolytes leads to

$$\alpha^{a}_{HR}\ u^{a}_{R^-} > \alpha^{a}_{HS}\ u^{a}_{S^-} \qquad (50)$$

and

$$\alpha^{b}_{HR}\ u^{b}_{R^-} > \alpha^{b}_{HS}\ u^{b}_{S^-} \qquad (51)$$

where α is the degree of dissociation of the subscripted acid. Conditions (50) and (51) have been used by the author (see later) as one of the criteria in the selection of a proper indicator solution.

(b) Concentration of indicator solution.

It has already been pointed out that when a boundary moves in a steady state the indicator ion-constituent must move at the same rate as the leading ion-constituent. This can occur only at one concentration of the indicator solution, called the Kohlrausch concentration, for each concentration of the leading solution. At the start of the moving boundary experiment the concentration of the indicator solution would, in general, not be at the Kohlrausch concentration and hence either the leading or the following solution (or both) should alter its concentration to make both ion-constituents move at the same velocity. The equality in rates is brought about by changes in the potential gradients in the solutions. Since the boundary moves towards the leading solution it seems reasonable to suppose that only the following solution adjusts its concentration. Kohlrausch was the first to show that this is so, and that the adjusted or Kohlrausch concentration C_{HS} behind the boundary is given by

$$\frac{C_{HS}}{C_{HR}} = \frac{T_{S}^{HS}}{T_{R.}^{HR}} \qquad (52)$$

where C_{HR} is the concentration of the leading solution.

3.2. EXPERIMENTAL

3.2.1. The moving boundary cell.

The falling moving boundary (m.b.) cell that was used is shown in Fig. (19), the parts of which are labelled. The stopcock S, having a bore of the same diameter as the m.b. tube, had been hand ground to obtain a perfect fit. The barrel of the stopcock was hollow to enable the thermostat oil to circulate through it and so prevent any local heating. The stopcock S, will for convenience of description, be considered to divide the cell into an anode and a cathode compartment, marked A and C in the figure. The m.b. tube had previously been calibrated by Spiro[59] by carrying out runs with KCℓ whose transference numbers are known.

3.2.2. The thermostat and thermoregulator.

The internal thermostat dimensions were:- length 60 cms, width 35 cms, and height 52 cms.. The two larger faces of the thermostat were made of glass to enable the boundary to be observed. A small glass window was installed on one of the other faces so that the cell could be aligned vertically. The bath fluid was Shell "Diala" oil, chosen on the criteria of adequate fluidity, transparency to the light beam and chemical stability.

The thermostat was mounted on a steel framework (of height 100 cms.) to provide a convenient height. The stirrer motor was mounted on a separate framework to avoid transmitting vibration to the thermostat and thus to the cell itself. The motor was a Hoover a.c. type 7389 HBQ 1188 and was used in conjunction with a reduction gear box to rotate the stirring

rods (with paddles) at 250 revolutions per minute.

The temperature in the oil thermostat was controlled to $\pm$ 0.002°C by using a large but conventional glass toluene thermoregulator coupled to a Sunvic '602V' relay tube. The heating element of power approximately 150 watts (resistance $\doteq$ 400 ohms), obtained by winding low thermal capacity Nichrome wire on a glass framework, was however placed inside the spirals of the toluene regulator. This was found to improve the sensitivity of the thermoregulator response.

3.2.3. The optical assembly.

A simple optical assembly, as shown in Fig. (20), was used to follow the boundary between the leading and following solutions. L was a 25 watt lamp bulb, and N a blackened cylindrical metal shield to prevent interference by stray light. S was a ground glass slide which helped to diffuse the light and to uniformly illuminate the rectangular opening R, of height 4 m.m. and length 6 cms. W and W' were the glass sided faces of the thermostat, C the m.b. cell and D a stand on which the telescope T could be slid up or down to follow the motion of the boundary. The light source A was attached by a string which passed over a set of pulleys to a counterbalancing weight; the latter could be raised or lowered while looking through the telescope so as to align the light behind the boundary.

3.2.4. Constant current regulator.

During a run the resistance of the moving boundary (m.b.) cell increases as the leading solution in the moving boundary tube is replaced by the following solution and a device is hence necessary for

keeping the current constant. Various complex constant current regulators have been described in the literature but the simple and effective semi-constant regulator described by LeRoy and Gordon[60] was used in a slightly modified form. The circuit diagram of the regulator used is shown in Fig. (21). The power source of 2,500 V was made up of 120 V. "EverReady Winner" batteries; the use of batteries eliminated the possibility of any a.c. component being present in the circuit. During a run about 600-1000 V. should always be present at the anode of the valves for the efficient running of the current regulator.

The current through the m.b. cell depends primarily on the grid voltage applied to the valves. The dependence of the current on the grid voltage is shown in the table below.

Grid Voltage (Volts)	Approximate Current (mA.)
+ 15	1.8
+ 12	1.5
+ 9.0	1.2
+ 6.0	1.0
+ 3.0	0.7
+ 1.5	0.6
0	0.5
- 1.5	0.3
- 3.0	0.2

The current through the cell was determined with the help of a Tinsley Vernier potentiometer. A 1000 Ω standard resistance was connected in series with the cell so that the same current passed through

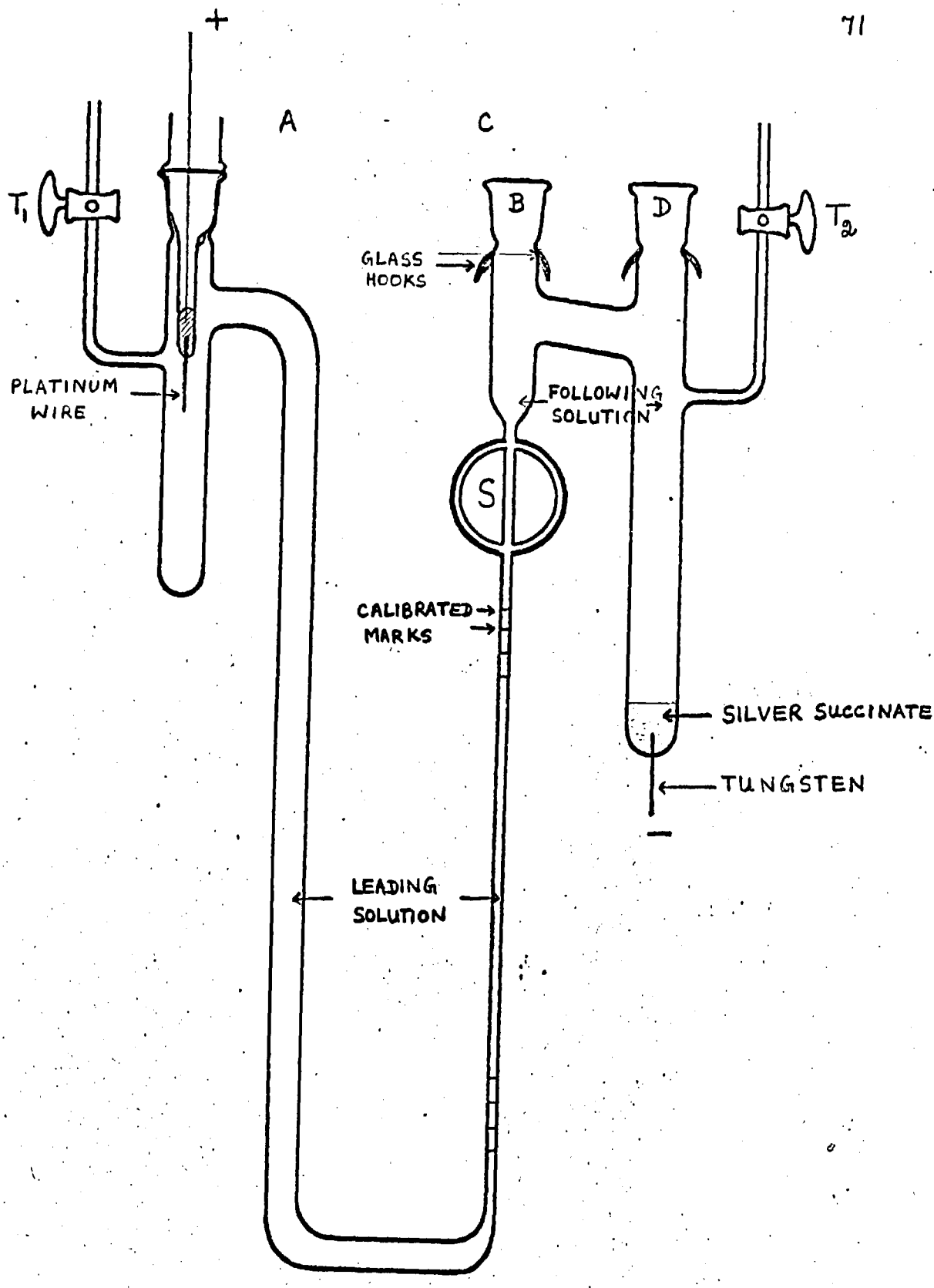


FIG. 19

THE MOVING BOUNDARY CELL

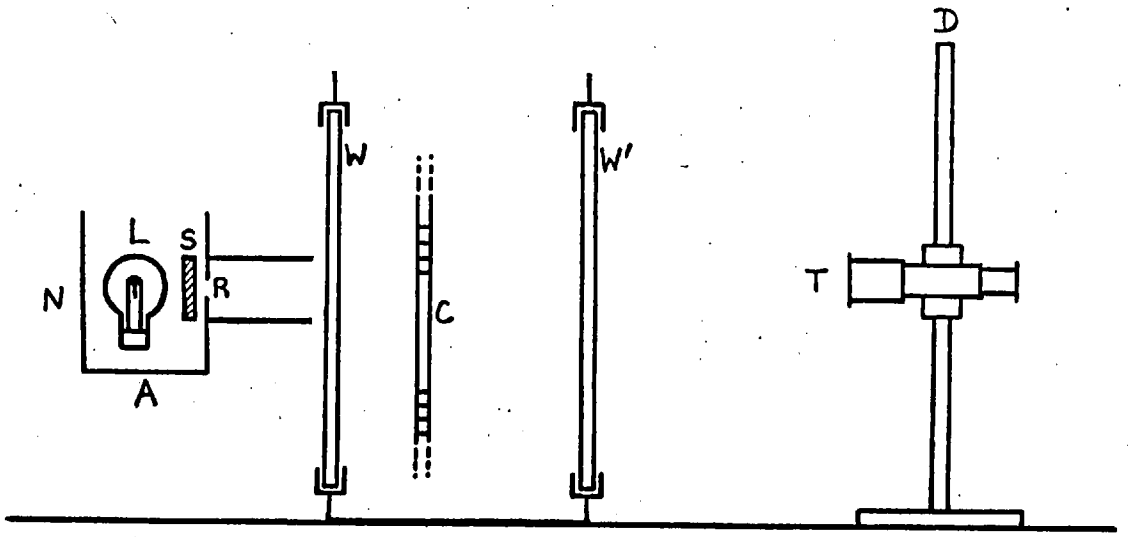


FIG. 20

THE OPTICAL ASSEMBLY

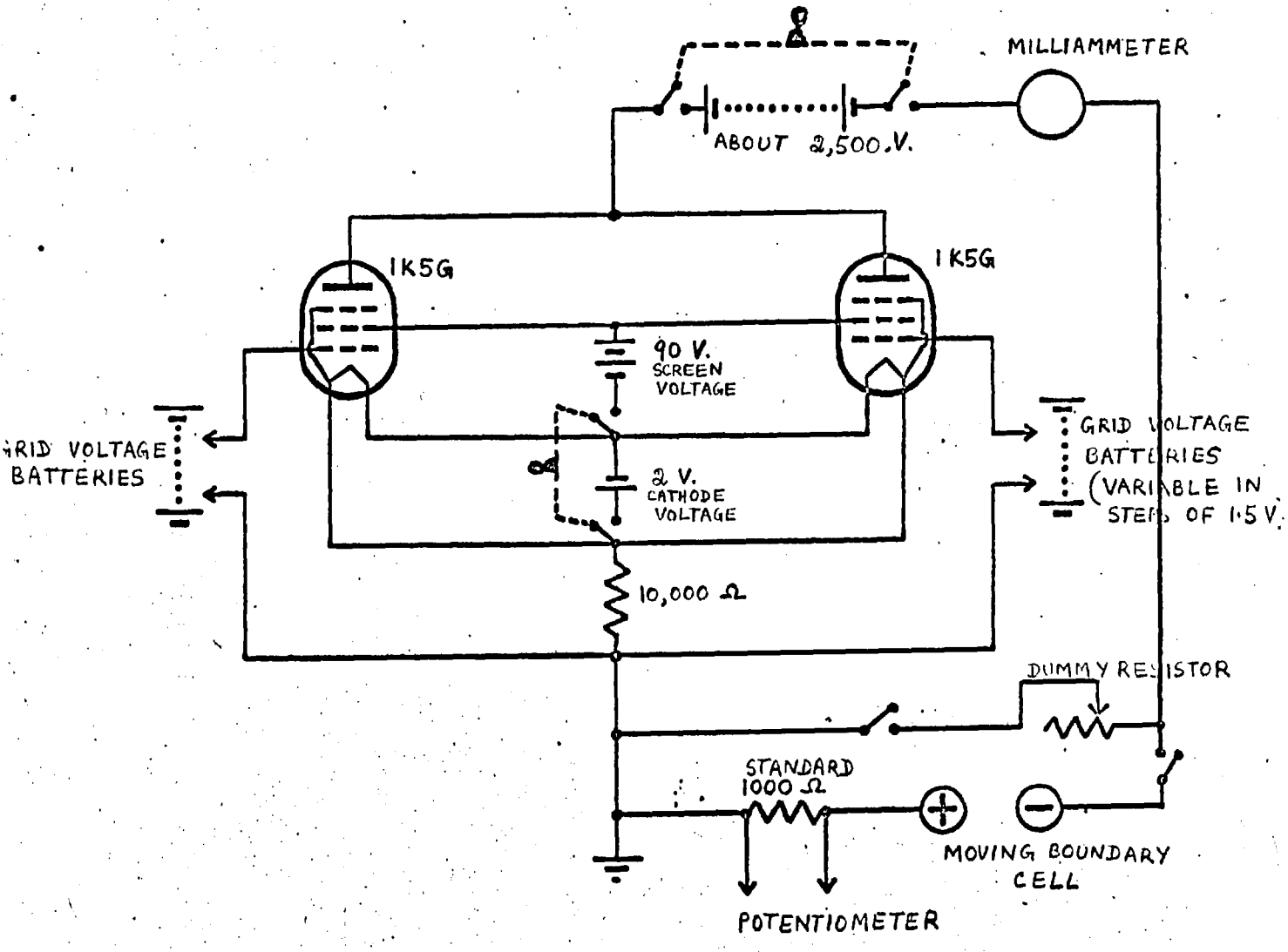

MILLIAMMETER
ABOUT 2,500.V.
1K5G
1K5G
90 V.
SCREEN
VOLTAGE
2 V.
CATHODE
VOLTAGE
GRID VOLTAGE
BATTERIES
GRID VOLTAGE
BATTERIES
(VARIABLE IN
STEPS OF 1·5 V.
10,000 Ω
DUMMY RESISTOR
STANDARD
1000 Ω
MOVING BOUNDARY
CELL
POTENTIOMETER

FIG. 21

both, and this current was measured by determining the potential drop across the 1000 Ω resistance and by using Ohm's law.

