Complexing in Unsymmetrical Electrolytes

A Thesis submitted to the University of Glasgow
for the Degree of
Doctor of Philosophy

presented by
Derek Midgley, B.Sc.

Department of Physical Chemistry
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Summary

The dissociation constants of d-tartaric acid have been determined from pH measurements at a number of temperatures and ionic strengths. The results are summarised in Table 1.

Table 1*

T°C.	medium	pK_1	pK_2	$10^3\sigma(pK_1)$	$10^3\sigma(pK_2)$
25	0.2 $(Me_4N)Cl$	2.81	3.93	1.1	8,8
25	0.1 $(Me_4N)Cl$	2.83	3.97	3.4	2,9
25	0.4 $(Me_4N)Cl$	2.83	3.88	0.8	2.1
15	0 corr	3.04	4.37	8,3	19.9
25	0 corr	3.06	4.26	2.7	4,9
35	0 corr	3.08	4.37	3.1	33.7

From the results at different temperatures, the Gibbs energy change, entropy change and enthalpy change for each dissociation at 25°C. The results are shown in Table 2.

Table 2

	$10^{-4}\Delta G^o$ j mole^{-1}	$10^{-3}\Delta H^o$ j mole^{-1}	ΔS^o j deg^{-1}mole^{-1}
First dissociation	1.75	- 3.23	- 69.5
Second dissociation	2.43	0.65	- 79.4

The effect of complexing between ligands and alkali metal ions has been discussed with respect to the apparent dissociation and stability constants obtained in constant ionic media and some literature values have been recalculated.

The stability constants of the sodium - tartaric acid system have been calculated from measurements with both sodium and proton sensitive glass electrodes. The agreement between the two methods is good. The mean values at 25°C. in 0.2M $(Me_4N)Cl$ are

K_{NaT} = (NaTar)/(Na)(Tar) = 2.0 $mole^{-1}$ litre

K_{NaHT} = (NaHTar)/(Na)(HTar) = 0.9 $mole^{-1}$ litre.

The stability constants of the potassium - tartaric acid system have been studied by means of pH measurements with a glass electrode. The constants, defined as above for the sodium tartrate system, lie within the ranges $0.6 \leq K_{KT} \leq 1.0$ $mole^{-1}$litre and $0.1_5 \leq K_{KHT} \leq 0.3_5$ $mole^{-1}$ litre.

The stability constants of the lanthanum tartrate system in the acid region have been investigated by means of pH measurements with a glass electrode. The results are shown in Table 3.

K_{101} = (MA)/(M)(A) , K_{102} = $(MA_2)/(M)(A)^2$, K' = (MHA)/(M)(HA), where (M), (A) etc. represent the various species' concentrations or activities, as appropriate.

Table 3*

T°C	medium	log K_{101}	log K_{102}	log K'	$10^3\sigma(\log K_{101})$	$10^2\sigma(\log K_{102})$	$10^2\sigma(\log K'$
25	0.2 $(Me_4N)Cl$	3.410	5.640	2.27	3.4	2.9	1.9
25	0.1 $(Me_4N)Cl$	3.676	6.128	2.44	2.2	0.7	0 9
25	0.4 $(Me_4N)Cl$	3.108	5.559	1.94	1.6	1.1	0 8
15	0 corr	4.852	7.41	3.10	3	12	-
25	0 corr	4.604	7.59	2.48	3	4	-
35	0 corr	4.876	7.93	2.70	4	5	-

The problems of calculating stability constants when protonated complexes coexist with the normal series of complexes have been discussed and some ALGOL programs written to perform the calculations.

From the results at different temperatures, the standard Gibbs energy change, entropy change and enthalpy change for each coordination reaction at 25°C. have been calculated. These results are given in Table 4.

Table 4

reaction	$-\Delta G^o \times 10^{-4}$ j $mole^{-1}$	$\Delta H^o \times 10^{-4}$ j $mole^{-1}$	ΔS^o j $deg^{-1} mole^{-1}$
M + A = MA	2.63	0.0	94.8
M + 2A = MA_2	4.33	4.47	295
M + HA = MHA	1.41	0.56	66

The published thermodynamic data for the complexing of lanthanides with divalent ligands has been reviewed and discussed in terms of the solvation and structure of the participating species.

The analytical uses of potentiometric titrations have been extended by the development of an improved linear titration plot method. Strong acid - strong base, weak acid - strong base, weak dibasic acid - strong base, weak acid - weak base, and precipitation titrations are included in the treatment. Allowance has also been made for activity coefficients. An ALGOL program has been written to undertake the calculations.

*The symbols in Tables 1 and 3 conform to those set out by L.G.Sillen and A.E.Martell in "Stability Constants", Chemical Society Special Publication No.17, London, 1964.

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g) Linear Titration Plots

Summary

The first and second dissociation constants of d-tartaric acid have been determined by means of pH studies with a glass electrode in 0.1, 0.2 and 0.4M tetramethylammonium chloride media at 25°C. The first and second stability constants of lanthanum tartrate and the first stability constant of lanthanum hydrogen tartrate have been found in the same conditions.

Thermodynamic constants at 15, 25 and 35°C. have also been determined for the above equilibria and standard Gibbs energy, enthalpy and entropy changes at 25°C calculated.

Potassium tartrate complexing has been investigated by means of pH measurements and stability constants for sodium tartrate complexing calculated from studies with both hydrogen and sodium sensitive glass electrodes.

An improved linear titration plot method of potentiometric analysis has been devised.

ALGOL programs for the English Electric KDF.9 computer have been written to facilitate many of the calculations involved in the above work.

Symbols & Notation

When tables of stability constants appear (Tables 1 in each of the Chapters 5 - 8), the symbols generally conform to those set out in "Stability Constants" by A.E. Martell and L.G. Sillen, Chemical Society Special Publication No. 17, London, 1964. Those used in this work are given below.

Medium: 0.1(KCl) - the ionic strength is maintained at 0.1 by the addition of KCl.

0.1 KCl - the background is 0.1M KCl.

0.1(K)Cl - the background has a constant chloride concentration of 0.1M and potassium is the principal counter-ion.

0 corr - some method of calculating activity coefficients has been applied.

$\rightarrow 0$ - extrapolation to infinite dilution.

var - the ionic strength varies.

Method: act - application of activity coefficients

cix - cation exchange

dil - dilatometry

dis - distribution methods

emf - emf measurements

H - hydrogen electrode

H;Ag,AgCl - hydrogen and silver-silver chloride electrodes kin - kinetics

M^+-gl - glass electrode responsive to M^+ ions

MHg - metal amalgam electrode

M^+-sel - electrode of the liquid ion exchanger, solid-state or impregnated types specific to M^+

pol - polarimetry

qh - quinhydrone electrode

sol - solubility

sp - spectrophotometry

tp - transport number

Symbols relating to the calculation of stability constants are given at the beginning of Chapter 3 and have the same meaning when they occur thereafter. Other symbols are defined locally.

Equations, figures and tables are numbered consecutively within each chapter by Arabic numerals. Each chapter is broken into sections identified by Roman numerals. For instance, in Chapter 2 we have Table 2, Eqn(2), Fig(2) and Section II. When the above are referred to in other chapters they are identified by Table 2.2, Eqn(2.2), Fig(2.2) and Section 2.II respectively. Literature references are numbered consecutively within each chapter and are listed at the end of that chapter.

Errors are always quoted as standard deviations.

Chapter 1

General Introduction

I. Ion Association

Ion association has long been a part of the theory of electrolyte solutions. After Faraday and Daniel had proposed, in 1833, that electrolysis consists of the transport of electricity by charged particles which are discharged at the electrodes, Clausius in 1857 suggested that ions are formed in solution simply by dissolving an electrolyte, the free ions being in dynamic equilibrium with undissociated solute molecules. By 1883 the theories of Arrhenius formed the basis for many modern treatments, but classical theories remained inadequate because of the neglect of the general interionic forces at work in electrolyte solutions. The development of theories of interionic forces, the most important of which was that of Debye and Hückel in 1923, enabled a clearer distinction to be made between the association of weak electrolytes and the classical "anomalous association" of strong electrolytes.

In 1926 Bjerrum, from considerations of the probability of the distance of approach, r, between ions of opposite charge $z_i e$ and $z_j e$, derived a relationship between the association constant, K, of an ion-pair and a certain minimum value of r and the distance of closest approach, a, of the two ions. The derivation has been given in many texts(1-3) and only the final expressions are given here. These are

$$K = (4\,N/1000)(|z_i z_j|\,e^2/\varepsilon kT)^3 Q(b) \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\; (1),$$

where $$Q(b) = \int_2^b \exp(x).x^{-4}dx \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\; (2),$$

$$x = |z_i z_j|\,e^2/r\varepsilon kT \quad\text{and}\quad b = |z_i z_j|\,e^2/a\varepsilon kT \quad .$$

The distance $q = |z_i z_j|e^2/2\varepsilon kT$, the ionic separation at which the mutual potential energy is equal to 2kT, is the radius of the sphere with a j-ion at its centre on which there is a minimum probability of finding an i-ion. Ions within this distance q are regarded as ion-pairs, while ions separated by distances greater than q are free ions which may be treated by Debye-Hückel theory. The Bjerrum treatment is a strictly electrostatic theory which takes no account of quantum-mechanical forces and applies only to nonpolarisable spherical ions in a structureless medium. The Bjerrum model is inadequate because, even for hard-sphere ions, interaction with the solvent and dielectric saturation invalidate the use of the macroscopic dielectric constant in regions close to the ions.

A more recent theory is that of Denison and Ramsey (4) and of Fuoss and Kraus (5), who regard only those ions in actual contact as forming ion pairs. They propose that the association constant must be given, to a first approximation, by

$$\ln K = \ln K^o + |z_i z_j|\,e^2/a\varepsilon kT \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\; (3),$$

where K^o is the association constant of two uncharged particles in the solution. There is, however, no really satisfactory general theory for the prediction of stability constants, even for hard-sphere ions.

In this work all forms of association, whatever the forces at work, are included in the term "complex" and no attempt is normally made to distinguish between them.

II. The Association or Stability Constant

The equilibrium

$$M^{m+} + A^{n-} \rightleftharpoons MA^{(m-n)+} \quad \ldots\ldots\ldots\ldots \quad (4)$$

may be described by means of a stability constant. Classically, this would be the stoichiometric stability constant,

$$K_c = \frac{MA}{M.A} ,$$

which, because of the non-ideality of electrolyte solutions, is not truly constant, but varies with concentration. The thermodynamic stability constant,

$$K = \frac{\{MA\}}{\{M\}\{A\}} = K_c . \frac{f_{MA}}{f_M . f_A} , \quad \ldots\ldots\ldots\ldots \quad (5),$$

is constant over the whole concentration range at a given temperature and pressure.

The dimensions of the stability constant depend on the concentration units used. If molar units are chosen, K for the equilibrium (4) will have the dimensions mole^{-1} litre, and for molal units $\text{mole}^{-1}\text{Kg}$. In general, molarities are experimentally more convenient than molalities, but they lack the latter's independence of temperature and pressure, which is a drawback if comparative studies in different conditions are desired. It is assumed, when solutions are made up by volume, that, if they are not prepared individually but by mixing stock solutions, the overall volume change is negligible, otherwise the concentrations and, hence, the stability constants will be inaccurate.

It should be noted that the conventional representation of equilibria, e.g. Eqn(4), is inaccurate. Eqn(4), if water is the solvent, should be written

$$M^{m+}_{aq} + A^{n-}_{aq} \rightleftharpoons MA^{(m-n)+}_{aq} + rH_2O \quad . . . . . (6),$$

where r is the difference in hydration of the complex and its constituent atoms. The equilibrium constant is

$$K' = \frac{\{MA\}\{H_2O\}^r}{\{M\}\{A\}} \quad . . . . (7).$$

If the activity of water is assumed to be equal to its concentration, Eqn(7) can be rewritten as

$$\ln K = \ln K' - r.\ln(H_2O) \quad . . . . (8).$$

K' is constant over the entire concentration range, provided the concentration of solute is not so high that the hydration of the various species is changed. Since K is a function of the free water concentration, it will not strictly be constant over a range of solute concentrations, even with molal units, when the total water concentration is independent of the solute concentration. With molar units the effect is more pronounced (see Section 7. IIIb). Marshall and Quist(6-8) find that Eqn(6) holds in water-dioxane mixtures as well as in water itself and that K' is constant over a series of different water-dioxane mixtures for a number of electrolytes and that similar behaviour is observed in water at different pressures and in carbon tetrachloride-nitrobenzene mixtures. The non-polar constituents of the solvents are assumed not to participate in the equilibrium or in solvation. Eqn(8) may be compared with Eqn(3). Marshall and Quist find that a plot of ln K against ln(H_2O) displays greater linearity than one of ln K against $1/\varepsilon$. They explain the relationship between ln K and the dielectric constant in terms of the dependence of the latter on the concentration of the polar constituent in the mixtures; K' itself is independent of the dielectric constant. If the solute concentration does not vary too much, the concentration of free solvent will be virtually constant and K will also be constant within experimental error.

If K_c can be obtained at some particular ionic strength, the determination of K requires the evaluation or elimination of the activity-coefficients term in Eqn(5). The following two sections are devoted to these two problems.

III. The Calculation of Activity Coefficients

The first important calculation of activity coefficients was that of Debye and Hückel(9), who obtained for the mean activity coefficient of ions in a binary electrolyte the limiting law

$$- \log f_{\mp} = |z_{+}z_{-}| A . I^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots \quad (9),$$

where $I = \frac{1}{2} \Sigma m_{i} z_{i}^{2}$ is the ionic strength (10) and A is a constant. For aqueous solutions at 25°, the activity coefficient of a z-valent ion is

$$-\log f_{z} = 0.509\ z^{2} I^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots \quad (9a).$$

In an attempt to extend the theory to higher concentrations, Debye and Hückel introduced a term which took into account the finite sizes of the ions. The resulting expression is

$$- \log f_{z} = A . z^{2} . I^{\frac{1}{2}} / (1 + B . a . I^{\frac{1}{2}}) \quad \ldots\ldots\ldots \quad (10),$$

where B is a fundamental constant and a is the distance of closest approach of the ions. An additional linear term has been introduced as an empirical correction to allow for short-range ion-solvent interactions

$$- \log f_{z} = A . z^{2} . I^{\frac{1}{2}} / (1 + B . a . I^{\frac{1}{2}}) - C' . I \quad \ldots \quad (11).$$

A simplified form of Eqn (10), containing no adjustable parameters, has been used by Guntelberg(11)

$$- \log f_{z} = A . z^{2} . I^{\frac{1}{2}} / (1 + I^{\frac{1}{2}}) \quad \ldots\ldots\ldots\ldots \quad (12).$$

Davies (12) proposed the formula

$$- \log f_{z} = A . z^{2} \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - C . I \right) \quad \ldots\ldots \quad (13),$$

with C = 0.2, which has the form of the modified Debye-Hückel equation suggested by Guggenheim(13). Davies(14) reassessed Eqn(13) in the light of more recent activity data and found that C = 0.3 gives a better fit for the electrolytes considered, with charge types as high as 3-1. Guggenheim(15) has criticised the use of Eqn(13) for charge types other than 1-1 and proposed the value C = 2.0 for 2-2 electrolytes. The use of this value for a number of bivalent metal sulphates(16), however, revealed a drift in K of 20-30%, which was not the case with C = 0.2(12). Rosseinsky(17) has suggested that this discrepancy arises from the interaction of the ion-pairs with the free ions in solution and has shown that allowing for this interaction is equivalent to the use of a low value of C.

Formulae for use at high concentrations have been devised by Robinson and Stokes(1) and for mixed electrolyte solutions by Harned(18) and Guggenheim(19,20). It should be pointed out that although it is sometimes convenient to calculate single ion activity coefficients, as above, these quantities have no physical meaning(21-23).

Using one of the above formulae, or one of the others referred to in standard works(1-3), the activity coefficients, and, hence, the thermodynamic stability constant, K, may be obtained. Alternatively the activity coefficient term may be eliminated by extrapolation. When the Debye-Hückel limiting law holds, log K_c may be plotted against $I^{\frac{1}{2}}$ and extrapolated to infinite dilution, where $K = K_c$. At higher concentrations, a plot of log $K_c + g.A.I^{\frac{1}{2}}/(1 + B.a.I^{\frac{1}{2}})$ against I gives an intercept equal to log K on extrapolation to I = 0.
If plots are made for several values of a, that value is chosen which gives the best linearity and then the slope is equal to q.C'.

The constant $g = \Sigma n_r z_r^2 - \Sigma n_p z_p^2$ and $q = N_r - N_p$, where n_r and n_p are the numbers of ions of charge z_r and z_p on the reactants and products sides respectively of the equilibrium equation. N_r and N_p are the total numbers of ions on each side of the equilibrium. C' and a are the parameters of Eqn(11).

IV. Constant Ionic Media

The earliest use of a constant ionic medium to control an equilibrium has been attributed to Bodländer by Grossman(24); who first published the method. J. Bjerrum(25) was the next to use the method in studying complex equilibria and for 30 years it has been extensively applied. The history of the method has been reviewed by Biedermann and Sillen(26) and by Sillen(27).

Lewis and Randall(10), who introduced the concept of the ionic strength, pointed out that activity coefficients are independent of the nature of the medium only at very low ionic strengths. Ellilä(29,30) has reported the dependence of the dissociation constant of acetic acid on the nature and concentration of the medium salt. The medium effect has been studied with organic acids(31 - 33) and cupric bromide(34) and sulphate(35) complexes. Leden(36) has discussed the influence of the medium on cadmium and silver sulphate complexes.

The variation in apparent stability constants measured in different media of the same ionic strength may arise either from activity coefficient changes due to specific ionic interactions or from complexing between the ions of the medium and the reacting species, which is discussed in Sections 3.X and 3.XI.

The concentration of the medium should be such that the reacting species make only a small contribution to the total ionic strength and that, if the ionic strength cannot strictly be maintained, the variation is negligible. On these grounds, a high ionic strength ($I > 1$) is to be preferred, but problems of complexing with the medium are greater and, if the results are to be extrapolated to infinite dilution, lower ionic strengths($I < 0.5$) should be chosen.

V. Experimental Methods

The various methods of investigating complexing have been described in standard texts, e.g. (1-3,14,28). Because of the intricacy of the system under study (lanthanum-tartrate complexes in acid solution), the conductivity method is not practicable. Spectrophotometry may be neglected on similar grounds, since, when the pH is high enough for the complication of protonated species to be avoided, hydrolysis of the lanthanum ion occurs(37). Polarography of lanthanum in a tetramethylammonium chloride medium has been attempted(38), but it was found that the polarographic wave was not diffusion controlled and was unreproducible and ill-defined.

With iterative calculations performed on a electronic computer, the data yielded by the potentiometric determination of pH can be successfully interpreted, even when there exists a variety of complex species. Moreover, unlike the ion exchange method, the concentration of metal is not restricted to trace levels and hence a wide range of metal-ligand ratios can be studied. For a titration-wise procedure, enabling a large number of data points to be gathered over a wide range of experimental conditions in a relatively short time, a glass electrode system is most convenient, and this was, therefore, used.

If a suitable electrode system exists, direct potentiometry provides an even better method, which is increasing in scope with the introduction of new ion-specific electrodes. A sodium-responsive glass electrode was used to study the complexing in the sodium - tartrate system.

VI. Thermodynamic Quantities

The derivation of the following equations may be found in numerous standard texts and they will merely be stated here.

$$\Delta G = \Delta H - T.\Delta S \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (14).$$

$$(\partial \Delta G/\partial T)_p = - \Delta S \text{ (the Gibbs-Helmholtz equation)}. \; . \; . \quad (15).$$

The Gibbs-Helmholtz equation can be written in the alternative forms:

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_P = -\frac{\Delta H}{T^2} \quad \ldots\ldots\ldots\ldots \quad (16)$$

or

$$\left[\frac{\partial(\Delta G/T)}{\partial(1/T)}\right]_P = \Delta H \quad \ldots\ldots\ldots\ldots \quad (17).$$

The equilibrium constant, K, of a reaction is related to the standard Gibbs energy change by

$$\Delta G^o = - RT\ln K \quad \ldots\ldots\ldots\ldots \quad (18).$$

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Chapter 2

Glass Electrodes for the Measurement of pH and pNa

Theoretical

I. The Origin of the Glass Electrode Potential

All aspects of the theory of glass electrodes have been discussed in the compilation edited by Eisenman(1) to which frequent reference will be made. The glass is not really an electrode but an electrolyte, forming a barrier between two solutions in which electrodes are immersed:

internal reference electrode | reference solution | glass electrode | test solution | external reference electrode (A)

There may be four contributions to the total e.m.f. of the cell associated with the glass: the interfacial potential differences at each glass surface and the diffusion potentials within the glass, at each side.

The interfacial potential has been derived in terms of the reaction constant for the ion-exchange reaction at a glass surface, the ion-exchange being assumed to reach equilibrium between the solution and the surface layers of the glass. For the reaction

$$i^+_{\text{glass}} + j^+_{\text{solution}} = j^+_{\text{glass}} + i^+_{\text{solution}}$$

the mass-action constant is $K_{ij} = (a_i . a'_j)/(a'_i . a_j)$, where the unprimed characters refer to the activities of the ions in solution and the primed ones to the activities in the glass phase.

At equilibrium the electrochemical potential of each species of ion is the same in both phases; hence

$$\mu_i + F\psi = \mu_i' + F\psi'$$

and

$$\mu_j + F\psi = \mu_j' + F\psi' \quad ,$$

where μ represents the chemical potential.

Since $\mu = \mu^o + RT\ \ln(a)$,

$F(\psi' - \psi) = \mu_i^o - \mu_i^{o'} + RT\ \ln(a_i/a_i')$, where μ^o and $\mu^{o'}$ are the appropriate standard chemical potentials. Since the anionic sites in the glass are fixed, the total number of cations in the glass is also fixed, i.e. $C_i + C_j = \text{constant} = C_o$. Assuming that the ionic activity coefficients within the glass are constant and the same for both ions, we can write

$$K_{ij} = a_i.C_j/(a_j.C_i) = a_i(C_o - C_i)/(a_j.C_i) \quad . \ . \ . \ . \ . . . \ (1).$$

Hence $a_i' = f.C_i = a_i.f.C_o/(a_i + K_{ij}.a_j)$, where f is the activity coefficient of the i and j ions in the glass, and

$$a_i/a_i' = (a_i + K_{ij}.a_j)/(f.C_o).$$

Therefore,

$$\psi' - \psi = \text{constant} + (RT/F)\ln\left[(a_i + K_{ij}.a_j)/(f.C_o)\right] .$$

Since f and C_o are constant this can be rewritten,

$$E = E^o + (RT/F)\ln(a_i + K_{ij}.a_j) \quad . \ . \ . \ . \ . \ . \ . \ . \ (2),$$

which is the boundary potential at one interface. Since the solution on the inner side of the glass is held constant, the total phase boundary potential for the electrode is also of the form (2), where E^o now includes the constant inner boundary potential. If the external reference electrode is, say, a saturated calomel electrode connected to the test solution via a salt bridge, and the liquid junction potential is assumed to be zero or constant, both the internal and external reference electrodes will make a constant contribution to the total cell potential, which will also be of the form (2). Eqn(2) is then a form of Nicolskii's(1b) equation for a cell of type (A). If the electrode responds to more than two ions, we obtain an extended form of Eqn(2),

$$E = E^{o} + (RT/F)\ln(a_i+K_{ij}.a_j+K_{ik}.a_k+ \, . \, .).$$

Eisenman et al.(47) introduced the equation,

$$E = E^{o} + n(RT/F)\ln\left[a_i^{1/n} + (K_{ij}.a_j)^{1/n}\right] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3),$$

where n depends on the particular pair of ions i and j and the composition of the glass. This equation was derived by assuming the ionic activities within the glass to vary as the nth power of the corresponding concentrations, i.e.

$$d\ln(a_i)/d\ln(C_i) = n.$$

Neither Eqn(3) nor Eqn(2) allows for the fact that when two ions of unequal mobilities interdiffuse there is established in the glass a local electric field which constrains both species to move at the same rate, for there cannot be a detectable difference in the number of ions entering and leaving a given macroscopic volume, or an excessively large electric field would arise. If the glass has a flat surface in the yz plane, the flows J_i and J_j of ions i and j are given by,

$$J_i = -D_i(\partial C_i/\partial x) - C_i v_i(\partial \psi/\partial x) ,$$

and $J_j = -D_j(\partial C_j/\partial x) - C_j v_j(\partial \psi/\partial x)$, where D's, C's and v's are diffusion coefficients, concentrations and mobilities in a unit field respectively and ψ is the electric potential. Now, $C_i + C_j = C_o$, a constant, $J_i = -J_j$ and $v = D(F/RT)$ for each ion. Hence it can be shown that

$$\partial\psi/\partial x = \left[(RT/F)(D_j - D_i)/(C_iD_i + C_jD_j)\right] \partial C_i/\partial x \; . \; . \; . \; . \; . \; . \; . \; . \; (4)$$

and $J_i = -\left[C_oD_iD_j/(C_oD_j + C_i\overline{D_i - D_j})\right] \partial C_i/\partial x$.

The potential difference between the surface and the unaffected material far from the surface can be obtained by integration of Eqn(4):

$$\Delta\psi = \int_{x=0}^{x=\infty} (\partial\psi/\partial x)dx$$

$$\Delta\psi = (RT/F) \int_{C_i'}^{C_o} (D_j - D_i)/(C_iD_i + \overline{C_o - C_i}D_j)dC_i .$$ where C_i' is the concentration of i at the surface immediately inside the glass. If D_i and D_j are independent of C_i, the integral becomes,

$$\Delta\psi = -(RT/F)\ln\left[C_oD_i/(C_i'D_i + C_j'D_j)\right] \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (5).$$

This derivation assumes that the activities of the ions in the glass are proportional to their concentrations; a more general treatment of diffusion potentials in glass is given by Doremus(1a).

Expressing the surface concentrations C_i' and C_j' in terms of solution activities and ion exchange equilibrium constants,

K_{ij} by means of Eqn(1), Eqn(5) becomes,

$$\Delta\psi = (RT/F)\ln\left[(a_i+(D_j/D_i)K_{ij}a_j)/(a_i+K_{ij}a_j)\right] \quad . \; . \; . \; . \; . \quad (6).$$

Adding Eqns(6) and (2), we obtain the total potential at the interface.

$$E = E^{o} + (RT/F)\ln(a_i+(D_j/D_i)K_{ij}a_j) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7).$$

If the same quantities are held constant as before the total cell potential will have the same form as Eqn(7).

Karreman and Eisenman(2) produced the equation,

$$E = E^{o} + n(RT/F)\ln\left[a_i^{1/n} + (u_j/u_i)(K_{ij}a_j)^{1/n}\right]. \; . \; . \; . \quad (8),$$

where u_i and u_j are the mobilities of the ions in the glass. Since the mobility ratio will not normally be known, it is convenient to use Eisenman's equation in the form,

$$E = E^{o} + n(RT/F)\ln\left[a_i^{1/n} + (K_{ij}^{pot}a_j)^{1/n}\right] \quad . \; . \; . \; . \; . \; . \; . \quad (9),$$

where $K_{ij}^{pot} = (u_j/u_i)^{n}K_{ij}$ and can be determined experimentally. If $a_i \gg K_{ij}a_j$(Eqn(3)) or $a_i \gg K_{ij}^{pot}a_j$(Eqn(9)) the cell e.m.f. is of the form,

$$E = E^{o} + (RT/F)\ln a_i \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10a),$$

Conversely, if $a_i \ll K_{ij}a_j$ or $a_i \ll K_{ij}^{pot}a_j$, the cell e.m.f. becomes

$$E = E^{o} + (RT/F)\ln a_j \, , \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10b),$$

where E^{o} now includes a term $(RT/F)\ln K_{ij}$ or $(RT/F)\ln K_{ij}^{pot}$. Since i is the ion initially in the glass and with most electrode glasses this is sodium, Eqn(10a) describes the potential of a sodium-sensitive glass electrode and Eqn(10b) the potential of an electrode responding to some other cation (including hydrogen), in each case the electrode being free from interference by other ions. When one of the terms a_i, $K_{ij}^{pot}a_j$ no longer dominates the other the electrode will show deviations from the "theoretical", i.e. Nernstian, response represented by Eqns(10a) and (10b) e.g. the "alkali error" exhibited by hydrogen-sensitive glass electrodes at high pH.

By adjusting the composition of the glass, electrodes of Nernstian response have been prepared for a number of different ions and these are now available commercially. The ordinary pH electrode uses a soda-silica-lime glass for which K_{NaH} is very large, hence the response. Addition of a small percentage of alumina reduces K_{NaH} to the extent that, provided the pH is not too low, a "theoretical" response to sodium ion is obtained. By varying the ratio of soda to alumina in the glass, electrodes suitable for other ions can be prepared. The physical basis for this behaviour has been described by Eisenman(1c).

II. The Definition of pH

The term "pH" as used in this work has no specific meaning attached to it and can be regarded as "the negative logarithm of some measurable or calculable function of hydrogen ion concentration in the solution under investigation". When a more precise definition is required it will be allotted its own symbol, after the fashion of Bates(3).

The pH concept was introduced by Sørensen(4) as a scale for hydrogen ion concentration pcH = -log c_H, where c_H is the molarity of the hydrogen ion. As a means of measuring pH Sorensen chose the cell

$$\text{Pt;H}_2\text{, soln.X} \,\big|\, \text{salt bridge} \,\big|\, \text{0.1M Calomel electrode} \;.\;.\;.\; \text{(B)},$$

allowing for the liquid junction potential by means of the Bjerrum extrapolation(5). Starting with a solution of known hydrogen ion concentration it was thought possible to calculate the pcH of a second solution from the e.m.f.s observed in cell (B) when each solution in turn was solution X.

Since Sørensen was restricted theoretically to the classical concepts of Nernst and Arrhenius and practically by limits to the Bjerrum extrapolation's applicability(6) this method was unsuccessful and even in a modern version where activities are used and the liquid junction potential "eliminated" by the use of a 3.5M or saturated KCl salt bridge, only a conventional scale results, defined in terms of operations and a specified formula.

Sørensen and Linderstrøm-Lang(7) proposed a new unit based on the hydrogen ion activity paH = $-\log a_H = -\log c_H f_H$ . .(11) where a_H is the hydrogen ion activity and f_H the activity coefficient. This scale is again a conventional one since the activity of a single ionic species lacks unique physical definition. It is now recognized(8) that the activity of a single ionic species plays no real part in the development of the e.m.f. of a galvanic cell, whether or not that cell incorporates a liquid junction. The quantity ptH has been introduced(9), defined by

ptH = $-\log c_H f_{\mp}$, where $f_{\mp}$ is the mean activity coefficient of a uni-univalent electrolyte in the solution. When the solution contains an unsymmetrical electrolyte or a mixture of electrolytes the assignment of a value to $f_{\mp}$ may be either inadequate or ambiguous and the ptH and paH scales become more or less equivalent.

Guggenheim(10) and Hitchcock(11) have advanced the idea of a unit

where m_H is the molality of the hydrogen ion and γ_H, γ_{Cl} are(12),

where m_H is the molality of the hydrogen ion and γ_H, γ_{Cl} are activity coefficients on the molality scale. This unit is physically defined at all ionic strengths and can be determined from measurements of cells without liquid junction of the type

$$\text{Pt};\text{H}_2,\ \text{Soln.X} + \text{MCl},\text{AgCl};\text{Ag} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (C).$$

The pwH is calculated from the e.m.f. of cell(C) by the expression

$$\mathrm{pwH} = \frac{F(E - E^{o})}{RT\ln 10} + \log m_{Cl} \quad .$$

The pwH concept would apply equally well to any system for which there existed a reversible electrode which could be used in a cell of type (C).

In practice an operational definition has gained wide acceptance, having been recommended by I.U.P.A.C.(12), and is formulated

$$\mathrm{pH(X)} = \mathrm{pH(S)} + \frac{(E_X - E_S)F}{RT\ln 10} \quad \ldots\ldots\ldots\ldots \quad (13).$$

In Eqn(13) pH(S) is the assigned pH of the standard and E_X and E_S are the values of the e.m.f. of a pH cell containing the unknown X and the standard S respectively. The cell may be of the type(B), but other electrodes may be chosen.

III. Liquid Junction Potentials

(a) General: The e.m.f. of a cell of type(B) can be represented by

$E = E^{O} + E_j - \frac{RT}{F} \log a_H$, where E^{O} includes the standard electrode potential for the cell and the contribution of the calomel half-cell and E_j is the liquid junction potential. The liquid junction potential is a complicated function of the activities a_i and transference numbers t_i of the ionic species i in the transition layer between the two sides 1 and 2 of the junction:

$$E_j = -\frac{RT}{F} \int_1^2 \Sigma \frac{t_i}{z_i} d\ln a_i \quad \ldots\ldots\ldots\ldots \text{(14)},$$

where z_i is the ionic charge on i.

Eqn(13) can be reformulated

$$pH(X) = pH(S) + \frac{(E_X - E_{j(X)} - E_S + E_{j(S)})F}{RT\ln 10} \quad \ldots\ldots \text{(13a)}.$$

If Eqn(13a) is to be a good pH scale then either the liquid junction potentials must be calculated or the difference $E_{j(S)} - E_{j(X)}$ must be negligible. An exact value for E_j can only be obtained from Eqn(14) if a_H is already known, apart from the need for knowing the variations in t_i across the junction and for attaching some significance to single ion activities. This problem has been discussed at length by Taylor(13) and Guggenheim(10,14), who showed that splitting the cell potential in the above way has no validity in thermodynamics, although it may for some purposes be convenient, and that an equation for the e.m.f. of the cell can be written without postulating single ion activities. It can be seen that an exact calculation of E_j is impossible, although approximate methods exist(15,16) and papers continue to be published on the subject(17-22).

The alternative to calculating E_j is to eliminate it from Eqn(13a) by a suitable choice of salt bridge such that E_j is constant i.e. $E_{j(X)} - E_{j(S)}$ is zero. The salt bridge in most common use is a concentrated(3.5M or saturated) solution of KCl.

The use of a salt bridge to connect two dilute solutions, as in cell(B), does not give a smaller potential that would be obtained if the two solutions were joined directly(18,23), although this procedure may be necessary in certain cases where the solutions would react chemically e.g. solutions of acids and bases or of silver and halide salts. If the solutions in the salt bridge and the reference half-cell are the same, the liquid junction potential will be reduced if the bridge is equitransferent i.e. if cations and anions each carry half the current. Grove-Rasmussen(24) has studied such bridges and reports an equimolar mixture of KCl and KNO_3 to be best (when the total molarity is 3.6) although in the limited number of cases studied the improvement is not great.

Accepting the presence of liquid junction potentials in real systems, methods have been proposed by Bjerrum(5) and Owen et al(25) to eliminate their effects by extrapolation to some state where they can be assumed to be zero. Bjerrum measures the potential across a cell using first one salt bridge and then another of half the concentration. The e.m.f.s are plotted against 1/c, c being the bridge concentration, and extrapolated to zero, corresponding to a bridge of infinite concentration, in which case the junction potential is assumed to be zero. Bjerrum's method is simple but there is evidence that it reduces the liquid junction potential to negligible proportions only when the observed difference of e.m.f. is small(6).

A method which has been used to determine thermodynamic dissociation constants of weak acids(26) and weak bases(27) and of solubility product constants and electrode potentials(25) is to measure the potentials of cells with a constant total molarity in all compartments (electrode half-cells and salt bridge) and with varying concentrations of reactants, the total being made up with inert electrolyte. The measured potentials are extrapolated to zero concentration of reactants, when the junction potential should be zero, the cell being uniform throughout. Repetition at a number of different total molarities, followed by extrapolation to zero concentration of inert electrolyte, yields the value of the property at infinite dilution. The method works well, but is lengthy and not easily suited to the relatively complex equilibria considered here.

(b) Structure of the Liquid Junction Boundary

When a junction is formed between solutions containing different electrolytes the potential depends on the composition of the transition layers between the two end solutions and if a reproducible potential is required it must be possible to duplicate the physical structure of the boundary. Guggenheim(28) identified four classes of boundary and studied them experimentally and theoretically.

(a) The continuous-mixture junction is formed by mixing the end solutions in continuously varying proportions, so that the composition at any point is a linear combination of these two solutions. This type of boundary is theoretically unstable, although the effect of this can be minimised if the transition layer is made sufficiently long. A junction of this type is troublesome to set up and is not used in practice,

(b) The free-diffusion boundary is formed by bringing the two solutions together in a tube. If cylindrical symmetry is achieved, the potential remains constant with time, while the transition layer increases in length. This type of junction is both stable and reproducible, but is not suited to a titration procedure because of the need for a new boundary for each addition.

(c) The constrained-diffusion junction is set up at a porous plug or membrane washed on the two sides by the end solutions. A steady state can theoretically be established, but is difficult to realize experimentally.

(d) "Sharp" junctions of indefinite type are formed by dipping tubes or capillaries containing the end solutions into a vessel containing the bridge solution or by dipping a tube filled with one solution directly into the other. Definite conditions for a steady state are lacking and such junctions may be subject to irregular fluctuations; on the other hand they are widely used, often with satisfaction.

Another type is the flowing junction in which the two solutions flow towards one another, meet and flow away together in parallel streams. The flowing junction is reproducible but not amenable to titration procedures.

(c) Calculation of Liquid Junction Potentials

Although it is not possible to calculate an exact value for the junction potential(vide super), by making suitable assumptions about activity coefficients and about concentration profiles in the transition layer expressions can be derived which can be usefully applied in many real cases.

Formulae have been proposed by Planck(15) for the constrained-diffusion junction and Henderson(16) for the continuous mixture type; no corresponding functions exist for the free-diffusion and "sharp" types, but the Henderson equation has been applied on the assumption that the junctions approximate to the continuous-mixture model.