3.2.5. Preparation of solutions.

(a) Conductivity water

Conductivity water, used for preparing all the required solutions, was obtained by distilling the distillate from a Manesty electric still with alkaline permanganate solution in a Pyrex glass still previously "pickled" in conc. hydrochloric acid. Only the middle third of the distillate was collected and this had a specific conductance between 1.3 and 1.7×10^{-6} $ohm^{-1}cm^{-1}$.

(b) Phosphoric acid solutions.

A small sample of B.D.H. AnalaR phosphoric acid ($\doteq$ 88% H_3PO_4) was solidified by cooling with liquid nitrogen and was used to 'seed' the main bulk of the AnalaR solution. Fine crystals of $H_3PO_4 \cdot \frac{1}{2} H_2O$ separated out almost instantaneously and were recrystallised by dissolving them in the minimum amount of hot conductivity water and cooling in ice. The dried crystals were used to prepare an approximately 0.25 M stock solution from which solutions of any desired concentration were obtained by weight dilution.

The stock solution was standardised gravimetrically by precipitating magnesium ammonium phosphate and igniting to the pyrophosphate following the procedure of Hofmann and Lundell[61]. A sintered silica Gooch crucible of fine porosity (porosity 3, Gallenkamp) was, however, used instead of a filter paper for filtering and igniting the precipitate. The analysis was carried out in duplicate, at the start, middle and end

of the series of runs. The accuracy in the value for the concentration was estimated to be better than ± 0.15%.

(c) D-Tartaric acid solutions.

These were prepared from a triply-recrystallised sample of B.D.H. AnalaR material after drying over silica gel in a vacuum desiccator. A small quantity of B.D.H. thymol (about 0.001 M) was added to the solutions to prevent any bacterial decomposition[62], and no solutions were kept for more than one week.

(d) Indicator solutions.

The indicator or following solutions were prepared from AnalaR reagents. Gravitational instability would occur in the falling boundary cell if the adjusted or Kohlrausch concentration is less than the indicator concentration started with. To avoid any possibility of this happening, indicator solutions having a concentration about 5% less than the Kohlrausch concentration were prepared and used.

All solutions were degassed before they were poured into the cell to prevent formation of air bubbles during a run. This was done by swirling the solutions for about 15 seconds in a flask subjected to the reduced pressure (about $\frac{1}{2}$ atm.) obtained with a water pump.

3.2.6. The Electrodes.

It is obvious that the experiment should be able to give the movement of the boundary due to electrical migration alone. One electrode compartment must therefore be closed to prevent bulk movement of the liquid and a non-gassing electrode must be used in this compartment. The non-gassing electrode should also have certain specific characteristics:

(i) the electrode reaction taking place should be quantitatively known to correct for the influence of the volume change, due to the electrode reaction, on the boundary movement.

(ii) it should not cause any other volume changes of unknown magnitude, for example, by reaction with or diffusion into the leading solution.

(iii) it should not introduce any fast moving ions which would cross the boundary.

No suitable anode in H_3PO_4 was found that fulfilled all the above requirements. Silver anodes were non-gassing but the Ag^+ formed was found to cross the boundary and deposit on the cathode. Evidently the concentration of the free PO_4^{---} ions in H_3PO_4, being very low ($K_3 \doteqdot 4 \times 10^{-13}$)[63], was not sufficient to precipitate the Ag^+ formed by anodic dissolution (Solubility Product of $Ag_3PO_4 \doteqdot 10^{-14}$)[64]. Lead was tried as anode, since its phosphate has a much lower Solubility Product ($\doteqdot 10^{-44}$)[65], but gassing was found to occur after a few hours with a current of 1 mA., when presumably the whole surface was coated with the phosphate.

Cd, Cu or Ag salt solutions of the indicator acid surrounding the tungsten electrode wire would have provided simple and convenient cathodes if it had not been for the uncertain volume changes caused by the diffusion of the salt and indicator solutions into each other. For strong electrolyte systems where the runs are fast and usually take only an hour or two, this neglect would not lead to an appreciable error. For anion-constituent transference measurements on weak acid solutions, however, a run may take several days; this is partly because the

transference number is small and partly because very low currents (usually < 1 mA.) have to be used to prevent boundary instability arising from excessive Joule heating. The error due to volume change on diffusion may thus introduce significant errors and was therefore investigated by dilatometer experiments using the $Cd(OAc)_2$ soln./Cd cathode.

The dilatometer used is shown in Fig. (22). The bulb had approximately the same dimensions and shape as the cathode chamber of the m.b. cell and was filled up as if for a run. The cadmium acetate solution was introduced with a pipette without touching the sides of the bulb and 0.1 M acetic acid solution was then slowly run down the walls to prevent any undue mixing with the heavier cadmium acetate solution. The dilatometer was placed in a thermostat at 25°C and the change in level in the capillary tube (see Fig. (22)) due to the diffusion of the salt and acid solutions into each other, was observed as a function of time.

The results for 2 M and 0.5 M $Cd(OAc)_2$ are shown in Fig. (23) where the decrease in volume ($-\Delta V$) is plotted against the time. The graph shows that even with 0.5 M cadmium acetate significant volume changes occur because of diffusion. The error in a T_- determination due to this volume change would obviously depend on the time taken for a run. For a slow run taking, say, 30 hours, the boundary sweeps out about 0.024 ml. per hour and since the volume decrease on diffusion, using 2 M cadmium acetate, is 0.0003 ml. per hour an error of about 1.2% would occur if diffusion is neglected. With 0.5 M cadmium acetate the error would be about 0.3%. This error is larger the lower the current and is increased even more when the T_- results are extrapolated to zero current.

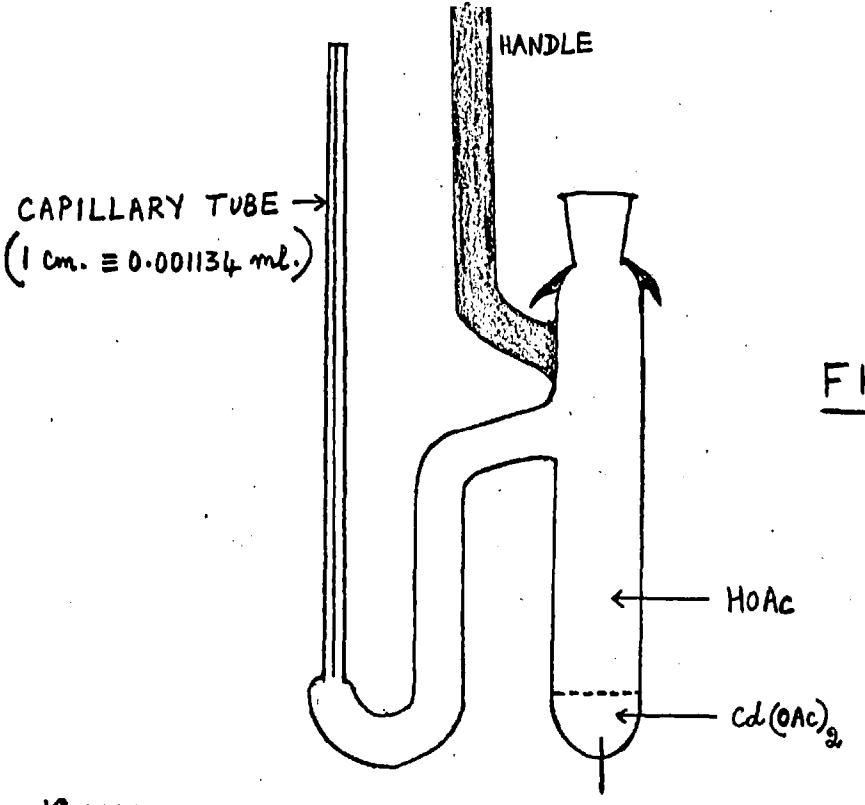

HANDLE
CAPILLARY TUBE →
(1 cm. ≡ 0.001134 ml.)
HOAc
Cd(OAc)2

FIG. 22

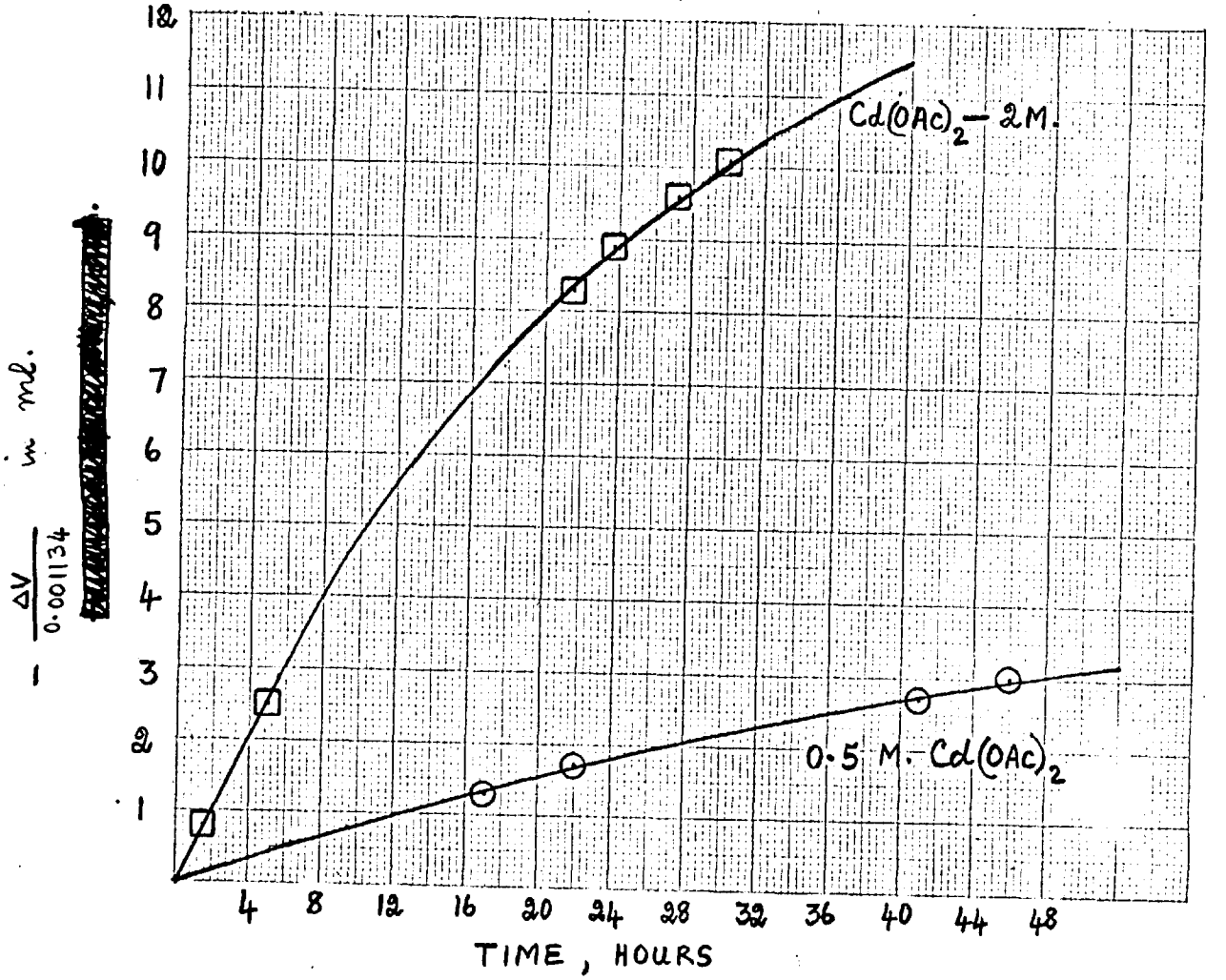

Cd(OAc)2 — 2M.
0.5 M. Cd(OAc)2
ΔV / 0.001134 in ml.
TIME, HOURS
1
2
3
4
5
6
7
8
9
10
11
12
4
8
12
16
20
24
28
32
36
40
44
48

FIG. 23

It is therefore necessary to correct each T_- value for diffusion before extrapolating to zero current. These corrections can be done only approximately because even in a dilatometer the volume change is reproducible to only about ± 15%, and because the electric migration of ions in a run will affect the diffusion process to some extent.