The Henderson treatment applies to junctions formed between solutions of the same total molarity such that the junction is of the continuous mixture type and the total molarity in all parts of the transition layer is the same as that in the two end solutions. It is further assumed that the activity coefficient and mobility of each ion are the same throughout the system. Let us consider the junction

$$y \text{ M KCl} \; \Big| \; y \text{ M HCl}$$

and suppose that some thin layer inside the transition region has a composition x parts KCl, 1-x parts HCl. Let u_H, u_K and v be the mobilities of the hydrogen, potassium and chloride ions respectively. The contribution of an ion i to the transport of 1 faraday of electricity, from right to left is $t_i = \frac{(\text{concentration of i})\text{x}(\text{mobility of i})}{(\text{concentration})\text{x}(\text{mobility})}$ then in the layer of composition xyM KCl, (1-x)y M HCl we have:

$$t_H = \frac{(1-x)y.u_H}{(1-x)y.u_H+x.y.u_K+y.v} \quad , \quad t_K = \frac{x.y.u_K}{(1-x)y.u_H+x.y.u_K+y.v} \quad \text{and}$$

$$t_{Cl} = \frac{y.v}{(1-x)y.u_H+x.y.u_K+y.v}$$

. In the conditions we have assumed Eqn(4) can be rewritten:

$$E_j = -\frac{RT}{F}\int_1^2 t_H d\ln c_H - \frac{RT}{F}\int_1^2 t_K d\ln c_K + \frac{RT}{F}\int_1^2 t_{Cl} d\ln c_{Cl} \quad .$$

Now $d\ln c_i = dc_i/c_i$ and so $d\ln c_H = -dx/(1-x)$,
$d\ln c_K = dx/x$ and $d\ln c_{Cl} = 0$.
We can now write:

$$E_j = \frac{RT}{F}\int_0^1 \frac{(1-x)u_H}{(1-x)u_H+x.u_K+v} \cdot \frac{dx}{1-x} - \frac{RT}{F}\int_0^1 \frac{x.u_K}{(1-x)u_H+x.u_K+v} \cdot \frac{dx}{x}$$

$$= \frac{RT}{F}(u_H-u_K)\int_0^1 \frac{dx}{x(u_K-u_H)+u_H+v} = \frac{RT}{F}\ln\frac{u_H+v}{u_K+v} \quad .$$

In the general case we indicate the concentrations of a cation i and an anion p in solution 1 by c_i and a_p respectively and their corresponding mobilities by u_i and v_p. In solution 2 these quantities are represented by the primed symbols c_i', a_p', u_i' and v_p'. The positive charge on i is w_i and the negative charge on p ~~by~~ is z_p. We can define the functions, for solution 1,

$$U_1 = u_i.c_i + u_j.c_j + u_k.c_k + \ldots \quad ,$$
$$V_1 = v_p.a_p + v_q.a_q + v_r.a_r + \ldots \quad ,$$
$$U_1' = u_i.w_i.c_i + u_j.w_j.c_j + \ldots \quad ,$$

and $$V_1' = v_p.z_p.a_p + v_q.z_q.a_q + \ldots \quad ,$$

Corresponding functions U_2, V_2, U_2' and V_2' can be defined for solution 2.

Now $$E_j = \frac{RT}{F} \cdot \frac{(U_1-V_1) - (U_2-V_2)}{(U_1'+V_1') - (U_2'+V_2')} \ln \frac{U_1'+V_1'}{U_2'+V_2'} \quad \ldots\ldots\ (15).$$

The Henderson equation has been extended by the addition of a salt effects term calculated from activity coefficients computed with the aid of Harned's rule(29) or Guggenheim specific interaction coefficients(30), this being done by Spiro(17) for the case of two electrolytes with a common ion and Covington(18) for a more general case.

(d) The Sillén Correction

If we consider the cell

$$\text{reference electrode} \left| \text{mM BA} \right| \text{hM HA, (m-h)M BA} \left| \text{pH electrode} \right. \quad \ldots\ (D)$$

we can simplify the Henderson equation to

$$E_j = - k \ln(1+ \frac{dh}{m}) \quad \ldots\ldots\ (16),$$

where $d = (\Lambda_{HA} - \Lambda_{BA})/\Lambda_{BA}$ and $k = (RT/F)\ln(10)$.

Equation (16) can be transformed to

$$10^{-E_j/k} - 1 = d.h/m \quad \ldots\ldots\ (17).$$

A plot of $10^{-E_j/k} - 1$ against h/m should be a straight line of slope d.

The e.m.f. of cell(D) is given by

$E = E^o + E_j - k\log h$, assuming that the activity coefficients are constant. A plot of $E+k \log h = E^o+E_j$ against h, when extrapolated to h = 0, gives the value of E^o, from which E_j can be calculated for each value of h and then substituted in Eqn(17). Sillén et al.(31,32) found that d did not vary with h, except when h was large, but that the empirically evaluated d differed considerably from that calculated from the conductivities of the pure components. If Eqn(17) gives a linear plot, it may be concluded that Eqn(16), with the empirical value of d, is a good approximation to the liquid junction potential.

Experimental

IV. Reagents

Distilled water was obtained from an all-glass still and was boiled to remove carbon dioxide before being used for titrations.

Tetramethylammonium chloride(B.D.H.Laboratory Reagent) was recrystallised from methanol/ether(33), or from methanol alone, and dried under vacuum over phosphorus pentoxide. Gravimetric analysis as silver chloride indicated a purity of 99.9 %. Since this compound is highly deliquescent, all weighings were performed on an Oertling electric balance inside a glove box fitted with a posting port. The atmosphere of the box was kept dry by means of dishes of phosphorus pentoxide.

Potassium hydrogen phthalate was prepared by recrystallising B.D.H.AnalaR material from distilled water. 0.05 m buffer solutions were made up by volume(34) with freshly boiled-out distilled water.

Phosphate buffer was made up with freshly boiled-out distilled water from B.D.H.AnalaR grade anhydrous disodium hydrogen orthophosphate and potassium dihydrogen orthophosphate, both used without further purification, and was 0.025 m in each constituent, being made up by volume(34).

Potassium nitrate and potassium chloride were each prepared by recrystallisation of B.D.H. AnalaR materials from distilled water.

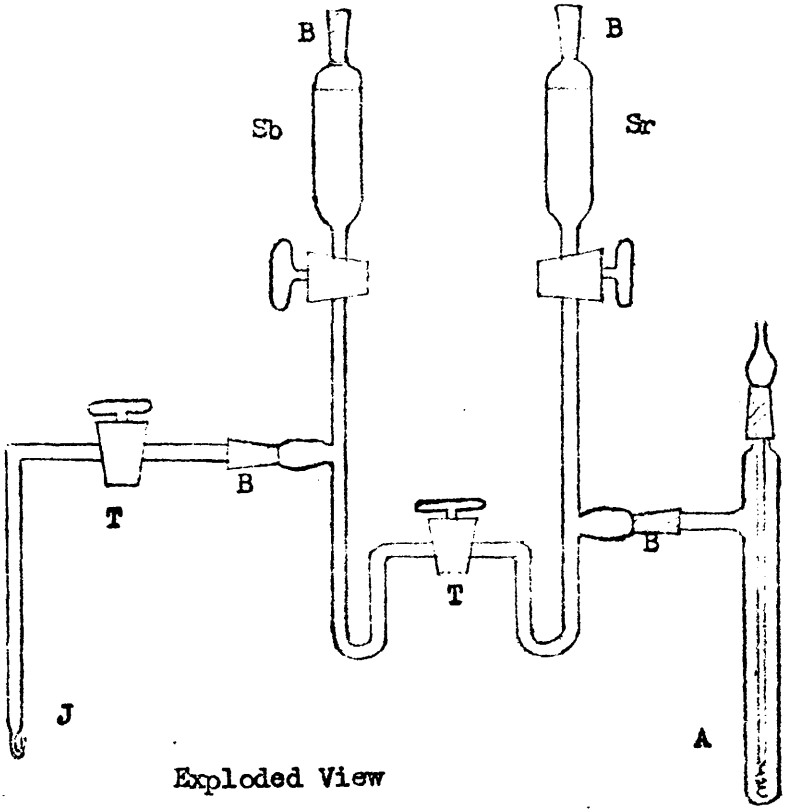
Sodium carbonate was made by heating sodium hydrogen carbonate (B.D.H. AnalaR grade), contained in a platinum dish, in an electric muffle furnace at 270°C for 90 minutes.

Constant-boiling hydrochloric acid was prepared by the method of Foulk and Hollingsworth(35) with the modifications suggested by Shaw(36) and Titus and Smith(37). The distillation was done in all-pyrex 'Quickfit' apparatus, the heat being supplied by an electric heating mantle.
A portion of the constant-boiling acid was diluted with distilled water and the concentration checked by gravimetric analysis as silver chloride, potentiometric titration with standard sodium carbonate solution and indicator titrations against sodium carbonate solution using screened methyl orange as indicator. The maximum difference between individual runs of any kind was 0.6%.

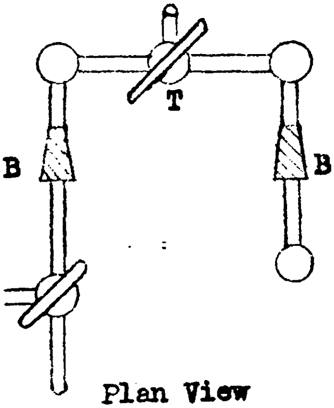
All the recrystallisations above were performed using pyrex apparatus, the filtration of solutions and collections of precipitates being done on sintered glass filters.

V. E.M.F. Measurements

(a) A Pye 7565 precision potentiometer with a five decade register (a sixth figure could be estimated) was used to measure



Exploded View



Plan View

Fig.1 The "Wilhelm" Bridge

Key: B - 'Quickfit' B.10 socket; T - three-way stopcock;
A - Ag,AgCl electrode; Sb - bridge solution;
Sr - bridge solution saturated with AgCl;
J - j-tube.

the potential of the cell

$$\begin{array}{l|c|c|c|c}\mathrm{Ag,AgCl} & \text{reference} & \text{bridge} & \text{test} & \text{glass}\\ & \text{solution} & \text{solution} & \text{solution} & \text{electrode}\end{array} \quad . \; . \quad (\mathrm{E}),$$

using an Electronic Instruments Ltd. 'Vibron' model 33B electrometer as a null detector. A Weston cell at 25°C was used as a standard. The geometry of the cell is illustrated in Fig.(1); it is of the 'Wilhelm' bridge design(38), containing a silver-silver chloride electrode of the thermoelectric type(39). The reference solution is identical to the bridge solution, except that a drop of silver nitrate solution was added before it was made up to the mark, so that any fresh solution run into the reference arm of the bridge was already saturated with silver chloride. The liquid junction between the reference and bridge solutions was formed in a three-way stopcock by flowing solution from the reservoirs through each side in turn. The junction between the bridge and test solutions was formed at the tip of a j-tube immersed in the test solution.

The experimental cells were immersed in a continuously stirred water bath of 60 litres capacity, maintained at the desired temperature by an electric heating element controlled by a mercury-toluene regulator fitted with a Sunvic Controls Ltd type TOL 3C thermoregulator proportioning head operating through an A.E.I. type EA4T electronic relay.

For temperature below room temperature the bath was kept cool by means of a Frigidaire refrigerator unit, the cooling coil of which, 20 feet of tinned copper tubing, was arranged round the stirrer at the bottom of the bath. When the bath was at room temperature cold water was passed through a cooler at one side of the bath in order to increase the sensitivity of the temperature control. The temperature was read on calibrated Beckmann thermometers and was maintained to ±0.02°. The temperature was found to be uniform throughout the bath. All the experimental work was done in a room maintained at 25±0.5°.

The metal frame supporting the Wilhelm bridge and the body of the water bath were earthed to a water pipe.

(b) The glass electrodes used were of the type GC33 manufactured by Electronic Instruments Ltd. These are screened electrodes with a fast response time. suitable for measurements in the pH range 0-11 and temperature range 0-50°C. When not in use the electrodes were stored in distilled water and they were also rinsed with distilled water whenever they were being changed from one solution to another. Before immersion in a fresh solution the stem of the electrode was wiped dry with a paper tissue and the water on the bulb allowed to drain to the neck, where it was absorbed on a tissue. There have been recent reports(40,41) of the effect of light on glass electrodes; in the present work the electrodes were kept in the open laboratory without any special precautions as to the light's reaching them. The laboratory,

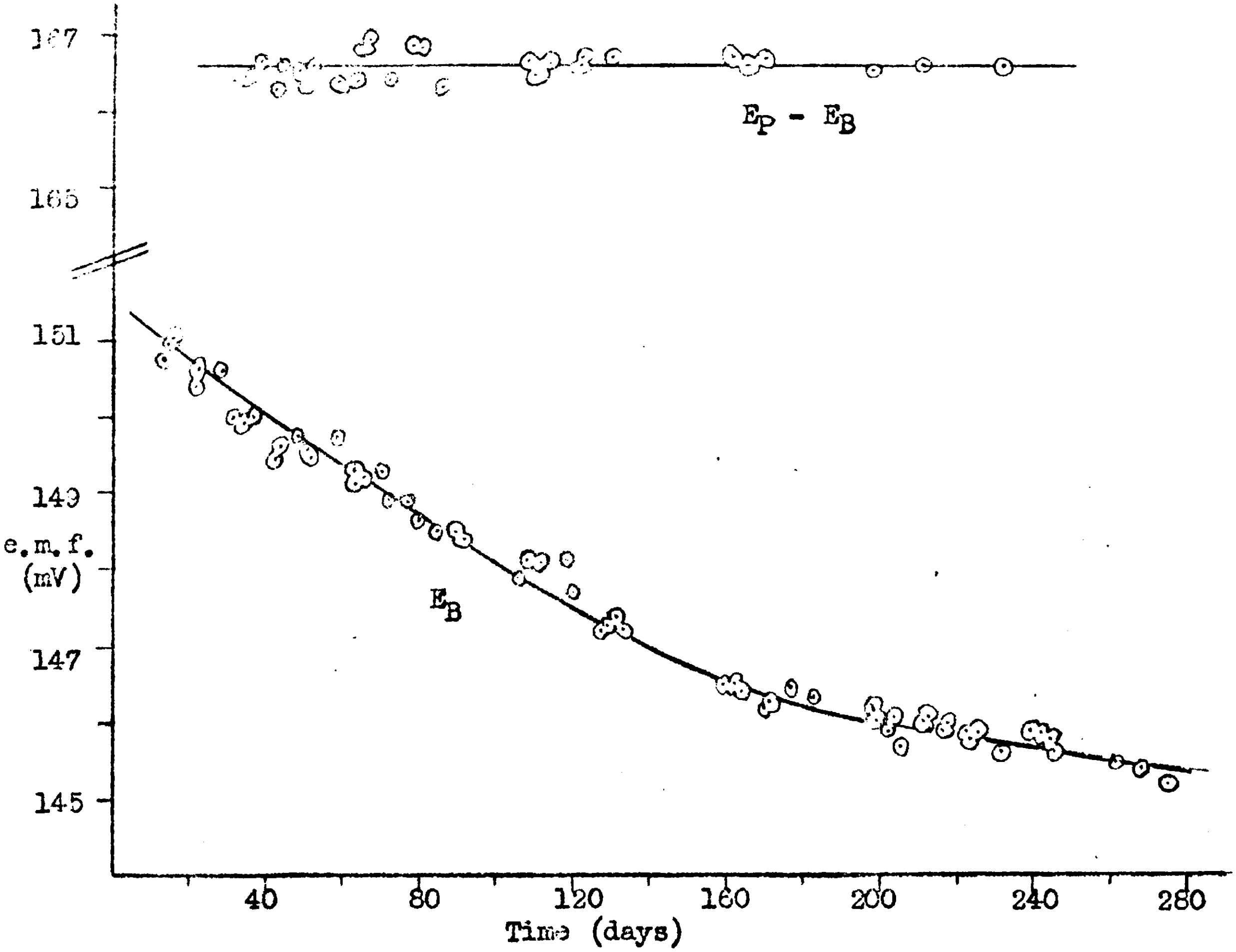


Fig. 2 Glass Electrode Y; T = 25°C. ; 0.2M Me_4NCl salt bridge

however, was in a shaded position and received no direct sunlight, illumination being provided by tungsten filament lamps which were on all the time work was in progress, hence the level of illumination was virtually constant.
The silver-silver chloride electrodes were also shaded, that in the Wilhelm bridge by a coat of black paint applied to the reference arm and that inside the glass electrode by the construction of the electrode itself. No behaviour of the glass electrode was noted which might be attributed to the effect of light.

The e.m.f., E_B, of cell (E) when the test solution was 0.05m potassium hydrogen phthalate was measured before and after every titration in order to check the constancy of the electrode during that particular titration and to enable the results of different titrations to be compared directly by dealing with the quantity $E_B - E_X$ rather than E_X, where E_X is the e.m.f. corresponding to some point in the titration. The e.m.f., E_p, when cell(E) contained phosphate buffer was also recorded periodically. Although E_B varied from day to day, $E_p - E_B$ was effectively constant over a long period of time, as can be seen in Fig(2).

(c) <u>pH Measurements in a Constant Ionic Medium</u>

If the medium succeeds in its purpose of keeping the activity coefficients constant, only hydrogen ion

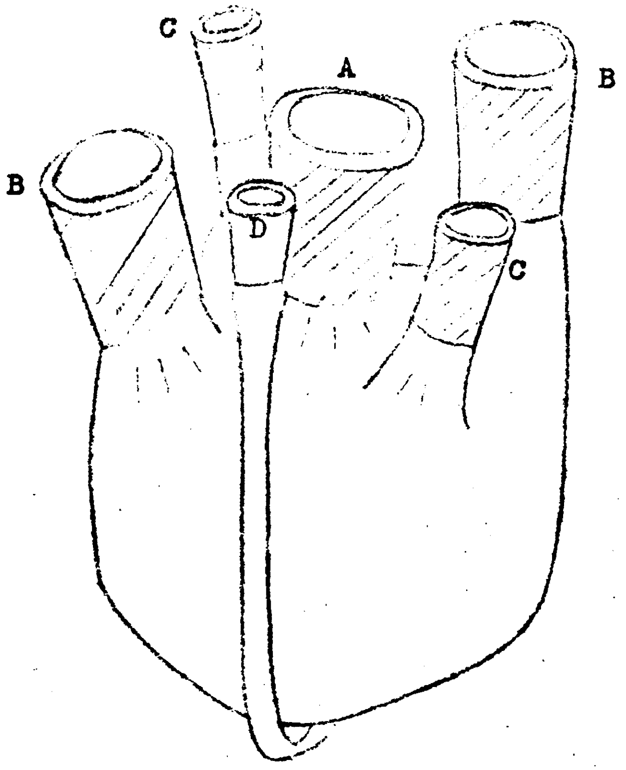


Fig. 3 Titration Flask

Key: A - B.24 socket; B - B.17 socket;
C - B.10 socket; D - B.7 socket.

concentrations are needed for the calculation of stability constants in that medium. The use of the operational definition of pH (Eqn(13)) to relate pH with e.m.f. measurements involves the assumption that the liquid junction potentials are the same in both the (S) and (X) solutions, which is unlikely if (S) is a standard buffer and (X) a solution of different pH and much higher ionic strength. Moreover, Eqn(13) furnishes a paH scale and assumptions must be made about the activity coefficient of hydrogen ion in the medium before the required concentration can be obtained. To avoid the above uncertainties it was decided to provide a more direct correlation between the e.m.f. of the cell and the hydrogen ion concentration in the medium.

Hydrochloric acid, made up to the required ionic strength, q, with Me_4NCl, was added to the titration cell depicted in Fig(3) containing qM Me_4NCl solution which had been freed from CO_2 by bubbling nitrogen through it. Cylinder nitrogen (British Oxygen Co. Ltd.) was passed through a series of presaturators

qM HCl, qM NaOH, qM Me_4NCl, qM Me_4NCl

before it reached the test solution. The presaturator solutions were at the same temperature (25°C) as the test solution. The e.m.f. was recorded after five minutes and checked after another five, before the next addition was made. Stirring was effected by the passage of nitrogen, which was

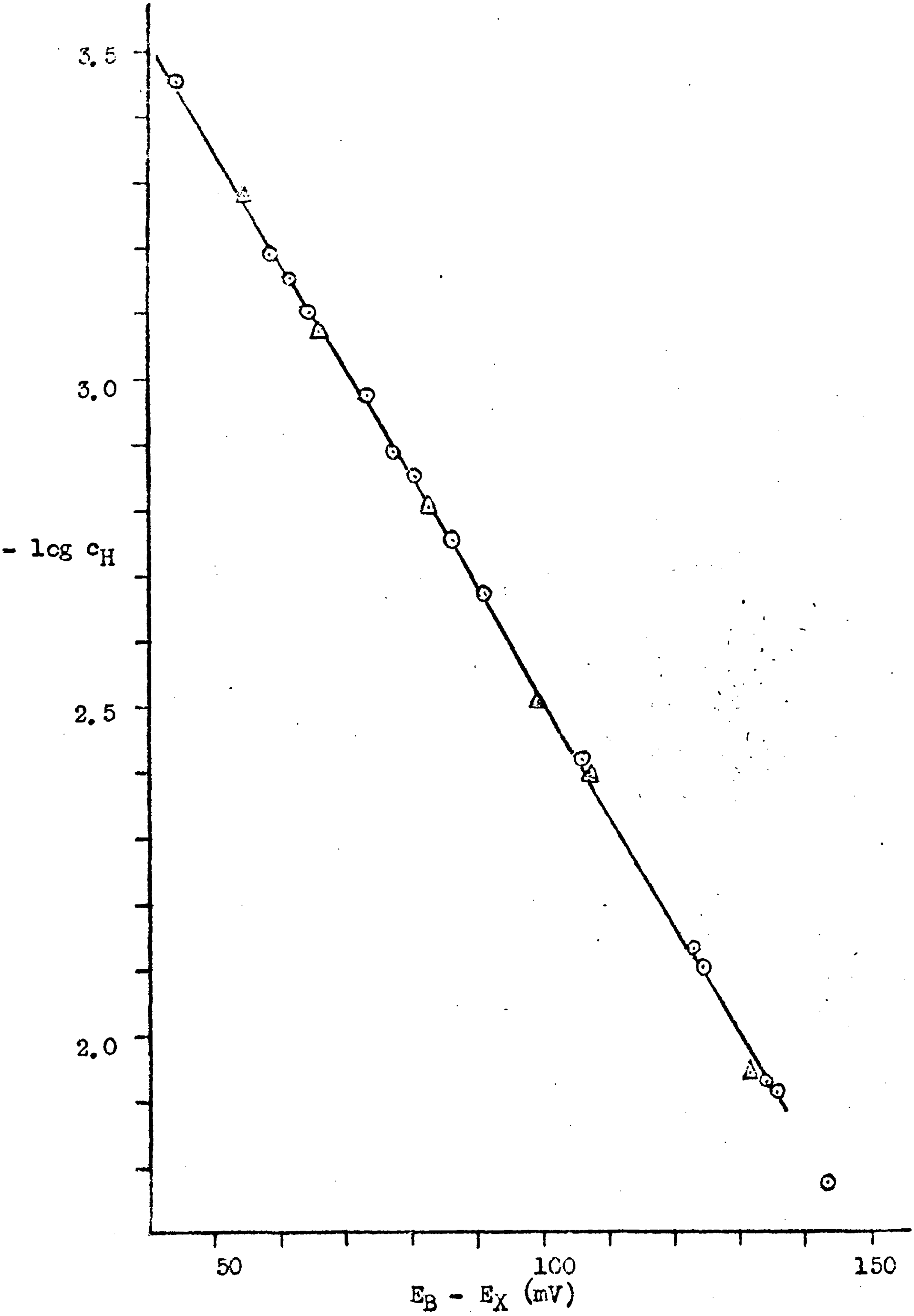


Fig. 4 Uncorrected Calibration Curve

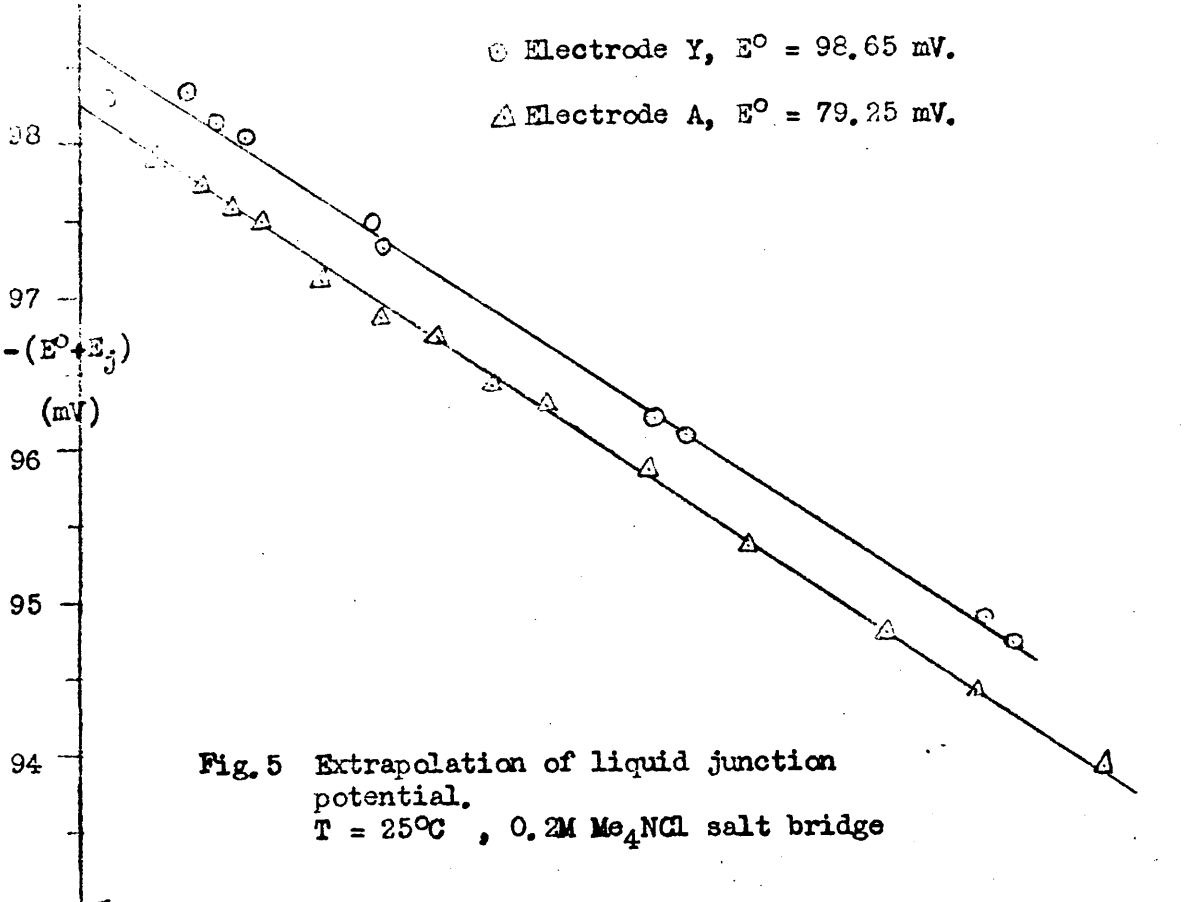


Fig. 5 Extrapolation of liquid junction potential.
$T = 25^\circ C$, 0.2M Me_4NCl salt bridge

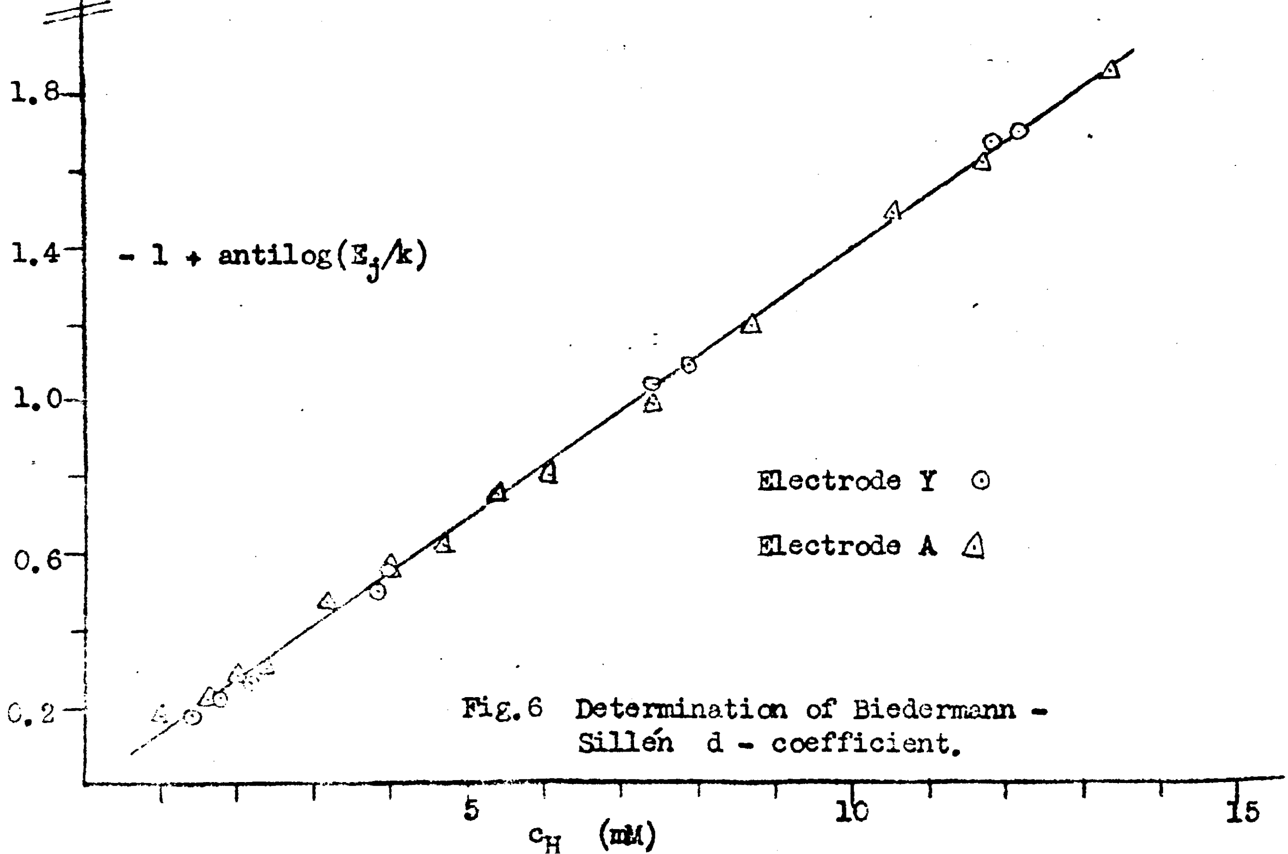


Fig. 6 Determination of Biedermann - Sillén d - coefficient.

maintained at all times. The titration was also performed in the reverse direction by adding standard solutions of sodium hydroxide or sodium carbonate to HCl solutions made up to qM in chloride with Me_4NCl. In this case an equal volume of (2q)M Me_4NCl was added from a second burette to maintain the ionic strength. Calibrations of this sort were carried out for ionic strengths of 0.1, 0.2 and 0.4M. Typical plots of E_B-E_X against $-\log c_H$ are shown in Fig(4) for a pair of runs at 0.2M. The deviation from linearity was systematic and was worse, the lower the ionic strength; it was therefore decided to apply a correction for liquid junction potential by Sillén's method (Section IIId). Typical plots (obtained from separate experiments) of $-(E^o + E_j)$ against c_H in a 0.2M medium are shown in Fig(5) for two different glass electrodes identified by the letters Y and A. Once the values E^o had been found, plots of $L = 10^{-E_j/k}-1$ against c_H were constructed for the two electrodes (Fig(6)). The data for the two runs are presented in Tables 1 and 2.

Table 1

Glass electrode Y; T=25°C; I = 0.2M; E^0 = 98.65 mV

10^3c_H M	$-\log c_H$	E_B-E_X mV	E^0+E_j mV	$-E_j$ mV	L
3.812	2.4189	104.75	97.46	1.19	0.050
7.403	2.1306	120.53	96.19	2.46	0.104
11.79	1.9285	131.05	94.75	3.90	0.166
12.16	1.9152	131.79	94.70	3.95	0.169
7.913	2.1016	122.12	96.06	2.59	0.109
3.995	2.3986	105.79	97.30	1.35	0.056
2.133	2.6711	90.39	98.02	0.63	0.027
1.770	2.7520	85.70	98.12	0.53	0.023
1.410	2.8507	80.07	98.33	0.32	0.019
0.348	3.4583	44.21	98.29	0.36	0.021

Table 2

Glass electrode A; T=25^0; I = 0.2; E^0 = 79.25mV

10^3c_H	$-\log c_H$	E_B-E_X	E^0+E_j	$-E_j$	L
M		mV	mV	mV	
0.807	3.0934	64.15	78.90	0.46	0.018
1.607	2.7940	81.66	78.70	0.55	0.022
2.003	2.6984	87.16	78.55	0.70	0.028
2.394	2.6210	91.66	78.47	0.78	0.030
3.168	2.4992	98.48	78.08	1.17	0.047
3.926	2.4060	103.75	77.84	1.41	0.056
4.649	2.3328	107.95	77.71	1.54	0.062
5.366	2.2704	111.33	77.40	1.85	0.075
6.061	2.2175	114.33	77.27	1.98	0.080
7.401	2.1307	119.05	76.85	2.40	0.098
8.691	2.0609	122.70	76.37	2.88	0.119
10.528	1.9773	127.06	75.79	3.46	0.144
11.685	1.9323	129.34	75.40	3.85	0.161
13.338	1.8748	132.24	74.90	4.35	0.183

The value of d in the Biedermann-Sillén equation obtained from the combined results of the two runs above is 2.79.

A value was also calculated for d from conductivity data for HCl(42) and Me_4NCl(43). $\Lambda^{0.2}_{Me_4NCl}$ was calculated by interpolation.

$$d_{lit} = (\Lambda^{0.2}_{HCl} - \Lambda^{0.2}_{Me_4NCl})/\Lambda^{0.2}_{Me_4NCl} = (388.09-92.29)/92.29 = 3.21$$

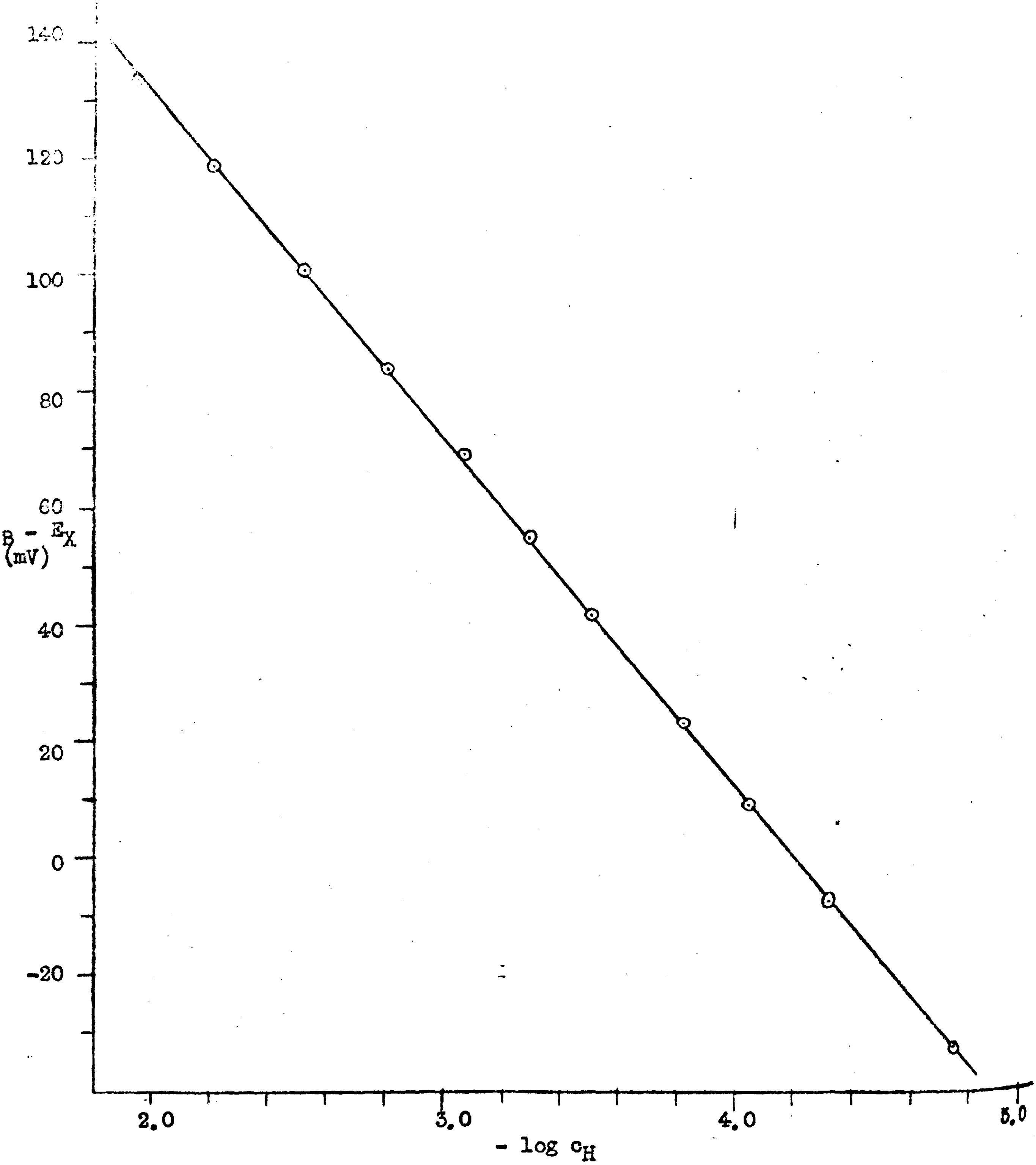


Fig. 7 Corrected Calibration for Glass Electrode Y at 25°C. 0.2M Me_4NCl Medium

The discrepancy between d_{obs} and d_{lit} is relatively small compared with the results in 3M $NaClO_4$(32). Using the empirical value of d, a correction for liquid junction potential was applied to the calibration data and $E_B-E_X+E_j$ plotted against -log c_H(Fig(7)). The corrected calibration curve is linear and of near-Nernstian slope over the measured range of 3 pH units. The good linearity of the corrected calibration curve and the L-c_H plot, Fig(6), is evidence that Eqn(16) adequately describes the liquid junction potential and it was used to correct the calibration curves at other values of the ionic strength.

Table 3

Calibration of Glass Electrodes at 25°C

Ionic strength	0.1	0.2	0.2	0.4
Electrode	A	Y	A	A
Number of runs	2	5	8	2
Number of points	23	54	80	28
d_{obs}	2.57	2.79	2.79	2.36
b	59.386	59.282	59.180	59.497
$10^2\sigma_b$	6.38	7.98	8.04	7.84
a	237.94	249.10	247.93	253.06
$10\sigma_a$	1.68	2.61	2.39	2.31
$10\sigma_y$	1.34	3.35	4.36	2.24

At each ionic strength the combined calibration data from a number of runs were fitted to an equation

$$y = E_B - E_X + E_j = a - b\log c_H$$

by least squares analysis. The results are presented in Table 3.

When using the above calibrations to obtain the pH from measurements of e.m.f., the calculation of E_j depends on the magnitude of the quantity we wish to determine and before the correction can be applied it is necessary to make an approximation to c_H. A least squares fit of the uncorrected calibration data was made to the equation

$$y' = E_B - E_X = a' - b'\log c_H$$

which provided a first estimate of c_H, which was then used to calculate the liquid junction correction. A new value of c_H was calculated from the corrected calibration and was inserted in Eqn(16) to give a new value for E_j. This process was repeated until successive values of E_j agreed within a specified limit (0.01 mV) and the current value of c_H accepted as the right one. An ALGOL program for the KDF.9 computer was written to carry out this procedure and a listing is given in Appendix 2a. To test this process the data of Table 1, which were not used for the calibration itself, were treated in the above way. The results are shown in Table 4. E_j^1 and pH^1 are the values obtained on the first application of the liquid junction correction.

Table 4

Glass Electrode Y at 25°C ; I = 0.2

-log c_H	E_j^1 mV	pH^1	E_j mV	pH
2.1306	2.31	2.1297	2.55	2.1258
1.9285	3.40	1.9339	3.93	1.9250
1.7755	4.45	1.7890	5.42	1.7727
2.1016	2.45	2.1005	2.72	2.0961
2.3986	1.33	2.3949	1.41	2.3937
2.6711	0.74	2.6646	0.76	2.6643
2.7520	0.62	2.7458	0.63	2.7456
2.8507	0.50	2.8428	0.51	2.8427
2.9768	0.38	2.9676	0.38	2.9676
3.1548	0.25	3.1588	0.25	3.1588
3.4583	0.13	3.4560	0.13	3.4561

The use of Eqn(16) when the Me_4N^+ ion is replaced by sodium or lanthanum ions or chloride is replaced by tartrate is justified on the grounds that the concentrations of these substitute ions are low and their mobilities not too different from those of the ions they replace.

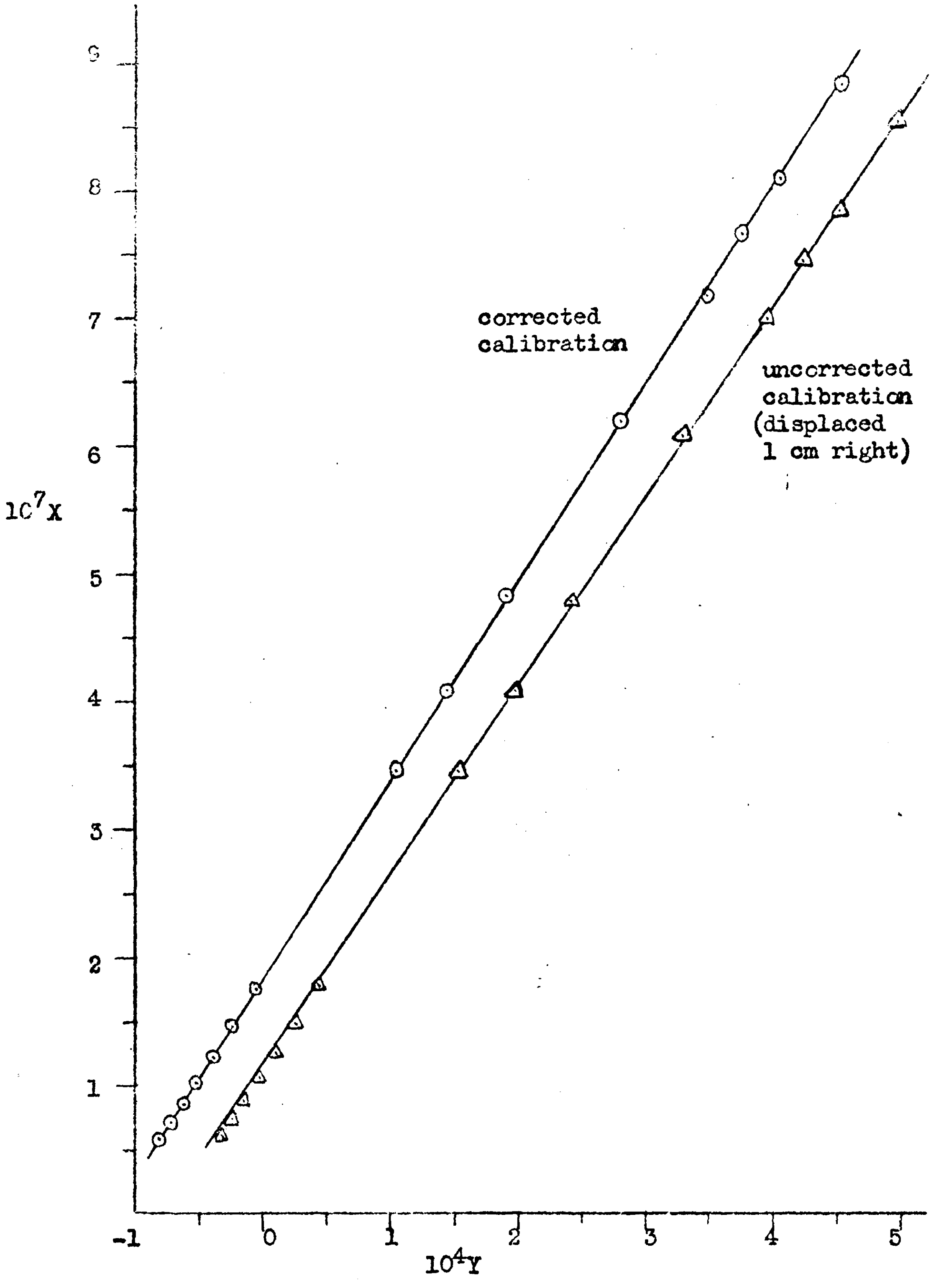


Fig. 8 Speakman plot for d-tartaric acid calculated for Run T. 5 .

Table 5

Limiting Equivalent Conductivities of Ions in Water at 25°C(44)

Me_4N	Na	La	Cl	Tartrate (46)
44.9	50.1	69.7	76.35	83.2

For the case of sodium this was tested experimentally when up to a third of the Me_4N^+ ion was replaced (see Section 5.III). No change in the e.m.f. was recorded. The difference between the Speakman plots (Section 4.III) for tartaric acid when the corrected and uncorrected calibrations are used is illustrated in Fig(8).

Unknown pH's at constant ionic strength were all calculated by the iterative method described above.

(d) pH Measurements at Different Ionic Strengths

When the ionic strength and, therefore, the activity coefficients vary during a run, it is not possible, as in Section Vc, to establish a simple relationship between $-\log c_H$ and the e.m.f. The pH scale chosen was

$$pH = -\log m_H - \log f_1,$$

where m_H is the molality of the hydrogen ion and f_1 the activity coefficient of a univalent ion calculated by the Davies equation. As before, a cell of type (E) was used. The salt bridge solution initially chosen was the 1.8M KCl - 1.8M KNO_3 mixture recommended by Grove-Rasmussen(24) as reducing liquid junction potentials compared with the

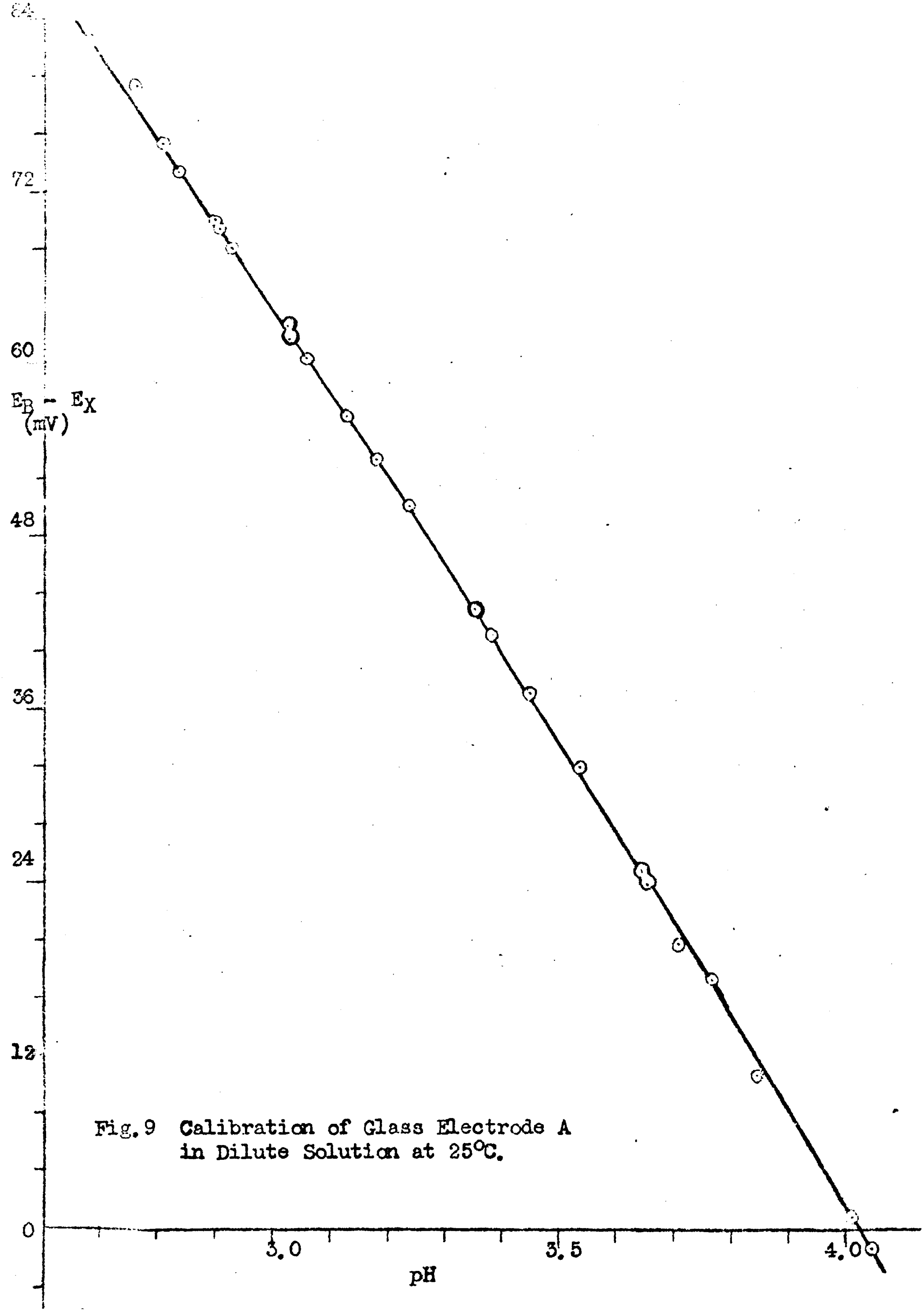


Fig. 9 Calibration of Glass Electrode A in Dilute Solution at 25°C.

normal KCl bridge, but it was found that a 0.18-0.18M mixture gave more stable potentials and so this mixture was preferred. The calibrations were performed by adding approximately 0.05m hydrochloric acid, prepared from constant boiling acid, from a weight burette to a weighed amount of distilled water which had previously been 'washed' with nitrogen for some hours and which had KCl added to it for some of the runs. During the calibration, nitrogen from a cylinder was bubbled through the test solution after first having passed through a series of presaturators,

0.1M HCl, 0.1M NaOH, distilled water, distilled water.

The presaturators containing the distilled water were immersed in the thermostat tank so that they were at the same temperature as the test solution. Weighings of less than 200g were done on a Stanton Unimatic single pan electric balance, while for greater weights a Sartorius chemical balance, with new Oertling stainless steel weights, was used. All weights were corrected for the buoyancy of air.

The calibration at 25° is shown in Fig.(9). The curve is non-linear, presumably because of liquid junction potentials rather than activity coefficient effects, since the presence of varying amounts of KCl does not affect the calibration. Measurements were made with phthalate buffer before and after each run to put the runs on a common basis, as in Section Vb.

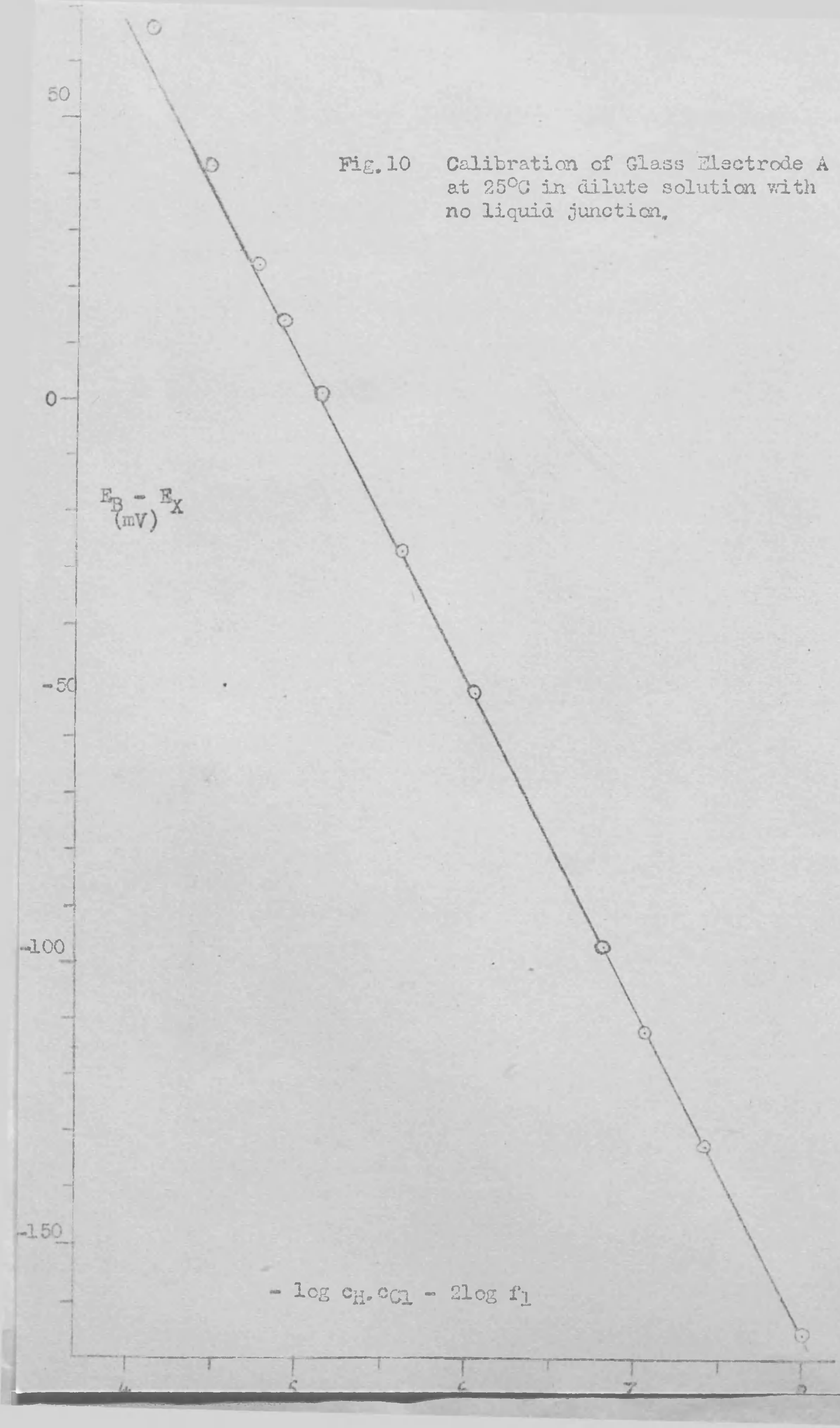


Fig. 10 Calibration of Glass Electrode A at 25°C in dilute solution with no liquid junction.

A calibration was also performed using the cell without liquid junction

glass electrode, test solution, AgCl,Ag . . . . . (F).

The calibration was done on a molar basis, hydrochloric acid solution being added from a burette to a cell of the type shown in Fig.(3) containing glass and silver-silver chloride electrodes. The Davies equation was again used to calculate activity coefficients. The resultant curve is plotted in Fig.(10) and is linear, hence we may assume that the curvature in the calibration with liquid junction is not a function of the electrode, but arises from the liquid junction itself. The calculation of liquid junction potentials in the circumstances of this calibration is very uncertain and it was decided to fit the data to an equation of the form

$$y = E_B - E_X = a + b(pH) + c(pH)^2 + d(pH)^3 + e(pH)^4$$

by the method of least squares and use this empirical relationship to calculate unknown pH's from measured e.m.f. s. The least squares fit was performed on the KDF.9 computer using a program written by Mr. G.M. Armitage, of this department. The adoption of this procedure involves the implicit assumption that the liquid junction potential is a function of the pH only, which can be justified by the agreement between calibrations with different amounts of added salt and the fact that the ionic strength does not vary over too wide a range. The results of the curve-fitting are given in Table 6.

Table 6

T^oC	a	10^2b	10^5c	10^7d	10^9e
15	4.0979	-1.6974	-2.8397	3.2031	-1.6834
25	4.0194	-1.4351	-4.0462	2.9235	-1.1368
35	4.0527	-1.4244	-3.0918	0.7121	0.2872

pNa Measurements

VI. The Meaning of pNa

The problem of definition is the same for pNa as for pH (Section II). Since all the present work on pNa measurements is at constant ionic strength, the definition

$$pNa = -\log c_{Na}$$

has been adopted, where c_{Na} is the molarity of the sodium ion.

Experimental

VII. Reagents

Sodium chloride(B.D.H.AnalaR grade) was recrystallised from distilled water. Hydrochloric acid and tetramethylammonium chloride were prepared as before (Section IV).

VIII. E.M.F. Measurements

(a)Apart from the glass electrodes the apparatus was as described in Section Va.

(b)The glass electrode used was an Electronic Instruments Ltd GEA.33 electrode with an internal silver-silver chloride standard. When not in use it was stored in 0.2M NaCl and was rinsed with the same solution when being transferred from one solution to another. Before the electrode was immersed in a new solution the stem was wiped with a paper tissue and the liquid on the bulb allowed to drain to the neck, where it was absorbed on a tissue.

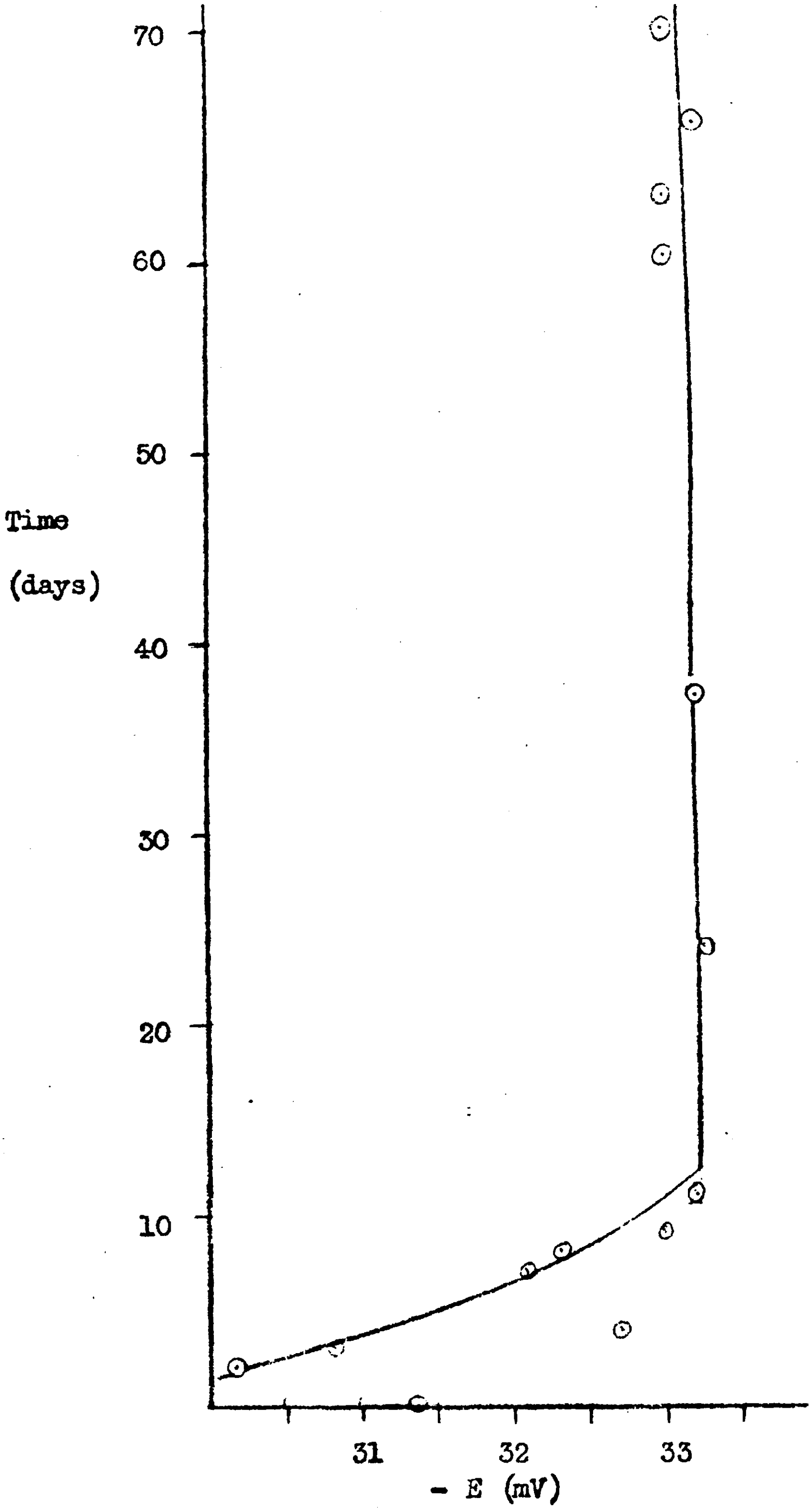
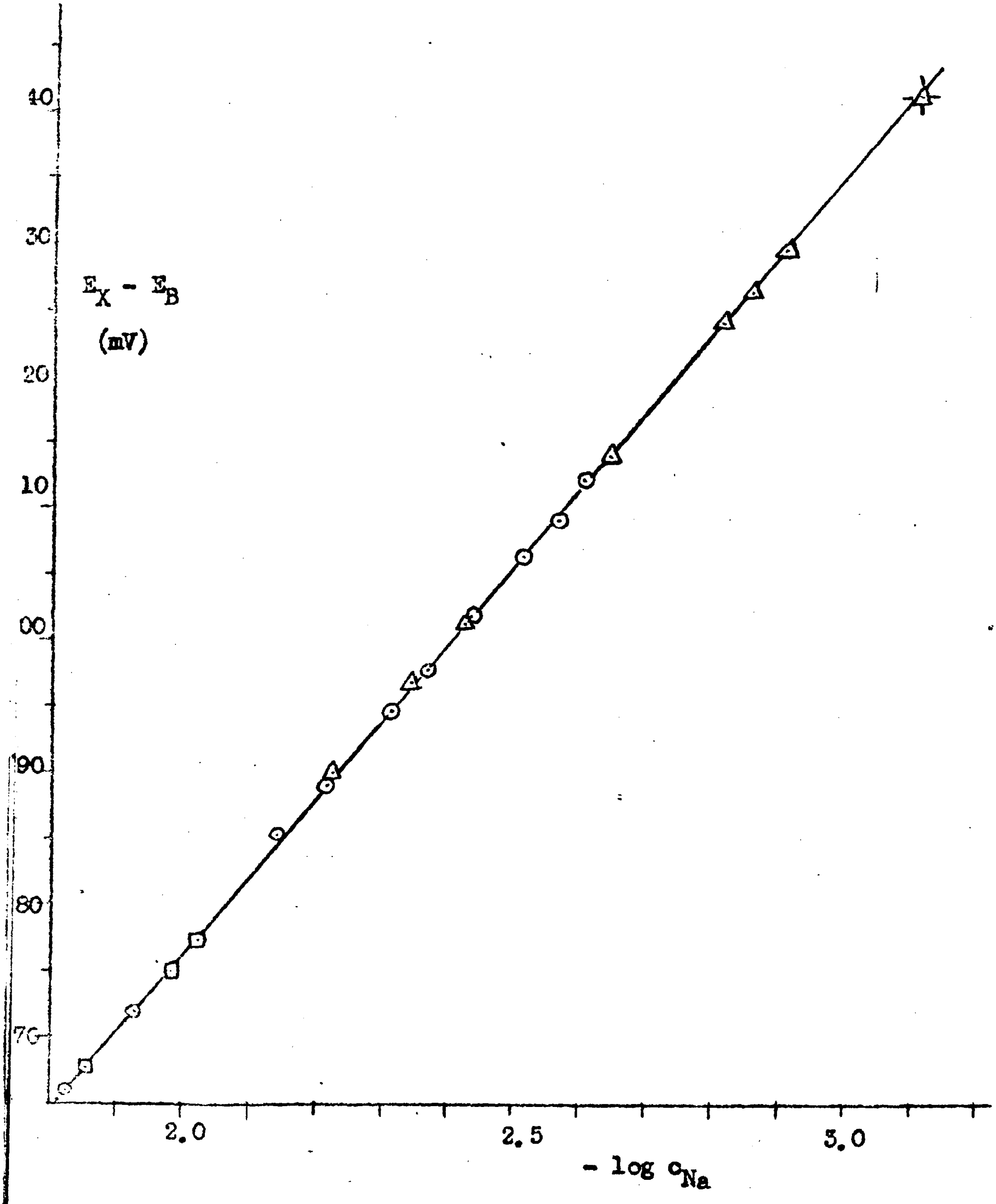


Fig. 11 Response of Na-selective electrode

Fig.12 Calibration of Sodium-responsive Glass Electrode at 25°C. in 0.2M (Me_4NCl) Medium.

○ △ + □ Represent individual runs.



Since all measurements were made at a constant ionic strength of 0.2, maintained with tetramethylammonium chloride, the salt bridge solution chosen was 0.2M Me_4NCl.A 0.2M NaCl solution was made to serve the same purpose in the pNa system as phthalate buffer did in the pH system and measurements of cell(V) containing 0.2M NaCl were made before and after every run. The e.m.f. s obtained from such measurements over a period of time are shown in Fig.(11). After an initial period of increase, the e.m.f. was much more stable than the buffer e.m.f. of a pH electrode, cf.Fig.(2).

The electrode was calibrated by adding 0.2M NaCl from a burette to the titration flask illustrated in Fig(3) containing 0.2M Me_4NCl. Nitrogen from a cylinder (British Oxygen Co.Ltd.), having first passed through a series of presaturators

0.2M HCl,0.2M NaOH,0.2M Me_4NCl,0.2M Me_4 NCl ,

was bubbled continuously through the solution to prevent the absorption of carbon dioxide. Several runs were performed and the results are shown in Fig.(12). The linearity of the plot indicates that liquid junction and activity coefficient effects can be neglected. The response was found to be reproducible in neutral solution, but was seriously affected by the presence of hydrogen ion.

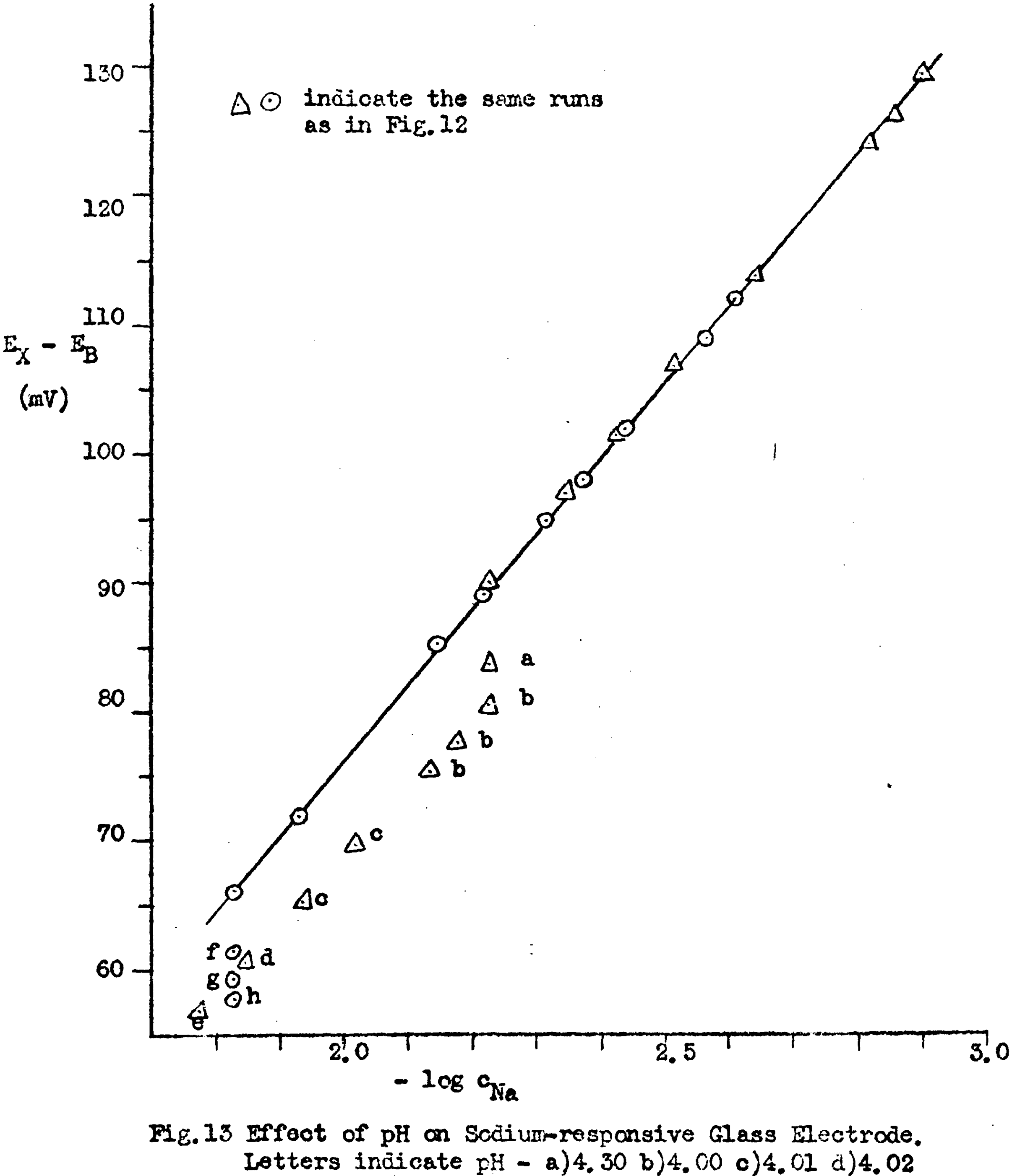


Fig. 13 Effect of pH on Sodium-responsive Glass Electrode. Letters indicate pH - a) 4.30 b) 4.00 c) 4.01 d) 4.02 e) 4.03 f) 4.11 g) 3.93 h) 3.81. Solid line is the calibration in neutral solution.

This effect is illustrated in Fig.(13) and has been discussed theoretically in Section I. The behaviour of the GEA.33 electrode in this respect has been described by Mattock(45). The existence of relationships such as Eqn(9) suggests that if the hydrogen ion activity were known, the sodium ion activity could be calculated, but the electrode behaved sluggishly in these circumstances and bi-ionic measurements would have been quite impracticable with a titration-wise procedure. After having been in a mixed hydrogen-sodium solution the electrode recovered its response if it was soaked in 0.2M NaCl overnight.

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Chapter 3

The Calculation of Stability Constants of Metal Complexes

Part 1: From pH measurements

When an equilibrium cannot be studied by measuring the concentrations of any of the species involved, it is necessary to measure the concentration of some other substance which reacts in a known way with one of the components of the equilibrium under study; this is most commonly hydrogen, which protonates the ligand to form an acid whose dissociation constants are known. Such an indirect method introduces more uncertainties into the calculation in that there will be errors associated with the dissociation constants of the protonated ligand, even if a rigorous mathematical treatment is possible, which will not be the case if the protonated ligand also forms complexes with the metal. Side reactions are often significant if the ligand is a polybasic acid, especially if any of the dissociation steps overlap; such is the case in the present work.

The subsequent calculations are developed for pH measurements made in mixtures of a metal salt, MY_m, a dibasic acid, H_2A, and a monoacid strong base, BOH. For the sake of clarity charges will be omitted from ionic formulae and the concentration of a species X^{z+} represented as X, its activity as $\{X\}$ and its activity coefficient as f_X. All the calculations are treated as if activity corrections were to be applied, but if the measurements are made in a constant ionic medium, the same equations hold with activities set equal to concentrations, i.e. activity coefficients assumed to be unity.

The following symbols are used throughout:

Ta	Total concentration of ligand
Tm	Total concentration of metal
Tb	Total concentration of base,
m	The positive charge on the metal ion ,
a	The negative charge on A, the least protonated form of the ligand,
Ka_1	first dissociation constant of the acid H_2A,
Ka_2	second dissociation constant of the acid,
I	the ionic strength,
Kw	the autoprotolysis constant for water.

The overall stability constants of the complexes are represented as K_{ijk}, where i, j and k are respectively the number of metal ions, protons and ligand molecules which compose the complex.

The following equations hold in all subsequent parts of this chapter:

$Ka_1 = \{H\}\{HA\}/\{H_2A\} = \{H\}\ HA.f_{HA}/(H_2A.f_{H2A})$ . . . . (1),

$Ka_2 = \{H\}\{A\}/\{HA\} = \{H\}\ A.f_A/(HA.f_{HA})$ . . . . . (2),

$Kw = \{H\}\{OH\} = \{H\}\ OH.f_H$ . . . . . (3)

I. The Formation of the Complexes MA and MA_2

This is the method of Gelles and Nancollas(1). The mass and charge balance equations are:

$Tm = M + MA + MA_2$ . . . . (4),

$Ta = H_2A + HA + A + MA + 2MA_2$ . . . . (5),

$mM + (m-a)MA + (m-2a)MA_2 + H + B = Y + OH + aA + (a-1)HA + (a-2)H_2A$ . . . . . . (6).

For the calculation of activity coefficients an initial approximation is made to the ionic strength I = mTm + Tb. Combining equations (3), (4), (5) and (6) we obtain

$a.Ta - m.Tm + Y - Tb + OH - H = HA + 2H_2A$, which may be expressed

$P - \{H\}/f_H + Kw/(\{H\}f_H) = HA(1 + 2\{H\}f_{HA}/(Ka_1.f_{H2A}))$. . . (7),

where P is in terms of known quantities. Eqn (7) can be solved for HA and hence H_2A and A calculated from eqns (1) and (2).

If we define a function $V = Ta - H_2A - HA - A = MA + 2MA_2$, then

$Tm - V = M - MA_2 = M(1 - K_{102}.A^2.f_M.f_A^2/f_{MA2})$ . . . (8),

and $2Tm - V = 2M + MA = M(2 + K_{101}.A.f_M.f_A/f_{MA})$ . . . (9).

Elimination of M from eqns (8) and (9), followed by rearrangement, gives,

$$\frac{V}{A^2(2Tm - V)} \cdot \frac{f_{MA2}}{f_M \cdot f_A^2} = K_{101} \cdot \frac{Tm - V}{A(2Tm - V)} \cdot \frac{f_{MA2}}{f_{MA} \cdot f_A} + K_{102} \quad . . . \quad (10),$$

which is of the form $y = mx + c$. If measurements are made in a number of different solutions and values of the function $y = \frac{V}{A^2(2Tm-V)} \cdot \frac{f_{MA2}}{f_M \cdot f_A^2}$ plotted against $x = \frac{Tm - V}{A(2Tm - V)} \cdot \frac{f_{MA2}}{f_{MA} \cdot f_A}$ the slope will be K_{101} and the intercept on the y-axis K_{102}. The concentrations of all the species can now be calculated and a new value of I, and hence the activity coefficients, obtained for every point. These improved estimates for the activity coefficients can be substituted in eqn (7) and the whole process repeated to give more accurate values of K_{101} and K_{102}, whence we obtain still better estimates of I and so on.
Iteration can continue until successive cycles give values of both K_{101} and K_{102} which agree within acceptable limits.

An ALGOL program for KDF.9 computer, written by Dr. H.S. Dunsmore, with some additions by the author, was used to perform the calculations. The slope and intercept of the x-y plot were calculated by the method of least squares.

II. The Formation of Complexes MA and MHA

The constants are

$$K_{101} = \{MA\}/\{M\}\{A\} \text{ and } K_{111} = \{MHA\}/\{M\}\{H\}\{A\}.$$

It is convenient to define a constant

$$K' = \{MHA\}/\{M\}\{HA\} = K_{111}.Ka_2 \quad \ldots\ldots\ldots\ldots \quad (11).$$

The mass and charge balance equations are,

$$Tm = M + MA + MHA \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12),$$

$$Ta = H_2A + HA + A + MA + MHA \quad \ldots\ldots\ldots\ldots \quad (13),$$

and $mM + (m-a)MA + (m+1-a)MHA + H + B = aA + (a-1)HA + (a-2)H_2A + OH + Y$ (14).

In contrast to the MA-MA_2 case, eqns(12) - (14) cannot be manipulated so as to eliminate all the metal-containing species and a knowledge of one of the stability constants is necessary in order to calculate the other. It will normally be possible to obtain an estimate of one of the constants by working in a comparatively high or low pH range and neglecting the other complex. The method will be demonstrated for each case in turn.

(a) K_{101} is known

Eqns (12), (13) and (14) can be combined and rearranged to give a function

$$Z = (a-1)Ta - m.Tm - Tb + Y - H + OH = H_2A - A - MA.$$

If an initial estimate $I = m.Tm + Tb$ is made to the ionic strength, activity coefficients can be calculated, H and OH obtained from H, eqn(3) and f_H and Z thus determined.