The runs with tartaric acid were performed using the $Cd(OAc)_2$ soln./Cd cathode before it was recognised that appreciable volume changes may occur because of diffusion. The dilatometer studies were carried out later to enable a correction to be made for this volume change.

The uncertain volume change because of diffusion could obviously be avoided if a suitable solid electrode could be devised. Granular silver oxide, covering the tungsten electrode wire, proved to be a non-gassing cathode but partially reacted with all the suitable indicator acids. For example, with succinic acid as the indicator solution the brown silver oxide granules gradually became whitish and this was shown, by its solubility in dil. ammonia, to be due to the formation of silver succinate. Since there was no gassing it appeared probable that silver succinate itself might be a suitable non-gassing cathode and this was found to be so. As the solubility of silver succinate is only 0.199g per litre[66] at 25°C any solution of the salt during a run would not introduce any significant volume change; this was also confirmed experimentally with the dilatometer. The volume change in the closed cathode compartment on passing a current was due only to the reduction of silver succinate to silver metal and could be calculated accurately since both are solids. The reduction was found to start at the top of the silver

succinate and gradually proceed downwards, and at the end of a run a layer of metallic silver could be seen above the unreduced silver succinate.

Silver succinate was prepared by stirring silver oxide into warm concentrated acetic acid solution, filtering and adding succinic acid solution to the filtrate. The precipitate was washed several times with dilute succinic acid solution and was allowed to stand in the same solution until it was required for a run. A freshly prepared sample was in the form of a fine suspension and on ageing the particles became larger and larger. T_- results, with the same solutions, were found to increase with the ageing of the silver succinate and reached a constant value after about 2 weeks' ageing; the difference in T_- between a fresh and a 2 weeks' aged sample was about 0.3%.

Semimicro analyses of a dried sample gave 14.9% C and 65.1% ash; $(CH_2COO\ Ag)_2$ requires 14.5% carbon and 65.1% silver. The density of the sample was determined using a specific gravity bottle and was fouhd to be $3.750 \pm 0.005\ g.cm^{-3}$.

3.2.7. Grease.

Purified vaseline grease was found to be satisfactory for some of the runs. Water-soluble impurities were removed by stirring the molten grease several times with water at about 60°C (the grease starts 'melting' at about 35°C) and subsequent drying in an oven at 50°C over silica gel. For the runs with 0.02 M phosphoric acid vaseline grease could not be used; this was due to softening of the grease and the consequent dislodging of the stopcock S at the high temperatures developed during a run. Edwards soft high vacuum grease was found to be satisfactory and was used

for all the runs with phosphoric acid as the leading solution. Vaseline grease was used for the tartaric acid runs.

3.2.8. A run.

After a run the thermostat oil was washed from the outside of the cell with $CC\ell_4$ and all greased joints were wiped with "Kleenex" tissues to remove as much of the grease as possible. The cell was then rinsed with alcohol and washed thoroughly with $CC\ell_4$. After rinsing with alcohol and water, the cell was filled with dichromate-nitric acid cleaning mixture and allowed to stand for about one hour. It was then rinsed a dozen times with distilled water and finally with conductivity water. The cell was dried by clamping it in an inverted position and passing dry nitrogen (obtained by passing commercial nitrogen through anhydrous $CaCl_2$, charcoal and finally glass wool) through it.

The stopcock S and tap T_2 were carefully greased and inserted at the appropriate positions in the cell (see Fig. (19)). After opening the stopcock S and taps T_1 and T_2 the anode compartment was rinsed three times, and then filled with the degassed leading solution to a level just above S. Air bubbles sticking to the grease around the stopcock S were removed with the help of a platinum wire introduced through B. After closing S more leading solution was poured into the anode compartment to fill it, and a platinum wire anode was introduced through A. The anode was kept open to allow escape of oxygen during a run.

The cathode compartment was washed thoroughly with distilled water by successively filling it and emptying it with the help of a glass tube connected to a suction pump. After rinsing with the following solution

either solid silver succinate or cadmium acetate solution was introduced above the tungsten electrode and the compartment was filled with the degassed following solution. Care was taken to prevent any undue mixing between the cadmium acetate and the following solution when the cell was filled. The B10 cones were then inserted into B and D and maintained tightly in position by springs held by glass hooks. The cathode compartment was the closed one in all the runs.

The cell was clamped firmly on to a retort stand and lowered into the thermostatic oil bath. The m.b. tube was aligned vertically to the rectangular bar of light from the light source and after connecting the leads and allowing the cell to attain thermal equilibrium, tap T_2 was closed, stopcock S fully opened and the appropriate current was switched on.

When the boundary crossed the calibrated marks on the moving boundary tube readings were taken both of the time, on a calibrated battery operated 'Secticon' clock, and of the potential drop across the 1000Ω standard resistor. Potential readings were also taken inbetween the calibrated marks to confirm the uniform drop of potential with time. Runs in which the potential drop was not uniform with time were discarded. Simultaneous visual observation of the boundary and the time when the boundary passed a calibrated mark was difficult; a metronome clicking at a beat a second was found useful for the timing[67].

The details of a typical run are presented below for run 13 with 0.04968 M H_3PO_4.

Date
23.3.63. Run 13

$m_{H_3PO_4}$ = 0.04968 M , $m_{(CH_2COOH)_2}$ = 0.049 M

Silver succinate cathode, Pt wire anode in H_3PO_4(gassing). Current of 0.3 mA (Grid = -1.5V) switched into cell at 17 G.M.T. hours.

Date
24.3.63.

Current through cell increased to 1.35 mA. (Grid = +10.5V) at 10 G.M.T. hours.

Results:-

Calibration mark	Time at which boundary passed calibration mark			Potential (V.) across 1000 Ω (= current, mA.)
	hr.	min.	Sec.	
1	10	35	45	1.35910
2	11	27	10	1.35724
4	13	11	10	1.35270
5	18	50	30	1.33774
6	19	38	10	1.33488

Calculation:-

$$T_- = V_F\, m = \frac{VF}{It}\, m$$

where I = current in amperes,

t = time taken (in seconds) by the boundary to sweep out the volume V (in litres) and

F = 96, 494 coulombs.

Calibration marks	V(ml.)	It (coulombs)	T_-
5 - 1	0.67097	40.033	0.08024
5 - 2	0.60080	35.843	0.08024
5 - 4	0.45903	27.388	0.08023
6 - 1	0.73489	43.855	0.08022
6 - 2	0.66474	39.665	0.08023
6 - 4	0.52297	31.210	0.08022

$\therefore$ T_- = 0.08023 at 1.35 mA .

3.3. $\lambda^{o}_{H_2PO_4^-}$ FROM TRANSFERENCE NUMBERS OF ORTHOPHOSPHORIC ACID.

3.3.1. Introduction.

Many attempts have been made to determine the limiting equivalent conductance of the $H_2PO_4^-$ ion at 25°C and these have yielded widely scattered results: 33.7[1] (conductances of NaH_2PO_4), 32.3[1](conductances of KH_2PO_4), 26.2 (Shedlovsky extrapolation[22] applied to conductances of H_3PO_4[1]), 16[68](e.m.f. of a cell with transference) and 41[69] (cation transference numbers of H_3PO_4). Recalculations of the conductance data of NaH_2PO_4 and KH_2PO_4 gave 33.0 and 31.5 respectively (see Fig. 4). It has already been pointed out in a previous section that the conductance and e.m.f. methods are not very satisfactory for this determination. The cation transference number method has the disadvantage of being complicated by hydrolysis occurring in the following solution. It was therefore decided to measure the anion constituent transference numbers of the acid, a procedure that is particularly suitable for determining the limiting equivalent conductances of the acid anions of polyprotic acids.

3.3.2. Preliminary experiments.

It has already been pointed out that a suitable indicator solution should satisfy mobility conditions (50) and (51) and should not lead to gravitational instability. Also because of the simple optical assembly used the indicator solution should give a visible boundary with the leading phosphoric acid solution. The mobility conditions are satisfied if the indicatr solution is appreciably less dissociated than the phosphoric acid solution (pK = 2.15)[83]. Except for malonic

acid, boundaries were visible with all the indicator solutions tried. Fumaric (pK = 3.02)[83], furoic (pK = 3.17)[83], phenoxyacetic (pK = 3.17)[83], mandelic (pK = 3.41)[83], formic (pK = 3.75)[83], lactic (pK = 3.86)[83], succinic (pK = 4.21)[83] and acetic (pK = 4.76)[83] acids, being less dense than the leading H_3PO_4 solution, gave stable descending boundaries and tartaric acid (pK = 3.03)[83] and citric acid (pK = 3.13)[83] were suitable indicators in a rising boundary cell. The boundaries became sharper when either the concentration of the leading solution or the current was increased.

The boundaries with acetic, formic, tartaric and citric acids appeared as dark lines when viewed near the upper edge of the rectangular bar of light but as a bright line near the lower edge (as seen through the telescope). With all the other indicator solutions the positions of the dark and bright lines were reversed.

Ag/Ag_2 succ. was used as the non-gassing cathode (see section 3.2.6). For a few runs Cd/0.5 M $Cd(OAc)_2$ solution was used instead of Ag/Ag_2 succ.

3.3.3. Results.

Transference number measurements were done at molar concentrations of 0.02031, 0.04968 and 0.09300 and these are given in Table XVIII. A 0.01 M solution could not be used since skew boundaries were obtained, due to Joule heating, at the high currents necessary for boundary visibility. At all these concentrations the transference numbers were studied as a function of the current and the results were extrapolated to zero current. This is shown in Figures (24) and (25). Acetic and

Table XVIII

m	electrode	indicator	indicator concentration (M)	current (mA)	T_-
0.02031	$Ag/Ag_2succ.$	HOAc	0.026	0.46	0.08028
			0.024	0.46	0.08018
			0.026	0.62	0.08033
			0.026	0.62	0.08027
			0.026	0.76	0.08046
			0.026	0.85	0.08012
			0.026	0.89	0.08018
			0.026	1.02	0.08044
			0.026	1.05	0.08038
		$H_2succ.$	0.020	1.03	0.08066
0.04968	$Ag/Ag_2succ.$	HOAc	0.064	0.39	0.08011
			0.058	0.92	0.08035
			0.064	1.20	0.08041
		$H_2succ.$	0.049	0.51	0.08010
			0.049	0.92	0.08024
			0.049	1.35	0.08033
			0.044	1.20	0.08030
	$Cd/Cd(OAc)_2$	HOAc	0.064	0.51	0.08045
			0.064	0.92	0.08061
			0.064	1.19	0.08075
0.09300	$Ag/Ag_2succ.$	HOAc	0.125	0.63	0.08114
			0.125	0.77	0.08112
			0.113	0.77	0.08103
			0.125	0.84	0.08106
			0.125	0.96	0.08124

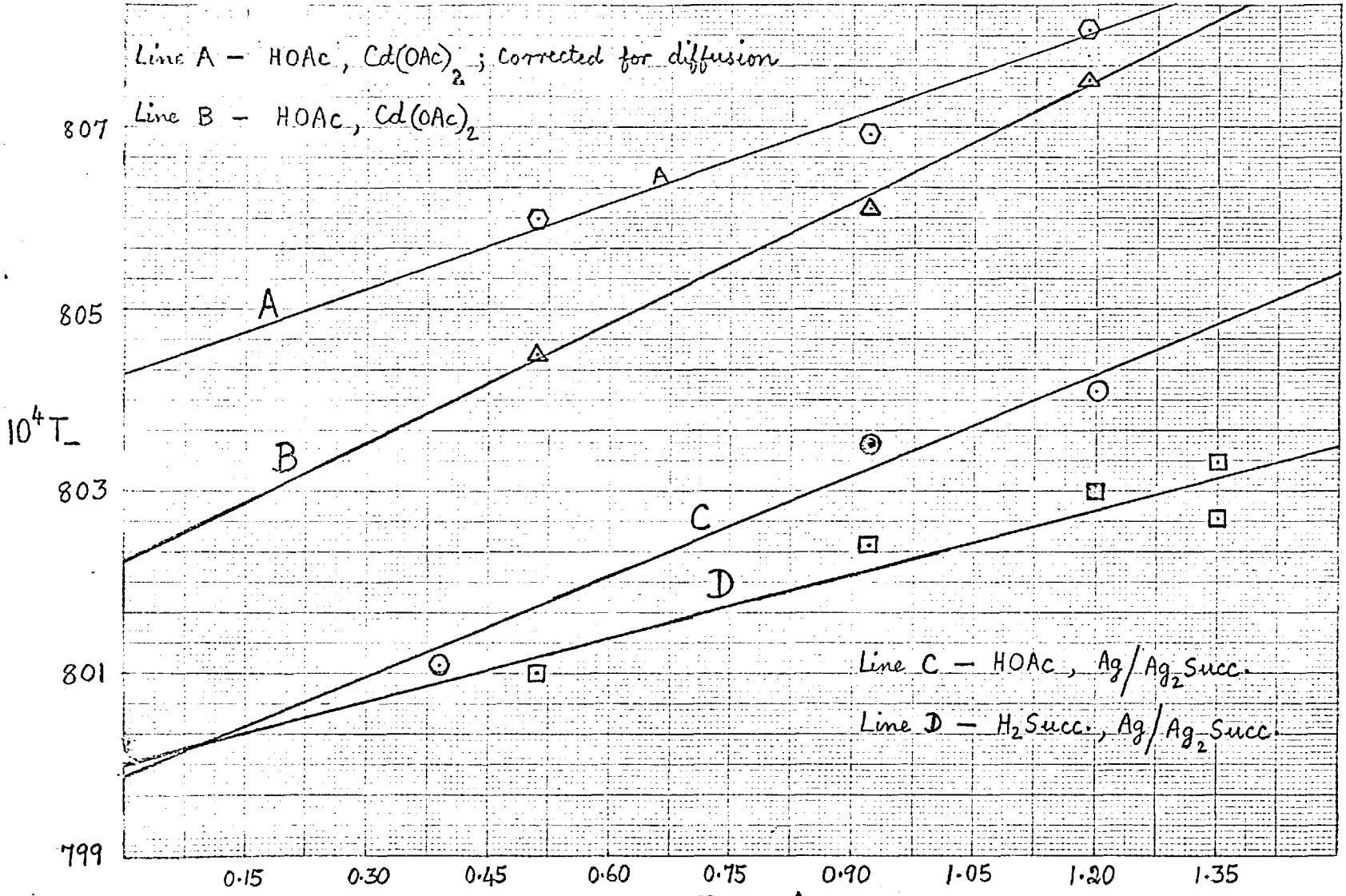


FIG. 24 (See Table XVIII)