From eqns(12) and (13) $M = Tm - Ta + H_2A + HA + A$. . . . . (15)

Now

$$Z = \{H\}HA.f_{HA}/(Ka_1.f_{H2A}) - Ka_2.HA.f_{HA}/(\{H\}.f_A) - K_{101}.M.A.f_M.f_A/f_{MA} .$$

$$Z = \frac{\{H\}HA.f_{HA}}{Ka_1.f_{H2A}} - \frac{Ka_2.HA.f_{HA}}{\{H\}\,f_A} - \frac{K_{101}.f_M.f_{HA}.Ka_2.HA(Tm - Ta)}{\{H\}\,f_{MA}}$$

$$- \frac{K_{101}.Ka_2.HA^2.f_M.f_{HA}(1 + \{H\}f_{HA}/(Ka_1.f_{H2A}) + Ka_2 f_{HA}/(\{H\}f_A)).}{\{H\}\,f_{MA}}$$

This can be rearranged to give a quadratic in HA of the form

$qHA^2 + rHA + s = 0$, where $s = Z$,

$$r = \frac{K_{101}.f_M.f_{HA}.Ka_2(Tm - Ta)}{\{H\}f_{MA}} + \frac{Ka_2.f_{HA}}{\{H\}\,f_A} - \frac{\{H\}\;f_{HA}}{Ka_1.f_{H2A}} ,$$

and

$$q = \frac{K_{101}.Ka_2.f_M.f_{HA}}{\{H\}\;f_{MA}} . \left\{ 1 + \frac{\{H\}\;f_{HA}}{Ka_1.f_{H2A}} + \frac{Ka_2.f_{HA}}{\{H\}\;f_A} \right\} .$$

HA can now be obtained as the roots $\dfrac{-r \pm\sqrt{r^2 - 4qs}}{2q}$ of the equation.

H_2A and A are calculated from HA and eqns(1) and (2) respectively. From eqn(15) we get M and hence MA and

$MHA.K_{111}$ can now be obtained, a better approximation made to I and the whole process repeated until consistency is achieved.

(b) K_{111} is known

Combination of (12), (13) and (14), followed by rearrangement gives

$$Z' = a.Ta - m.Tm - H - Tb + Y + OH = 2H_2A + HA + MHA \quad . \ . \ . \ . \ (16).$$

Combining eqns(1), (2), (3), (11), (15) and (16) gives, after rearrangement,

$$HA^2\left(\frac{K'.f_{HA}.f_M}{f_{MHA}} \left(1 + \frac{\{H\}\ f_{HA}}{Ka_1.f_{H2A}} + \frac{Ka_2.f_{HA}}{\{H\}\ .f_A} \right) \right)$$

$$+ \quad HA\left(1 + \frac{K'.f_{HA}.f_M}{f_{MHA}}(Tm - Ta) + \frac{2\{H\}\ f_{HA}}{Ka_1.f_{H2A}}\right) - Z' = 0 \quad . \ . \ . \ (17).$$

which is a quadratic of the form $q'HA^2 + r'HA + s' = 0$ and can be solved for HA. Once HA is known, H_2A and A can be obtained from eqns(1) and (2) and then, from eqn(15), M is calculable. MHA follows from eqn(11) and finally MA from eqn(12). K_{101} can now be determined. A better value of I can be calculated and the cycle repeated until successive values of K_{101} agree within a desired limit.

The above methods have been described by Nancollas(2), but a closer mathematical analysis reveals certain restrictions as to the possible solutions of the equations of the form

$$q.HA^2 + r.HA + s = 0$$

in both (a) and (b) above. A knowledge of these restrictions can lead to a considerable saving in the time of calculation.

The coefficients q, r and s are functions of quantities which are physically meaningful only if they are positive and HA itself must be positive. If the roots are $R_1 = (-r + \sqrt{r^2 - 4qs})/2q$ and $R_2 = (-r - \sqrt{r^2 - 4qs})/2q$ then, since q is always positive, we arrive at the classification given in Table 1 as to whether the roots are meaningful ("yes") or not ("no").

Table 1

s	r	R_1	R_2
-	+,0	yes	no
-,0	-	yes	no
+,0	+,0	no	no
+	-	yes	yes

In case (b) s is always negative and hence only root R_1 need be considered, but in case (a) both roots must be checked.

In practice it is found that in the course of a single titration control may switch from one root to the other.

In view of the duplication of calculation usually involved in method (a) and the tendancy of errors in the approximation of the larger K_{101} to obscure the trends in the calculated values of K_{111}, it has been found more convenient to adopt method (b), varying the given K_{111} systematically and taking that value which leads to a minimum in the standard deviation of the calculated K_{101}. This method has been found to succeed when others fail, especially where the stability constants are small, e.g. alkali metal complexes.

Calculations were carried out on the English Electric KDF.9 computer, using an ALGOL program originally written by Dr. H.S. Dunsmore, but extended by the author.

III. The Formation of Complexes MA, MA_2 and MHA

The constants are $K_{101} = \frac{\{MA\}}{\{M\}\{A\}}$, $K_{102} = \frac{\{MA_2\}}{\{M\}\{A\}^2}$ and $K_{111} = \frac{\{MHA\}}{\{M\}\{H\}\{A\}}$. Again it is convenient to define $K' = K_{111}.Ka_2$. The mass and charge balance equations are:

$$Tm = M + MA + MA_2 + MHA \quad \ldots\ldots\ldots\ldots \quad (18),$$

$$Ta = H_2A + HA + A + MA + 2MA_2 + MHA \quad \ldots\ldots\ldots \quad (19),$$

$$mM + (m-a)MA + (m-2a)MA_2 + (m+1-a)MHA + H + B$$
$$= Y + OH + aA + (a-1)HA + (a-2)H_2A \quad \ldots\ldots\ldots \quad (20).$$

Combination of equations (3), (18), (19) and (20) yields a function

$$Z'' = aTa - mTm - B - H + OH + Y = HA + 2H_2A + MHA.$$

$$\text{Hence } HA = Z''/(1 + \frac{2\{H\}f_{HA}}{Ka_1 . f_{H2A}} + \frac{K'.M.f_M.f_{HA}}{f_{MHA}}) \quad . . . . (21).$$

If Eqn(21) is to be solved for HA the activity coefficients must be calculated using an approximate value for the ionic strength and both K' and M must also be estimated.

By an apt choice of experimental conditions and use of the methods demonstrated in Section II it will normally be possible to obtain an estimate for K', however rough, and M may initially be set to zero (or any more realistic value which earlier calculations may provide). HA can now be calculated and hence, from Eqns (1) and (2), A and H_2A.

We can define

$$V'' = Ta - A - HA - H_2A = MA + 2MA_2 + MHA, \text{ where } MHA$$

is also known, and set up functions

$$y'' = \frac{(V''-MHA)f_{MA2}}{A^2.f_A^2.f_M(2Tm-V''-MHA)} \quad \text{and } x'' = \frac{(Tm-V'')f_{MA2}}{A.f_A.f_{MA}(2Tm-V''-MHA)}$$

analogous to the functions y and x respectively in Section I which have the property that $y'' = K_{101}.x'' + K_{102}$. A plot of y'' against x'' will therefore have a slope of K_{101} and an

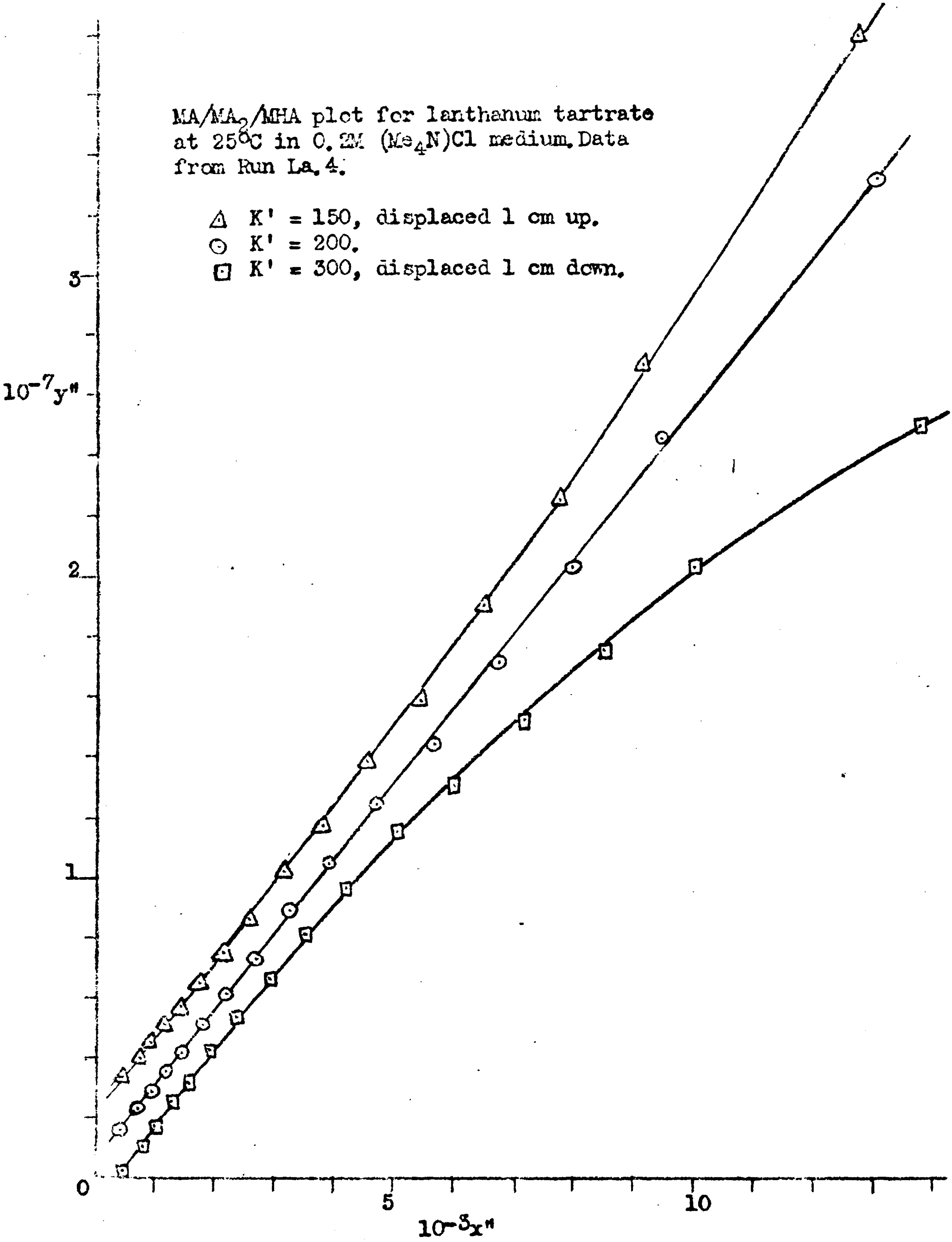
MA/MA$_2$/MHA plot for lanthanum tartrate at 25°C in 0.2M (Me$_4$N)Cl medium. Data from Run La. 4.
△ K' = 150, displaced 1 cm up.
⊙ K' = 200.
⊡ K' = 300, displaced 1 cm down.
$10^{-7}y''$
0
1
2
3
$10^{-3}x''$
5
10

Fig. 1

intercept of K_{102}. Knowing the values of the stability constants and of A, we can now calculate the concentrations of all the species present, i.e. we have a new value for M which can be substituted in Eqn (21), thus starting the cycle again. The procedure is repeated until consistent values for the stability constants are obtained and used to calculate the concentrations of all species in order to determine the ionic strength more accurately. New activity coefficients are derived and substituted in Eqn (21) when the whole process starts once more. This doubly cyclical operation is repeated until consistent stability constants are achieved at the end of both cycles.

The accuracy of the above procedure depends on the closeness of the independently estimated value of K_{111} to the true one, a poor estimate resulting in considerable curvature of the y"-x" plot. During the course of this work it was observed that deviations from linearity occurred in a regular way (Fig. 1) and that this could be used to improve the above method. In order to test the y"-x" plot for curvature it is fitted to a second order equation by the method of least squares and the sums of the squares of the deviations of the points calculated for both the first and second order fits. If these two quantities agree within a prescribed limit the first order line is assumed to be a "good" one and the value of K_{111} employed in its calculation assumed to be a "good" value, otherwise K_{111} is adjusted in the manner below.

The second order curve is tested for the direction of its deviation from linearity by comparing the area under the curve with the area under the straight line between its extremities. The algebraic differences between these two areas is designated D_i, where

D_i = (area under curve)-(area under line) for the ith value of K_{111} tried. If D_i is negative K_{111} is increased by a given proportion and conversely if it is positive. The new K_{111} is substituted in Eqn(21) and the entire process repeated. This procedure is carried out until two successive differences D_j and D_k are of opposite sign, when a new value, K''_{111}, is assigned to K_{111} by means of the relation

$$K''_{111} = K'_{111}\left(1 - \frac{D_k}{|D_j - D_k|}\right),$$ where K'_{111} is the kth value of K_{111} . . . . (22)

Alternatively K''_{111} may be set equal to the arithmetic or geometric mean of the jth and kth values.

The calculation is again carried through from Eqn (21) onwards, a new value for K_{111} being henceforth determined by an equation of the form (22), where D_j and D_k are the least negative and least positive values (or vice versa) of D_1 so far obtained. Iteration continues in this way until a "good" value of K_{111} is attained, as defined above.

In practice it is found that five or six values of K_{111} need to be tried before arriving at a "good" one, but data of high quality are required, since the curvature should not be masked by random scatter of the points.

The calculations were performed on an English Electric KDF.9 Computer, using a program originally written by Dr. H.S. Dunsmore, with the addition of the trial value adjustment section by the author. The slope and intercept of the x"-y" plot were determined by the method of least squares. The program is given in Appendix 2b.

IV. The Formation of Complexes MA and M_2A_2

The constants are

$$K_{101} = \frac{\{MA\}}{\{M\}\{A\}} \quad \text{and} \quad K_{202} = \frac{\{M_2A_2\}}{\{M\}^2\{A\}^2} .$$

The mass and charge balance equations are:

$$Tm = M + MA + 2M_2A_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (23),$$

$$Ta = H_2A + HA + A + MA + 2M_2A_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (24),$$

and

$$mM + (m-a)MA + 2(m-a)M_2A_2 + B + H = Y + OH + aA + (a-1)HA + (a-2)H_2A \quad \ldots\ldots \quad (25).$$

Combination of Eqns (3), (23), (24) and (25) gives

$$HA + 2H_2A = aTa - m.Tm - B - H + OH + Y,$$

which can be solved for HA with the aid of Eqn (1). A and H_2A are now calculated from Eqns (2) and (1) respectively. Combination of Eqns (23) and (24) gives

$$M = Tm - Ta + H_2A + HA + A.$$ We can write

$$Tm - M = MA + 2M_2A_2$$
$$= K_{101}.M.A.(f_M.f_A/f_{MA}) + 2K_{202}(M.A.f_M.f_A)^2/f_{M2A2} \quad ,$$

which can be transformed to

$$\frac{Tm - M.}{M^2.A^2} \cdot \frac{f_{M2A2}}{(f_M.f_A)^2} = \frac{K_{101}}{M.A} \cdot \frac{f_{M2A2}}{f_M.f_A.f_{MA}} + 2K_{202} \quad . . . (26a),$$

or $$\frac{Tm - M.}{M.A} \cdot \frac{f_{MA}}{f_M.f_A} = 2K_{202}.M.A.\frac{f_M.f_A.f_{MA}}{f_{M2A2}} + K_{101} \quad . . (26b).$$

Equations (26a) and (26b) are of the form y = m.x + c, where the slope and intercept are in (26a) K_{101} and $2K_{202}$ and in (26b) K_{202} and K_{101} respectively. If no dimerisation takes place, i.e. $K_{202} = 0$, Eqn (26a) should be extrapolated through the origin and Eqn (26b) should be a horizontal straight line. As before activity coefficients are dealt with by iteration in the ionic strength expression.

Eqn (26b) is the same as that of Leden (4). For a series of polymers M_iA_i, i = 1, .. N, we can write, neglecting activity coefficients,

$$Tm - M = \sum_{i=1}^{N} i.K_{10i}.M^i.A^i \quad ,$$

which can be solved for the N K_{10i} if at least N distinct measurements are made. Solving by simultaneous equations is likely to be unsatisfactory unless the data is of the highest precision and alternatively the graphical extrapolation method of Hedström (5) may be used.

An ALGOL program for the KDF.9 computer was written by the author to deal with the calculations for the $MA-M_2A_2$ case. The slope and intercept of the x-y plot were calculated by the method of least squares. The program is given in Appendix 2c.

V. The complexes MA, MA_2 and MA_3

The stability constants are

$$K_{101} = \frac{\{MA\}}{\{M\}\{A\}} \ , \ K_{102} = \frac{\{MA_2\}}{\{M\}\{A\}^2} \ \text{and} \ K_{103} = \frac{\{MA_3\}}{\{M\}\{A\}^3} \ .$$

The mass and charge balance equations are

$$Tm = M + MA + MA_2 + MA_3 \quad \ldots\ldots\ldots\ldots\ldots \quad (27),$$

$$Ta = H_2A + HA + A + MA + 2MA_2 + 3MA_3 \quad \ldots\ldots\ldots \quad (28)$$

and

$$H + B + m.M + (m-a)MA + (m-2a)MA_2 + (m-3a)MA_3$$
$$= Y + OH + a.A + (a-1)HA + (a-2)H_2A \quad \ldots\ldots\ldots \quad (29).$$

Combination of Eqns (27), (28) and (29) gives

$$HA + 2H_2A = Y + OH + a.Ta - m.Tm - B - H,$$

which, together with Eqn (1) gives HA and hence H_2A. Eqn (2) is then used to calculate A. We can now construct a function

$$V = Ta - H_2A - HA - A,$$

and hence the functions

$$Tm - V = M - MA_2 - 2MA_3,$$

$$2Tm - V = 2M + MA - MA_3$$

and

$$3Tm - V = 3M + 2MA + MA_2$$

From the above four functions we derive

$$\frac{V.f_{MA3}}{A^3.f_A^3.f_M(3Tm-V)} = K_{103} + K_{102}.\frac{f_{MA3}(2Tm-V)}{A.f_A.f_{MA2}(3Tm-V)} + K_{101}.\frac{f_{MA3}(Tm-V)}{A^2.f_A^2.f_{MA}(3Tm-V)},$$

which is of the form

$$x = K_{103} + y.K_{102} + z.K_{101} \quad \ldots\ldots\ldots (30a).$$

$$\text{Hence } x.y = y.K_{103} + y^2.K_{102} + y.z.K_{101} \quad \ldots\ldots\ldots (30b)$$

$$\text{and } x.z = z.K_{103} + y.z.K_{102} + z^2.K_{101} \quad \ldots\ldots\ldots (30c).$$

Equations of the types (30a-c) can be set up for each data point and then summed over all n points. Hence

$$\Sigma x = n.K_{103} + \Sigma y.K_{102} + \Sigma z.K_{101} \quad \ldots\ldots\ldots (31a),$$

$$\Sigma xy = y.K_{103} + \Sigma y^2.K_{102} + \Sigma yz.K_{101} \quad \ldots\ldots\ldots (31b),$$

$$\text{and } \Sigma xz = z.K_{103} + \Sigma yz.K_{102} + \Sigma z^2.K_{101} \quad \ldots\ldots\ldots (31c).$$

Eqns (31a-c) can now be solved simultaneously for K_{101}, K_{102} and K_{103}. An ALGOL program for the KDF.9 computer has been written by Dr. H.S. Dunsmore to deal with the above calculations.

VI. Other Complexes

In the preceding sections it has not been necessary to assume values for more than a single stability constant in order to determine the others and there has existed some criterion to judge the validity of the assumption. When measurements are made in particular conditions other complexes may be present e.g. when the ratio of Ta to Tm is large and the pH is low MHA_2 may exist or when the absolute values of Tm and Ta are large and the pH is high, but < 7, the neutral species M_aA_m may appear in solution prior to precipitation. In solving for the two above complexes we must know K_{101}, K_{102} and K_{111} and considerable uncertainty must be attached to any value of a fourth stability constant so calculated, depending on the accuracy with which the other three are known.

It is convenient to define the following functions:

$$Q = \frac{\{H\} f_A}{Ka_2 . f_{HA}} \;, \quad R = \frac{\{H\}^2 f_A}{Ka_1 . Ka_2 . f_{H2A}} \;, \quad Fma = f_M . f_A / f_{MA} \;,$$

$$Fmaa = f_M . f_A^2 / f_{MA2} \quad \text{and} \quad Fmha = f_M . f_A / f_{MHA}$$

VI(a) Complexes MA, MA_2, MHA, MHA_2

The mass and charge balance equations are:

$$Tm = M + MA + MA_2 + MHA + MHA_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (32),$$

$$Ta = H_2A + HA + A + MA + MHA + 2MHA_2 + 2MA_2 \quad \ldots\ldots\ldots\ldots \quad (33),$$

and

$$m.M + (m-a)MA + (m-2a)MA_2 + (m+1-a)MHA + (m+1-2a)MHA_2 + B + H$$

$$= Y + OH + a.A + (a-1)HA + (a-2)H_2A \quad \ldots\ldots\ldots\ldots \quad (34).$$

Eqns (32), (33) and (34) can be combined and rearranged to give a function

$$P = Y + OH + a.Ta - m.Tm - H - B = MHA + MHA_2 + HA + 2H_2A.$$

$$P - Tm = A(Q + 2R) - M(1 + K_{101}.A.Fma + K_{102}.A^2.Fmaa) \quad \ldots (35).$$

$$Ta - 2Tm = A(1 + Q + R) - M(2 + K_{101}.A.Fma + K_{111}.A.\{H\}.Fmha) \ldots (36).$$

Elimination of M from Eqns (30) and (31) results in a polynomial in A:

$$A^3 K_{102}.Fmaa(1 + Q + R) \quad + \quad A^2 \left[K_{102}.Fmaa(2Tm-Ta) + K_{101}.Fma(1-R) - K_{111}\{H\}Fmha(Q+2R)\right] + A\left[1 - Q - 3R + K_{101}.Fma(Tm-Ta+P) - K_{111}\{H\}Fmha(Tm-P)\right] + 2P - Ta = 0,$$

which, given an initial estimate for A, can be solved for A by the Newton-Raphson method (see Section VII). Once A is known Eqns (35) or (36) can be solved for M and hence MA, MA_2 and MHA calculated from the appropriate stability constant. MHA_2 is then the residual in Tm, and K_{112} follows immediately.

VI(b) Complexes MA, MHA, MA_2 and M_aA_m

The mass and charge balance equations are:

$$Tm = M + MA + MA_2 + MHA + a.M_aA_m \quad \ldots\ldots\ldots\ldots (37),$$

$$Ta = H_2A + HA + A + MA + MHA + 2MA_2 + m.M_aA_m \quad \ldots\ldots (38),$$

and $m.M + (m-a)MA + (m+1-a)MHA + (m-2a)MA_2 = Y + OH + a.A + (a-1)HA + (a-2)H_2A \quad \ldots\ldots\ldots\ldots (39)$.

Combination of Eqns (37), (38) and (39) yields

$$P = Y + OH - H - B + a.Ta - m.Tm = MHA + HA + 2H_2A \ldots (40).$$

Rearrangement and expansion of (40) gives an expression for HA,

$$HA = P/(K_{111}.Ka_2.M.Fmha + 1 + 2Q) \quad \ldots\ldots\ldots\ldots (41).$$

Insertion of a trial value for M in Eqn (41) enables a first estimate of HA to be made. H_2A and A can then be calculated from Eqns (1) and (2). We can now define a function

$G = Ta - A - HA - H_2A$. Then

$m.Tm - a.G = m.M + (m-a)MA + (m-2a)MA_2 + (m-a)MHA$, which can be rearranged and expanded to give

$$M = (m.Tm - a.G)/(m + (m-a)K_{101}.A.Fma + (m-2a)K_{102}.A^2.Fmaa + (m-a)K_{111}.\{H\}.A).$$

This new value of M is substituted in Eqn (41) and the whole process repeated. This goes on until successive values of both HA and M agree within specified limits, when the concentrations MA, MA_2 and MHA can be calculated from the stability constants. Eqn (37) is then used to calculate the concentration of the neutral complex and in consequence the stability constant K_{aOm}.

In both sections VI(a) and VI(b) activity corrections can be made in the usual way by iteration in the ionic strength equation, but as the system becomes more involved such iterations become less reliable and in the present work have not been tried experimentally.

ALGOL programs to deal with both VI(a) and VI(b) above have been written by the author.

VII. The Equilibrium Constant Refinement Program GAUSS G

GAUSS G is a program designed by Tobias (6) to refine values of equilibrium constants for generalised complex formation reactions. Originally written in FORTRAN 60, a WHETSTONE ALGOL translation for the English Electric KDF.9 computer has been prepared and is listed in Appendix 2d.

The non-linear Gauss method is used and all derivatives are obtained numerically. The complete program will handle any of the following four types of systems (1) hydrolysis of an aquo-metal ion only (2) complex formation with a ligand which is the conjugate base of a weak acid and for which the acid dissociation constants are known (3) acid dissociation equilibria for any weak acid (4) complex formation between the ligand and the metal ion where either protonation of the ligand or hydroxo complexing of the metal ion occurs simultaneously.

Gauss Method Least Squares

The problem is to assign values to a collection of variables such that $\sum_i R_i^2$ is a minimum, where R_i is the residual for the ith experimental observation of some quantity which is a function of the variables in which we are interested. By the residual we mean the difference between the observed value of the measured quantity and the value calculated from a trial set of values for the variables inserted in the equation for the experimental quantity. In this particular case the experimental quantity is $\bar{H}_i$, the analytical hydrogen concentration of the ith experimental solution, and the variables some or all of the stability constants $k_1, k_2, \ldots k_N$ which describe the behaviour of all the species present in solution in terms of the free metal concentration, M_i, the free ligand concentration, A_i, and the hydrogen ion concentration, H_i, neglecting the solvent and "inert" background electrolyte. The total metal concentration, $\bar{M}_i$, total ligand concentration, $\bar{A}_i$, analytical hydrogen concentration, $\bar{H}_i$, and free hydrogen concentration, H_i, are known.

If we wish to refine n of the N constants, then by differentiating $\sum_i R_i^2$ term by term we obtain n equations of the form

$$2 \sum_i R_i \frac{\partial \bar{H}_i}{\partial k_j} = 0$$

Now $R_i = -\bar{H}_{i(obs)} + \bar{H}_{i(calc)} = -\bar{H}_{i(obs)} + f(k_1, k_2, \ldots k_n, k_{n+1} \ldots k_N, H_i, M_i, A_i)$.

Using the initial trial values of the stability constants we obtain a calculated initial value ${}^o\bar{H}_i$ for the analytical hydrogen concentration and consequently an initial residual ${}^oR_i = {}^o\bar{H}_i - \bar{H}_{i(obs)}$. Provided ${}^o\bar{H}_i$ is a reasonable approximation we can express the best calculated $\bar{H}_i$ by means of Taylor's theorem thus:

$${}'\bar{H}_i = {}^o\bar{H}_i + \left(\frac{\partial f}{\partial k_1}\right) dk_1 + \left(\frac{\partial f}{\partial k_2}\right) dk_2 + \ldots,$$ neglecting

second and higher order terms and where dk_j is the required shift in the jth stability constant. The best residual can now be expressed

$${}'R_i = {}^oR_i + \left(\frac{\partial f}{\partial k_1}\right) dk_1 + \left(\frac{\partial f}{\partial k_2}\right) dk_2 + \ldots.$$

The n normal equations now become

$$\sum_i \left\{ \left(\frac{\partial f_i}{\partial k_1}\right) dk_1 + \left(\frac{\partial f_i}{\partial k_2}\right) dk_2 + \ldots\ldots + {}^oR_i \right\} \left(\frac{\partial f_i}{\partial k_j}\right) = 0$$

which can be expressed in matrix notation as

$$\begin{vmatrix} \sum_i\left(\frac{\partial f_i}{\partial k_1}\right)\left(\frac{\partial f_i}{\partial k_1}\right) & \sum_i\left(\frac{\partial f_i}{\partial k_1}\right)\left(\frac{\partial f_i}{\partial k_2}\right) & \cdots\cdots \\ . & . & \cdots\cdots \\ . & . & \cdots\cdots \\ . & . & \cdots\cdots \\ . & . & \cdots\cdots \end{vmatrix} \begin{vmatrix} dk_1 \\ dk_2 \\ dk_3 \\ . \\ . \end{vmatrix} = \begin{vmatrix} -\sum_i {}^{o}R_i\left(\frac{\partial f_i}{\partial k_1}\right) \\ . \\ . \\ . \\ . \end{vmatrix}$$

Having obtained the requisite mathematical formula we have now to calculate $\bar{H}_i$ from the experimental data. If a complex is composed of m metal ions, a ligand ions and either h hydrogen ions or h hydroxide ions its concentration is $k_{mhn}.M_i^m.A_i^a.H_i^h$ where k_{mhn} is the appropriate stability constant and h is -1x the number of hydroxide ions if it is a hydroxo complex. The procedure adopted depends on whether $\bar{M}_i = 0, \bar{A}_i = 0$ or neither is zero.

1) $\bar{M}_i = 0$

This is the case where no metal is present and the constants being refined are the dissociation constants of an acid. There are two mass balance equations in total ligand and analytical hydrogen concentration:

$$F = -\bar{A}_i + A_i + \sum_a \sum_h a k_{0ha} A_i^a . H_i^h$$

$$G = -\bar{H}_i + H_i - Kw/H_i + \sum_a \sum_h h k_{0ha} A_i^a . H_i^h$$

F is considered an identity in the experimental data and is used to calculate A_i in the following way

An estimate is made to A_i, which may be $\bar{A}_i$, or any other guess for which there are grounds, and used together with the trial k's to calculate

$$L = A_i + \sum_a \sum_h a.k_{Oha}.A_i^a.H_i^h \text{ , which is then compared}$$

with $\bar{A}_i$. If $L - \bar{A}_i$ is within a specified limit the trial value of A_i is assumed to be the true one, otherwise a new value is calculated by the Newton-Raphson method i.e. $x_2 = x_1 - x_1.f(x_1)/f'(x_1)$ where x_1 and x_2 are the trial and improved values respectively, $f(x_1)$ is the value of the function at x_1 and $f'(x_1)$ the gradient to the function at x_1. In this case

$$f(x_1)/f'(x_1) = (L-\bar{A}_i)/(A_i + \sum_a \sum_h a^2.k_{Oha}.A_i^a.H_i^h).$$

The new A_i is used to calculate a new L and so on until the desired limit is reached. G can now be calculated. If the variance in a quantity X is represented s_X we can write, treating the equations in the variances in G and F as vectors,

$$s_F = \underset{\sim}{t}.F_{\bar{A}_i}.s_{\bar{A}_i} + \underset{\sim}{u}.F_{\bar{H}_i}.s_{\bar{H}_i} + \underset{\sim}{v}.F_{A_i}.s_{A_i} + \underset{\sim}{w}.F_{H_i}.s_{H_i} \quad ,$$

$$s_G = \underset{\sim}{t}.G_{\bar{A}_i}.s_{\bar{A}_i}. + \underset{\sim}{u}.G_{\bar{H}_i}.s_{\bar{H}_i} + \underset{\sim}{v}.G_{A_i}.s_{A_i} + \underset{\sim}{w}.G_{H_i}.s_{H_i} \quad ,$$

where

$$F_{H_i} = (\partial F/\partial H_i), \; G_{H_i} = (\partial G/\partial H_i) \text{ etc.}$$

Since F is regarded as an identity, $s_F = 0$.

Evaluating the derivatives, we find

$F_{\bar{A}_1} = -1$, $F_{\bar{H}_1} = 0$, $G_{\bar{H}_1} = -1$ and $G_{\bar{A}_1} = 0$. F_{H_1}, F_{A_1}, G_{H_1} and G_{A_1} can be calculated from the equations in F and G respectively and $s_{\bar{A}_1}$, $s_{\bar{H}_1}$ and s_{H_1} the variances in the experimental data, are known. The equation in s_F is used to calculate the unknown s_{A_1} in terms of known variances.

$$\underset{\sim}{v}.s_{A_1} = (\underset{\sim}{t}.s_{\bar{A}_1} - \underset{\sim}{w}.F_{H_1}.s_{H_1})/F_{A_1} \ .$$

Then $s_G = -\underset{\sim}{u}.s_{\bar{H}_1} + \underset{\sim}{t}.G_{A_1}.s_{\bar{A}_1}/F_{A_1} + (G_{H_1} - G_{A_1}.F_{H_1}/F_{A_1}).\underset{\sim}{w}.s_{H_1}$.

If it is assumed that there is no correlation between the errors in F and G, taking the result of $(s_G.s_G)$, we obtain the variance in G, s_G^2, in terms of known quantities.

$$s_G^2 = s^2_{\bar{H}_1} + G^2_{A_1}.s^2_{\bar{A}_1}/F^2_{A_1} + (G_{H_1} - G_{A_1}.F_{H_1}/F_{A_1})^2.s^2_{H_1} \ .$$

2) $\bar{A}_1 = 0$.

If in part (1) above $\bar{A}_1$, A_1 and a are replaced in every instance by $\bar{M}_1$, M_1 and m respectively, the equations hold for this case also.

(3) $\bar{M}_i \neq 0$, $\bar{A}_i \neq 0$

There are three mass balance equations in total metal, total ligand and analytical hydrogen ion concentrations.

$$E = -\bar{M}_i + M_i + \sum_m \sum_h \sum_a m.k_{mha}.M_i^m.A_i^a.H_i^h = 0,$$

$$F = -\bar{A}_i + A_i + \sum_m \sum_h \sum_a a.k_{mha}.M_i^m.A_i^a.H_i^h = 0,$$

$$G = -\bar{H}_i + H_i - Kw/H_i - \sum_m \sum_h \sum_a M_i^m.A_i^a.H_i^h \quad .$$

The equations E and F are considered identities in the experimental data and iteration is carried out in the total metal and total ligand mass balance equations simultaneously to obtain M_i and A_i.

Let $f(M,A) = \bar{M}_{obs} - \bar{M}_{calc}$ and $g(M,A) = \bar{A}_{obs} - \bar{A}_{calc}$, where $M, \bar{M}, A$ and $\bar{A}$ are the free metal, total metal, free ligand and total ligand concentrations respectively. The correct values for M and A are those for which

$$f(M,A) = g(M,A) = 0.$$

Expanding in Taylor's series and neglecting second and higher order terms,

$$f(M,A) = f(M_1,A_1) + f'_M(M_1,A_1).X_M + f'_A(M_1,A_1).X_A = 0,$$

$$g(M,A) = g(M_1,A_1) + g'_M(M_1,A_1).X_M + g'_A(M_1,A_1).X_A = 0,$$

where X_M and X_A are the required shifts in M and A from the trial values M_1 and A_1 and f'_M, f'_A, g'_M and g'_A are the first derivatives with respect to the free metal concentration and free ligand concentration respectively. In matrix notation these equations become

$$\begin{vmatrix} f'_M & f'_A \\ g'_M & g'_A \end{vmatrix} \begin{vmatrix} X_M \\ X_A \end{vmatrix} = \begin{vmatrix} -f \\ -g \end{vmatrix}$$

As before new values are calculated for M and A from the trial values and these new values tested in the equations for E and F. If E and F are satisfied within an agreed limit the values of M and A are assumed to be the true ones, otherwise the cycle is repeated and a further improvement in M are A made.

Treating the equations in the variances in E, F and G as vectors,

$$s_E = \underset{\sim}{t}.E_{\bar{M}}.s_{\bar{M}} + \underset{\sim}{u}.E_{\bar{A}}.s_{\bar{A}} + \underset{\sim}{v}.E_{\bar{H}}.s_{\bar{H}} + \underset{\sim}{w}.E_M.s_M + \underset{\sim}{x}.E_A.s_A + \underset{\sim}{y}.E_H.s_H ,$$

$$s_F = \underset{\sim}{t}.F_{\bar{M}}.s_{\bar{M}} + \underset{\sim}{u}.F_{\bar{A}}.s_{\bar{A}} + \underset{\sim}{v}.F_{\bar{H}}.s_{\bar{H}} + \underset{\sim}{w}.F_M.s_M + \underset{\sim}{x}.F_A.s_A + \underset{\sim}{y}.F_H.s_H ,$$

$$s_G = \underset{\sim}{t}.G_{\bar{M}}.s_{\bar{M}} + \underset{\sim}{u}.G_{\bar{A}}.s_{\bar{A}} + \underset{\sim}{v}.G_{\bar{H}}.s_{\bar{H}} + \underset{\sim}{w}.G_M.s_M + \underset{\sim}{x}.G_A.s_A + \underset{\sim}{y}.G_H.s_H .$$

$E_M = (\partial E/\partial M)$, $G_{\bar{A}} = (\partial G/\partial \bar{A})$ etc. and $\underset{\sim}{t}, \underset{\sim}{u}$, etc. are unit vectors. Since both E and F are regarded as identities , $s_E = s_F = 0$.

Also $E_{\bar{A}} = E_{\bar{H}} = F_{\bar{M}} = F_{\bar{H}} = C_{\bar{M}} = C_{\bar{A}} = 0, \quad E_{\bar{M}} = F_{\bar{A}} = G_{\bar{H}} = -1$

and the derivatives with respect to M, A and H can be calculated. The equations in s_E and s_F can now be solved for the unknown variances s_M and s_A.

$$\underset{\sim}{w} \cdot s_M = \frac{\underset{\sim}{t} \cdot F_A \cdot s_{\bar{M}} - \underset{\sim}{u} \cdot E_A \cdot s_{\bar{A}} + (E_A \cdot F_H - E_H \cdot F_A) \cdot \underset{\sim}{y} \cdot s_H}{E_M \cdot F_A - F_M \cdot E_A}$$

$$\underset{\sim}{x} \cdot s_A = \frac{\underset{\sim}{t} \cdot F_M \cdot s_{\bar{M}} - \underset{\sim}{u} \cdot E_M \cdot s_{\bar{A}} + (E_M \cdot F_H - F_M \cdot E_H) \cdot \underset{\sim}{y} \cdot s_H}{F_M \cdot E_A - E_M \cdot F_A}$$ we can now express s_G

in terms of known quantities.

$$s_G = -\underset{\sim}{y} \cdot s_{\bar{H}} + \frac{\underset{\sim}{t} \cdot s_{\bar{M}} \cdot (G_M \cdot F_A - F_M \cdot G_A)}{E_M \cdot F_A - F_M \cdot E_A} - \frac{\underset{\sim}{u} \cdot s_{\bar{A}} (G_M \cdot E_A - E_M \cdot G_A)}{E_M \cdot F_A - F_M \cdot E_A}$$

$$+ \underset{\sim}{y} \cdot s_H \frac{(G_M \cdot E_A \cdot F_H - G_M \cdot E_H \cdot F_A - G_A \cdot E_M \cdot F_H - G_A \cdot F_M \cdot E_H)}{E_M \cdot F_A - F_M \cdot E_A} + \underset{\sim}{y} \cdot s_H \cdot G_H .$$

Rearranging and taking the product $s_G \cdot s_G$ we obtain

$$s_G^2 = s_{\bar{H}}^2 + s_{\bar{M}}^2 \frac{(G_M \cdot F_A - F_M \cdot G_A)^2}{(E_M \cdot F_A - F_M \cdot E_A)^2} + s_{\bar{A}}^2 \frac{(G_M \cdot E_A - E_M \cdot G_A)^2}{(E_M \cdot F_A - F_M \cdot E_A)^2}$$

$$+ s_H^2 \left\{ \frac{E_H (G_A \cdot F_M - F_A \cdot G_M) \pm F_H (G_M \cdot E_A - G_A \cdot E_M)}{F_A \cdot E_M - F_M \cdot E_A} + G_H \right\}^2 .$$

We have now in each of the three cases calculated the free metal concentration, the free ligand concentration and the variance in the residual in $\bar{H}_i$.