VARIATION WITH CURRENT OF T_- IN 0·04968 M H_3PO_4

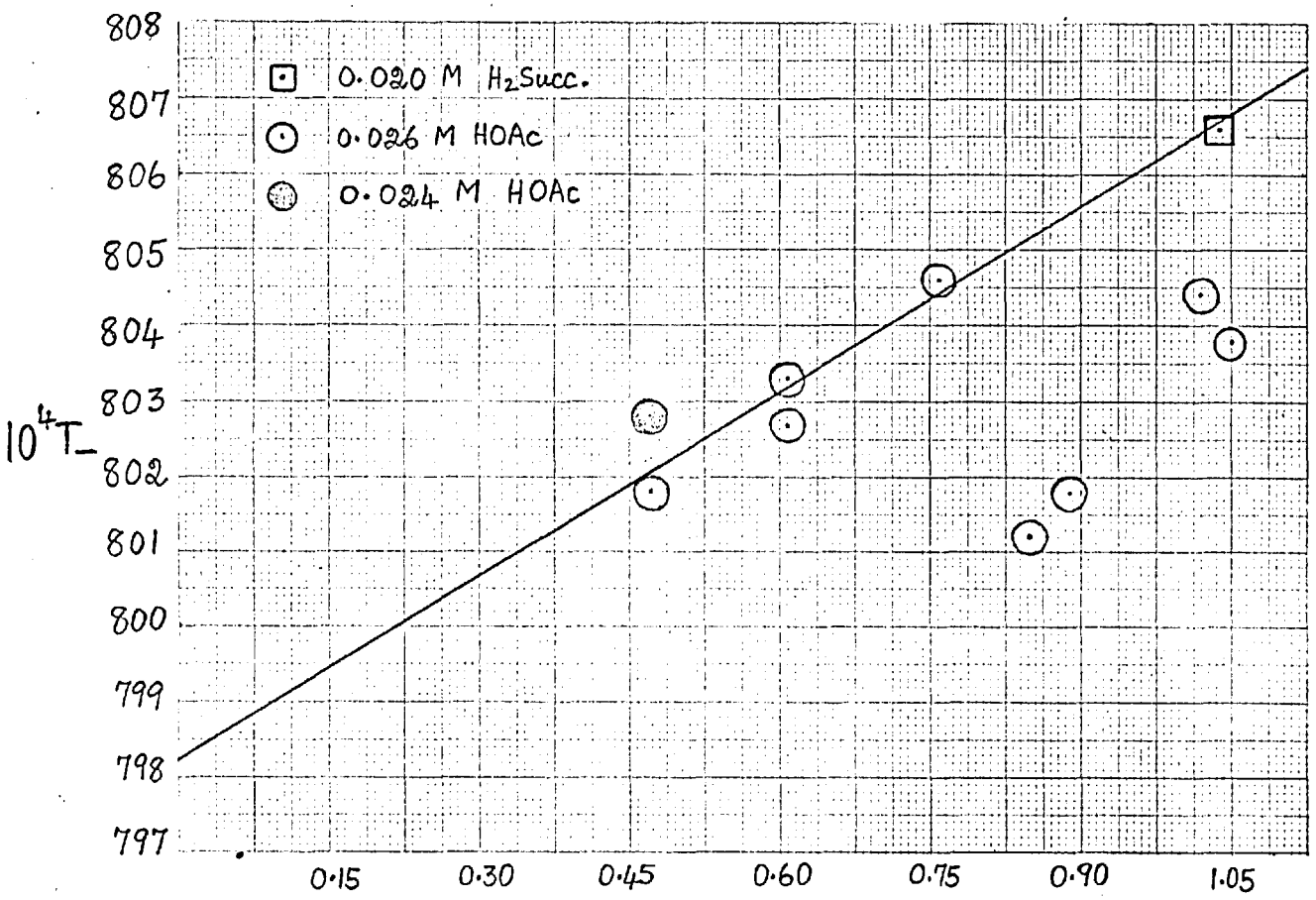


FIG. 25

VARIATION WITH CURRENT OF T_- IN 0.02031 M H_3PO_4. THE NON-GASSING ELECTRODE WAS $Ag/Ag_2Succ.$ RESULTS FOR $I > 0.8$ mA. WERE NEGLECTED WHEN DRAWING THE GRAPH SINCE SKEW BOUNDARIES WERE OBTAINED.

succinic acids were used as the indicator solutions since they gave the sharpest boundaries; the former was used at all concentrations of H_3PO_4 and both were employed with the 0.04968 M solution to test whether the results were independent of the following electrolyte.

The 0.04968 M H_3PO_4 solution was studied in detail; runs were performed varying the current, the following electrolyte and its concentration and the type of non-gassing electrode (see Fig. (24)). The general rise of transference number with increasing current has been shown very recently to be a consequence of Joule heating[70]. This heating effect would be expected to be greater the weaker the indicator electrolyte and this is borne out by the greater current dependence of T_- with the weaker indicator, acetic acid (line C), compared with succinic acid (line D). The points on lines C and D show that T_- is not significantly affected by changing the indicator concentration by 10% and the fact that the intercepts of these lines with the zero-current axis are almost identical proves that the transference numbers are independent of the nature of the following electrolyte. The points on line B were found with a different non-gassing electrode — Cd/0.5 M $Cd(OAc)_2$ solution. The results have to be corrected for diffusion between the $Cd(OAc)_2$ and indicator solutions (see section 3.2.6); the points on line A give the corrected transference numbers. The results obtained with the different electrodes agree after the necessary corrections (see below) have been applied. The transference number results at zero current for the various concentrations are given in column 4 of Table XIX . The T_- results at I=0 have to be corrected for the conduction due to the solvent (solvent correction) and for the volume change in the closed

compartment because of the electrode reaction (volume correction). These will now be considered.

Table XIX

m	α	electrode	$T_-(I=0)$	Solvent correction	Volume correction	T_- (corrected)
0.02031	0.486	Ag/Ag_2succ.	0.07981	0.00001	- 0.00008	0.07974
0.04968	0.358	Ag/Ag_2succ.	0.08000	-	- 0.00020	0.07980
		$Cd/Cd(OAC)_2$ soln.	0.08043	-	- 0.00063	0.07980
0.09300	0.283	Ag/Ag_2succ.	0.08094	-	- 0.00036	0.08058

3.3.4. The solvent and volume corrections.

The solvent correction was first applied by Longsworth in 1932[91]. Assuming that the solute does not alter the concentration and mobilities of the impurities in the solvent he derived the following relationship

$$T_- = T_{-(obs.)} + T_{-(obs.)} \frac{k_{solvent}}{k_{solution}} \qquad (53)$$

k is the specific conductance and $T_{-(obs.)}$ and T_- the experimental and corrected transference numbers respectively. The equation shows that the solvent correction becomes more and more important as the solution becomes more and more dilute. Equation (53) should be modified for acidic solutions since $k_{solvent}$ changes when solutions are made. This is because the specific conductance of conductivity water is in the main due to dissolved carbon dioxide and when any acid solution is prepared the ionisation of H_2CO_3 is suppressed. $k_{solvent}$ (in the solution) was therefore obtained by subtracting the conductance due to H_2CO_3 from

the experimentally determined specific conductance of conductivity water. This was done as follows:- pH of conductivity water (experimentally measured) = 5.5. If acidity is due only to H_2CO_3 then

$$(H^+) = (HCO_3^-) \doteq 10^{-5.5} \doteq 3.2 \times 10^{-6}$$

Since $\Lambda_{H^+HCO_3^-} = \Lambda^o_{H^+HCO_3^-} = 395 \text{ cm}^2\text{ohm}^{-1}\text{equiv.}^{-1}$,

$$k_{H_2CO_3} = \frac{\Lambda C}{1000} = 395 \times 3.2 \times 10^{-6} \times 10^{-3}$$

$$= 1.25 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}.$$

k of conductivity water was about 1.5×10^{-6}

$\therefore$ $k_{solvent}$ in the solution $= 0.25 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$.

The specific conductance of the solutions can be calculated from known equivalent conductances and dissociation constants and therefore the solvent correction can be worked out from equation (53). Column 5 of Table XIX shows that the solvent correction is negligible for all the solutions.

The necessity for volume corrections was first pointed out by Lewis[71] in 1910. This correction is given by

$$T_- = T_{-(obs.)} - m\Delta V_F/1000 \qquad (54)$$

where ΔV_F is the volume change in cm^3 in the closed compartment per faraday of electricity passed through the cell. The method of calculating ΔV_F has been given in detail[72]. For the silver/silver succinate cathode

$$\Delta V_F = V_{Ag} - \frac{1}{2} V_{Ag_2 \text{ succ.}} + \frac{1}{2} \bar{V}_{H_2\text{succ.}} - T_- \bar{V}_{H_3PO_4}$$

and for the cadmium/cadmium acetate cathode

$$\Delta V_F = \frac{1}{2} V_{Cd} - \frac{1}{2} \bar{V}_{Cd(OAc)_2} + \bar{V}_{HOAc} - T_- \bar{V}_{H_3PO_4}$$

where T_- is the anion constituent transference number and $\bar{V}_{H_3PO_4}$ the partial molal volume in the H_3PO_4 solution and where the other $\bar{V}$ values refer to the following solution containing succinic or acetic acid. Values of V_{Ag} (10.3 cm^3/mole)[73], V_{Cd}(13.0)[73] and $\bar{V}_{HOAc}$ (51.9)[74] are given in the literature, $\bar{V}_{H_2succ.}$ (82.5) and $\bar{V}_{H_3PO_4}$ (43.3) were calculated from published density data[75,76] while $V_{Ag_2succ.}$ (88.5 - see section 3.2.6.) and $\bar{V}_{Cd(OAc)_2}$ in the 0.5 M $Cd(OAc)_2$ solution (84.3) were obtained from the author's density measurements. The partial molal volumes were calculated from density data using the equation[72]

$$\bar{V} = m' \frac{d\phi}{dm'} + \phi$$

$$\phi = \frac{V - V_o}{m}$$

where V is the colume of an m' molal solution and V_o is the volume of 1000 g. of pure water. The density results for $Cd(OAc)_2$ solutions and the stages in the calculation for determining $\bar{V}_{Cd(OAc)_2}$ are given below:-

molar conc.	density (ρ)	molal conc. (m')	$V(= \frac{100+Mm'}{\rho})$	ϕ	$\bar{V}$
0.35	1.0501	0.361	1031.53	79.2	
0.50	1.0722	0.522	1044.88	80.3	84.3
0.65	1.0940	0.688	1059.03	81.5	

It follows that ΔV_F = +3.9 and +12.7 cm^3/faraday for the silver/silver succinate and cadmium/cadmium acetate cathodes respectively. Column 6 of Table XIX gives the volume corrections for the various solutions. The last column in the Table gives the T_- value at zero current after applying the solvent and volume corrections. It can be seen that the results obtained with the two electrode systems (0.04968 M H_3PO_4) are in good agreement.

3.3.5. Discussion and determination of $\lambda^o_{H_2PO_4^-}$.

The transference numbers in Table XIX are plotted against $\sqrt{cm}$ in Fig. 26. α was calculated taking K_1 as 7.516×10^{-3} [81]. The dashed line is a naive extrapolation to infinite dilution and gives T^o_- = 0.0782 which, since $\lambda^o_{H^+}$ = 349.8, leads to $\lambda^o_{H_2PO_4^-}$ = 29.7 $cm^2 ohm^{-1} equiv.^{-1}$. This value does not agree with any of the figures obtained by earlier workers and, what is more important, the T_- versus $\sqrt{cm}$ relationship differs completely from the limiting Debye-Hückel-Onsager (D-H-O) slope. According to the D-H-O theory, for uni-univalent electrolytes, T_- at any concentration should be given by

$$T_- = \frac{\lambda_-}{\lambda_+ + \lambda_-} = \frac{\lambda^o_- - S_{(\lambda)}\sqrt{\alpha m}}{\lambda^o_- - S_{(\lambda)}\sqrt{\alpha m} + \lambda_+ - S_{(\lambda)}\sqrt{\alpha m}} \qquad (55)$$

It will be shown later that $\lambda^o_{H_2PO_4^-}$ = 32.3 and the T_- values calculated on this basis using the D-H-O equation are given by line B in the graph. The discrepancy between the experimental T_- values and that predicted by the D-H-O theory cannot be attributed to hydrogen ion proton-jumps since the transference numbers of HCl solutions obey the theory[77]. It has been shown in Part I of the thesis that the conductance data provides

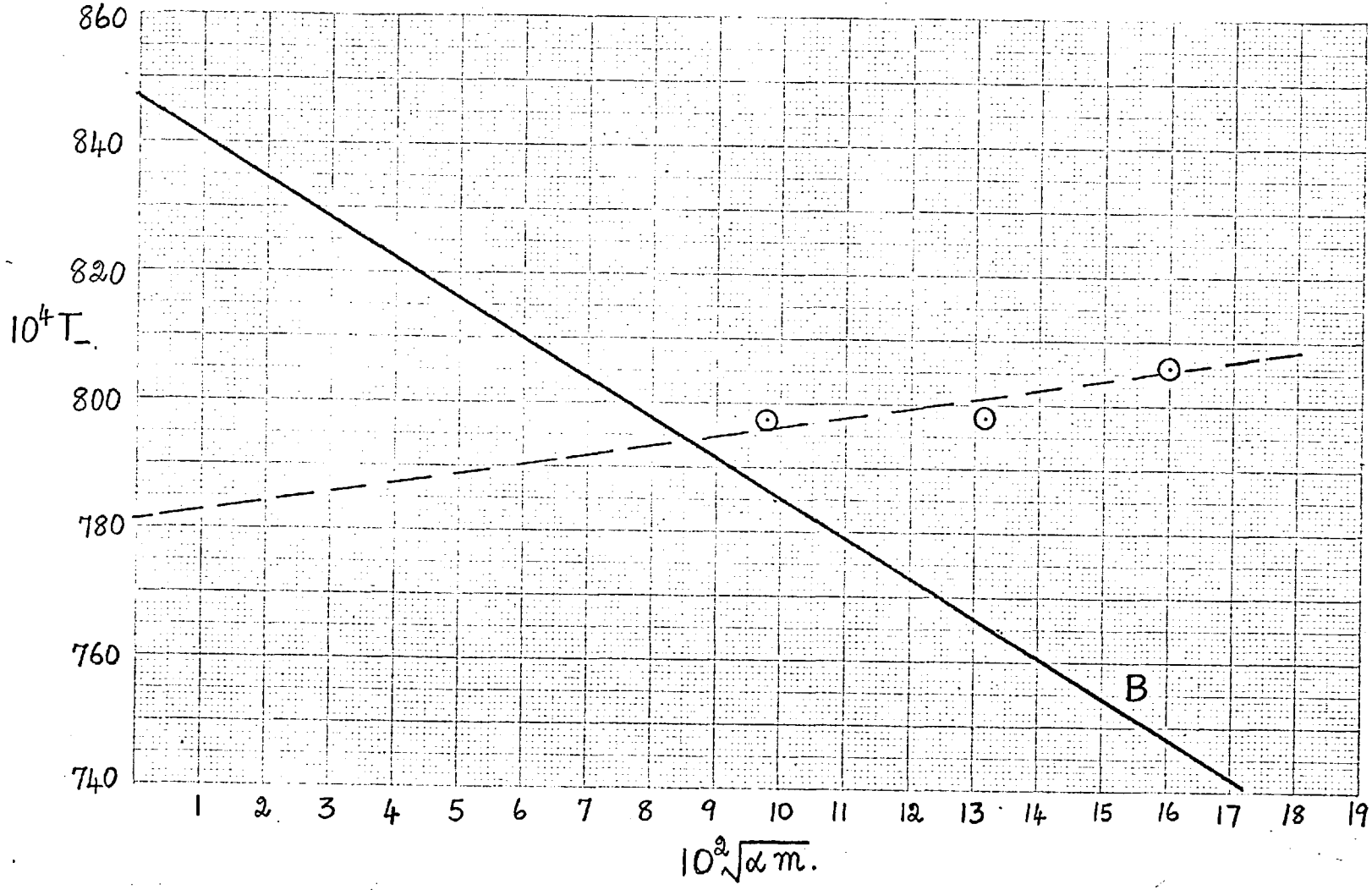


FIG. 26

DEPENDENCE OF T_- ON $\sqrt{\alpha m}$. THE FULL LINE HAS THE D-H-O LIMITING SLOPE CORRESPONDING TO $\lambda^0_{A-} = 32.3$, THE DASHED LINE IS A NAIVE EXTRAPOLATION.

strong evidence for the presence of complex ions of the type $H_2PO_4^- \cdot H_3PO_4$. The transference results, as well as some other observations, can be explained also by the presence of the complex ion $H_2PO_4^- \cdot H_3PO_4$.

The effect of the presence of the complex ion on the anion constituent transference number and the calculation of $\lambda^o_{H_2PO_4^-}$ will now be considered. For simplicity H_3PO_4 will be represented as HA (since H_3PO_4 is monoprotic within the concentration range of the investigation) and therefore the complex ion becomes AHA^-. The equilibria in solution are therefore

$$HA \rightleftharpoons H^+ + A^-$$

$$A^- + HA \rightleftharpoons AHA^-$$

If α is the degree of dissociation of HA and β the degree of formation of AHA^- the concentrations of the various species in an m molar solution of the acid are given by

$$(HA) = m(1-\alpha-\beta) \quad , \quad (H^+) = m\alpha \quad , \quad (A^-) = m(\alpha-\beta)$$

$$(AHA^-) = m\beta \quad \text{so that}$$

$$K_1 = \frac{(H^+)(A^-)\, f_{\pm}^2}{(HA)} = \frac{m(\alpha-\beta)\alpha\, f_{\pm}^2}{(1-\alpha-\beta)} \qquad (56)$$

$$K_{AHA^-} = \frac{(AHA^-) f_{AHA^-}}{(A^-)(HA) f_{A^-}} = \frac{\beta}{m(\alpha-\beta)(1-\alpha-\beta)} \qquad (57)$$

K_{AHA^-} is the stability constant of the complex.

The transference number of the A ion constituent is by equation (36) given by

$$T_{A^-} = \frac{m_{A^-}\,\lambda_{A^-} + 2m_{AHA^-}\,\lambda_{AHA^-}}{m_{H^+}\,\lambda_{H^+} + m_{A^-}\,\lambda_{A^-} + m_{AHA^-}\,\lambda_{AHA^-}}$$

$$= \frac{(\alpha-\beta)\,\lambda_{A^-} + 2\beta\,\lambda_{AHA^-}}{\alpha\,\lambda_{H^+} + (\alpha-\beta)\lambda_{A^-} + \beta\lambda_{AHA^-}}$$

$$= \frac{\lambda_{A^-} + \left(\frac{\beta}{\alpha}\right)(2\lambda_{AHA^-} - \lambda_{A^-})}{\lambda_{H^+} + \lambda_{A^-} - \left(\frac{\beta}{\alpha}\right)(\lambda_{A^-} - \lambda_{AHA^-})}$$

$$= \frac{\lambda_{A^-}}{\lambda_{H^+} + \lambda_{A^-}}\,(1 + \phi) \qquad (58)$$

where $\phi \doteq \left(\frac{\beta}{\alpha}\right)\left(\frac{2\lambda_{AHA^-} - \lambda_{A^-}}{\lambda_{A^-}} + \frac{\lambda_{A^-} - \lambda_{AHA^-}}{\lambda_{H^+} + \lambda_{A^-}}\right)$

The problem is to determine λ_{A^-} using equation (58) from the experimental transference numbers. This cannot be done uniquely since there are three unknown parameters in the equation — λ_{A^-}, λ_{AHA^-} and K_{AHA^-} (K_{AHA^-} should be known to determine β/α). It is therefore necessary to fit equation (58) to the experimental results by suitably selecting the three unknown parameters. This was done by the following method.

A reasonable pair of values were first chosen for $\lambda^{\circ}_{A^-}$ and $\lambda^{\circ}_{AHA^-}$. The necessary λ values at the appropriate ionic strengths were then calculated using the conductance equation (8) and were inserted into equation (58) along with the experimental T_- values to obtain β/α. K_{AHA^-} was then calculated using equation (57). Successive approximations were needed to determine the correct ionic strength of the solution

($\mu = \alpha m$) since the value of α depends on that of β, (see equation (56)). Various pairs of values for $\lambda^{o}_{A^-}$ and $\lambda^{o}_{AHA^-}$ were tried until the same result was obtained for K_{AHA^-} at each molarity m. The stages in the calculation are presented below for a successful pair of λ^{o} values.

$$\lambda^{o}_{A^-} = 32.35 \quad , \quad \lambda^{o}_{AHA^-} = 25.2$$

m	$\alpha(K_{AHA^-} = 3)$	$\frac{\lambda_{A^-}}{\lambda_{H^+} + \lambda_{A^-}}$	ϕ	β/α	K_{AHA^-}
0.02031	0.4856	0.07848	0.01606	0.02997	3.04
0.04968	0.3635	0.07647	0.04355	0.08369	3.03
0.09300	0.2964	0.07472	0.07843	0.1547	2.99

It can be seen that the data - i.e. $\lambda^{o}_{A^-} = 32.35$, $\lambda^{o}_{AHA^-} = 25.2$ cm^2 ohm^{-1} equiv.$^{-1}$ and $K_{AHA^-} = 3$ litre mole^{-1} is consistent with equation (58), at all the concentrations at which T_- results are available. However, $\lambda^{o}_{A^-}$ cannot be uniquely fixed at 32.35 since constancy in K_{AHA^-} is also attained with other sets of parameters, e.g. with

$$\lambda^{o}_{A^-} = 32.27 \quad , \quad \lambda^{o}_{AHA^-} = 23.4 \quad , \quad K_{AHA^-} = 4.6$$

This can be seen from Table XX where the K_{AHA^-} results at the three concentrations are given for various assumed values for $\lambda^{o}_{A^-}$ and $\lambda^{o}_{AHA^-}$.

In the calculations given above equation (8), in which the distance of closest approach of the ions ($\mathring{a}$) is assumed to be $3\mathring{A}$, was used. If $\mathring{a}$ is assumed to be $6\mathring{A}$ and the Stokes equation[78]

$$\frac{\lambda_{A^-}}{\lambda_{H^+} + \lambda_{A^-}} = \frac{\lambda^{o}_{A^-} - 30.3\sqrt{\alpha m} \,/\, (1 + 0.3291\, \mathring{a}\sqrt{\alpha m}}{\wedge^{o} - 60.6\sqrt{\alpha m} \,/\, (1 + 0.3291\, \mathring{a}\sqrt{\alpha m}}$$

Table XX

$\lambda^{o}_{H_2PO_4^-}(A^-)$	$\lambda^{o}_{AHA^-}$	K_{AHA^-} at 0.02031 M	K_{AHA^-} at 0.04968 M	K_{AHA^-} at 0.09300 M
32.35	20.0	9.1	12.6	22.4
	22.0	5.2	5.7	6.5
	24.0	3.6	3.7	3.8
	25.0	3.1	3.1	3.1
	25.2	3.0	3.0	3.0
	25.2	3.3*	3.1*	3.1*
	26.0	2.8	2.7	2.6
	28.0	2.2	2.2	2.1
	32.35	1.6	1.5	1.4
32.30	25.0	3.4	3.3	3.2
32.35	25.0	3.1	3.1	3.1
32.40	25.0	2.7	3.0	3.0
32.27	23.4	4.6	4.5	4.6

* Calculated with each T_{-}(corr.) result in Table XIX increased by 0.0001 to test the effect on K_{AHA^-} of experimental errors.

used for calculating the transference numbers, constancy at the various concentrations of K_{AHA^-} can be achieved with, for example,

$$\lambda^{o}_{A^-} = 32.20 \ , \ \lambda^{o}_{AHA^-} = 23.4 \ , \ K_{AHA^-} = 3.0$$

Transference measurements alone therefore do not provide a unique value for $\lambda^{o}_{A^-}$. However, it can be seen that $\lambda^{o}_{A^-}$ is relatively insensitive to the choice of the other parameters and so it can be fixed fairly exactly at

$$\lambda^{o}_{H_2PO_4^-} = 32.3 \pm 0.1 \ cm^2 ohm^{-1} \ equiv.^{-1}$$

In passing it may be mentioned that the above analysis indicates a value between 23 and 26 for $\lambda^{o}_{AHA^-}$ and 3 and 6 for K_{AHA^-} .

3.3.6. Conductances of H_3PO_4 solutions.

The conductance data for H_3PO_4 has already been partially treated (see section 2.4) and it was pointed out that they indicate the presence of complex ions of the type $A.HA^-$ in solution. The subject will now be treated quantitatively so as to estimate a value for $\lambda^{o}_{A^-}$ after allowing for the presence of AHA^- ions.

The conductance data have to be first corrected for viscosity changes in the medium by multiplying it by $\frac{\eta}{\eta_o} - S_{(\eta)}\sqrt{\alpha m}$ (see section 2.4.).

$$\frac{\eta}{\eta_o} - S_{(\eta)}\sqrt{\alpha m} = 1 + B_i \alpha m + B_u(1-\alpha)m$$

B_i and B_u were determined (section 2.4) from viscosity data on the appropriate salts[79] and H_3PO_4[80]. It was found that

$$B_i = 0.37 \quad \text{and} \quad B_u = 0.22 \ .$$

$\lambda^{o}_{A^-}$ was then calculated using the method given in section 2.3; the only difference being that the D-H-O limiting law was used instead of the conductance equation (8). The plot of $\lambda^{o}_{A^-}$ against $\sqrt{m}$ forms curve A in Fig. 27 and it can be seen that $\lambda^{o}_{A^-}$ increases with increasing concentration. A horizontal plot would have been expected if H_3PO_4 solutions had contained only H^+ and A^- ions.