Numerical Derivatives

Before the shifts in the stability constants can be calculated the derivatives $(\partial f_i/\partial k_j)$ must be evaluated. This is done by repeating the above procedure with the set of stability constants $k_1, k_2, \ldots k_j' \ldots k_n \ldots k_N$, where $k_j' = k_j + \Delta k_j$ and so obtaining new values $M_i', A_i', \bar{H}_{i(calc)}'$ and then again with the set containing $k_j'' = k_j - \Delta k_j$ and obtaining M_i'', A_i'' and $\bar{H}_{i(calc)}''$. Then $(\partial f_i/\partial k_j) = (\bar{H}_i' - \bar{H}_i'')/2\Delta k_j$. This must be done for each of the n constants to be refined and so the calculation of an $\bar{H}_i$ must be done a total of 2n+1 times. The variance in the residual is calculated only once. In the program the derivatives are obtained with respect to $\log(k_j)$ and $\Delta\log(k_j)$ usually set to 0.0004, corresponding to a 0.01% change in k_j; in this case the shifts will also be in the logarithms of the constants. Before summation of

the $\left(\frac{\partial f_i}{\partial k_j}\right)\left(\frac{\partial f_i}{\partial k_k}\right)$ or $-\ {}^{o}R_i\left(\frac{\partial f_i}{\partial k_j}\right)$ a weighting factor w_i may be

$\left(\frac{\partial r_i}{\partial k_j}\right)\left(\frac{\partial r_i}{\partial k_k}\right)$ or $-\ {}^{o}R_i\left(\frac{\partial r_i}{\partial k_j}\right)$ a weighting factor w_i may be

applied by multiplying each derivative or residual by $w_i = 1/\sqrt{s_G^2}$, where s_G^2 is as defined in the previous sections.

Observations

With relatively weak complexes under study it was found that GAUSS G produced certain spurious results. In the numerical differentiation procedure the derivatives ($\partial f_i/\partial k_j$) could turn out zero even if the concentration of the species concerned was not negligible, provided it was an unprotonated complex. Increasing $\Delta\log(k_j)$ by a factor of ten had no effect in the particular instance. The matrix inversion part of the program (written by the author) did not fail when this occurred and the program carried a false calculation through to completion. The output looked "reasonable" but was characterised by extremely small shifts in the input constants and sometimes by negative standard deviations. The program was modified to print a warning message whenever this phenomenon occurred. When the constants were very small (e.g. sodium tartrate complexes) refinement was not possible for the above reason.

The matrix inversion method used by the author is not the best, nor is that in Tobias's program, the procedure of Blackburn (7) having advantages over both.

Part 2: From pM Measurements

The symbols and notation are the same as in Part 1. Since all the measurements in the present work were made in a constant ionic medium, activity coefficients have been omitted, but, if required, they could be calculated by iteration in the ionic strength expression, as in Part 1.

The calculations correspond to measurements of pM made in solutions containing a metal salt MY_m and either an acid H_jA and at least j equivalents of the metal hydroxide $M(OH)_m$ or the metal salt of the ligand acid. Y is assumed to be univalent. Each method is developed first assuming no hydrolysis of the ligand to take place and second allowing for hydrolysis, in which case the pH also must be measured.

VIII The Formation of the MA Complex

(a) It is assumed that the unbound ligand exists only as the unprotonated form A^{a-}, and the mass balance equations are therefore:

$$Ta = A + MA$$

and $$Tm = M + MA.$$

Then MA = Tm - M and A = Ta - MA, hence K_{101} can be calculated.

(b) Hydrolysis takes place such that the unbound ligand exists as both $HA^{(a-1)-}$ and A^{a-}. It is assumed that the pH is measured and Ka_2 is known. The mass balance equations now become

$$Ta = HA + A + MA$$

and $$Tm = M + MA.$$

Then $MA = Tm - M$ and $A = \dfrac{Ta - MA}{1 + H/Ka_2}$ and K_{101} is calculated. An ALGOL program to deal with both VII(a) and VII(b) is included in Appendix 2e.

IX Complexes MA and M_2A

(a) No hydrolysis of the ligand

The mass balance equations are:

$$Ta = A + MA + M_2A \quad \ldots\ldots\ldots\ldots\ldots (42),$$

and $$Tm = M + MA + 2M_2A \quad \ldots\ldots\ldots\ldots\ldots (43),$$

Eqns (42) and (43) can be written

$$Ta = A(1 + K_{101}.M + K_{201}.M^2) \quad \ldots\ldots\ldots (44),$$

$$Tm - M = A(K_{101}.M + 2K_{201}.M^2) \quad \ldots\ldots\ldots (45).$$

Elimination of A between Eqns (44) and (45), followed by rearrangement, gives

$$\frac{(M - Tm)}{M^2(Tm-M-2Ta)} = \frac{(Tm-M-Ta)}{M(Tm-M-2Ta)} K_{101} + K_{201} \quad \ldots\ldots\ldots (46).$$

A plot of $y = \dfrac{(M - Tm)}{M^2(Tm-M-2Ta)}$ against $x = \dfrac{(Tm-M-Ta)}{M(Tm-M-2Ta)}$ is a straight line of gradient K_{101} and intercept K_{201}.

The analogy between Eqn (46) and the Speakman plot for the dissociation constants of a dibasic acid should be noted (cf. Section 4.III).

(b) Hydrolysis of the ligand to form HA

The mass and charge balance equations are:

$$Ta = A + HA + MA + M_2A \quad \dots\dots\dots\dots \quad (47),$$

$$Tm = M + MA + 2M_2A \quad \dots\dots\dots\dots \quad (48)$$

and

$$M + H = a.M + (a-1)HA + (a-m)MA + (a-2m)M_2A + \\ + Y + OH \quad \dots\dots \quad (49).$$

Equation (49) can be rearranged to give

$$HA = Y + OH - H + a.Ta - m.Tm.$$

Substituting for HA in Eqn (47) and eliminating A from Eqns (47) and (48) gives

$$\frac{(M - Tm)}{M^2(Tm-M-2Ta+2HA)} = \frac{(Tm-M-Ta+HA)}{M(Tm-M-2Ta+2HA)} K_{101} + K_{201} .$$

A plot of $y' = \frac{(M - Tm)}{M^2(Tm-M-2Ta+2HA)}$ against $x' = \frac{(Tm-M-Ta+HA)}{M(Tm-M-2Ta+2Ha)}$ is a straight line of gradient K_{101} and intercept K_{201}.

An ALGOL program to deal with both cases (a) and (b) above is included in Appendix 2f.

Part 3: Complexing between the Reactants and the Medium.

X. Metal - Medium Complexing

Let us consider a system in which a metal, M^{m+}, and an acid, H_2A, form the complexes MA and MA_2 (cf Section 1). If the metal ion, whether already complexed or not, forms further complexes with the anion, X^-, of the constant ionic medium, we have also the species MX, MX_2, MX_3, . . MAX, MAX_2, . . . , MA_2X, MA_2X_2, ... The stability constants of these additional complexes are represented by K_{ijkn}, where i, j and k are as defined earlier and n is the number of anions X^- incorporated in the complex. Hence

$$K_{ijkn} = \frac{M_iH_jA_kX_n}{M_iH_jA_k . X^n} .$$

It is assumed that the complexing with the medium is so weak and the metal concentration so low, that the ionic strength is virtually constant and activity coefficients have, therefore, been omitted.

The mass and charge balance equations are:

$$Tm = (M + MX + MX_2 + . .) + (MA + MAX + . .) + (MA_2 + MA_2X + . .)$$
$$= M(1 + K_{1001} . X + K_{1002} . X^2) + MA(1 + K_{1011} . X + . .)$$
$$+ MA_2(1 + K_{1021} . X + . . .) \quad . . . . . . (50),$$

$$Ta = H_2A + HA + A + MA(1 + \Sigma K_{101n} . X^n) + 2MA_2(1 + \Sigma K_{102n} . X^n) \quad . . . . . (51),$$

$$Tx = X + \Sigma n.K_{101n}.M + \Sigma n.K_{101n}.MA + \Sigma n.K_{102n}.MA_2 \quad . . . . (52),$$

$$M(m + \Sigma(m-n)K_{100n}.X^n) + MA(m - a + \Sigma(m-a-n)K_{101n}.X^n)$$
$$+ MA_2(m - 2a + \Sigma(m-2a-n)K_{102n}.X^n) + H + B + Tx$$
$$= Y + OH + a.A + (a-1) + (a-2)H_2A + X \quad . . . . (53).$$

Combination of Eqns (3) and (50)-(53) gives

$$HA + 2H_2A = a.Ta - m.Tm + Y - Tb + OH - H.$$

This equation may be transformed to Eqn (7), and is, therefore, independent of any complexing with the medium. The concentrations A, HA and H_2A can be calculated as before and the function $V = Ta - H_2A - HA - A$ defined in the same way. Now,

$$V = MA(1 + \Sigma K_{101n}.X^n) + 2MA_2(1 + \Sigma K_{102n}.X^n),$$

$$Tm - V = M(1 + \Sigma K_{100n}.X^n) - MA_2 (1 + \Sigma K_{102n}.X^n) \quad . . . .(54)$$

and

$$2Tm - B = 2M(1 + \Sigma K_{100n}.X^n) + MA(1 + \Sigma K_{101n}.X^n) \quad . . . .(55).$$

Elimination of M from Eqns (54) and (55), followed by rearrangement, gives

$$\frac{V}{A^2(2Tm-V)} = K_{101}.\frac{R_{101}}{R_{100}}.\frac{Tm-V}{A(2Tm-V)} + K_{102}.\frac{R_{102}}{R_{100}} \quad ,$$

where $R_{ijk} = 1 + \sum_n K_{ijkn}.X^n$.

Since Tx » Tm, X and hence the factors R_{ijk} are virtually constant and plot of $V/(A^2(2Tm-V))$ against $(Tm-V)/(A(2Tm-V))$ will be a straight line of slope $K_{101}.R_{101}/R_{100}$ and intercept

$K_{102}.R_{102}/R_{100}$, which would be the apparent values of the stability constants assuming no complexing with the medium occurred. An equivalent relationship has been reported by Dunsmore, Hietanen and Sillén (8).

If these apparent constants are used to calculate the concentrations of the metal ion and its complexes, the true and apparent concentrations are related as shown below:

$$M(\text{apparent}) = R_{100}.M(\text{true}) \quad ,$$
$$MA(\text{apparent}) = R_{101}.MA(\text{true}) \quad ,$$
$$MA_2(\text{apparent}) = R_{102}.MA_2(\text{true}) \quad .$$

Comparisons between stability constants for a series of metals with the same ligand in the same medium must be treated with suspicion if complexing with the medium can occur.
It should be noted that the discrepancy is greater if only the free metal ion forms complexes with the medium.
Comparisons between the stability constants for a series of ligands with the same metal should be valid, especially if the complexed species do not form further complexes with the medium, even though only the apparent constants are available.
An experimental test of the validity of such comparisons is provided by the data of van Uitert, Fernelius and Douglas (9) for complexing between a series of divalent metals and the ligands dibenzoylmethane(dibenz) and acetylacetone(acac) in

a 75% (volume) dioxan - 25% water mixtures. The concentration of the various anions is 0.02M. The results are summarised in Table 2. The figures represent logK(ClO_4^-) - logK(anion).

Table 2

metal	anion	dibenz	acac
Mg	NO_3^-	0.43	0.32
Mn	NO_3^-	0.37	0.35
Mn	Cl^-	0.74	0.79
Zn	NO_3^-	0.36	0.41
Zn	Cl^-	1.60	1.73
Co	NO_3^-	0.39	0.46
Co	Cl^-	0.77	0.80
Ni	NO_3^-	0.31	0.49
Ni	Cl^-	0.68	0.85
Fe	Cl^-	0.51	0.52
Pb	NO_3^-	0.98	1.13

The agreement between the two sets of figures is quite good, indicating that similar effects are at work in both series of complexes. A contribution to these effects may arise from the influence of specific ion interactions on the activity coefficients, but in the circumstances of the experiments this is unlikely to be of major importance.

XI. Ligand - Medium Complexing

A model system was constructed to illustrate the effect of ligand-medium complexing. 10 ml of a 0.05M solution of a dibasic weak acid H_2A were mixed with 40 ml of distilled water and 50 ml of a 0.4M solution of a uni-univalent electrolyte, MY. This solution was titrated with 0.1M base solution, which was also 0.2M in MY. The total concentration of MY was thus 0.2M throughout. The dissociation constants of the acid are $Ka_1 = 1.5 \times 10^{-3}$mole litre^{-1} and $Ka_2 = 1.0 \times 10^{-4}$mole litre^{-1}. The complex species MA^- is formed and has a stability constant $K_{101} = 4.0$mole^{-1}litre; no other complex is formed. It is assumed that the solution behaves ideally or alternatively that the activity coefficients are constant. The pH in the solution for each addition of titrant was calculated on the KDF.9 computer using a program adapted by the author from the part of the GAUSS G program (Section VII) which calculates the free metal and free ligand concentrations.

There are three mass balance equations in total metal, total ligand and analytical hydrogen ion concentration.

$$E = -\bar{M} + \sum_m \sum_h \sum_a m.K_{mha}.M^m.A^a.H^h = 0,$$

$$F = -\bar{A} + \sum_m \sum_h \sum_a a.K_{mha}.M^m.A^a.H^h = 0$$

and

$$G = -\bar{H} + \sum_m \sum_h \sum_a h.K_{mha}.M^m.A^a.H^h = 0.$$

In the above M, A and H are the concentrations of free metal, free ligand and free hydrogen respectively, the corresponding barred symbols being the total metal, total ligand and analytical hydrogen concentrations. The complex species comprising m metal ions, a ligand molecules and h protons has a stability constant K_{mha}. Iteration is carried out in all three mass balance equations simultaneously to obtain the unknown M, A and H.

We define the functions $e(M,A,H) = \overline{M}_{obs} - \overline{M}_{calc}$, $f(M,A,H) = \overline{A}_{obs} - \overline{A}_{calc}$ and $g(M,A,H) = \overline{H}_{obs} - \overline{H}_{calc}$. The correct values of M, A and H are those for which $e(M,A,H) = f(M,A,H) = g(M,A,H) = 0$. Expanding in Taylor's series and neglecting second and higher order terms, we obtain

$$e(0) = e(1) + e'_M(1).X_M + e'_A(1).X_A + e'_H(1).X_H = 0,$$

$$f(0) = f(1) + f'_M(1).X_M + f'_A(1).X_A + f'_H(1).X_H = 0$$

and $$g(0) = g(1) + g'_M(1).X_M + g'_A(1).X_A + g'_H(1).X_H = 0,$$

where e(0) is the value of e(M,A,H) with the true values of M, A and H and e(1) is the value with a set of trial concentrations. $e'_M(1)$, $e'_A(1)$ and $e'_H(1)$ are the first derivatives of e(M,A,H) at the trial concentrations with respect to the free metal, free ligand and free hydrogen ion concentrations respectively. A corresponding set of

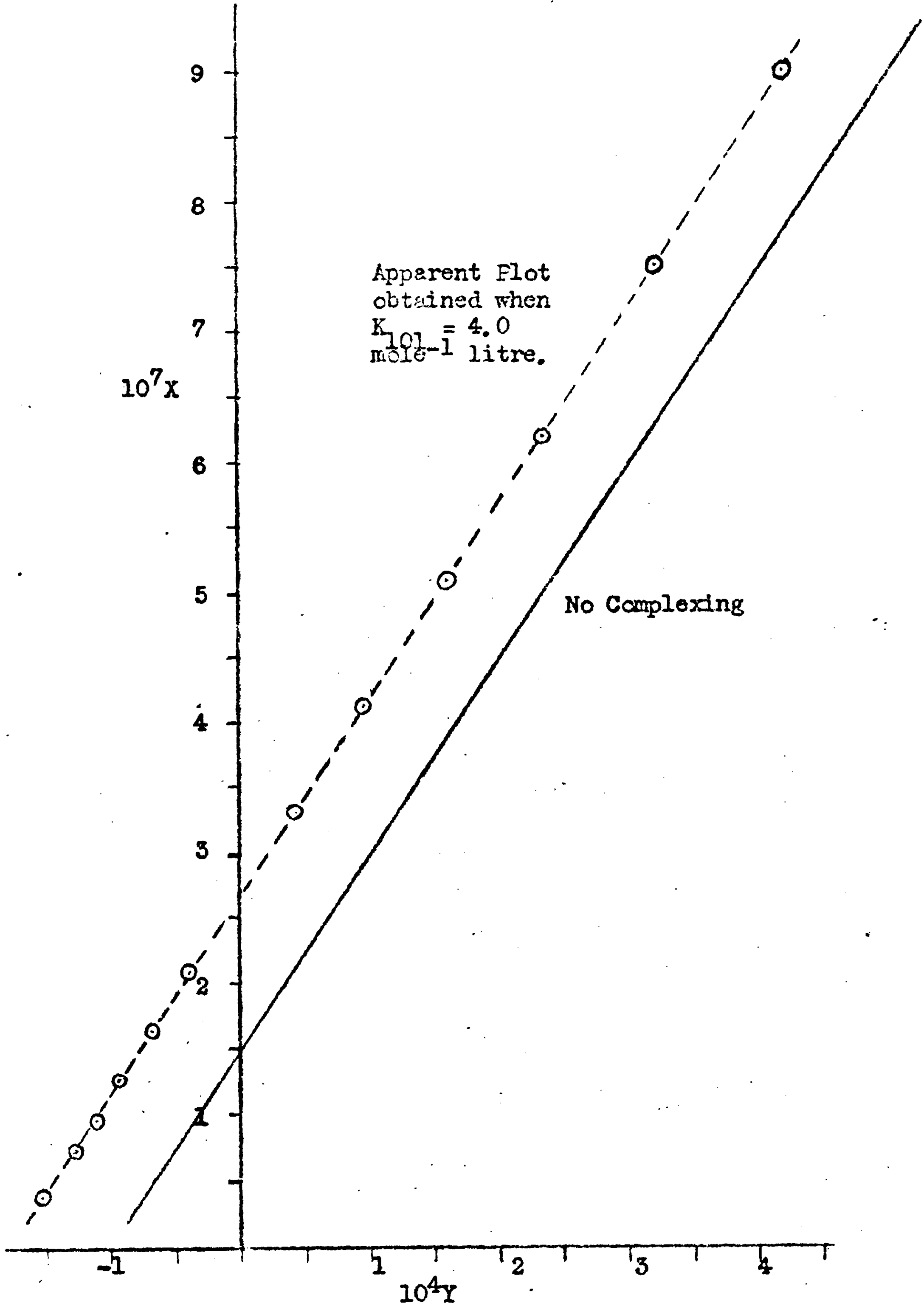

Fig. 2 Speakman Plot for Dibasic Acid complexing with the Background Medium. True $Ka_1 = 1.5\times10^{-5}$ mole litre^{-1}, True $Ka_2 = 1.0\times10^{-4}$ mole litre^{-1}.

definitions exists for the f- and g-functions. X_M, X_A and X_H are the required shifts to the trial values. In matrix notation the above equations become

$$\begin{vmatrix} e'_M(1) & e'_A(1) & e'_H(1) \\ f'_M(1) & f'_A(1) & f'_H(1) \\ g'_M(1) & g'_A(1) & g'_H(1) \end{vmatrix} \begin{vmatrix} X_M \\ X_A \\ X_H \end{vmatrix} = \begin{vmatrix} -e(1) \\ -f(1) \\ -g(1) \end{vmatrix} .$$

The equations are solved for the shifts by means of a matrix inversion routine developed by Blackburn(7) and the new values for the concentrations tested in the equations for E, F and G. If E, F and G are satisfied within a specified limit, the current values of M, A and H are accepted as the true ones, otherwise the procedure is repeated until agreement is reached. When the pH's had been calculated the data were treated by Speakman's method (Section 4. III) as if no complexing took place. The resultant plot is shown in Fig (2) and the calculated dissociation constants given in Table 3.

Table 3

	10^3Ka_1	10^4Ka_2
actual	1.5000	1.0000
calculated	1.4999	1.7992

The molar concentrations of the various species in solution are given in columns 1-6 of Table 4. The concentrations calculated from the dissociation constants obtained by the Speakman method are given in columns 7-9.

Table 4

ACTUAL						CALCULATED		
pH	10M	10^4MA	10^4A	10^3HA	10^4H_2A	10^4A	10^3HA	10^4H_2A
2.7710	1.9990	1.0449	1.3067	2.2142	25.011	2.3512	2.2142	25.012
2.8369	1.9987	1.2918	1.6156	2.3523	22.831	2.9062	2.3524	22.831
2.9056	1.9984	1.5979	1.9988	2.4842	20.582	3.5978	2.4840	20.582
2.9772	1.9980	1.9747	2.4706	2.6039	18.296	4.4449	2.6039	18.296
3.0515	1.9976	2.4337	3.0455	2.7049	16.016	5.4800	2.7048	16.016
3.1286	1.9970	2.9867	3.7387	2.7801	13.782	6.7272	2.7799	13.783
3.2087	1.9964	3.6450	4.5641	2.8228	11.639	8.2087	2.8229	11.639
3.3781	1.9947	5.3113	6.6562	2.7871	7.7802	11.967	2.7872	7.802
3.4682	1.9937	6.3298	7.9366	2.7002	6.1243	14.267	2.7001	6.1249
3.5629	1.9925	7.4723	9.3746	2.5646	4.6772	16.848	2.5645	4.6776
3.6634	1.9913	8.7349	10.965	2.3803	3.4446	19.700	2.3803	3.4447
3.7715	1.9899	10.109	12.700	2.1495	2.4253	22.809	2.1495	2.4253
4.0253	1.9868	13.153	16.549	1.5611	0.9817	29.703	1.5611	0.9819

Clearly the Speakman method reproduces accurately the concentrations of the protonated species but adds the neglected complex concentration to that of the free ligand. Corresponding to Eqn (4.7) we now write, neglecting activity coefficients,

$$Ta = A\left(1 + \frac{H}{Ka_2} + \frac{H^2}{Ka_1.Ka_2} + K_{101}.M \right) \quad . \ . \ . \ . \ . \ (55).$$

Eliminating A from Eqns (4.6) and (55) we obtain

$$H^2 \left(\frac{2Ta}{N} - 1\right) = H\left(1 - \frac{Ta}{N}\right)Ka_1 + Ka_1.Ka_2(1 + K_{101}.M) \quad . \ . (56).$$

Comparison of Eqns (56) and (4.8) shows that treating the data on a simple Speakman basis will result in the correct value for Ka_1, and that Ka_2 will be too large by a factor $r = (1 + K_{101}.M)$, provided r is virtually constant.
Since K_{101} is small and Tm is large (4.0 mole^{-1}litre and 0.2M respectively in the present example), the free metal concentration and, therefore, r vary only a little.
The concentrations of the protonated species are obtained from Ka_1 and Eqn (4.6) and A from HA and Eqn (4.2), hence good approximations can be made to HA and H_2A, but, if Ka_2(apparent) = $r.Ka_2$(true), then A(apparent) = r.A(true).

If these apparent constants are used in the calculation of the stability constants of the complexes formed between the ligand A and a second metal P the error will reappear in the results. Let us consider the formation of two complexes PA and PA_2 and obtain values for the stability constants by the method of Gelles and Nancollas (Section I). As before the concentrations of the protonated species would be calculated accurately, since we have a good approximation to Ka_1. The apparent concentration of A would, however, again be r times the true value. Neglecting activity coefficients, we can write Eqn (10) in the form

$$V/(\ A^2(2Tm-V)\ ) = K_{101}(Tm-V)/(\ A(2Tm-V)\ ) + K_{102},$$

or

$$y = K_{101}\cdot x + K_{102}.$$

If the apparent concentration of A is used in calculating y and x, we obtain

$$y(\text{apparent}) \simeq y(\text{true})/r^2 \quad \text{and} \quad x(\text{apparent}) \simeq x(\text{true})/r \ ,$$

which results in

$$K_{101}(\text{apparent}) \simeq K_{101}(\text{true})/r \quad \text{and} \quad K_{102}(\text{apparent}) \simeq K_{102}(\text{true})/r^2.$$

It should be noted that the apparent stability constants, together with the apparent concentration of A, will enable a good approximation to be made to the concentrations of the metal-containing species P, PA and PA_2, since the factors r, r^{-1}, r^2, r^{-2} will cancel. As the r-factor is a function of the ligand and the medium, the comparison of the apparent stability constants of a series of ligands with the same metal ion in a given medium will subject to uncertainty, although the trends with a series of metals and the same ligand should be reliable.

XI(b) If the ligand and the medium form both MA and MHA complexes, instead of Eqn(55) we write, neglecting activity coefficients,

$$Ta = A\left(1 + \frac{H}{Ka_2} + \frac{H^2}{Ka_1.Ka_2} + K_{101}.M + K_{111}.H.M\right) \quad . \; . \; . \; (57),$$

and instead of Eqn (4.6)

$$N = HA + 2H_2A + MHA = A\left(\frac{H}{Ka_2} + \frac{2H^2}{Ka_1.Ka_2} + K_{111}.H.M\right). \; . \; . \; (58).$$

Eliminating A from Eqns (57) and (58), we obtain,

$$H^2\left(\frac{2Ta-N}{N}\right) = H\left(\frac{N-Ta}{N}\right)(1 + Ka_2.K_{111}.M)Ka_1 + Ka_1.Ka_2(1 + K_{102}.M) \; . \; . \; . \; . \; (59)$$

Comparison of Eqn (59) with Eqn (4.8) shows that if, as before, M is practically constant, Speakman's method overestimates Ka_1 by a factor $s = (1 + Ka_2.K_{111}.M)$ and Ka_2 by the factor $t = (1 + K_{101}.M)/(1 + Ka_2.K_{111}.M)$. In these circumstances a good approximation can be made to HA, but not to H_2A or A. The following relationships describe the effect of ligand-medium complexing on the concentrations of the acid species as calculated by Speakman's method

$$HA(\text{apparent}) \simeq HA(\text{true}),$$

$$H_2A(\text{apparent}) \simeq H_2A(\text{true})/s$$

and

$$A(\text{apparent}) \simeq t.A(\text{true}).$$

Application of apparent constants obtained in this way to the calculation of the stability constants of the complexes PA and PA_2 formed between a second metal ion, P, and the ligand results in the same relationships between the apparent and true concentrations of the uncomplexed acid species as above. It is also true that

$$(A + HA + H_2A)_{\text{apparent}} \simeq (A + HA + H_2A + MA + MHA)_{\text{true}},$$

hence the function V in Section I can be obtained quite accurately and we can, again neglecting activity coefficients, write Eqn (10) in the form

$$V/(\ A^2(2Tm - V)\ ) = K_{101}(Tm-V)/(\ A(2Tm-V)\ ) + K_{102} \quad . \ . \ (60).$$

The use of A(apparent) in Eqn (60) results in

$K_{101}(\text{apparent}) \simeq K_{101}(\text{true})/t$ and $K_{102}(\text{apparent}) \simeq K_{102}(\text{true})/t^2$.

The concentrations of the metal-containing species P, PA and PA_2 can be calculated to a good approximation from the apparent values of A, K_{101} and K_{102}, since the t-factors cancel. Comparison with Section XIa shows that, if the medium and the stability constant of the MA complex are the same in each case, more accurate stability constants are obtained in the circumstances of this section, since $r > t$. An experimental test of the effect on the apparent dissociation constants of tartaric acid is described in Section 7.IV.

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Chapter 4

Tartaric Acid

I. Introduction

Although tartaric acid and its salts have been used as constituents of buffer solutions for the regulation of acidity (1-3), the dissociation constants are not well characterised. This lack arises partly from the complex composition of solutions containing these substances: the ratio of the first dissociation constant to the second is about 20 and hence the two dissociative steps overlap to such an extent that appreciable amounts of molecular tartaric acid and both the primary and secondary tartrate ions exist simultaneously in tartrate buffer solutions. The problem of calculating the concentrations of all three species must be overcome before the dissociation constants can be obtained. A further problem is the complexing reported between alkali metal ions and α-hydroxyacids. Tetramethylammonium ion does not form complexes in these circumstances (4, 5) and in this work the base (Me_4NOH) and background electrolyte (Me_4NCl) were chosen accordingly. Complexing with sodium and potassium is the subject of the next two chapters and the topic is discussed as a whole in Chapter 7.

Calculation

II. The dissociation constants of a dibasic weak acid can, if they are sufficiently different, i.e. $Ka_1 > 10^3 Ka_2$, be calculated as if each dissociation step were the dissociation of a monobasic acid. If necessary, after first estimates have been obtained for the constants, allowance can be made for one dissociation in determining the equilibrium constant for the other and this procedure repeated until successive values of the constants agree within some arbitrary limit. An iterative method of this kind becomes less efficient as the difference between the constants diminishes and, if the equilibria are such that all three acid species coexist in significant quantities, is impracticable. Speakman (6) has devised a method which gives both constants simultaneously. We can define the equations

$Ka_1 = \{H\}\{HA\}/\{H_2A\} = H.HA.f_H.f_{HA}/(H_2A.f_{H2A})$ . . . . (1),

$Ka_2 = \{H\}\{A\}/\{HA\} = H.A.f_H.f_A/(HA.f_{HA})$ . . . . (2),

$Kw = \{H\}\{OH\} = H.OH.f_H.f_{OH}$ . . . . (3),

$Na + H = HA + 2A + OH$ (Electroneutrality) . . . . (4),

$Ta = H_2A + HA + A$ . . . . (5).

III Speakman's Method

Combining Eqns (1)-(4) and rearranging, we obtain

$$HA + 2H_2A = A\left(\frac{\{H\}f_A}{Ka_2.f_{HA}} + \frac{\{H\}^2 f_A}{Ka_1.Ka_2.f_{H2A}}\right)$$

$$= 2Ta - Na - \{H\}/f_H + Kw/(\{H\}.f_{OH}) = N \quad . . . . (6).$$

From Eqns (1), (2) and (5) we obtain

$$Ta = A\left(1 + \frac{\{H\}f_A}{Ka_2.f_{HA}} + \frac{\{H\}^2 f_A}{Ka_1.Ka_2.f_{H2A}} \right) \quad . . . . (7).$$

Eliminating A from Eqns (6) and (7) gives

$$\frac{\{H\}^2 f_A}{f_{H2A}}\left(\frac{2Ta}{N} - 1\right) = \frac{\{H\}f_A}{f_{HA}}\left(1 - \frac{Ta}{N} \right)Ka_1 + Ka_1.Ka_2 \quad . . . (8).$$

A plot of $X = \frac{\{H\}^2 f_A}{f_{H2A}}\left(\frac{2Ta}{N} - 1\right)$ against $Y = \frac{\{H\} f_A}{f_{HA}}\left(1 - \frac{Ta}{N}\right)$ is a straight line of the form $X = m.Y + c$, where the slope $m = Ka_1$ and the intercept on the X-axis, $c = Ka_1.Ka_2$.

If the titration is performed in a constant ionic medium, the activity coefficients in the above equations can be set equal to unity and concentration dissociation constants will result. When activity coefficients are to be calculated an initial estimate must be made to the ionic strength

$$I = Na + H \quad .$$

An approximate set of dissociation constants is then calculated as above and a better estimate of the ionic strength obtained

$$I = \tfrac{1}{2}\left(3Na + \frac{3\{H\}}{f_H} - \frac{2Ta - Na - \{H\}/f_H}{1 + 2f_H\cdot\{H\}/Ka_1} \right) \quad .$$

Hence a more accurate set of activity coefficients can be calculated and used to compute new values for the dissociation constants. The process is repeated until successive cycles yield dissociation constants which agree within a specified limit.

The slope and intercept of Eqn (8) were calculated from the set of quantities (Y, X) by the method of least squares. All calculations were carried out on a KDF.9 computer using a program written by Dr. H.S. Dunsmore and modified by the author.

IVa. Bates's Method for Ka_2 (7, 8)

Measurements made with the cell

$$Pt \,|\, H_2 \text{, test solution, AgCl, Ag,}$$

where the test solution contains the salts NaHA, Na_2A and NaCl in the proportions 1:q:r, give rise to the quantity pwH, defined by

$$pwH = -\log m_H - \log f_H f_{Cl},$$

m_H being the molality of the hydrogen ion.

The equilibria obtaining in the solution are

$$HA^- = H^+ + A^{2-}$$

and

$$2HA^- = H_2A + A^{2-} .$$

If m is the stoicheiometric molality of NaHA, we can write the equilibrium concentrations of HA^- and A^{2-} as

$$m_{HA} = m - m_H - 2m_{H2A} \quad \ldots\ldots\ldots\ldots \quad (9)$$

and

$$m_A = q.m + m_H + m_{H2A} \quad \ldots\ldots\ldots\ldots \quad (10).$$

The ionic strength $I = (1+r+3q)m + 2m_H + m_{H2A}$ . . . . (11).
If $f_H.f_{HA}.m_H/f_{H2A}$ is taken equal to $f_H.f_{Cl}.m_H$, i.e. to 1/(antilog pwH), a reasonable assumption in dilute solution, we obtain from Eqns (1) and (9)

$$m_{H2A} = (m - m_H)/(2 + Ka_1 \text{ antilog pwH}) \quad . . \quad (12).$$

We can calculate m_H from the measured pwH if a suitable expression is adopted for the activity coefficients, such as

$$-\log f_z = \frac{A.z^2.I^{\frac{1}{2}}}{1 + B.a.I^{\frac{1}{2}}} - b.I \quad \ldots\ldots\ldots\ldots\ldots \quad (13)$$

where z is the charge on the ion, A and B are the Debye-Hückel parameters and a and b are adjustable parameters. Iteration through Eqns (11) and (12) to constant m_H and m_{H2A} is followed by calculation of m_{HA} and m_A. The value of Ka_1 obviously affects the outcome of the above process, but if the conditions are such that m_{H2A} is small, the effect of an inaccuracy in Ka_1 will also be small.

Eqn (2) can be written in the form

$$pKa_2 = pwH - \log \frac{m_A}{m_{HA}} + \frac{2.A.I^{\frac{1}{2}}}{1+B.a.I^{\frac{1}{2}}} - 2.A.b.I \quad \ldots\ldots\ldots (14),$$

which can be rearranged to give

$$pKa_2' = pKa_2 + 2.A.b.I = pwH - \log \frac{m_A}{m_{HA}} + \frac{2.A.I^{\frac{1}{2}}}{1+B.a.I^{\frac{1}{2}}} \quad \ldots\ldots (15).$$

pKa_2' is, assuming a reasonable value for a and allowing for the errors involved in the iteration to find m_A, m_{HA} and I, a function of known quantities.

A plot of pKa_2' against I will be a straight line of intercept pKa_2 and slope 2.A.b.

The thermodynamic value of Ka_2 obtained in this way can be used in conjunction with another set of experimental data to provide an improved estimate of Ka_1.

IVb. Bate's Method for Ka_1

With the same notation as above, we obtain from Eqns (1) and (2)

$$-\tfrac{1}{2}\log(Ka_1.Ka_2)' = -\tfrac{1}{2}\log(Ka_1.Ka_2) + A.b.I$$

$$= pwH - \tfrac{1}{2}\log \frac{m_A}{m_{H2A}} + \frac{A.I^{\frac{1}{2}}}{1 + B.a.I^{\frac{1}{2}}} \quad \ldots\ldots\ldots (16).$$

As before we can calculate m_{H2A} and I from the measured pwH and iteration through Eqns (11) - (13). Eqn. (10) then yields m_A. A plot of $-\tfrac{1}{2}\log(Ka_1.Ka_2)'$ against I is a straight line of slope A.b and intercept $-\frac{1}{2}\log(Ka_1Ka_2)$. Using the previously obtained value of Ka_2, Ka_1 can be calculated and then used to calculate a better value for Ka_2 in the same way as before. Iteration is carried through both stages to constant Ka_1 and Ka_2.

The experimental conditions are such that, in determining Ka_2, q has values 1.5 - 3 and for Ka_1, q = 0.

IVc. Allowance for the Complex NaA^-

Bates does not consider the possibility of sodium complexing, but if we insert an additional iterative loop in his procedure, compensation can be made, provided that the stability constant of the complex is known.

If the NaA^- complex is formed and NaHA complexing can be neglected, we can write

$$K_{101} = \frac{\{NaA^-\}}{\{Na\}\{A^{2-}\}} = \frac{m_{NaA}\cdot f_{NaA}}{m_{Na}\cdot f_{Na}\cdot m_A\cdot f_A} \quad \ldots\ldots\ldots\ldots \text{(17)},$$

$$m_A = q.m + m_H + m_{H2A} - K_{101}.m_{Na}.m_A.f_A \qquad \text{(cf. Eqn(10));}$$

i.e.

$$m_A = (q.m + m_H + m_{H2A})/(1 + K_{101}.m_{Na}.f_A) \quad \ldots\ldots \text{(18)}$$

and $$m_{Na} = (1 + 2q + r)m/(1 + K_{101}.m_A.f_A) \quad \ldots\ldots\ldots \text{(19)}.$$

Iteration through Eqns (10), (18), (19) and (13) to constant m_A, m_{HA} and I, followed by substitution in Eqn (15) enables Ka_2 to be determined as before.