It is possible to correct for the influence of AHA^- ions on the conductance by applying equation (26)

$$\lambda_{H^+} + \lambda_{A^-} = \frac{\Lambda}{\alpha} + \frac{\beta}{\alpha}(\lambda_{A^-} - \lambda_{AHA^-}) \qquad (59)$$

To do this K_{AHA^-}, $\lambda^{o}_{A^-}$ and $\lambda^{o}_{AHA^-}$ should be known. $\lambda_{A^-} - \lambda_{AHA^-}$ was assumed to be 8 and K_{AHA^-} was taken as 3 litre mole^{-1} (that given by the T_- results). The values calculated for the first and second terms on the right hand side of the equation at the various concentrations are given in the following table.

m	$K_{AHA^-} = 0$ $\frac{\Lambda}{\alpha}$	$K_{AHA^-} = 3$ $\frac{\Lambda}{\alpha}$	$K_{AHA^-} = 4.5$ $\frac{\Lambda}{\alpha}$	$K_{AHA^-} = 3$ $\frac{\beta}{\alpha}(\lambda_{A^-} - \lambda_{AHA^-})$	$K_{AHA^-} = 4.5$ $\frac{\beta}{\alpha}(\lambda_{A^-} - \lambda_{AHA^-})$
0.004	372.70	373.16	373.31	0.03	0.04
0.012471	370.44	370.97	371.17	0.14	0.19
0.02	371.03	370.88	370.80	0.26	0.34
0.05	372.69	366.83	364.32	0.75	0.93
0.10	377.27	359.16	352.35	1.48	1.78

The second term can be seen to contribute only a small amount and λ_{A^-} is therefore not very sensitive to the value assumed for $\lambda^{o}_{AHA^-}$. λ_{A^-} results

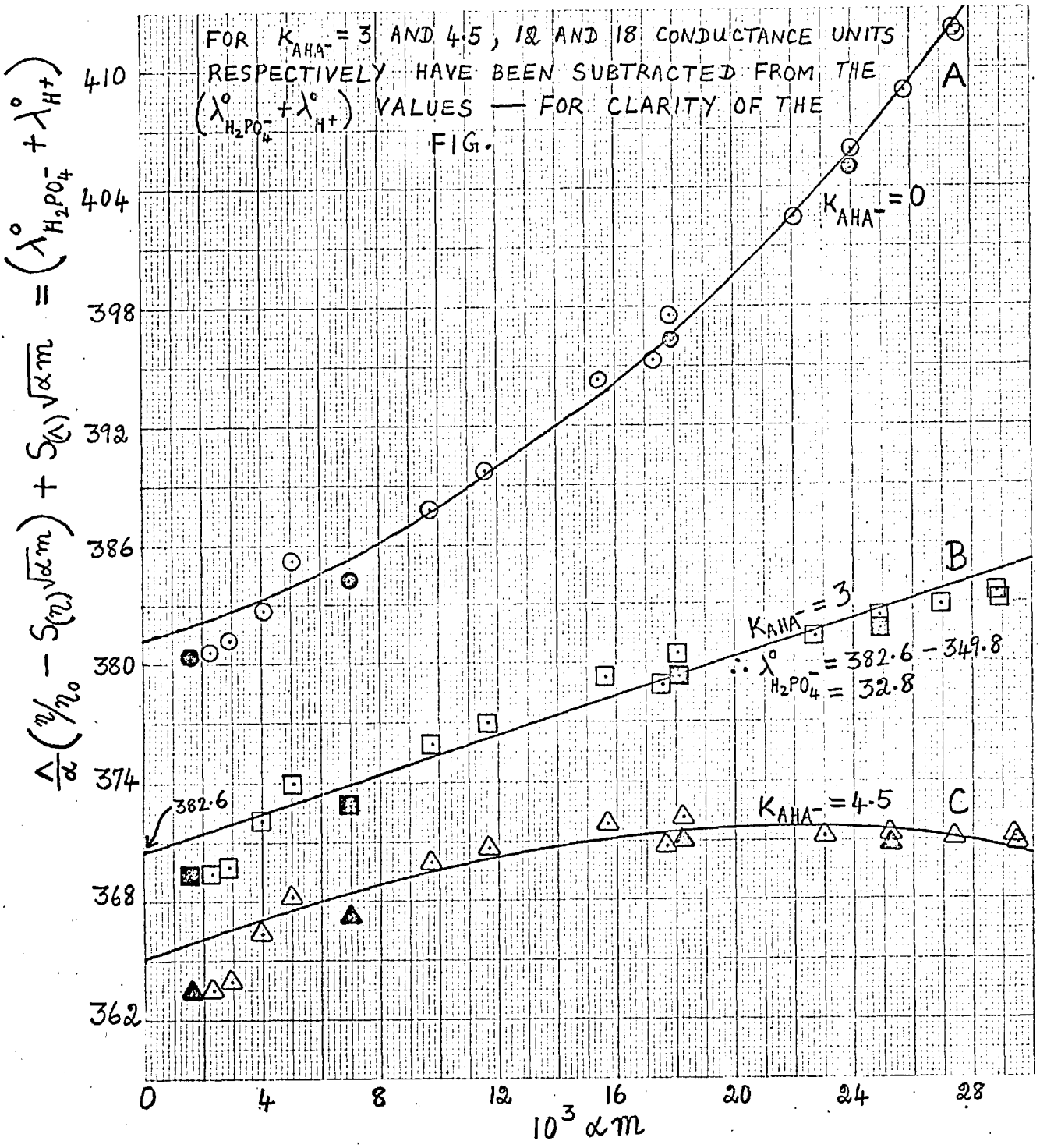


FIG. 27: PLOTS OF $\left(\lambda^\circ_{H_2PO_4^-} + \lambda^\circ_{H^+}\right)$ VERSUS αm FOR VARIOUS VALUES OF K_{AHA^-}.

⊙ H_3PO_4 CONDUCTANCE DATA OF MASON AND CULVERN[1]

◉ CONDUCTANCE DATA OF NOYES[101]

are, however, quite sensitive to changes in a and therefore to K_{AHA^-} (see equation 59); the results when K_{AHA^-} = 3 and 4.5 are given on lines B and C respectively in Fig. 27. The line C curves back so that K_{AHA^-} = 4.5 is clearly too large. The line B is a straight line of slope equivalent to an $\mathring{a}$ of 9$\mathring{A}$. This appears to be too high a value for the distance of closest approach but since neither the viscosity correction nor the theoretical equation itself are devoid of uncertainty the result is not unsatisfactory. Extrapolation leads to $\lambda^o_{A^-}$ = 32.8 ± 1 cm^2 ohm^{-1} $equiv.^{-1}$ in good agreement with that obtained from transference measurements.

3.3.7. Cation transference numbers of H_3PO_4 solutions.

Recently cation constituent transference numbers of dilute H_3PO_4 solutions have been measured[69] by using KH_2PO_4 as the following electrolyte. On the implicit assumption that the hydrogen ion constituent is present only in the leading solution, Kerker et al calculated T_+ using equation (38)

$$T_+ = V_F\, m_H \qquad (38)$$

and by extrapolating the results to infinite dilution obtained T^o_+ = 0.895. This is equivalent to a $\lambda^o_{A^-}$ of 41.0, a value about 25% higher than that obtained by the other methods. Their results were

m	T_+
0.0088	0.9005
0.0220	0.9040
0.0352	0.9063
0.0440	0.9090

The main reason for this large difference is that hydrolysis in the following KH_2PO_4 solution was neglected. The leading solution (a) contains

the species H_3PO_4 , H^+ and $H_2PO_4^-$ and the following solution (b) the species K^+ , $H_2PO_4^-$, H^+ , H_3PO_4 and HPO_4^{--} . It is clear, since H^+ ions are present in the following solution also, that the m.b. equation (37)

$$T_H^a - T_H^b = V_F (\bar{m}_H^a - \bar{m}_H^b) \qquad (37)$$

should have been used to calculate T_H^a instead of equation (38). The cation transference number measurements are therefore re-interpreted below using equation (37) in order to obtain a value for λ_A^o- . The detailed calculations were lengthy and involved several sets of successive approximations; in outline the procedure for a given concentration of the leading solution was as follows.

The composition of the adjusted following solution for any particular concentration of the leading solution was calculated from Kerker's experimental results by the following method.

(i) An approximate value for the concentration of the following solution (KH_2PO_4) was determined, assuming no hydrolysis in it, by using the Kohlrausch relation (equation (52)).

$$\frac{m^b_{KH_2PO_4}}{m^a_{H_3PO_4}} = \frac{T_{K^+}}{T_{H^+}} \qquad (60)$$

The concentrations of H^+, $H_2PO_4^-$, HPO_4^{--} and K^+ and the ionic strength μ in this solution was then calculated using the method given in section 1.2. K_1 was taken as 7.516×10^{-3} [81] and K_2 as 6.339×10^{-8} [82] mole litre^{-1}.

(ii) $T^b_{K^+}$ is related to the conductances and concentrations of the ions in the solution by equation (36) and can be calculated by

$$T^{b}_{K^+} = \frac{\lambda_{K^+}\ m_{K^+}}{\lambda_{K^+}\ m_{K^+} + \lambda_{H_2PO_4^-}\ m_{H_2PO_4^-} + \lambda_{H^+}\ m_{H^+} + 2\lambda_{HPO_4^{--}}\ m_{HPO_4^{--}}} \quad \ldots(61)$$

λ_i values at the required ionic strength were obtained by correcting the λ^o_i values using equation (8). $\lambda^o_{K^+}$ and $\lambda^o_{H^+}$ were taken as 73.52 and 349.81 respectively. $\lambda^o_{HPO_4^{--}}$ is not known accurately. As results of 57[84] and 53.4[85] have been reported, a value of 55 was assumed. A value of $\lambda^o_{H_2PO_4^-}$ was provisionally chosen (see later).

Since K^+ ions are present only in the following solution, its concentration ($\bar{m}^b_{K^+}$) was determined using the m.b. equation in the simplified form (equation (38))

$$\bar{m}^b_{K^+}\ V_F = T^b_{K^+} \qquad (62)$$

V_F being obtained from Kerker's experimental results. For example, $V_F = \frac{0.9090}{0.0440}$ for the 0.0440 M. solution. $\bar{m}^b_{K^+}$ so determined was closer to the Kohlrausch concentration than that calculated by step (i). The same procedure was repeated with successive new values for $\bar{m}^b_{K^+}$ until a self-consistent result was obtained. This represented the concentration of K^+ in the adjusted following solution and the concentrations of H^+, $H_2PO_4^-$ and HPO_4^{--} in equilibrium with it were then determined (section 1.2.).

By applying the m.b. equation (37) to the hydrogen ion constituent in the leading and following solutions it is possible to determine T^a_H making use of Kerker's experimental results (which gives V_F). To do this $\bar{m}^a_H$, $\bar{m}^b_H$ and T^b_H must be calculated. The constituents should be so defined that no species formed by their dissociation is present in either the leading or the following solution. In the system considered either

H^+ , K^+ and HPO_4^{--} or H^+, K^+ and PO_4^{---} can therefore be selected as the ion constituents. Taking the first set only, the equivalent concentrations of the hydrogen ion constituent in the leading and following solutions are given by

$$\bar{m}_H^a = m_{H^+}^a + m_{H_2PO_4^-}^a + 2m_{H_3PO_4}^a = 2m^a$$

$$\bar{m}_H^b = m_{H^+}^b + m_{H_2PO_4^-}^b + 2m_{H_3PO_4}^b = m^b$$

where m^a is the molarity of the phosphoric acid in the leading solution. T_H can be easily calculated from the concentrations and conductances of the ions in the following solution by applying equation (36)

$$T_H^b = \frac{\lambda_{H^+} m_{H^+} - \lambda_{H_2PO_4^-} m_{H_2PO_4^-}}{\lambda_{H^+} m_{H^+} + \lambda_{H_2PO_4^-} m_{H_2PO_4^-} + \lambda_{K^+} m_{K^+} + 2\lambda_{HPO_4^{--}} m_{HPO_4^{--}}} \quad .. (63)$$

T_H^a may now be determined from equation (37) and will be represented as T_H^a (expt.)

T_H^a can also be calculated, T_H^a (calc.), without using the experimental transference results by applying equation (36)

$$T_H^a \text{ (calc.)} = \frac{\lambda_{H^+} m_{H^+} - \lambda_{H_2PO_4^-} m_{H_2PO_4^-}}{\lambda_{H^+} m_{H^+} + \lambda_{H_2PO_4^-} m_{H_2PO_4^-}} \quad (64)$$

The ionic concentrations were calculated from the known values for the dissociation constants of phosphoric acid, and the ionic conductances at the required ionic strength were obtained with equation (8).

It is obvious that the values of T_H^a (expt.) and T_H^a (calc.) are dependent on the choice of the value for $\lambda^o_{H_2PO_4^-}$. By trial and error a value of $\lambda^o_{H_2PO_4^-}$ was selected so as to make T_H^a (expt.) identical with T_H^a (calc.). The value of $\lambda^o_{H_2PO_4^-}$ so obtained is based on the assumption that the conductance equation (8) applies to all the ions in the leading and following solutions. This involves the assumption that $\mathring{a} = 3\mathring{A}$. The detailed results of the calculations for the 0.022 M H_3PO_4 are presented below.