Experimental

V. Reagents AnalaR grade d-tartaric acid(B.D.H.) was recrystallised from distilled water and dried at 120°C. The crystals were ground in an agate mortar and dried again. A solution of the acid was titrated with standard sodium hydroxide solution(B.D.H. volumetric solution) with phenolphthalein as indicator; the results were theoretical.

Tetramethylammonium hydroxide was prepared in two ways, by ion-exchange and from silver hydroxide.

(1) The Ion-Exchange Method

Amberlite IRA.400 anion exchange resin(B.D.H. Analytical Grade) was washed with distilled water and the "fines" decanted off. The resin was transferred to a pyrex column, 55 cm long and 2 cm in diameter, which was fitted with a sintered glass plug and a stopcock. The resin was then washed twice with cycles of 0.5M hydrochloric acid, distilled water, methanol, distilled water and 0.5M sodium hydroxide. Distilled water was run through the column until the eluate was neutral. The capacity of the column of resin was about seven times the amount of material to be exchanged.

Tetramethylammonium chloride was dissolved in boiled-out distilled water and nitrogen passed through the solution for an hour to remove dissolved carbon dioxide. The approximately 0.5M solution was introduced slowly at the top of the column

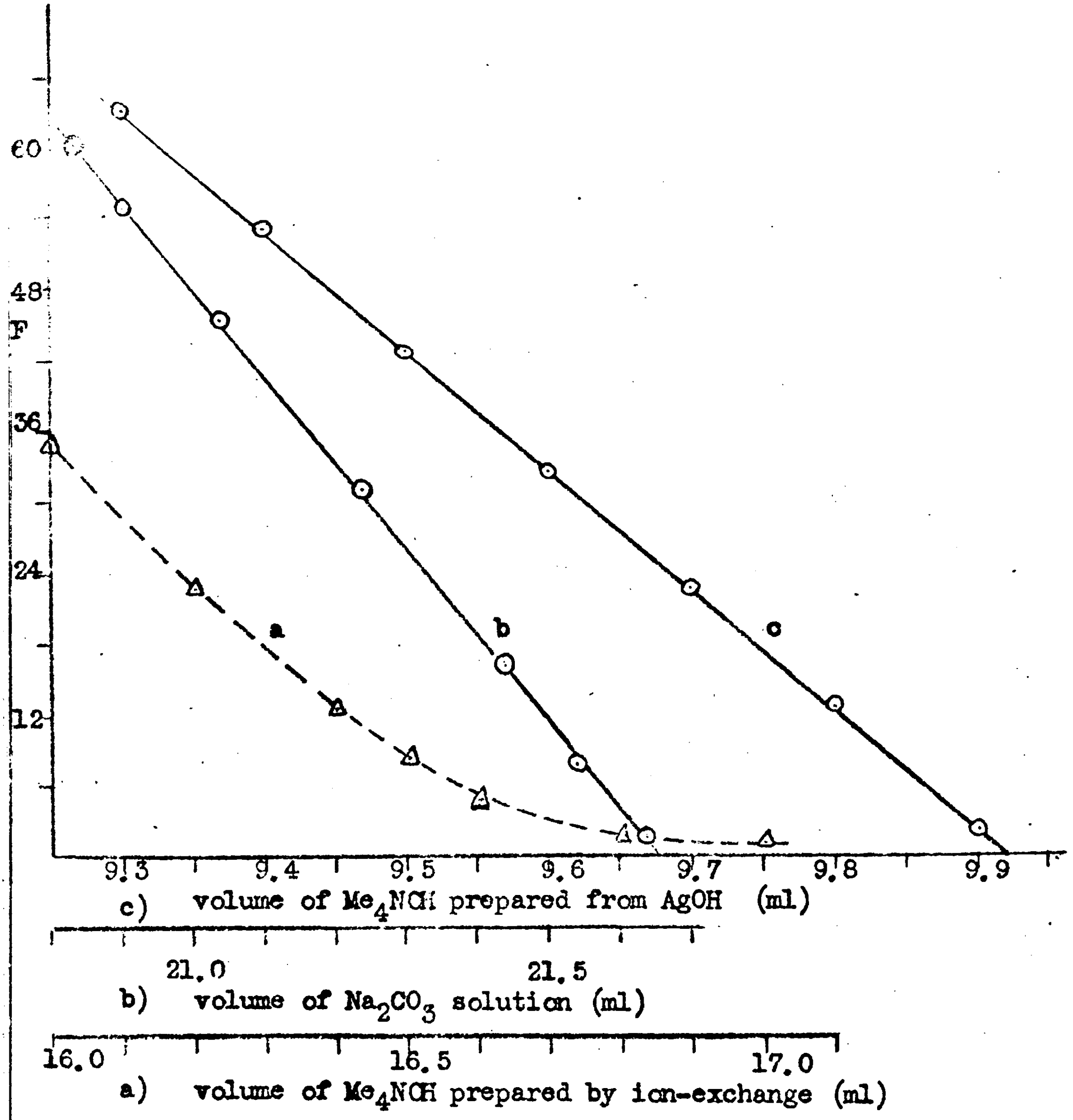

Fig.1 Gran Plots for the Titration of Hydrochloric Acid with
a) Me_4NOH prepared by ion-exchange,
b) Na_2CO_3 solution,
c) Me_4NOH prepared from AgOH.

and the eluate discarded until it was basic, when it was run into a flask through which was flowing a continuous stream of nitrogen. The system was closed to the atmosphere except for a nitrogen leak. The column was eluted with water to remove all the tetramethylammonium hydroxide and the eluate made up with boiled-out distilled water. The solution was dispensed through the usual syphon arrangement.

The Me_4NOH solution was analysed by potentiometric titration against standard hydrochloric acid, the results being treated by Gran's method (Chapter 9). A typical plot for Me_4NOH prepared by ion exchange is shown in Fig.1a; this behaviour was repeated by several samples prepared from two different batches of resin. Since sodium carbonate solutions gave linear plots (Fig.1b) the curvature cannot be attributed to the effects of absorbed carbon dioxide.

Amberlite IRA.400 is a strongly basic anion exchanger formed of a polystyrene matrix cross-linked with 3-5% of divinyl benzene, its basic character arising from $-NMe_3^+$ groups on the benzene rings of the polystyrene. Baumann (13) reports that at 90°C IRA.400 loses 15% of its capacity in 3 days when in the hydroxide form, but is much more stable in the carbonate and bicarbonate forms. The presence of the strongly basic hydroxide ion enables the Hofmann degradation to occur, producing amines and, if alkenes cannot be formed, alcohols.

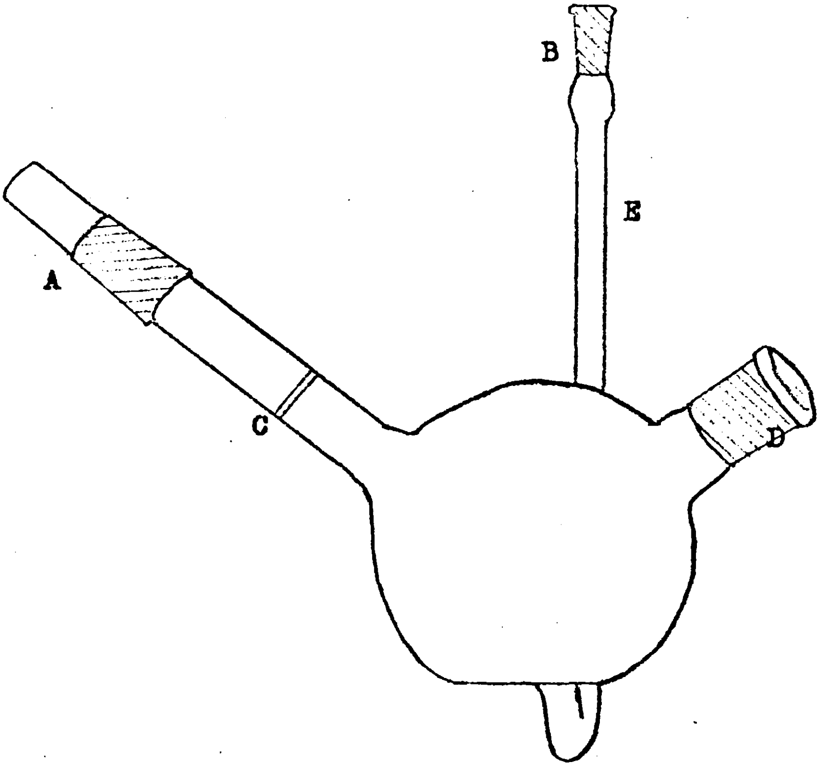

Fig. 2 Tetramethylammonium Hydroxide Preparation Vessel.

Key: A B.19 cone, B B.7 socket, C porous glass sinter, D B.19 socket, E capillary.

The Me_4NOH solutions had an amine smell and the presence of weak bases such as amines would give a Gran plot of the type observed. An anion exchange membrane, Amfion A-104, of similar composition and capacity showed no loss in weight after being immersed in chloride solutions for six months (9) and solutions of Me_4NOH prepared from silver hydroxide were stable for weeks at least, lending weight to the view that decomposition occurs when the resin is in the hydroxide form. It has also been observed (12) that mixed-bed exchangers release weakly basic polyelectrolytes into the bathing solution. Me_4NOH prepared by this method would be quite useless for accurate work.

(2) Preparation from Silver Hydroxide

Tetramethylammonium hydroxide has been prepared (10) by reacting tetramethylammonium halides with silver hydroxide and filtering off the insoluble silver salts. In the present case this was done in the apparatus shown in Fig.(2). AnalaR silver nitrate (B.D.H.) was dissolved in the mixing chamber of the cell and the solution flushed with nitrogen for two hours. Saturated sodium hydroxide solution, made from B.D.H.AnalaR pellets, was added to the solution and the resultant brown sludge agitated by means of a magnetic stirrer until the supernatent liquid was clear. A further portion of NaOH solution was added to check that precipitation was complete. The cell was rotated through 120°, so that the silver hydroxide collected above the sinter, where it was washed with hot, boiled-out, distilled water until the filtrate was neutral. Nitrogen was passing the whole time and assisted the rate of filtration by forcing the solution through the sinter when the stopper was in place. The cell was returned to its original position and the silver hydroxide washed into the mixing chamber with cold boiled-out distilled water. Tetramethylammonium chloride was added and stirred with the silver hydroxide for at least two hours. The cell was again turned into the filtering position, with the B.19 ground glass cone fitting into a B.24 "Quickfit" conical flask via an adaptor with a small hole between the ground glass surfaces to serve as an air leak. The spout of the reaction vessel was extended so that the mouth came below the level of the ground glass surfaces in the receiving flask. The solution was forced into the flask by the pressure of nitrogen and the residue washed with two 100ml portions of boiled-out distilled water. The filtrate was made up with distilled water and the flask fitted with a syphon head. During the mixing periods the spout was protected from the atmosphere by means of a "Sofnolite" guard tube fitted to a necked-down glass tube with a B.19 socket at one end which fitted the cone on the spout.

Even with a large excess of silver over tetramethylammonium ion, the solution was always found to contain some chloride, which was determined gravimetrically as AgCl. The solution was analysed for OH^- by potentiometric titration against standard hydrochloric acid solution. The data were treated according to Gran's method and a typical plot is shown in Fig. 1c. Solutions which had been stored for some weeks still gave linear plots. The concentrations were also checked by titration against hot solutions containing weighed amounts of potassium hydrogen phthalate with phenolphthalein as indicator. The maximum difference between any pair of potentiometric and indicator titrations was less than 0.4%. All the Me_4NOH used in titrations to determine stability constants was prepared in this way.

All other reagents were prepared as described in Section 2.IV.

VI. Apparatus All graduated glassware was of grade A standard. Pipettes, burettes and 100ml flasks were calibrated with distilled water at 25°C. Glassware was cleaned in chromic acid and/or 'pyroneg' (an alkaline detergent) solution, rinsed with distilled water and dried with AnalaR acetone. When molal units were used titrations were performed with a weight burette. Weighings of more than 200g were done on a Sartorius chemical balance capable of weighing up to 2Kg.

Oertling stainless steel weights were used. Smaller weighings were done on a Stanton Unimatic single-pan electric balance.

The apparatus for the potentiometric titrations was described in Section 2.V.

VII. pH Titrations in Constant Background Media

Test solutions were made up by pipetting 2q M Me_4NCl, distilled water and tartaric acid solution into the cell illustrated in Fig.(2.3), such that the total chloride concentration was q M and the tartaric acid concentration was between 0.5 and 5% that of the chloride. Me_4NOH solution was added from a burette and -2q M Me_4NCl (adjusted for the concentration of chloride in the base) added from a second burette, so that the chloride concentration remained the same. Nitrogen from a cylinder (British Oxygen Co. Ltd.) was bubbled through the solution throughout the titration in order to prevent the absorption of carbon dioxide and to effect mixing. The nitrogen passed through a train of presaturators,

qM HCl, qM NaOH, qM Me_4NCl, qM Me_4NCl ,

before entering the reaction vessel. The details of e.m.f. measurement and correction for liquid junction potentials have been given in Section 2.Va-c. Measurements were made with phthalate buffer before and after each titration.

The titration cell was maintained at 25°C, which was also the temperature of the room.

The data for the three runs with q = 0.1 (glass electrode A) are given in Tables T.1 - T.3, for the eleven runs with q = 0.2 (glass electrode Y) in Tables T.4 - T.14 and for the two runs with q = 0.4 (glass electrode A) in Tables T.15 and T.16, which are to be found in Appendix 1a.

VIII. pH Titrations in Dilute Solution

Test solutions were made up from weighed portions of tartaric acid and distilled water. Me_4NOH solution was added from a weight burette. All weights were corrected for the buoyancy of air. Nitrogen was passed continuously during the titration and went through a series of presaturators

0.1M HCl, 0.1M NaOH, distilled water, distilled water,

the last two stages of which were at the same temperature as the cell, before entering the solution. The details of e.m.f. measurement and temperature control have been given in Section 2.V.

Two runs were done at each of the temperatures 15°C. and 25°C. and one run at 35°C. The data are presented in Tables T.19 - T.23 in Appendix 1a.

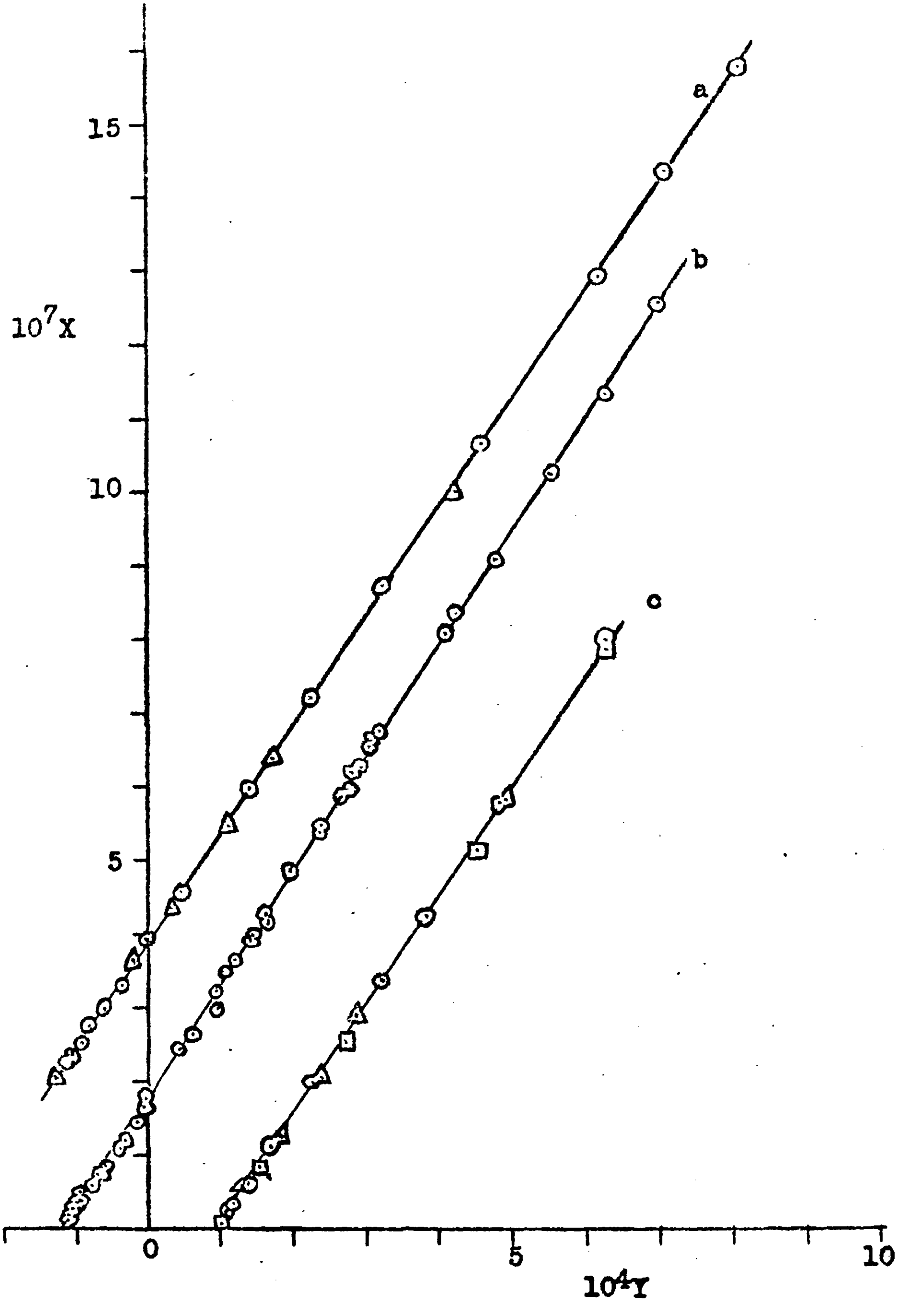

Fig. 3 Speakman Plots for Tartaric Acid at 25°C.
a) I = 0.4, alternate points plotted, displaced 2 cm up. Run 15 (⊙) and Run 16 (△).
b) I = 0.2, every fourth point plotted.
c) I = 0.1, alternate points plotted, displaced 2 cm right. Runs 1 (○), 2 (△) and 3 (□).

Results

IX. In Constant Ionic Background

The data were treated by Speakman's method (Section III). The dissociation constants were calculated for each run individually and the average constants for a particular medium obtained by combining all the data for that medium and calculating as for a single run. Plots for the combined data in the three media are shown in Fig (3) and the results for the individual runs in the 0.2M medium summarised in Table 1. The two groups of runs T.4-7 and T.8-14 were performed with completely different sets of reagents.

Table 1

0.2M Me_4NCl Medium ; T = 25°C.

Run	*Ta(mM)	10^3Ka_1 mole litre^{-1}	10^4Ka_2 mole litre^{-1}
T.4	4.56	1.55	1.18
T.5	10.4	1.53	1.20
T.6	7.95	1.52	1.19
T.7	10.1	1.56	1.19
T.8	5.48	1.54	1.16
T.9	2.61	1.53	1.15
T.10	8.64	1.53	1.18
T.11	4.47	1.55	1.18
T.12+13**	1.15	1.52	1.10
T.14	1.84	1.52	1.13

* Ta is the median value of the total acid concentration during the run.

** Runs T.12 and T.13 were combined because so few points were obtained in the first buffer region.

The values of the dissociation constants calculated from the combined data in each medium are presented in Table 2.

Table 2

medium	Runs	Points	$10^3 Ka_1$ mole/l.	$10^6 \sigma_{Ka_1}$	$10^4 Ka_2$ mole/l.	$10^7 \sigma_{Ka_2}$
0.1	3	47	1.494	12.3	1.066	6.98
0.2	11	182	1.540	4.01	1.173	24.0
0.4	2	52	1.472	2.66	1.308	6.04

The results were extrapolated to infinite dilution by plotting

$$E_c = - \log K_c + \frac{r.A.I^{\frac{1}{2}}}{1 + B.a.I^{\frac{1}{2}}} = - \log K_{th} + r.A.b.I$$

against the ionic strength (cf. Eqn (15)), where K_c and K_{th} are the dissociation constants in the particular medium and at infinite dilution respectively, A and B are the Debye-Hückel parameters, a and b are variable parameters and r is an integer characteristic of the dissociation concerned. For Ka_1, $r = 2$ and for $Ka_1.Ka_2$, $r = 6$. Values of E_c are calculated as a is varied systematically and fitted to the equation

$$E_c = p.I + q$$

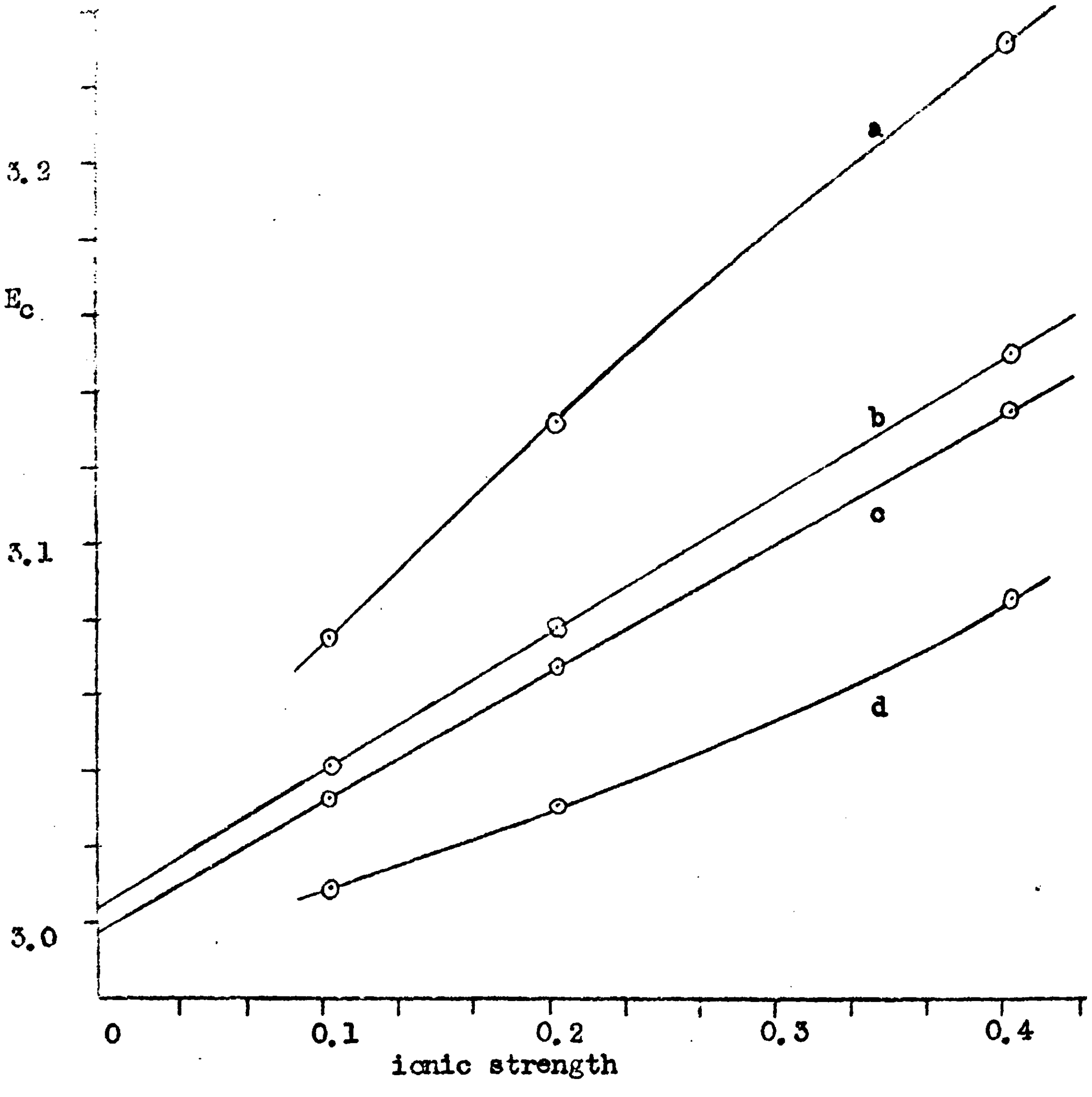

Fig.4 Extrapolation of pKa_1 of d-tartaric acid at 25°C.
a) a = 3.0 b) a = 5.0 c) a = 5.5 d) a = 7.5.

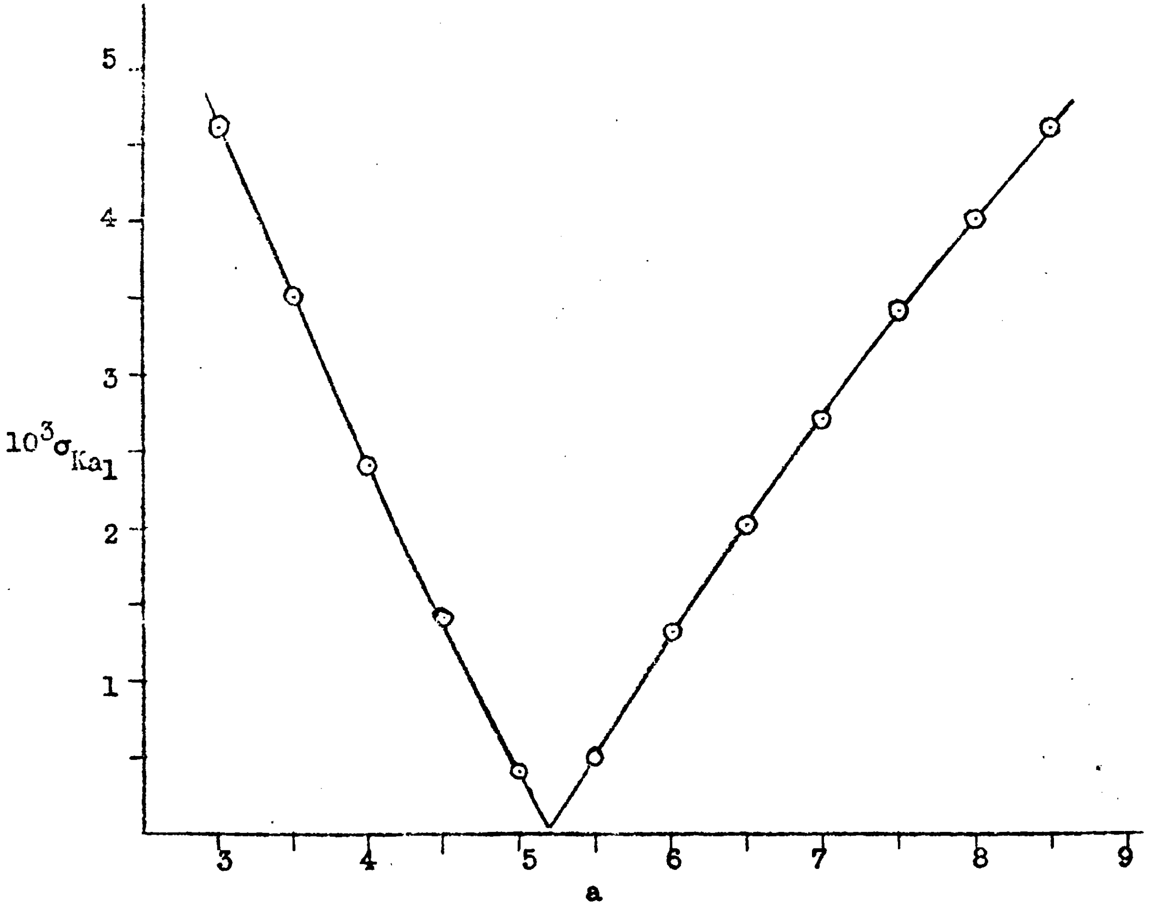

Fig. 5 Standard deviation in the extrapolated value of pKa_1 for tartaric acid at 25°C as a function of a

by the method of least squares. The a-value which leads to the best straight line for the E_c-I plot (Fig.4) is assumed to be the right one. $-\log K_{th}$ is taken to be equal to the best value of q, the standard deviation of which is at a minimum when the E_c-I plot is linear. A plot of the standard deviation, σ_q, is shown in Fig. 5 for the Ka_1 case. The corresponding value of b is calculated from p/(r.A). For Ka_1, the minimum occurs at a = 5.25, giving $-\log Ka_1 = 3.002$ and b = 0.34. The same value of a yields $-\log(Ka_1.Ka_2) = 7.369$ with b = 0.23. The minimum in σ_q for $(Ka_1.Ka_2)$ is at a = 10.15, for which $-\log(Ka_1.Ka_2) = 7.250$ and b = 0.07. The second dissociation constant is obtained from

$$-\log Ka_2 = \log(Ka_1)_{min} - \log(Ka_1.Ka_2)_{min},$$

which in this case yields $pKa_2 = 4.248$.

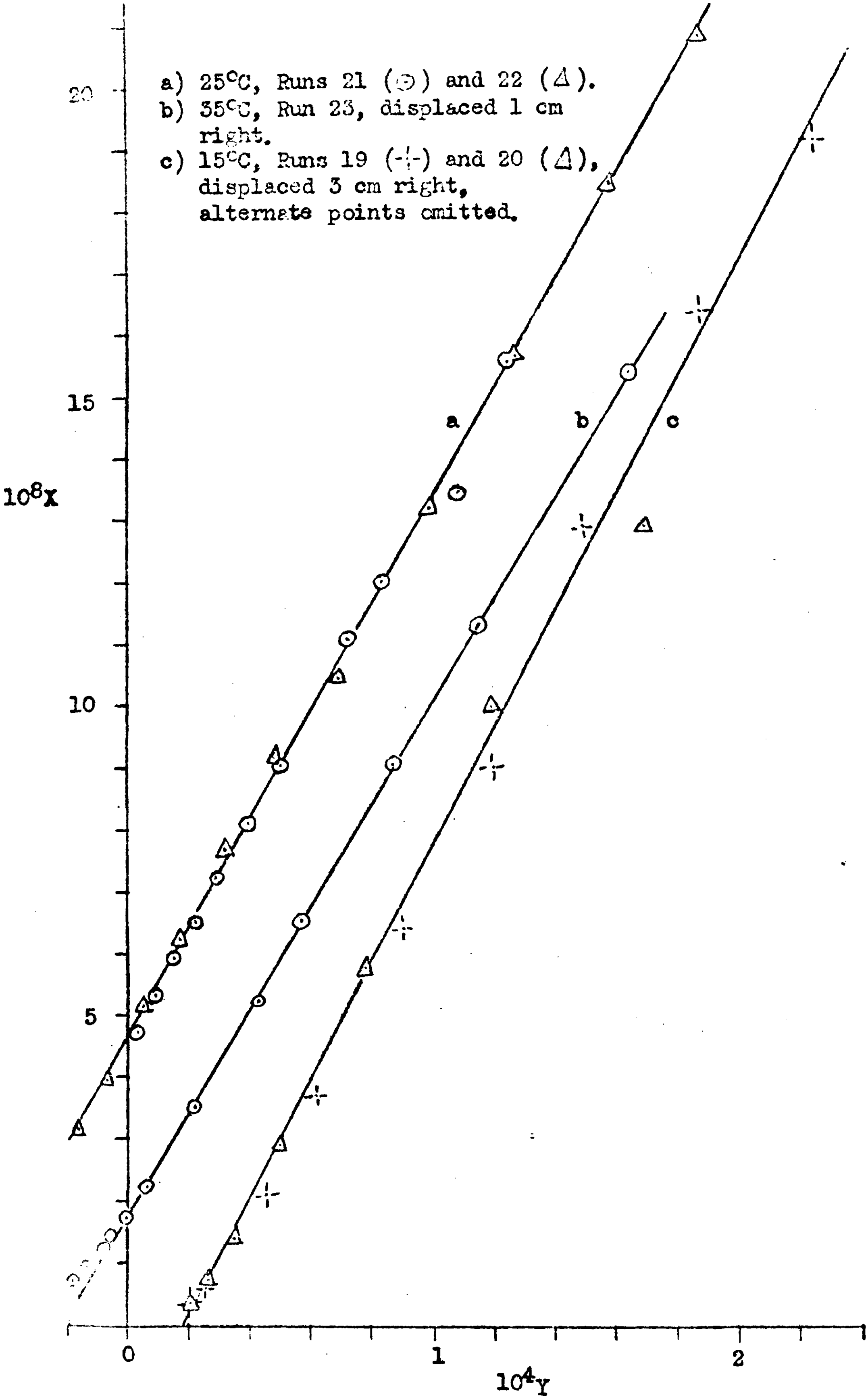

Fig. 6 Speakman Plots for Tartaric Acid

X. In Dilute Solution

The data were treated by Speakman's method (Section III), activity coefficients being calculated from

$$- \log f_z = A.z^2(I^{\frac{1}{2}}/(1 + B.a.I^{\frac{1}{2}}) - b.I),$$

where z is the ionic charge and A, B, a and b are as defined in the previous section. In the range of ionic strengths concerned ($8.5 \times 10^{-4} - 6.5 \times 10^{-3}$) the values of a and b chosen had little effect on the calculated value of the dissociation constants and their standard deviations. At constant b(0.1), varying a from 1.0 to 8.0 produced a 0.3% change in Ka_1 and a 0.6% change in σ_{Ka_1}. At constant a(2.6) a variation in b from -2.0 to 0.5 changed Ka_1 by 0.5% and σ_{Ka_1} by 0.6%. There was less than 1% difference in Ka_1 over any combination of a and b tried. The results with a = 7.0 and b = 0.2 are given in Table 3 and illustrated in Fig.(6).

Table 3

T°C.	Runs	Points	10^4Ka_1 mole Kg^{-1}	$10^6\sigma_{Ka_1}$	10^5Ka_2 mole Kg^{-1}	$10^7\sigma_{Ka_2}$
15	2	32	9.043	17.4	4.228	19.8
25	2	22	8.640	5.41	5.447	6.22
35	1	13	8.284	5.76	4.319	34.9

The values of $\log Ka_1$ and $\log Ka_2$ were fitted to the equation

$$-\log K = A/T + B + C.T \quad ,$$

where T is the temperature in degrees Kelvin, by substituting for K and T and solving the sets of three equations simultaneously. The coefficients are given in Table 4.

Table 4

	A	B	C
First dissociation	0	2.497	0.0019
Second dissociation	3014	-197.8	0.3387

The Gibbs energy change, enthalpy change and entropy charge for each dissociation in the standard state can be expressed in terms of the above coefficients.

$$\Delta G^o = -2.3026RT\log K \quad .$$

$$\Delta H^o = 2.3026R(A - CT^2) \quad .$$

$$\Delta S^o = 2.3026R(-B - 2CT) \quad .$$

The values of these thermodynamic quantities at 25°C are set out in Table 5 and compared with those of Bates and Canham (11).

Table 5 : Thermodynamic Data at 25°C.

	ΔG^o j mole^{-1}	ΔH^o j mole^{-1}	ΔS^o j deg^{-1}mole^{-1}	reference
First dissociation	17500	- 3230	- 69.5	This work
	17330	3100	- 47.7	Bates & Canham
Second dissociation	24300	650	- 79.4	This work
	24920	990	- 80.3	Bates & Canham

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Chapter 5

Sodium Tartrate Complexes

I. Introduction

The widespread use of sodium salts as background media in studies of complexing requires that sodium ions do not form complexes with the ligand, since, even if the stability of such a complex is low, with sodium concentrations up to 3M, a large proportion of the ligand will be present as the sodium complex and calculations ignoring this fact will be considerably in error.

That sodium and the other alkali metal ions do form complexes with certain organic ligands has been recognised for some time as a result of a number of different physical observations. Jardetzky & Wertz(1) recorded the Na^{23} spin resonance spectra of sodium salts as a function of concentration. With the salts of carboxylic, sulphonic and sulphanilic acids the amplitude was proportional to concentration and the line widths constant, whereas with the salts of the corresponding hydroxy-acids the line widths increased and the amplitudes reached a plateau or went through a maximum, these effects being more pronounced when substitution was in the ortho- or α-position.

The interpretation of such spectra is more than a matter of ion-pairing(2), but the line widths have been shown to have a linear correlation(3) with the stability constants of the same series of compounds determined with the use of cation-sensitive glass electrodes(4,5). Erickson & Alberty(6) measured the proton magnetic resonance spectra in D_2O of the methylene protons of the malate salts of the alkali metals and tetramethylammonium ion. The alkali metal salts produced sharper peaks as their concentrations increased, but tetramethylammonium malate exhibited no such effect, having a spectrum matching that obtained by extrapolating the alkali metal spectra to zero concentration. Eigen(7) has studied alkali metal complexes of EDTA, nitrilotriacetic acid(NTA), iminodiacetic acid and adenosine triphosphate by ultrasonic absorption techniques and also found that tetramethylammonium ion does not form complexes in the same conditions. EDTA complexes of sodium have also been studied by proton magnetic resonance spectroscopy(8) and by Na^{23} nuclear magnetic resonance(9). Stability constants have been reported for a number of sodium complexes and these are summarised in Table 1.

The evidence points to the unsuitability of sodium salts and, to a lesser extent, potassium salts (see Chapter 6) as background media when chelating ligands are involved. There is, however, no objection to tetramethylammonium salts as far as complexing between ligand and background is concerned.

Table 1

Stability Constants of Sodium Complexes

ligand	T°C.	medium	K_{101}	method	ref.
EDTA	20	0.2(KCl)	45.7	H;Ag,AgCl	(10)
	25	$0.1(Me_4NCl)$	66	H^+-gl	(11)
		0 corr	410	Na^+-gl	(12)
HEEDTA*	25	0.7-1.0	9.6	Na^{23}n.m.r.	(9)
NTA	25	0.7-1.0	8.7	Na^{23}n.m.r.	(9)
	20	→0	140	H	(17)
N-(o-sulphophenyl -IDA*	20	0.1 KCl	9.5	H	(18)
N-(o-carboxyphenyl) -IDA*	20	0.1 KCl	9.5	H	(18)
malate		$0.28(Me_4NBr)$	2.0	H^+-gl	(13)
	30	var	1.1	Na^+-gl	(4)
	25	var-0.17	1.9	Na^+-gl	(5)
citrate	25	var-0.17	5.0	Na^+-gl	(5)
thiosulphate	25	→0	4.8	sol	(19)
	15	0 corr	3.5	sp	(20)
	25	0 corr	3.8	sp	(20)
	35	0 corr	4.0	sp	(20)
trimetaphosphate	25	0 corr	25.1	Na^+-gl	(14)
($P_3O_9^{3-}$)	25	→0	15	con	(21)
	25?	$0.56?(Me_4NNO_3)$	0.8	CuHg $\boxed{K_{102}=1.0}$	(22)
tetrametaphosphate	25	0 corr	133.3	Na^+-gl	(14)
($P_4O_{12}^{4-}$)	25	→0	550	con	(21)
	25	0 corr	600	H^+-gl	(23)

Table 1 (continued)

ligand	T°C.	medium	K_{101}	method	ref.
pyrophosphate ($P_2O_7^{4-}$)	25	→0	220 20(K_{102}) 20($Ka_4.K_{111}$)	con	(24)
	25	2.0(KNO_3)	1.6 0.16(K_{102}) 0.3($Ka_4.K_{111}$)	H^+-gl	(22)
	25	→0	166 250(K_{102}) 33($Ka_4.K_{111}$)	H^+-gl	(22)
	25	1.0(Me_4NCl)	10	H^+-gl	(25)
	25	0 corr	200	H^+-gl	(26)
	40	0 corr	200	H^+-gl	(26)
triphosphate	25	0 corr	370	con	(24)
($P_3O_{10}^{5-}$)	25	Na_5L var	6300(K_{102})	con, tp	(22)
	25	1.0(Me_4NCl)	60	H^+-gl	(22)
	25	1.0(Me_4NCl)	44	H^+-gl	(27)
	25-40	0 corr	630(25°,40°)	H^+-gl	(26)
orthophosphate	25	0.2 Pr_4NX**	4.0	H^+-gl	(15)
AMP*	25	0.2 Pr_4NX**	2.9	H^+-gl	(15)
ADP*	25	0.2 Pr_4NX**	6.7	H^+-gl	(15)
ATP*	25	0.2 Pr_4NX**	14.3	H^+-gl	(15)
	30	0.1 buffer	15	sp [buffer = N-ethylmorpholine]	(28)

* HEEDTA = N'-(2-hydroxyethyl)ethylenediamine-N,N,N'-triacetic acid;

IDA = iminodiacetic acid;

AMP, ADP and ATP are adenosine mono-,di- and triphosphate respectively.

** The medium is "tetrapropylammonium halide".

Experimental

II. Reagents Disodium tartrate (Hopkin & Williams Ltd. Laboratory Reagent) and sodium chloride(B.D.H.AnalaR grade) were recrystallised from distilled water.

Approximately 0.1M sodium hydroxide solution was prepared by dilution, with freshly boiled-out distilled water, of a saturated solution made up from NaOH pellets(B.D.H.AnalaR grade), all vessels being flushed with nitrogen before use. The dilute solution was stored in and dispensed from the usual syphon arrangement and was analysed by titration against potassium hydrogen phthalate with phenolphthalein as indicator and by potentiometric titration against standard hydrochloric acid solutions, the results being treated by Gran's method(16).

Hydrochloric acid potassium hydrogen phthalate and tetramethylammonium chloride were prepared as in Chapter 2 and d-tartaric acid and tetramethylammonium hydroxide as in Chapter 3.

III. pH Titrations

Electronic Instruments Ltd GC33B glass electrodes were used to measure pH. Their calibration and treatment differed in no way from the procedures detailed in Section 2.IV. Since the complexing between sodium and tartrate ions is weak, relatively high concentrations of sodium ion were used in order to produce sufficiently large pH shifts and it was thought

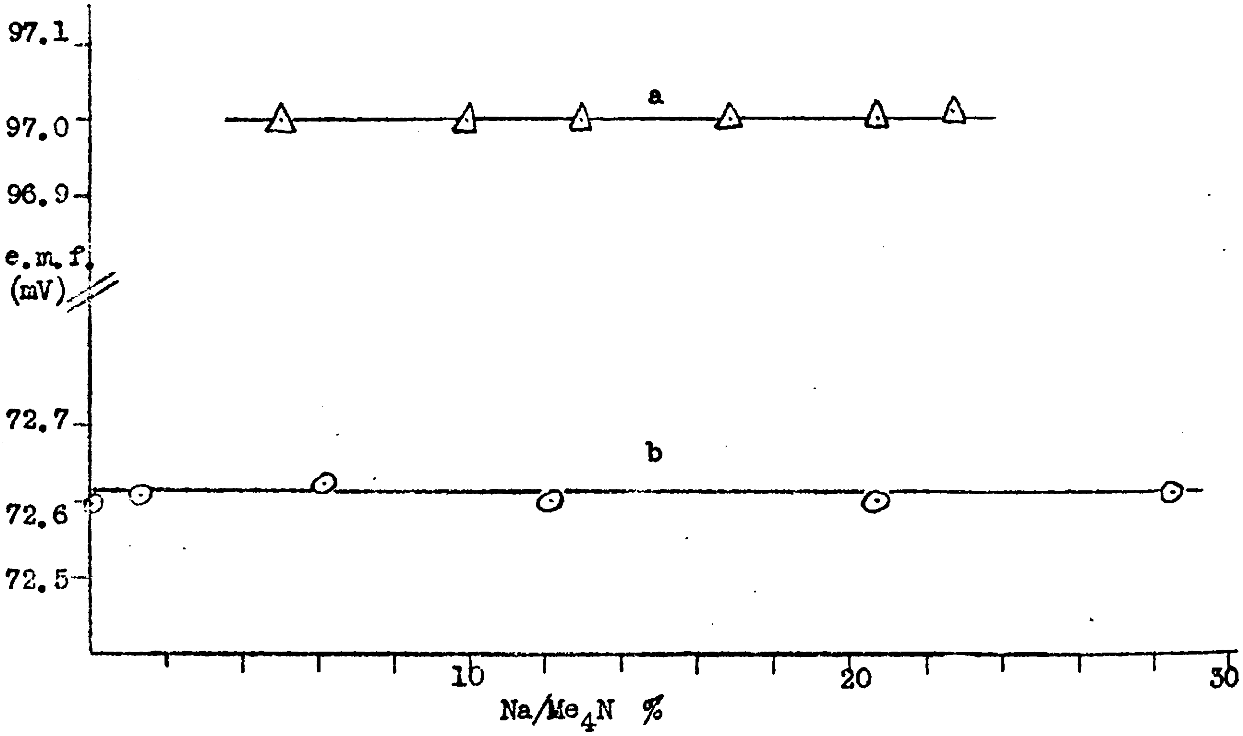

Fig.1 Effect of Composition of Medium on e.m.f. at Constant pH

a) $-\log c_H = 3.00$ b) $-\log c_H = 2.61$

$I = 0.2$ $T = 25°C.$

wise to check if a part of the shift in EMF arose from the influence of sodium ion on the liquid junction potential or on the activity coefficients in solutions of constant total molarity. Titrations were performed at two different pH's in which NaCl-HCl mixtures were added to Me_4NCl-HCl mixtures containing the same fraction of HCl. The total molarity was 0.2 in each case. The results are shown in Fig.(1).from which it can be seen that any such effects were negligible. The electrode system was calibrated and unknown pHs obtained according to the procedures detailed in Section 2.Va-c.

Volumes of 0.4M Me_4NCl, distilled water, 0.2M NaCl and approximately 0.05M tartaric acid solutions were pipetted into the flask illustrated in Fig.2.3 in such proportions that the chloride concentration was 0.2M.A solution of Me_4NOH or NaOH was added from a calibrated burette and Me_4NCl solution added from another to maintain the chloride concentration. Readings were taken after 5 minutes and checked after a further period. The temperature was maintained at 25°C in a water bath, as in Section 2.Va. Nitrogen which had been bubbled through a series of presaturators(0.2M HCl, 0.2M NaOH, 0.2M Me_4NCl, 0.2M Me_4NCl) was passed continuously to mix the solutions and prevent absorption of carbon dioxide at the higher pHs. Two titrations were performed with NaOH and two with Me_4NOH, a different glass electrode being used for each pair.

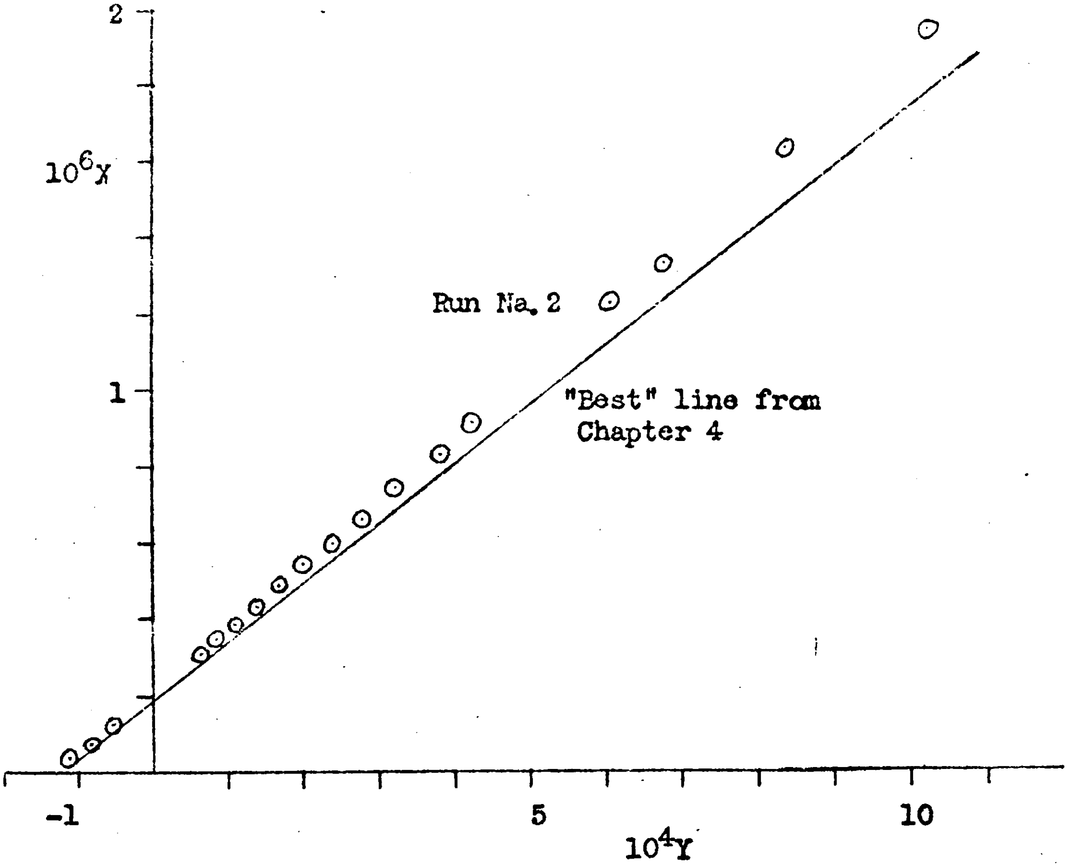

Fig. 2 Speakman Plot for Run Na. 2 .

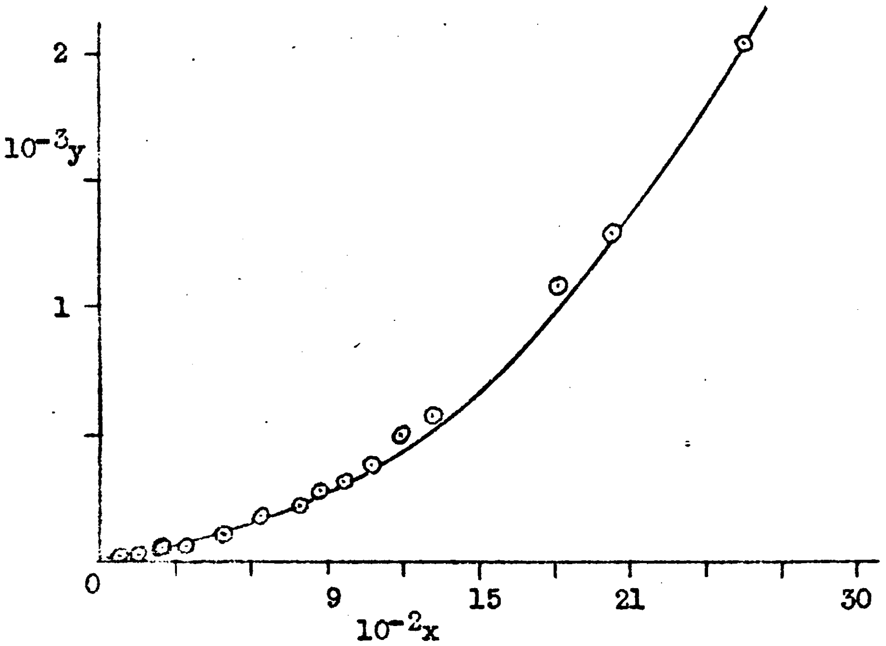

Fig. 3 Gelles - Nancollas Plot for Run Na. 2

IV. pNa Titrations

The performance and operation of the Electronic Instruments Ltd GEA33 electrode have been described in Section 2.VIII.

Equal volumes of boiled-out distilled water and 0.4M Me_4NCl solution were mixed and 0.0666M disodium tartrate solution added. Successive additions of 0.2M NaCl solution were made from a calibrated burette. The titration vessel was either the 250ml five-necked flask used above or a 100ml four-necked flask of similar design, but without the B.24 socket. Nitrogen was passed continuously as above, and the details of the temperature control are the same. In the first run the pH was also measured. Four titrations were performed in all.

V. Results and Calculation

(a) pH Titrations

The data are presented in Appendix 1b. Runs Na.1 and Na.2 were performed with NaOH and glass electrode Y and Runs Na.3 and Na.4 with Me_4NOH and glass electrode A.

The data were first treated as if no complexing took place and Speakman's method(Section 4.II) was used to calculate the apparent dissociation constants of tartaric acid.
The results for Run 2 are plotted in Fig.(2) and the "best" plot from Chapter 4 shown for comparison. The results for

all the runs are summarised in Table 2.

Table 2

Apparent Dissociation Constants of Tartaric Acid

10^2Na	10^3Ka$_1$	10^4Ka$_2$	Source
2.9	1.57	1.20	Run Na.1
10.4	1.69	1.30	Run Na.2
2.0	1.72	1.21	Run Na.3
2.0	1.67	1.30	Run Na.4
-	1.54	1.17	Chapter 2

The sodium concentrations in column 1 are median values for the runs concerned.

The apparent dissociation constants lie outside the range found for the individual tartaric acid runs of Chapter 4, indicating that complexing probably occurs(see Section 3.XI).

The data were then processed by the method of Gelles and Nancollas(Section 3.I). A typical plòt, again for Run 2, is shown in Fig(3). It should be noted that in Runs 1 and 2 the cation of the base/itself is taking part in the complexing, i.e. B = M, and the equations of Chapter 3 must consequently be modified by setting the concentration of B equal to zero, the actual concentration of base being included in the total metal concentration.

The curvature, increasing as the pH falls, in the Gelles and Nancollas plot indicates that complexing is not restricted to the types MA and MA_2, but probably involves

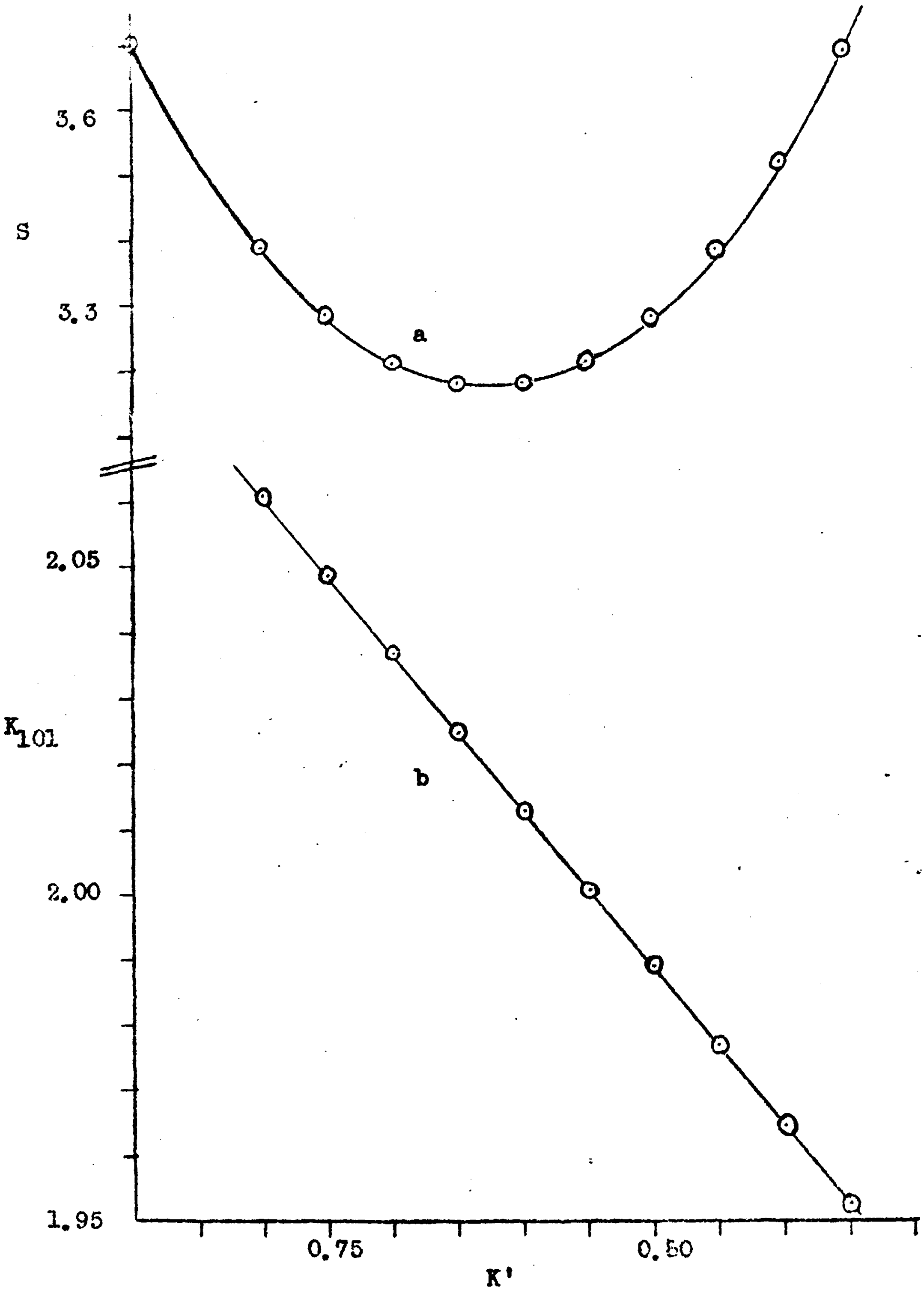

Fig. 4 Variation of a) S and b) K_{101} with input value of K' for Run Na, 2.

the type MHA also. The curve in Fig.(3) is tending towards the origin and therefore MA_2 formation is slight and may be negligible.

An approximation to K_{101} was obtained from the slope of the Gelles-Nancollas plot in the higher pH region(3.5-4.5) and used to calculate a value of K_{111} by the method described in Section 3.II(a). Treatment as an MA-MA_2-MHA system (Section 3.III) emphasised the negligibility of the MA_2 complex. The "best" values of K_{101} and K_{111} were obtained by the method of Section 3.II(b). A plot of S, the sum of the squares of deviations in K_{101}, against the trial values of $K' = K_{111}.Ka_2$ is given in Fig(4a) for the data of Run Na.2.Fig(4b) illustrates the linear relationship between trial values of K' and the resulting mean calculated K_{101}, again for Run Na.2.
The results for all the runs are summarised in Table 3.
The errors quoted in Tables 3-5 are standard deviations.

Table 3

Stability Constants of Sodium-Tartrate Complexes

Run	K_{101}(mole^{-1}litre)	K'(mole^{-1}litre)
Na.1	1.7±0.03	0.65
Na.2	2.0±0.07	0;78
Na.3	5.9±0.12	2.9
Na.4	7.6±0.27	1.5

The disparity between the first and second pairs of results is obvious. It was decided to do more tartaric acid runs with the electrode used in Runs Na.3 and Na.4. The procedure was identical with that for tartaric acid runs T.4 - T.14, except for the use of glass electrode A. The experimental data for the two additional runs, T.17 and T.18, are given in Appendix 1a. The combined data for the two runs lead to the following values for the dissociation constants:

$Ka_1 = 1.59\text{x}10^{-3}$ mole litre^{-1} and $Ka_2 = 1.19\text{x}10^{-4}$ mole litre^{-1}.

Runs Na.3 and Na.4 recalculated with the above dissociation constants and redesignated Na.3a and Na.4a give the results in Table 4.

Table 4

Run	K_{101}(mole^{-1} litre)	K'(mole^{-1} litre)
Na.3a	3.1±0.11	1.2
Na.4a	4.8±0.28	‹0.4

The pH range of Runs Na.3 and Na.4 is such that the value of K' tried has relatively little effect on the calculated value of K_{101}, although the standard deviation in K_{101} is more sensitive. In Run Na.4a both K_{101} and the standard deviation reach steady values for K' ‹ 0.4. It is assumed that there is some small systematic error between the two sets of pH measurements and that the use of the second set of dissociation constants in Runs Na.3a and Na.4a compensates for this to some extent. The weighted mean of Runs Na.1, Na.2, Na.3a and Na.4a is K_{101} = 1.9±0.03 mole^{-1}litre and the mean of Runs Na.1, Na.2 and Na.3a gives K' = 0.9±0.3 mole^{-1}litre. Refinement of the stability constants by the GAUSS G procedure (Section 2.VII) proved impossible, since the constants are so small that the derivatives were zero even when Δlogk was made much larger than normal.

(b) pNa Titrations

Four titrations were done and the data are given in Appendix 1b. Treatment of the data by the method of Section 3.IX gave no hint of M_2A formation and MA_2 complexing was discounted on the basis of the pH titrations, so only the MA complex was considered. The stability constant, K_{101}, was calculated as described in Section 3.VIII. During Run Na.5 the pH was also recorded and a hydrolysis correction applied to the results as in Section 3.VIIIb. The difference in the values of K_{101} with and without the correction was so small, 0.4% of the standard deviation, that the effect was neglected in subsequent runs. The results for each run are summarised in Table 5.

Table 5

Stability Constants of Sodium Tartrate Complexes

Run	K_{101}(mole^{-1}litre)
Na.5	3.0 ± 0.35
Na.6	2.1 ± 0.36
Na.7	1.4 ± 0.22
Na.8	5.0 + 0.59

The weighted mean of the above runs is $K_{101} = 2.6 \pm 0.1$ mole^{-1} litre.

(c) Results The final value of K_{101} was taken as the weighted mean from Runs 1, 2, 3a, 4a and 5 - 8. Hence, $K_{101} = 2.0 \pm 0.03$ mole^{-1} litre. Runs 1, 2 and 3a yield the mean value $K' = 0.9 \pm 0.3$ mole^{-1} litre.

VI. Discussion

Although small stability constants must always be regarded with caution, the agreement between a number of runs covering a fairly wide range of pH(2.5 - 7.0) and sodium ion concentration (0.005 - 0.1M), by two different methods is good enough to justify some confidence in the result. It may be objected that the difference between the total sodium concentration and the free sodium concentration as determined by the electrode calibration could be a spurious effect caused by activity coefficient changes brought about by the difference in composition of the medium between the calibration and the experiment. If we relate the e.m.f.s and pNas of two solutions by the equation

$$(E_1 - E_2)/k = pNa_1 - pNa_2,$$

then taking $pNa = -\log c_{Na} - \log f_{Na}$ and (by analogy with Guggenheim & Turgeon(29)) $-\log f_{Na} = AI^{\frac{1}{2}}/(1+I^{\frac{1}{2}}) - b_{NaCl} \cdot c_{Cl} - b_{NaT} \cdot c_T$, where c_{Cl} and c_T are the concentrations of chloride and tartrate ions respectively. If we assume that no complexing takes place, then c_T = Ta and c_{Na} = Tm and c_{Cl} is known. For the data of Run Na.5, c_{Cl} = Tm - 2Ta. We can now write

$$(E_1 - E_i)/k = \text{Constant} + \log Tm_i - b_{NaCl}(Tm_i - 2Ta_i) - b_{NaT} \cdot Ta_i$$

Since E_i, Tm_i and Ta_i are known, the b-coefficients can be found by solving simultaneous equations. A few points from Run Na.5 yield the values

$$b_{NaCl} = -70 \text{ and } b_{NaT} = -200.$$

Although the above treatment involves extrathermodynamic assumptions, the b-coefficients are so large and negative that complexing must surely be invoked in order to explain the observed behaviour. The true(29) value of b_{NaCl} is 0.15.

Comparison of K_{101} for sodium tartrate with the constants for the malate and citrate complexes in roughly the same conditions shows that the constants are all of the same order and in the expected series

$$\text{citrate} > \text{tartrate} > \text{malate}.$$

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Chapter 6

Potassium Tartrate Complexes

I. Introduction

Complexing studies in which potassium salts are used to maintain a constant ionic strength would be seriously compromised if the ligand in question were to form complexes with potassium. There is now an accumulation of evidence that potassium does complex with certain ligands, one of which would be expected to be tartrate.

Proton magnetic resonance spectroscopy (1) revealed changes in the spectrum of potassium malate as the concentration (in D_2O) increased. The spectrum of the tetramethylammonium salt, however, differed only in its intensity as the concentration changed. Extrapolation of the results for potassium malate to infinite dilution produced a spectrum of the same form as the tetramethylammonium one. Eigen (2) has studied EDTA, nitrilotriacetic acid and adenosine triphosphate complexes by ultrasonic absorption. Stability constants have been reported for a number of complexes and are summarised in Table 1.

Table 1

Stability Constants of Potassium Complexes

ligand	T°C.	medium	K_{101}	method	ref.
malate		0.28(Me_4NBr)	1.7	H^+-gl	(3)
	25	var - 0.17	1.5	K^+-gl	(4)
citrate	25	var - 0.17	3.9	K^+-gl	(4)
EDTA	25	0.1(Me_4NCl)	3.5	H^+-gl	(5)
	25	1.0(Me_4NCl)	4.9	H^+-gl	(5)
thiosulphate	25	→0	8.3	sol	(6)
	15	0 corr	7.1	sp	(7)
	25	0 corr	10.0	sp	(7)
orthophosphate	25	0.2**	3.1	H^+-gl	(8)
$P_2O_7^{2-}$	25	1.0(Me_4NCl)	6.3	H^+-gl	(9)
	25	0 corr	200	H^+-gl	(10)
	40	0 corr	200	H^+-gl	(10)
$P_3O_{10}^{5-}$	25	1.0(Me_4NCl)	24.0	H^+-gl	(11)
	25	1.0(Me_4NCl)	24.5	H^+-gl	(12)
	25	0 corr	630	H^+-gl	(10)
	40	0 corr	630	H^+-gl	(10)
AMP*	25	0.2**	1.6	H^+-gl	(8)
ADP*	25	0.2**	5.5	H^+-gl	(8)
ATP*	25	0.2**	11.5	H^+-gl	(8)

*AMP, ADP and ATP are adenosine mono-, di- and triphosphate respectively.

**The medium is "tetrapropylammonium halide".

Experimental

II. Reagents Potassium chloride and d-tartaric acid(B.D.H. AnalaR grade materials) were recrystallised from distilled water. Tetramethylammonium chloride and tetramethylammonium hydroxide were prepared as described in Sections 2.IV and 4.V respectively.

III. pH Measurements An Electronic Instruments Ltd. GC33 glass electrode was used to measure pH in a 0.2M Me_4NCl medium at 25°C. The details of glass electrode calibration and e.m.f. measurement are given in Sections 2.IV and 2.V. The electrode used in this part of the work was electrode 'A'.

10ml 0.04825M tartaric acid, 10ml 0.2M KCl, 30ml distilled water and 40ml 0.4M Me_4NCl were added to the titration vessel(Fig.(2.3)) by means of calibrated pipettes. Additions of tetramethylammonium hydroxide solution were made from a calibrated burette and the e.m.f. recorded 0.4M Me_4NCl was added from a second calibrated burette to maintain the chloride ion concentration.

Nitrogen from a cylinder (British Oxygen Co. Ltd.) was passed continuously, both to stir the solution and to prevent the absorption of carbon dioxide. The nitrogen passed through a train of presaturators

0.2M HCl; 0.2M NaCl; 0.2M Me_4NCl; 0.2M Me_4NCl

at 25°C. before it reached the test solution. Measurements with phthalate buffer in the cell were made before and after the titration. The e.m.f.'s were corrected for liquid junction potential according to the procedure given in Section 2.Vc and the pH's calculated from the calibration. The data are presented in Appendix 1c.

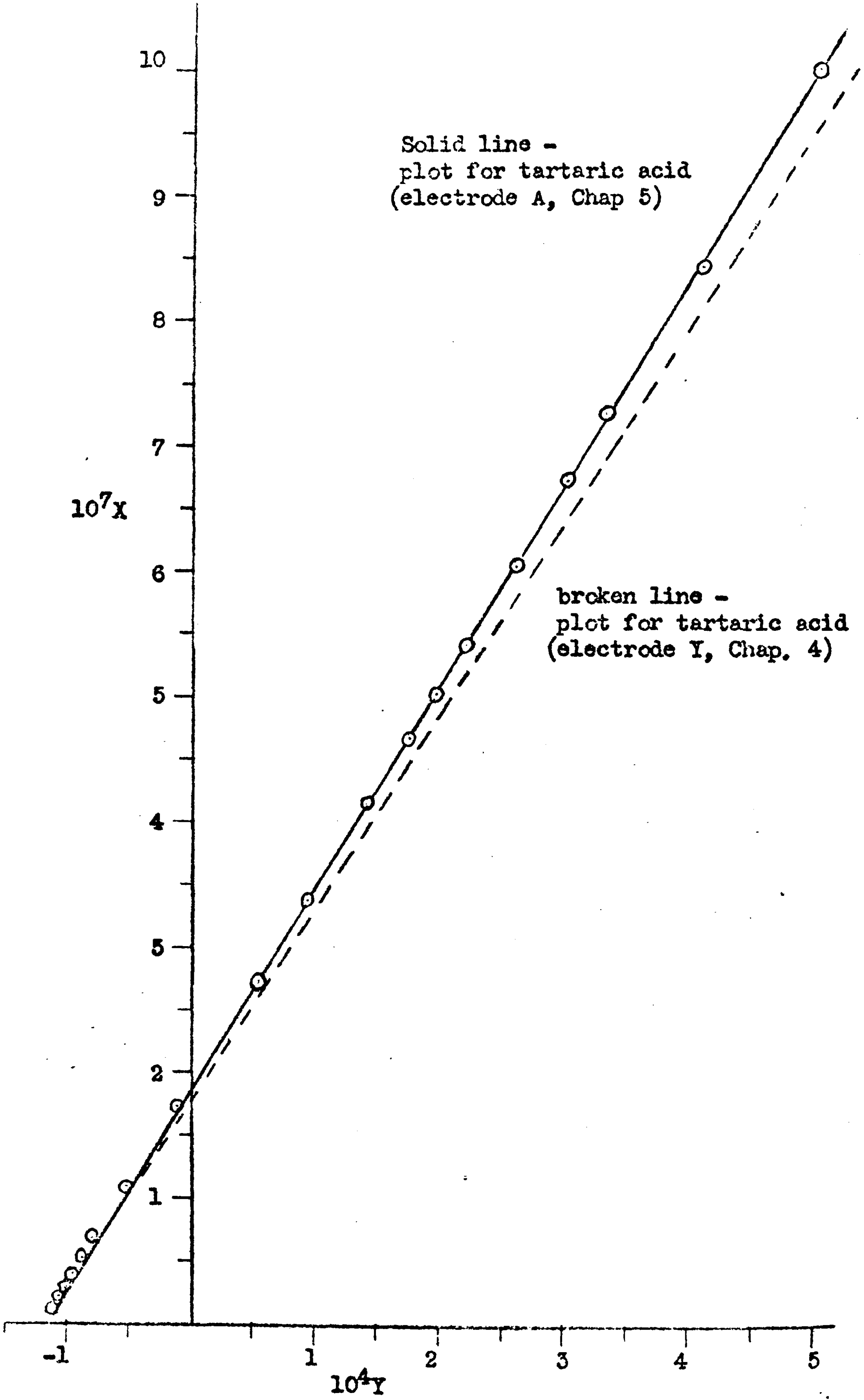

Fig.1 Speakman Plot for Run K.1 . ⊙

Calculation

IV. The results were first treated by Speakman's method (Section 4.III), as if no complexing occurred, and apparent stability constants for tartaric acid obtained. The plot is shown in Fig.(1), along with the "best" result from Chapter 4 for comparison(broken line). The result for the additional runs done with glass electrode **A** (Chapter 5) is also shown (continuous line). Comparing the results from glass electrode **A**, with and without potassium present, it can be seen that although there are deviations at higher pH s in the more acidic region the plots virtually coincide.

The conclusion is that **MHA** complexing is probably negligible, while **MA** complexing occurs to some small extent.

Comparison with the first set of tartaric acid results would suggest that both **MA** and **MHA** complexes existed. The results are listed in Table 2.

Table 2

electrode	$10^3 Ka_1$	$10^4 Ka_1$	comment
Y	1.54	1.173	Chapter 4
A	1.59	1.19	Chapter 5
A	1.61	1.20	potassium present

The difference between the dissociation constants obtained with electrode **A** in the absence and presence of potassium ions is within the experimental uncertainty, leading to the conclusion that complexing must be negligible. The deviation

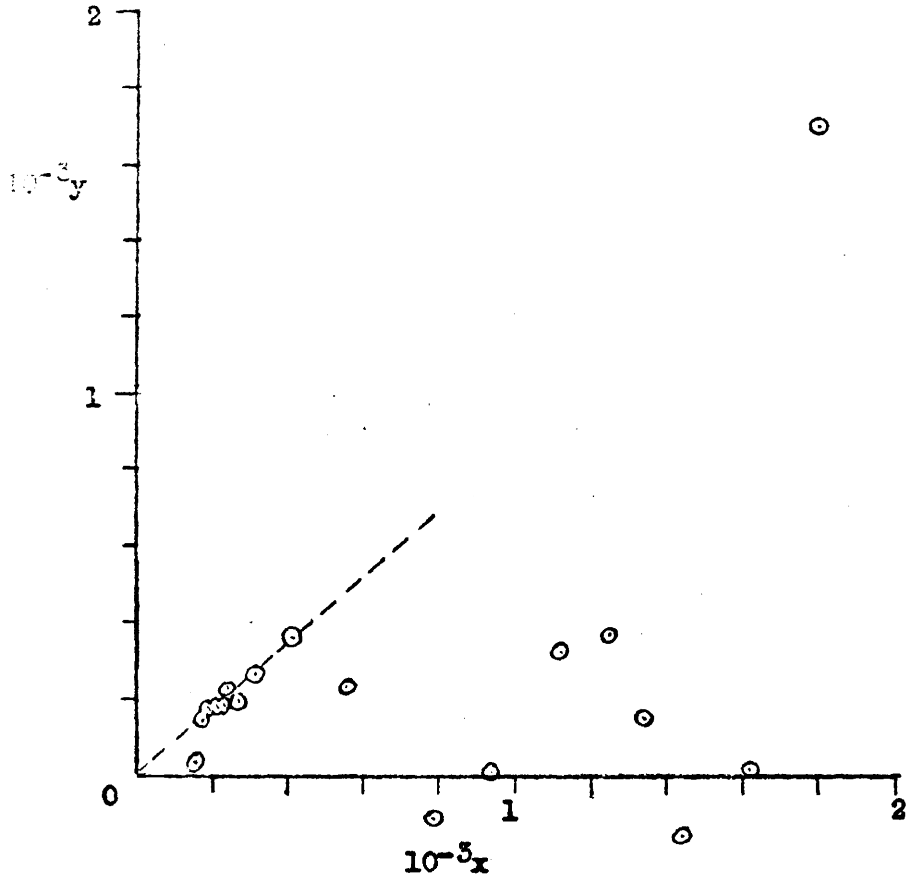

Fig. 2 Gelles - Nancollas Plot for Potassium Tartrate.

from linearity in the higher pH region, however, is more marked than was the case in any run with no potassium present, which may indicate the existence of a weak **MA** complex at these pH's. Using the dissociation constants measured with electrode **A**, stability constants were calculated for potassium complexes.

Treatment of the data by the method of Gelles and Nancollas (Section 3.I) for **MA** and MA_2 complexes gave the result illustrated in Fig.(2). The earlier findings are reinforced: in the more acidic region, where **MA** formation would be negligible, the points are scattered about the x-axis, while at higher pH's the plot may be interpreted as a straight line passing through the origin. The slope of this line (determined graphically) gives K_{101} and the intercept K_{102}.

K_{101} = 0.86 mole^{-1}.litre K_{102} = 0.0 mole^{-2}.litre^{2}

If **MA** is assumed to be the only complex formed and K_{101} is calculated individually for each point, we obtain the mean

K_{101} = 0.7 mole^{-1}.litre

with a standard deviation of 0.75. If only the last eleven points are considered the result is

K_{101} = 0.8$\pm$0.25 mole^{-1}.litre.