$\lambda^o_{H_2PO_4^-}$ (assumed)	$m^b_{KH_2PO_4}$ (eq.60)	T^b_K+(eq.61)	$\bar{m}^b_K$+(eq.62)	T^b_H(eq.63)	T^a_H(expt.) (eq. 37)	T^a_H(calc.) (eq. 64)
37.0	0.01630	0.6716	0.01634	- 0.3138	0.8227	0.8209
36.7	0.01640	0.6736	0.01639	- 0.3118	0.8227	0.8223

It can be seen that the T_+ results at 0.022 M H_3PO_4 indicate a $\lambda^o_{H_2PO_4^-}$ of 36.7 since it leads to T^a_H(calc.) = T^a_H(expt.). The results obtained similarly for all the concentrations are given in the following table.

$m_{H_3PO_4}$	0.0088	0.0220	0.0352	0.0440
$\lambda^o_{H_2PO_4^-}$	35.6	36.7	36.7	36.0

Mean = 36.3 $cm^2 ohm^{-1} equiv.^{-1}$.

As shown earlier the author's T_- results and Mason and Culvern's conductance data suggest the presence of $(H_3PO_4.H_2PO_4)^-$ ions in solutions of H_3PO_4. To allow for this, the calculation has to be slightly altered. In the leading solution H^+, $H_2PO_4^-$ and $(H_3PO_4.H_2PO_4)^-$ ions will be

present and therefore T_H^a(calc.) will be given by

$$T_H^a \text{ (calc.)} = \frac{\lambda_{H^+}\, m_{H^+} - \lambda_{H_2PO_4^-}\, m_{H_2PO_4^-} - 3\lambda_{AHA^-}\, m_{AHA^-}}{\lambda_{H^+}\, m_{H^+} + \lambda_{H_2PO_4^-}\, m_{H_2PO_4^-} + \lambda_{AHA^-}\, m_{AHA^-}}$$

The procedure for determining $\lambda^o_{H_2PO_4^-}$ is the same as in the former case, except for the different definition of T_H^a (calc.). $\lambda^o_{AHA^-}$ was assumed to be 25. The results are given below

$m_{H_3PO_4}$	0.0088	0.0220	0.0352	0.0440
$\lambda^o_{H_2PO_4^-}$	35.4	36.2	35.9	35.0

Mean = 35.6 $cm^2 ohm^{-1} equiv.^{-1}$.

The mean $\lambda^o_{A^-}$ of the recalculated results, 35.6, is much closer to the value of 32.3 obtained by the author's anion transference measurements than the uncorrected figure of 41.0 $cm^2 ohm^{-1} equiv.^{-1}$.

3.4. $\lambda^{o}_{HT^-}$ FROM TRANSFERENCE NUMBERS OF D-TARTARIC ACID

3.4.1. Introduction.

In part I of this thesis the relevant literature conductance data have been analysed to furnish figures for $\lambda^{o}_{HT^-}$ where HT^- stands for the bitartrate ion. Values of 32.7 and 27.0 $cm^2 ohm^{-1} equiv.^{-1}$ were obtained from conductance measurements on the acid and its ammonium hydrogen salt respectively. Anion transference measurements were therefore carried out to fix this quantity more exactly.

3.4.2. Preliminary experiments.

The work of the author was a continuation of that done by Marsh and Spiro in Australia. Preliminary work had shown that indicator solutions of citric, furoic, malic, mandelic, phenoxyacetic or succinic acids gave no visible boundaries with a leading tartaric acid solution. and that only acetic or propionic acids were suitable indicators. Also T_- had been determined at some indicator concentrations but not at the Kohlrausch concentration and Joule heating inside the moving boundary tube had already been investigated.

Results.

2 M.$Cd(OAc)_2$/Cd was used as the non-gassing cathode in all the runs and therefore the results have to be corrected for mutual diffusion between the $Cd(OAc)_2$ solution and the HOAc indicator. The volume changes from diffusion were not suspected until the runs were completed and the results published.[70] Dilatometer experiments were later carried out (see section 3.2) to estimate these volume changes and therefore to apply a correction to the T_- results. This can be done easily from the

known volume of the calibrated moving boundary tube (about 0.735 ml. between lines 1 and 6) and ΔV due to diffusion ($\doteq$ - 0.000284 ml. per hour, see section 3.2.6.). For example a run with 0.1 M H_3PO_4 using a current of 1 mA took 26 hours and 20 minutes. An error of about 1% is therefore caused by diffusion. The results are given in Table XXI where column 4 gives the experimental T_- values assuming tartaric acid is a 1:1 electrolyte and column 5 that after correcting for diffusion. The results at the lowest currents are seen to be not very reproducible and are relatively inaccurate, e.g. the 2 runs with a current of 0.22 mA (m = 0.05 M) differ by about 0.7%. This is probably the result of the errors due to diffusion becoming larger as the runs becomelonger. The results do not show a significant current dependence, presumably because this is masked by the relatively large errors caused by the uncertain volume corrections. An average value of the T_- results was therefore taken at each of the concentrations after discarding the runs at the lowest currents. These are given in column 3 of Table XXII. The equations for the solvent and volume corrections have been discussed earlier. The solvent correction was found to be negligible and the volume correction is given by $m\frac{\Delta V_F}{1000}$,

where

$$\Delta V_F = \frac{1}{2} V_{Cd} - \frac{1}{2} \bar{V}_{Cd(OAc)_2} + \bar{V}_{HOAc} - T_- \bar{V}_{H_2T}$$

Numerical values of V_{Cd} (13.0 $cm^3 mole^{-1}$)[73] and $\bar{V}_{HOAc}$ (51.9)[74] are given in the literature, and $\bar{V}_{H_2T}$ (83) and $\bar{V}_{Cd(OAc)_2}$ (122) were obtained from Marsh's density determinations. It therefore follows that ΔV_F = - 9 cm^3/faraday. The transference numbers with diffusion, solvent and volume corrections applied are given in the last column of Table XXII

Table XXI

m_{H_2T}	m_{HOAc}	I(mA.)	T_- [a]	T_- (d.corr.) [b]
0.01	0.013	0.43	0.07387	0.07404
	0.013	0.56	0.07392	0.07405
	0.013	0.56	0.07400	0.07413
0.05	0.064	0.22	0.07319	0.07487
	0.064	0.22	0.07270	0.07438
	0.064	0.36	0.07305	0.07408
	0.064	~~0.049~~ 0.49	0.07323	0.07400
	0.07	0.49	0.07330	0.07406
	0.064	0.61	0.07349	0.07410
	0.064	0.61	0.07333	0.07394
	0.064	0.87	0.07354	0.07397
	0.064	1.00	0.07369	0.07406
0.10	0.128	0.46	0.07334	0.07496
	0.128	0.70	0.07357	0.07464
	0.128	1.00	0.07384	0.07459

a - experimental results

b - results after correcting for diffusion.

Table XXII

m	α	T_- (I=0) [a]	T_- (corr.) [b]
0.01	0.274	0.0740	0.0741
0.05	0.138	0.0740	0.0745
0.10	0.101	0.0746	0.0755

a - at zero current with diffusion correction applied.

b - with volume and solvent correction applied also.

and will be referred to as T_{expt}.

These have been calculated using the equation

$$T_{expt} = mV_F \qquad (65)$$

on the assumption that tartaric acid behaves as a 1:1 electrolyte. Since K_2 is 4.30×10^{-5} [86] it can be easily shown (method of calculation was given in section 2.3) that in 0.1 M and 0.01 M solutions 0.7% and 2% of the HT^- ions are dissociated to T^{--} respectively. The T_- results have therefore to be corrected for secondary dissociation and this was done as follows. Since H^+, HT^- and T^{--} ions are present in solution H^+ and T^{--} ions should be chosen as the ion constituents and therefore applying equation (36)

$$T_{T^{--}} = \frac{2m_{HT^-}\lambda_{HT^-} + 2m_{T^{--}}\lambda_{T^{--}}}{m_{H^+}\lambda_{H^+} + m_{HT^-}\lambda_{HT^-} + 2m_{T^{--}}\lambda_{T^{--}}} = 2m\,V_F \qquad (66)$$

In equation (66) the factor of 2 arises since the equivalent concentration of a 1:2 electrolyte is twice its molarity. Comparison of equations (65) and (66) shows that

$$T_{expt} = \frac{1}{2}T_{--} = \frac{m_{HT^-}\lambda_{HT^-} + m_{T^{--}}\lambda_{T^{--}}}{m_{H^+}\lambda_{H^+} + m_{HT^-}\lambda_{HT^-} + 2m_{T^{--}}\lambda_{T^{--}}} \qquad (67)$$

The relationship between T_{expt} and T_{HT^-} becomes clearer if the equilibrium concentrations in an m molar solution of tartaric acid, i.e. $(H_2T) = m(1-\alpha)$, $(HT^-) = m(\alpha-\beta)$, $(T^{--}) = m\beta$, $(H^+) = (\alpha+\beta)$, are inserted into equation (67). Then

$$T_{expt} = \frac{(\alpha-\beta)\,\lambda_{HT^-} + \beta\lambda_{T^{--}}}{(\alpha+\beta)\lambda_{H^+} + (\alpha-\beta)\lambda_{HT^-} + 2\beta\lambda_{T^{--}}}$$

$$= \frac{\lambda_{HT^-} + \left(\frac{\beta}{\alpha-\beta}\right)\lambda_{T^{--}}}{\lambda_{H^+} + \lambda_{HT^-} + \left(\frac{2\beta}{\alpha-\beta}\right)(\lambda_{H^+} + \lambda_{T^{--}})} \qquad (68)$$

But $$T_{HT^-} = \frac{m_{HT^-}\,\lambda_{HT^-}}{m_{H^+}\,\lambda_{H^+} + m_{HT^-}\,\lambda_{HT^-}} = \frac{\lambda_{HT^-}}{\lambda_{H^+} + \lambda_{HT^-}} \qquad (69)$$

Equations (68) and (69) show that T_{HT^-} becomes equal to T_{expt} either when β/α is very small (i.e. no appreciable dissociation of HT^- ions into T^{--}) or when the tartrate terms in the numerator and the denominator of equation (68) just balance each other so that

$$\frac{\lambda_{T^{--}}}{\lambda_{HT^-}} = \frac{2(\lambda_{H^+} + \lambda_{T^{--}})}{\lambda_{H^+} + \lambda_{HT^-}} \qquad (70)$$

In the present case condition (70) applies if $\lambda^o_{T^{--}} = 59.9$ and it so happens that values of 59.6[4] and 63.2[38] have been reported from conductance measurements on salts. The numerical value of T_{HT^-} is therefore identical with that of $T_{expt.}$

The variation of T_{HT^-} with $\sqrt{\mu}$ does not obey the D-H-O theory (see section 3.3, Fig. 26) and is similar to that found for H_3PO_4. Complex ions of the same type are therefore probably present in solution. Unfortunately, conductance data are available only up to a concentration of 0.008 M[38] and the results (see section 1.3, Fig. 16) seem to indicate the absence of complex ions up to this concentration.

The T_{HT^-} results may be used to calculate $\lambda^o_{HT^-}$ by allowing for

the presence of complex ions using the method given in section 3.3.5. This rather laborious procedure was not used in this case partly because the T_{HT^-} results are of lower precision as a result of the somewhat uncertain correction for diffusion and partly because the T_- value at the lowest concentration, 0.01 M, is very probably not influenced by the presence, if any, of the complex ions. This is borne out by the conductance data discussed earlier. A reasonably accurate value for $\lambda^o_{HT^-}$ may therefore be obtained by taking only the T_- result at 0.01 M and treating it by the following procedure.

$$T_{HT^-} = \frac{\lambda_{HT^-}}{\lambda_{H^+} + \lambda_{HT^-}}$$

λ_{H^+} at the ionic strength corresponding to the 0.01 M solution may be calculated by equation (8)

$$\lambda_i = \lambda^o_i - \frac{S_{(\lambda)}\sqrt{cm}}{1 + \sqrt{cm}} \qquad (8)$$

Since T_{HT^-} at 0.01 M is 0.0741, λ_{HT^-} is obtained as 27.56 from which, by again using equation (8), λ^o_{HT} may be calculated. A value of 29.4 $cm^2 ohm^{-1} equiv.^{-1}$ was obtained. When complex ion formation was not taken into account and no corrections were made for the volume change due to diffusion, $\lambda^o_{HT^-}$ was derived as 27.6[70]. It would clearly be desirable to repeat some of the tartaric acid transference number work with a non-gassing electrode of the silver/silver succinate type where diffusion corrections are not needed.

DISCUSSION OF LIMITING CONDUCTANCES

In Part I of the thesis $\lambda^{o}_{HA^-}$ values have been evaluated for diprotic (or effectively diprotic) acids from published conductance data on the acids or their acid salts. In Part II the same quantity was determined more accurately from the author's anion transference number measurements on phosphoric and tartaric acids. These results are presented together in Table XXIII. For phosphoric acid the results obtained by the different methods are in good agreement: 32.3 (anion transference numbers of H_3PO_4), 33.0 (conductances of NaH_2PO_4), 31.5 (conductances of KH_2PO_4) and 32.8 (conductances of H_3PO_4). $\lambda^{o}_{H_2PO_4^-}$ may therefore be fixed fairly exactly at 32.3 $\pm$ 0.1 $cm^2 ohm^{-1} equiv.^{-1}$. The transference measurements of tartaric acid suggest a value of 29.4 $\pm$ 0.2 for the limiting equivalent conductance of the bitartrate ion but conductance measurements on the acid and the acid salt lead to values which are about 11% higher and 8% lower respectively. The only available data for determining $\lambda^{o}_{HA^-}$ for malic, maleic, fumaric and O-phthalic acids are conductances of dilute solutions of the ammonium hydrogen salts and the scatter in the results indicates an uncertainty of about $\pm$ 3 conductance units; the absolute accuracy is undoubtedly even lower. The conductances of the acid and its acid salt lead to results in fair agreement in the case of malonic, succinic and glutaric acids but yield values differing by several conductance units for adipic, pimelic and suberic acids. It can be seen from Table XXIII that $\lambda^{o}_{HA^-}$ may be fixed within, say, one conductance unit for only malonic, succinic, glutaric, tartaric and phosphoric acids. The final column in the Table gives the "best" values of $\lambda^{o}_{HA^-}$ for these acids.

Table XXIII

Limiting Ionic Conductances in $cm^2 ohm^{-1} equiv.^{-1}$

Acid	$\lambda^o_{HA^-}$ from acid	$\lambda^o_{HA^-}$ from acid salt	$\lambda^o_{HA^-}$ from T_- detns.	"Best" $\lambda^o_{HA^-}$
Malonic	38.2	39.1		38.7
Succinic	35.3	36.5		35.9
Glutaric	29.4	29.5		29.5
Adipic	20.0	29.1		-
Pimelic	22.6	29.4		-
Suberic	18.0	27.2		-
Malic	-	29.8		-
Maleic	-	44.8		-
Fumaric	-	42.3		-
O-Phthalic	-	32.5		-
Tartaric	32.7	27.0	29.4	29.4
Phosphoric	32.8	33.0 31.5	32.3	32.3

Table XXIV

Acid	$\lambda^o_{HA^-}$	$\lambda^o_{A^{--}}$	$\lambda^o_{HA^-} / \lambda^o_{A^{--}}$	r_s (A°)
Malonic	38.7	64	0.60	2.36
Succinic	35.9	60	0.60	2.55
Glutaric	29.5	56	0.53	3.10
Tartaric	29.4	60	0.49	3.11
Phosphoric	32.3	55	0.59	2.83

The only theoretical relationship available for predicting λ^o for an ion is that obtained by the application of Stokes' law to the motion of the ions in an electric field. According to Stokes' law the velocity (v) of a spherical particle of macroscopic dimensions moving in an ideal hydrodynamic continuum is given by[92]

$$v = \frac{F}{6\pi \eta r_s} \tag{71}$$

where F is the electric force acting on the particle of radius r_s, and η is the viscosity of the medium. In terms of ion conductances the above equation becomes[92]

$$\lambda_i^o = \frac{0.8147 \times 10^{-8} \ |z_i|}{\eta \times r_s} \tag{72}$$

where r_s is the Stokes radius or the radius of the solvated ion. For particles that are not spherical equation (72) has to be modified. The correction term can be obtained approximately by measuring the dimensions of molecular models and then theoretically calculating the ratio of the frictional resistance of the particle (of any shape) to the resistance of a sphere of the same volume.[93]

Since the ions considered in this discussion are roughly spherical[94], equation (72) may be used to estimate the radius of the solvated ion and this is given in the final column of Table XXIV. Construction of molecular models (Stuart and Briegleb models) showed that r_s and the radii obtained from the molecular models (r_m) are of the same order of magnitude, except for the $H_2PO_4^-$ ion. In the latter case $r_s > r_m$ indicating solvation of the $H_2PO_4^-$ ion. Further support for solvation of the $H_2PO_4^-$

ion is furnished by comparison of the conductances and structures of the ions $H_2PO_4^-$, HSO_4^- and ClO_4^-. All have the same structure (tetrahedral) and virtually the same radius[95] but $\lambda^o_{ClO_4^-} = 67.3$,[96] $\lambda^o_{HSO_4^-} \doteq 50$[97] and $\lambda^o_{H_2PO_4^-} = 32.3$. It therefore seems reasonable to correlate the decrease in conductance with solvation due to hydrogen bonding through the -OH groups of the acid anion and the increased charge densities on the remaining -O groups. For the acid anions of malonic, succinic, glutaric and tartaric acids $r_s \doteq r_m$ and apparently no solvation is indicated. It is, however, more likely that these ions are actually solvated in solution but that too small a radius was predicted due to the inapplicability of Stokes' law to small ions. Robinson and Stokes[98] have shown that Stokes' law is applicable only for ions having a radius of about five angstroms or greater and that for smaller ions the radii predicted by equation (72) are too small. They studied tetra-alkyl ammonium ions and found that r_m was greater than r_s when r was greater than about five. Their results are given in the following Table.

Ion	r_m(Å)	r_s(Å)	r_m/r_s
$N(CH_3)_4^+$	3.47	2.04	1.70
$N(C_2H_5)_4^+$	4.00	2.81	1.42
$N(C_3H_7)_4^+$	4.52	3.92	1.15
$N(C_4H_9)_4^+$	4.94	4.71	1.05
$N(C_5H_{11})_4^+$	5.29	5.25	1.01

r_m = radius estimated from molecular volumes or models.

r_s = radius calculated from λ^o_+ by Stokes' law.

The results for the tetra alkyl ammonium salts indicate the inapplicability of Stokes' law to ions with $r_s < 5\text{Å}$ and therefore not much reliance can be placed on the values of r_s given in Table XXIV.

Various attempts have been made in the literature to find the relationship between the limiting equivalent conductances of the acid anions ($\lambda^o_{HA^-}$) and the corresponding divalent ions ($\lambda^o_{A^{--}}$). For example, Chandler[99] suggested that $\lambda^o_{HA^-} = 0.6\ \lambda^o_{A^{--}}$ while Jeffery and Vogel[3] postulated that the correct relationship is given by $\lambda^o_{HA^-} = 0.53\ \lambda^o_{A^{--}}$. In column 4 of Table XXIV is shown the relationship between $\lambda^o_{HA^-}$ and $\lambda^o_{A^{--}}$ for the acids whose $\lambda^o_{HA^-}$ values are reasonably reliable and it is clear that $\lambda^o_{HA^-} / \lambda^o_{A^{--}}$ varies between 0.5 and 0.6.

It can be seen from equation (72) that $\lambda^o_{HA^-} = 0.5\ \lambda^o_{A^{--}}$ if Stokes' equation is applicable and if the radius of the solvated species is the same for both the divalent and the univalent acid anion. Since the A^{--} and HA^- ions are nearly spherical[94] and have virtually the same crystal radius (H^+ ions are much smaller than the A^{--} ions), any inapplicability of the Stokes' equation should cause nearly the same error for the two ions. The ratio of the conductances should therefore not be very much affected and $\lambda^o_{HA^-} / \lambda^o_{A^{--}}$ should be about 0.5. It therefore appears that r_s is different for the HA^- and A^{--} ions because of different degrees of solvation. The divalent ion having a higher charge density would be expected to be solvated more, and hence the ratio of $\lambda^o_{HA^-} / \lambda^o_{A^{--}}$ should in general be greater than 0.5. The ion-solvent interaction also depends on the presence or absence of internal hydrogen bonding. For example the acid malonate ion has been shown to be internally hydrogen bonded[100].

It should therefore be less solvated than the corresponding divalent ion where internal hydrogen bonding is not possible.

A general numerical relationship cannot therefore be expected between $\lambda^{o}_{HA^-}$ and $\lambda^{o}_{A^{--}}$ since the mobility of an ion depends on interactions that are specific to the ion concerned.

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APPENDIX I

See Section 1.2

EXPLANATION OF THE PROGRAMME

```
TITLE
SELVA SALT HYDROLYSIS
CHAPTERo

1)READ(C)
READ(D)
READ(Dn)
NEWLINE
NEWLINE
READ(Cn)
READ(V)
READ(Vn)
PRINT(C)o,5

A=o
B=o
F=1
Fn=1
JUMPDOWN2

PRINT(A)o,5
PRINT(B)o,5
Gn=CA-CB
PRINT(Gn)o,5
NEWLINE
H=C-CA-CB
PRINT(H)o,5
Hn=2CA
PRINT(Hn)o,5
PRINT(G)o,5
U=340.8-110.48G
U=1000UGn
PRINT(U)o,5
NEWLINE
Un=o.2292V+30.3
Un=V-UnG
Un=1000UnC
PRINT(Un)o,5
W=Cn+W
Wn=o.666666W
X=Cn+2V
X=Un/X
```

$C \equiv m$
$D \equiv K_1$
$D^n \equiv K_2$

$C^n \equiv \lambda^o_{A^{--}}$
$V \equiv \lambda^o_{M^+}$
$V^n \equiv \Lambda_{expt.}$

$A \equiv \alpha$
$B \equiv \beta$
$F \equiv f_{\pm}^2$
$F^n \equiv f_{A^{--}}$

Calculating and printing instructions.

$G^n \equiv (H^+)$

$H \equiv (HA^-)$
$H^n \equiv (A^{--})$

$U \equiv 10^6 K_{H^+}$

$U^n \equiv 10^6 K_{M^+}$

```
XN=XSQRT(X)
XN=1+XN
XN=1.5654X/XN
XN=XNN+90.9-0.2292*V-30.3
XN=CN-XNG
XN=1000XNHN
PRINT(XN)0,5
Y=1000VNC
Y=Y-XN-HN-U
PRINT(Y)0,5
YN=0.001Y/H
Z=1-0.2292G
ZN=YN+30.36
ZN=ZN/Z
PRINT(ZN)0,5
JUMP1
0)END

2)E=1-A-B
E=CFE
E=D/E+1
EN=1-A-B
EN=DNENENF/D
EN=EN/EN
AN=XSQRT(EEN)
BN=XSQRT(EN/E)
E=1-A/AN
E=EE
JUMP4,E≥0.000000001
EN=1-B/BN
EN=ENEN
JUMP4,EN≥0.000000001
JUMP3

4)A=A+0.5AN-0.5A
B=B+0.5BN-0.5B
G=XSQRT(G+2AG-BG)
GN=1+G
G=G/GN
F=XEXP(-2.3478G)
FN=FF
JUMP2

3)RETURN
XSQRT
XEXP
CLOSE
→
*********************************
```

$X^n \equiv 10^6 k_A$--

$Y \equiv 10^6 k_{HA}$-

$Z^n \equiv \lambda^\circ_{HA}$-

Calculation of α and β by iteration using equations (5), (6) and (7). (See Section 1.2)

} To check convergence of iteration.

APPENDIX II

(See Section 2.3)

```
TITLE
SELVA ACID EQUILIBRIA I
CHAPTER 0

1)READ(C)
READ(D)
READ(D2)
READ(C2)
READ(V2)
NEWLINE
NEWLINE
PRINT(C)0,4

Z2=2C
Z=DD+4CD
Z=XSQRT(Z)
Z=Z-D
A=Z/Z2
Z=XSQRT(CA)
Z2=1+Z
F=XEXP(-2.3478Z/Z2)
F2=FF
D=D2/C
B=B/F2
JUMPDOWN2

NEWLINE
PRINT(A)0,4
PRINT(B)0,4
U=CA+CB
PRINT(U)0,4
U2=CA-CB
PRINT(U2)0,4
NEWLINE
V=AC
PRINT(V)0,4
V=2CB
PRINT(V)0,4
X=CA+2CB
X=XSQRT(X)
X2=1+X
X=X/X2
PRINT(X)0,4
X2=349.8-110.48X
Y=1000X2
PRINT(Y)0,4
NEWLINE
Y2=349.8+C2
C=0.66666Y2
C2=C2+699.6
C2=C/C2
```

EXPLANATION OF THE PROGRAMME

$C \equiv m$
$D \equiv K_1$
$D^2 \equiv K_2$
$C^2 \equiv \lambda^\circ_{A^{--}}$
$V^2 \equiv \Lambda_{expt.}$

Approximate values for α, β, $f_\pm^2$ and $f_{A^{--}}$.

$A \equiv \alpha$

$F \equiv f_\pm^2$
$F^2 \equiv f_{A^{--}}$
$B \equiv \beta$

Calculating and printing instructions.

$W \equiv (H^+)$

$W^2 \equiv (HA^-)$

$V \equiv (A^{--})$

$Y \equiv 10^6 K_{H^+}$

```
H=XSQRT(GM)
H=1+H
H=1.5654GM/H
H=HYM-110.48+90.9
H=GM-HX
H=1000HV
PRINT(H)0,4
VM=1000VMC
VM=VM-H-Y
PRINT(VM)0,4
HM=0.001VM/HM
PRINT(HM)0,4
HM=HM+30.3X
U=1-0.2392X
HM=HM/U
PRINT(HM)0,4

JUMP1
0)END

2)Z=D/C
Z=Z/E
ZM=ZZ+4Z+4BB
ZM=XSQRT(ZM)
ZM=ZM-Z
AM=ZM/2
Z=AM-B
ZM=AM+B
Z=Z/ZM
DM=DMZ/C
DM=DM/EM
Z=1-A/AM
Z=ZZ
JUMP1,Z≥0.000000000001
ZM=1-B/BM
ZM=ZMZM
JUMP4,ZM≥0.000000000001
JUMP3

4)A=A+0.5AM-0.5A
B=BM
E=XSQRT(CA+2CB)
EM=1+E
F=XEXP(-2.3478E/EM)
FM=FF
JUMP2
3)RETURN
XSQRT
XEXP
CLOSE

→
**********
```

$H \equiv 10^6 k_A$--

$V^n \equiv 10^6 K_{HA}$-

$H^n \equiv \lambda^\circ_{HA}$-

Calculation of α and β by iteration using equations (16), (17) and (7). (See Section 2.3)