Considering the system as a mixture of **MA** and **MHA** complexes gives, by the method of Section 3.IIb, the values

K_{101} = 0.6$\pm$0.15 mole^{-1}litre and K' = 0.14 mole^{-1}litre,

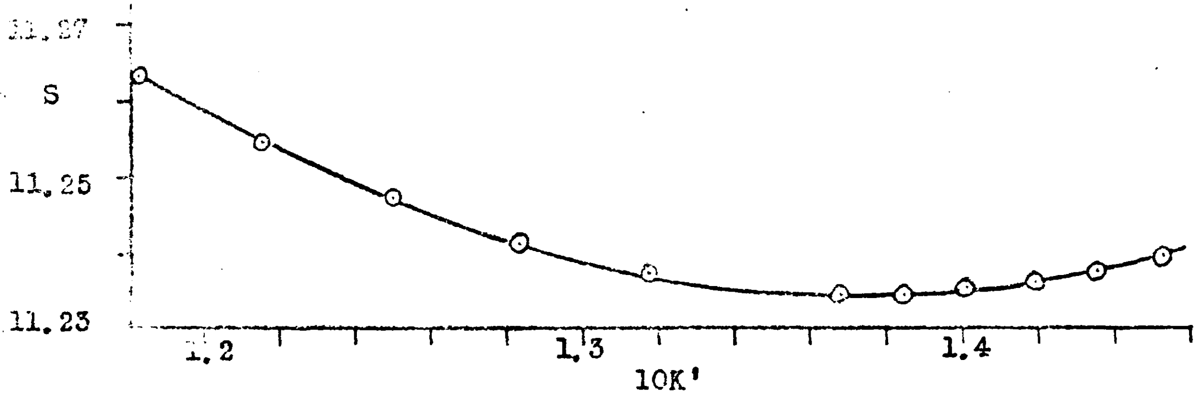

Fig. 3a Potassium Tartrate - effect of K' on S
(all points)

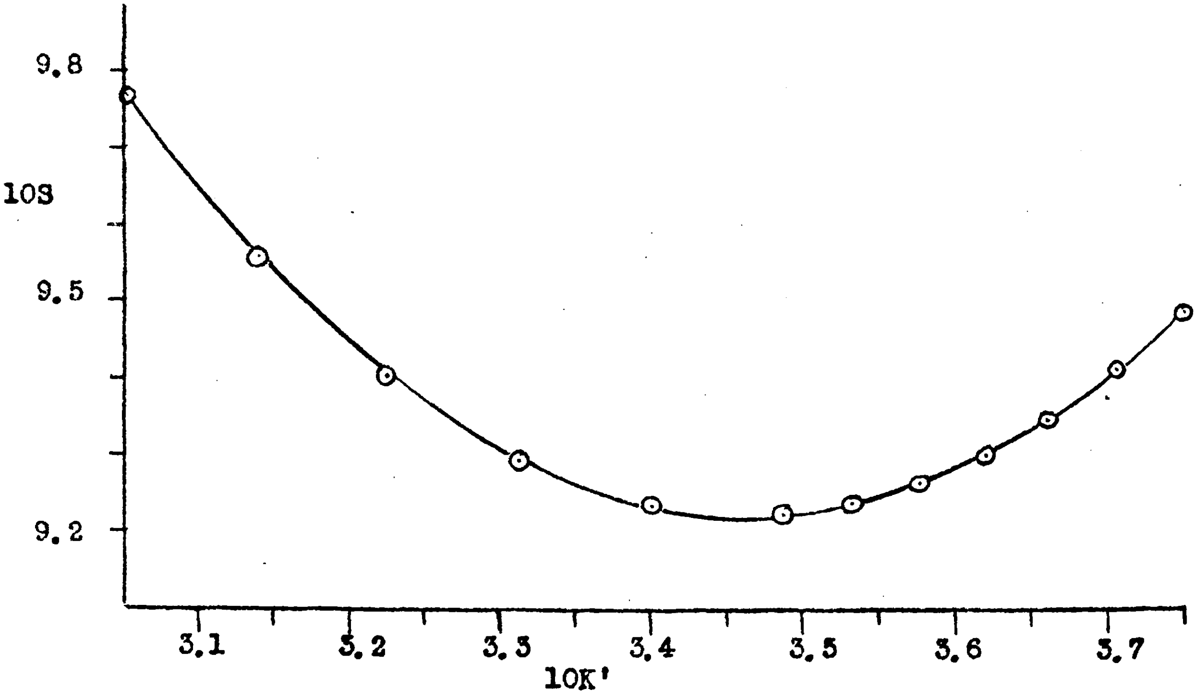

Fig. 3b Potassium Tartrate - effect of K' on S
(last 12 points only)

S is the sum of the squares of the deviations in K_{101}.

where $K' = Ka_2.K_{111}$ and all points are included in the calculation. Omitting points in the lower half of the pH range, the values were

$$K_{101} = 1.0\pm0.1 \text{ mole}^{-1}\text{litre and } K' = 0.35 \text{ mole}^{-1}\text{litre.}$$

Plots of S, the sum of the squares of the deviations, are shown in Figs(3a) and (3b) for the two cases.

The significance of results calculated from a single run is slight when the degree of complexing is so small, but it is probable that the potassium tartrate system has stability constants in the range

$$0.6 \leq K_{101} \leq 1.0$$

and $$0.1_5 \leq K' \leq 0.3_5$$

V. Discussion

Although not much confidence can be placed in the above results, experience with the sodium tartrate results in the previous chapter leads us to believe that potassium tartrate complexing is a real effect. Comparison with the constants for malate and citrate complexes in Table 1 shows that the figures found here are of the same order, as was the case with the corresponding sodium complexes.

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Chapter 7

d-Tartaric Acid and its Alkali Metal Complexes - a Discussion

I. The dissociation constants of tartaric acid have been measured a number of times and in a variety of media. The results are summarised in Table 1.

Table 1 - the Dissociation Constants of d-Tartaric Acid

T°C	medium	pKa_1	pKa_2	$-\log(Ka_1Ka_2)$	method	date	ref.
15	→0	3.057	4.381	7.438	H;Ag,AgCl	1951	(1)
15	0 corr	3.04	4.37	7.41	H^+-gl	1969	(2)
16.8	0 corr	2.93	-	-	qh	1928	(3)
17.6	0 corr	-	4.23	-	qh	1928	(3)
18	0 corr	3.02	4.55	7.57	emf	1928	(4)
20	0 corr	2.98	4.39	7.37	qh	1938	(5)
20	→0	3.044	4.372	7.416	H;Ag,AgCl	1951	(1)
20	0 corr	2.89	4.52	7.41	H	1965	(6)
25	0 corr	-	4.29	-	sol	1926	(7)
25	0 corr	2.98	4.34	7.32	H;Ag,AgCl	1934	(8)
25	→0	2.52	4.16	6.68	con	1940	(9)
25	→0	3.036	4.366	7.402	H;Ag,AgCl	1951	(1)
25	→0	2.95	4.44	7.39	H^+-gl	1951	(10)
25	0 corr	3.03	4.45	7.48	H^+-gl	1959	(11)
25	0 corr	3.036	-	-	con	1959	(11)
25	0 corr	3.11	4.26	7.37	H^+-gl	1961	(12)
25	0 corr	3.01	4.55	7.56	H^+-gl	1964	(13)

Table 1 (continued)

T°C	medium	pKa_1	pKa_2	$-\log(Ka_1Ka_2)$	method	date	ref.
25	$\to 0$	3.00	4.25	7.25	H^+-gl	1969	(2)
25	0 corr	3.06	4.26	7.32	H^+-gl	1969	(2)
35	$\to 0$	3.019	4.367	7.386	H;Ag,AgCl	1951	(1)
35	0 corr	3.08	4.37	7.45	H^+-gl	1969	(2)
50	0 corr	2.94	4.39	7.33	H;Ag,AgCl	1934	(8)
50	$\to 0$	3.021	4.391	7.412	H;Ag,AgCl	1951	(1)
74	0 corr	3.01	4.51	7.52	H;Ag,AgCl	1934	(8)
20	0.1($NaClO_4$)	2.80	3.96	6.76	H^+-gl	1964	(14)
25	0.1 Me_4NCl	2.83	3.97	6.80	H^+-gl	1969	(2)
25	0.136(KNO_3)	2.81	3.95	6.76	H^+-gl	1960	(15)
25	0.2(KCl)	2.88	3.94	6.82	H	1938	(16)
25	0.2 Me_4NBr	2.95	3.98	6.93	H^+-gl	1963	(17)
25	0.2 Me_4NCl	2.81	3.93	6.74	H^+-gl	1969	(2)
25	0.4 Me_4NCl	2.83	3.88	6.71	H^+-gl	1969	(2)
20	1.0 $NaClO_4$	2.37	3.41	5.78	H^+-gl	1957	(18)
20	1.0 $NaNO_3$	2.66	3.61	6.27	H^+-gl	1969	(19)
25	1.0(KNO_3)	2.60	3.77	6.37	H^+-gl	1964	(20)
25	1.0 $Na(ClO_4)$	2.59	3.84	6.43	H^+-gl	1968	(21)
18	var	3.01	4.55	7.56	con,kin	1924	(22)
20	var	3.05	4.13	7.18	qh	1924	(23)
18	var	2.90	4.02	6.92	H	1925	(24)
25	var	-	4.40	-	kin	1927	(25)
18	var	2.93	3.99	6.92	H	1934	(26)
?	var	2.75	3.99	6.74	H^+-gl+pol	1960	(27)

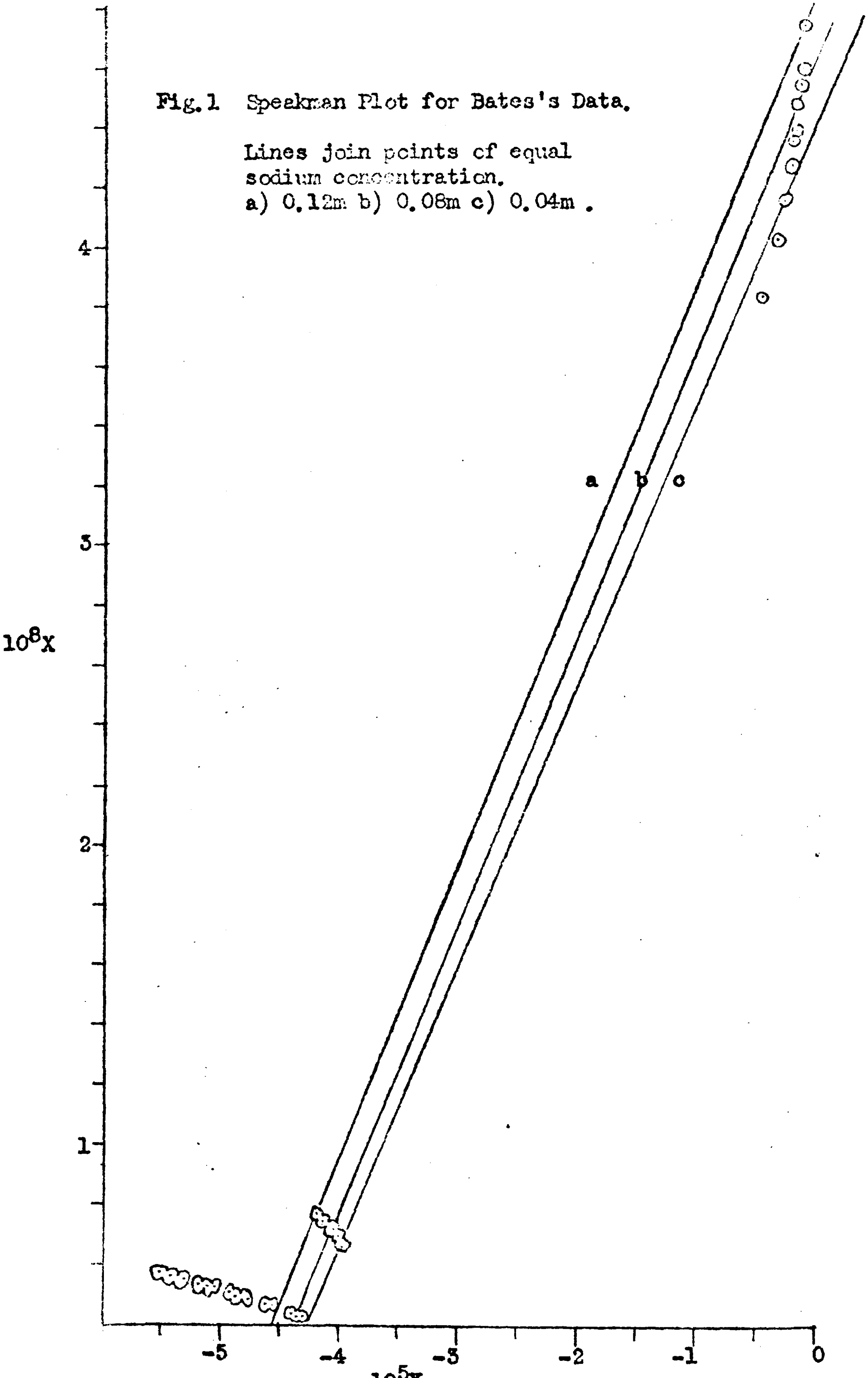

Fig. 1 Speakman Plot for Bates's Data.

Lines join points of equal sodium concentration.
a) 0.12m b) 0.08m c) 0.04m .

Bates and Canham (1) have measured the dissociation constants at a number of temperatures other than those given above and all these extra results are summarised in Table 2.

Table 2

$T^{o}C$	0	5	10	30	40	45
pKa_1	3.118	3.095	3.075	3.025	3.018	3.020
pKa_2	4.426	4.407	4.391	4.365	4.372	4.380

In most of the work cited in Table 1 sodium ion was present to some extent, since, even when a potassium salt was used as a background medium (15,16,20), sodium hydroxide served as the titrant. Tetramethylammonium salts, which do not form complexes with α-hydroxyacids (28,29), have been used as background media in this work and by Wu and Hsu(17). All the results corrected to infinite dilution, apart from the present work, were obtained in the presence of sodium. Only Frei (6) makes allowance for sodium complexes.

II. The most extensive and accurate measurements have been made by Bates and Canham (1), but their method (Section 4.IV) involves the presence of fairly high concentrations of sodium ion(up to 0.416m). The application of Speakman's method (Section 4.III) to these data results in a plot of marked curvature, Fig(1). The lines on the graph are drawn through points with approximately equal sodium concentrations. As would be expected if sodium complexing occurs, the higher the concentration, the higher the apparent dissociation

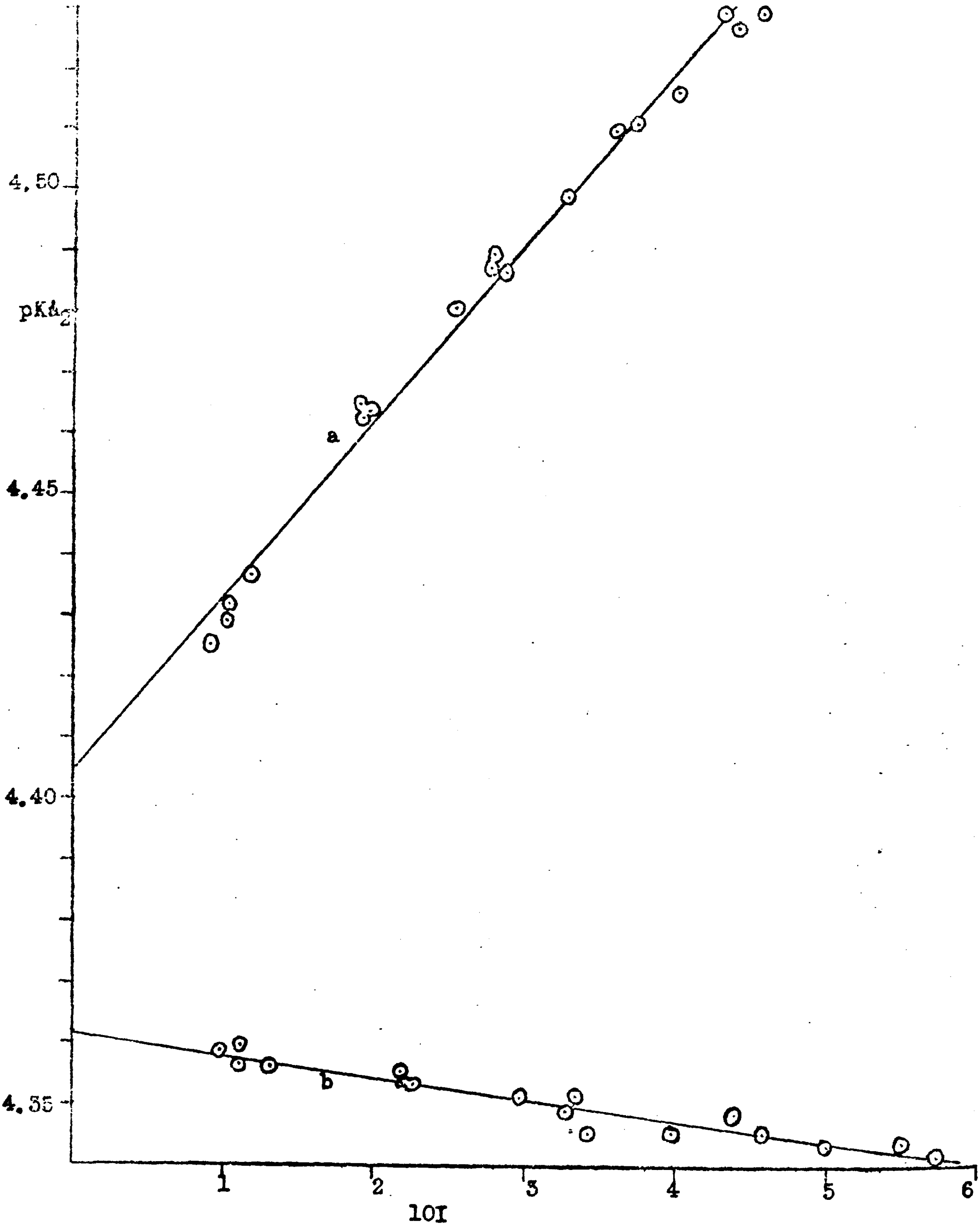

Fig. 2 Recalculation of Bates's Data with a) K_{101} = 6.45 b) K_{101} = 0.0 .

constants.

Series 1a of the Bates and Canham data was recalculated according to the method for Ka_2 described in Section 4.IVc. It was assumed that no sodium-hydrogen tartrate complexing took place. The value of K_{101} for sodium tartrate (6.45 $mole^{-1}$ Kg) was obtained by applying an activity correction to the value in 0.2M medium (Chapter 5). Values of 13.0 and 0.0 were also tried. Both the Ka_1 value from this work (8.64×10^{-4} mole Kg^{-1}) and Bates and Canham's own (9.1×10^{-4} mole Kg^{-1}) were tried. The parameter a in Eqn(4.15) was set equal to 6.0. The iterative calculations were carried out on a KDF.9 computer, using a program written by the author. The results for $Ka_1 = 8.6 \times 10^{-4}$ are shown for $K_{101} = 6.45$ and $K_{101} = 0.0$ in Fig(2). From Eqn(4.15), the slopes of the lines in Fig(2) are equal to 2A.b. Changing Ka_1 had little effect on the results, which are summarised in Table 3.

Table 3

$10^4 Ka_1$	8.64	8.64	8.64	9.10	9.10
K_{101}	0.0	6.45	13.0	0.0	6.45
pKa_2	4.362	4.405	4.445	4.363	4.406
10A.b.	-0.18	1.42	2.67	-0.17	1.43

Negative values of b, which are obtained when there is assumed to be no complexing with sodium, are a sign of association(30). The use of $K_{101} = 6.45$ gives $b = 0.28$, which is close to the value, 0.3, adopted by Davies (31) for strong electrolytes of the type 1:1 and 1:2.

IIIa The only spectroscopic evidence for alkali metal tartrate complex formation consists of optical rotation studies by Britton & Jackson(26) and Katzin and Gulyas(27). The former found that the molar rotation of disodium tartrate solutions decreases as the concentration increases, while the molar rotation of the potassium and ammonium salt solutions increased, but at different rates. The molar rotations of all three salts converged at low concentrations. Katzin and Gulyas, working at constant tartrate concentration and variable pH, explained the variation in the specific rotation in terms of contributions from tartrate and hydrogen tartrate ions and molecular tartaric acid, related by means of the acid dissociation constants, but reported that the optical rotation depended, to a greater extent than would be expected from activity effects, on the cation of the base used to neutralise the acid. The results of both groups seems to indicate some specific interaction between tartrate ions and the alkali metals, especially sodium.

IIIb Stability constants for complexes between tartrate ion and alkali metal ion have been reported by Frei(6) and Wu and Hesu(17). The latter performed pH titrations at 25°C. with a glass electrode. Their method consisted in titrating a tartaric acid solution in a 0.2M background medium of the alkali metal salt with potassium hydroxide solution, having first determined the mixed dissociation constants of the acid by titration with Me_4NOH in a tetramethylammonium salt medium. A single titration was done in each medium. Their results are given in Table 4.

Table 4

The stability constants of alkali metal and ammonium tartrate complexes at 25°C. and I = 0.2.

	Li^+	Na^+	K^+	Rb^+	NH_4^+	Cs^+
$-\log K_{101}$	0.76	0.56	0.40	0.36	0.32	0.30
$-\log K'$	0.42	0.20	0.04	0.08	-0.01	0.00

$K' = Ka_2.K_{111}$

The figures for sodium and potassium complexes are roughly double those found in this work. Part of this difference must be caused by the change of medium, but a more important factor is the uncertainty in the values of the acid dissociation constants. The application of Speakman's method (Section 4.III) to their data produces, when hydrogen ion activities are used, a curved plot which levels off at low pH's. The value of the first dissociation constant is approximately half that reported in the original paper. When an activity coefficient is applied to the pH's, the concentration first dissociation constant resulting from a Speakman plot is roughly double the reported mixed constant. In view of this uncertainty the agreement between the metal tartrate stability constants of Wu and Hsu and those found in this work is fair.

IIIc From pH measurements with the hydrogen electrode at 20°C. Frei(6) has reported thermodynamic stability constants for sodium - tartrate complexes: K_{101} = 96.2 mole^{-1} litre and K' = 29.2 mole^{-1} litre. Frei's activity coefficient corrections are, however, open to question, e.g. for a 0.01M solution of tartaric acid he reports an ionic strength of 0.00476 and an activity coefficient f = 0.541, whereas at the same ionic strength the Davies equation(31) gives f = 0.943. Frei sets out elsewhere (32) his method of calculating activity coefficients. Electrolytes are described in terms of an activity coefficient f and a dissociation constant K(K^o at infinite dilution) or degree of dissociation α. K having been obtained by an approximate method, K^o is determined by extrapolation to zero ionic strength and the activity coefficients calculated from the relation(for symmetrical electrolytes)

$$K^{o} = K.f^{2} .$$

A relationship, which is assumed to hold for all electrolytes of the same charge type, is established empirically between the ionic strength and the activity coefficient determined in this way.

The application of this method to solutions of 1:1 electrolytes reveals some anomalies. The ionic strengths of the solutions listed in the second table in the paper not only differ from the ionic strengths given for the same solutions in the third table, but are greater than the molarities of the solutions, which is absurd. Moreover, the mean ionic activity coefficients calculated in this way are smaller than literature values(33) for the stoichiometric activity coefficients, which again is absurd.

Frei's dissociation constants for tartaric acid and stability constants for sodium tartrate complexes were calculated by using the above relationship between I and f, successive approximations being made to the ionic strength until constant values of f were obtained. For comparison, calculations using the Davies equation were performed here on some of the data. The first dissociation constant of d-tartaric acid was calculated from pH measurements of tartaric acid solutions of a range of concentrations (0.005 - 2.0M), neglecting the effects of the second dissociation.

The results, using both Frei's method and the Davies equation (b = 0.2), are shown in Table 5. The average of the recalculated constants gives pKa_1 = 3.04, which is in better agreement with literature values (Table 1) than Frei's figure. Although the concentration of the A^{2-} species is negligible with respect to the total acid concentration, relative to the concentration of the protonated anion HA^- it is not, e.g. in 0.01M solution A/Ta - 10^{-5} and A/HA - $2x10^{-2}$. Assuming a value for Ka_2 ($4.3x10^{-5}$ mole $litre^{-1}$) and allowing for A^{2-} in the calculations produces a value of 8.61 mole $litre^{-1}$ from the data at 0.01M.

Table 5

The first dissociation constant of d-tartaric acid at 20°C

		Frei			Davies		
M	pH	10^3I	f	10^3Ka_1	10^3I	f	10^4Ka_1
0.005	2.77	2.65	0.644	1.23	1.78	0.954	8.95
0.010	2.59	4.76	0.541	1.26	2.72	0.944	9.08
0.015	2.49	6.54	0.496	1.24	3.45	0.938	9.07
0.020	2.42	8.02	0.473	1.21	4.08	0.933	9.07
0.025	2.36	9.62	0.455	1.24	4.70	0.929	9.39

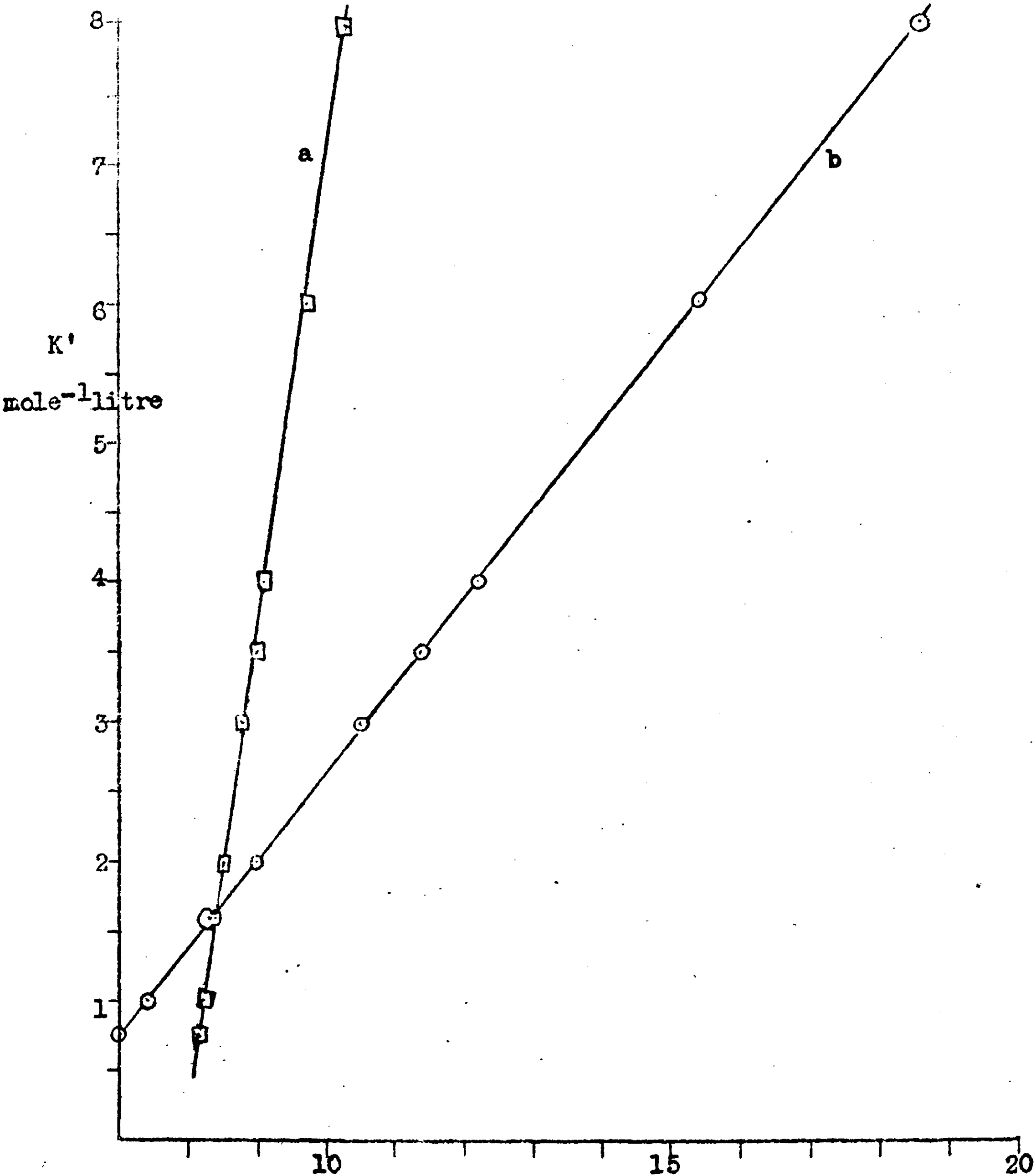

Fig. 3 Recalculation of Frei's Data, Using the Davies Equation.
a) half-neutralised b) three quarters neutralised .

Frei has calculated the second dissociation constant of tartaric acid from a similar series of measurements with three quarters neutralised acid and the stability constants of sodium tartrate from measurements with one quarter ($K' = Ka_2.K_{111}$) and one half(K_{101}) neutralised acid. Frei calculated activity coefficients as described above and obtained the results $K_{101} = 96.2$ mole^{-1} litre and $K' = 29.2$ mole^{-1} litre. Frei's data were recalculated using the method of Section 3. IIb, activity coefficients being calculated with Eqn(2.13). ($a = 7.0, b = 0.2$). Bates and Canham's(1) values of the dissociation constants of tartaric acid were used. The calculated value of K_{101} for both the half and three quarters neutralised series was a linear function of the trial value of K', as illustrated in Fig(3). The value of K' which produced identical values of K_{101} for both series of measurements was selected as the "best". This gives

$K' = 1.65$ mole^{-1} litre and $K_{101} = 8.4$ mole^{-1}litre.

The standard deviations in K_{101} for the two series of measurements are 1.7 (three quarters neutralised) and 4.7 (half neutralised). Correction of the values obtained at 25°C in 0.2M medium(Chapter 5) to infinite dilution by means of the Davies(31) Equation($b = 0.3$) yields the values

$K' = 1.6$ mole^{-1}litre and $K_{101} = 6.5$ mole^{-1}litre, which are in good agreement with the recalculated values from Frei's data at 20°C. The stability constants of sodium tartrate complexes from various sources are summarised in Table 6.

Table 6

Stability Constants of Sodium - Tartrate Complexes

T^oC	medium	$K'(\text{mole}^{-1}\text{l.})$	$K_{101}(\text{mole}^{-1}\text{l.})$	ref.
20	0 corr.	29.2	96.2	(6)
20	0 corr.	1.7	8.4	(6)+(2)
25	0 corr	1.6	6.5	(2)
25	0.2M Me_4NCl	0.9	2.0	(2)
25	0.2M Me_4NBr	1.6	3.6	(17)

It should be noted that Frei's results were obtained in the concentration range 0.005M-2.0M, within which the total water concentration is not even approximately constant. It may be calculated from the density data(34) that the water concentrations in 0.005, 0.1 and 1.0M tartaric acid solutions are 55.37, 54.93 and 50.76M respectively. In these circumstances one would expect conventional equilibrium constants to show a drift as the concentration changed, which is not the case with Frei's own calculations. The data which has been recalculated in the present work was taken from the range up to 0.1M.

IV. Prediction of Apparent pK Values

Using the relationships developed in Section 3.XIb between the true and apparent values of the dissociation constants it is possible to predict the apparent pK values of tartaric acid in the presence of sodium or potassium. The data and stability constants of the two previous chapters have been used. The predictions are summarised in Table 7.

Table 7

Apparent pKs for tartaric acid in complexing media.

Run	Ion	10^2Tm(M)	pK_1(calc)	pK_1(obs)	pK_2(calc)	pK_2(obs)
Na.1	Na^+	2.9	2.80	2.80	3.92	3.92
Na.2	Na^+	10.4	2.78	2.77	3.89	3.89
Na.3	Na^+	2.0	2.80	2.77	3.92	3.92
Na.4	Na^+	2.0	2.80	2.78	3.92	3.88
K.1	K^+	2.0	2.81	2.79	3.93	3.92

It should be noted that the metal concentrations are fairly low in the above examples and are only roughly constant (see Appendices 1b and 1c). The values of Tm in Table 7 are median values. In runs Na.1 and Na.2 the concentrations are slowly increasing, while in the others Tm decreases.

In these circumstances, the agreement between observed and calculated values is quite good.

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Chapter 8

Lanthanum Tartrate Complexes

I. Introduction

Extensive reviews of rare earth complexing have recently been published (1,2) and a brief review of tartrate complexes (3). Rare earth tartrates have been touched upon by Ryabchikov and Korchemnaya (4) in their review covering mainly Russian work.

Pastorek (5) has reported infrared spectra and thermal analyses for the following solid compounds prepared from alkaline solution: $LaT'.4H_2O$, $La_4T''_3.14H_2O$, $KLaT''.3H_2O$, $K_2LaT''OH.4H_2O$, $K_2LaTT'.4H_2O$, $K_3LaT'_2.4H_2O$, $K_4LaT'T''.5H_2O$, where $T = C_4H_4O_6{}^{2-}$, $T' = C_4H_3O_6{}^{3-}$ and $T'' = C_4H_2O_6{}^{4-}$. Davidenko (6) reports the solid compounds $LaT'.3H_2O$ and $La_2T_3.9H_2O$ and also the following species: LaT^+, $LaT_2{}^-$, $LaT'T^{2-}$ and $LaT'_2{}^{3-}$. From solubility measurements Davidenko postulates the complexes $La(OH)T_2{}^{2-}$ and $La(OH)_2T_2{}^{3-}$. Shevchenko(7) has recorded the infrared spectrum of $La_2T_3.9H_2O$. In contrast to the variety of species above, Zvayagintsov and Tikhonov(8) and Katzin and Barnett(9) find from spectroscopic studies that only one complex is present in the alkaline solution for the tartrates of praseodymium, neodymium and erbium. Gallet and Pâris(100) have studied cerous and dysprosium tartrate by means of thermometric titrations and found three complexes of the type LnT, Ln_2T_3 and LnT_2.

Work on lanthanide Tartrates in acid solution is summarised in Table 1.

Table 1 - Stability Constants of Lanthanide Tartrate Complexes

Metal	Ligand	Method	T°C	Medium	$\log K_{101}$	$\log K_{102}$	logK'	ref.
La[1]	dl	dis	25	0.0597($NaClO_4$)	3.75	6.02		(10)
La[2]	dl	H^+-gl	20	0.1(KNO_3)	3.46±0.45	5.52±0.45		(11)
La		dis	25	1($NaClO_4$)	2.08			(12)
La	d?	H	25	var			2.5	(13)
La[3]	d?	H	25	var	3.68	6.37	6.32 (K_{201})	(14)
La		emf			3.06	4.25		(15)
La[4]	?	H^+-gl	23 -25	0.2(KCl)	3.10			(16)
La	?	sol			2.36	6.10		(6)
La	d	H^+-gl	25	0.2	3.06		1.19	(17)
Pr		H^+-gl	20	var	4.77			(18)
Eu		dis	20	0.1 NH_4Cl		6.79		(19)
Eu[5]	d	tp	25	0.1($NaNO_3$)	6.11	9.34		(20)
Ce	d	H	25	0.3			2.45	(21)
Y	d?	H	25	var	4.07	6.89	2.82	(22)
Eu[6]	dl	dis	25	0.0597($NaClO_4$)	4.07	7.18		(23)
	d	dis	25	0.0597($NaClO_4$)	4.07	7.16		
	meso	dis	25	0.0597($NaClO_4$)	4.78	7.94		

Notes: The following metals have also been studied 1) Ce, Pm, Tm, Y. 2) Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y. 3) Ce. 4) Ce, Eu. 5) Ce. 6) Tb.

Mattern's(12) figure is based on a single experimental measurement and cannot be regarded as reliable. The work by Pastorek and Březina (13,14,22) ignores activity coefficients without maintaining a constant ionic strength, which must lead to considerable errors with highly charged ions. Moreover, their calculations are based on the premise that only one complex is present in significant amounts for a given metal: ligand ratio, which is not borne out by any of the other work. Reservations about Wu and Hsu's(17) results are the same as those set out in Section 7.IIIb. The constants quoted are fairly scattered, particularly the second consecutive constant $k_{102} = K_{102}/K_{101}$.

II. Choice of Ionic Medium

For the reasons given in the previous four chapters, the presence of tartaric acid precludes the use of the customary sodium or potassium salt media and therefore a tetramethylammonium salt was chosen. For similar reasons, it is desirable that the anion of the medium should not form complexes with lanthanum ions and the three commonest medium anions, chloride, perchlorate and nitrate were compared in this respect. Stability constants have been reported for the chloride and nitrate complexes of many of the rare earth elements, principally lanthanum, cerium and europium. Constants have also been quoted for cerous perchlorate complexes. The constants for the lanthanum and cerous complexes are listed in Table 2.

For the seven lanthanides for which comparison in the same conditions can be made, the chloride complex was found to be less stable than the nitrate complex in all determinations except one. Most of the constants were obtained by distribution methods at high ionic strengths where the composition of the medium varied considerably; it is likely, therefore, that the reported constants include the effects of activity coefficient variations caused by specific ion interactions. With such unstable complexes, the contribution of such effects to the apparent constants may be considerable. Knoeck(24) has obtained infra-red and Raman spectroscopic evidence for the species $LaNO_3^{2+}$ and has determined its stability constant in a 0.1M medium. Knoeck states that the constant for a possible chloride complex must be much smaller. Garnsey and Ebdon(25) have made ultrasonic measurements on the nitrates of a number of lanthanides, including lanthanum, and conclude that inner-sphere complexing occurs, calculating the stability constants

Table 2 - lanthanum and cerous complexes

T°C.	medium	K_{LnCl} mole^{-1}l.	K_{LnNO_3} mole^{-1}l.	K_{LnClO_4} mole^{-1}l.	method	ref.
Lanthanum						
22	1.0($HClO_4$)	0.9	1.3	-	dis	(26)
25	4.0 $NaClO_4$	1.7	-	-	dis	(27)
?	1.0	0.7	-	-	?	(28)
?	0.1(KCl)	-	29	-	NO_3^- sel	(24)
25	1.0($NaClO_4$)	0.75	0.55	0.51($LaClO_3$)	dis	(12)
Cerous						
22	1.0($HClO_4$)	0.9	1.3	-	dis	(26)
26.6	1.14(ClO_4)	-	-	1.2	sp	(29)
26.6	5.11(ClO_4)	-	-	0.4	sp	(29)
30	1.0($NaClO_4$)	-	2.9	-	dil	(30)
25	0 corr	-	-	4.4	sp	(31)
25		1.5	2.6	-	act/cix	(32)
25	1 H(ClO_4)	0.8	1.63	-	dis	(33,34)

for the $NdNO_3^{2+}$ and $GdNO_3^{2+}$ species. The same authors studied neodymium and gadolinium chlorides and perchlorates and found no absorption in the range measured, indicating either that the concentration of inner sphere complexes is very low or that the volume change is very small. It is unlikely that the absorption would lie outwith the range studied.

Robinson and Stokes(35) state that conductivity of lanthanum chloride solutions obeys the Onsager limiting law up to 0.001N and then deviates from it in the manner of unassociated, e.g. sodium chloride, rather than associated, e.g. cadmium sulphate, electrolytes. The evidence for perchlorate complexing with the lanthanides is slight, although complexes have been reported(36) with a number of other metal ions. Krumholtz(37) has interpreted the uv absorption spectra of Nd^{3+} in $HClO_4$ solutions in terms of ion pairing, but Karraker(38) in his extensive studies of the same phenomena in chloride and perchlorate solutions finds the explanation in a change in coordination number at higher concentrations. Ion exchange studies(39) on lanthanide and actinide ions in HCl solutions show that the affinity of a cation exchanger for lanthanides increases with the concentration of HCl, in contrast to the behaviour with the trivalent actinides, which form chloro-complexes(36,40). This difference between the two groups of ions has been used to effect group separation by ion exchange (39,41-43) and solvent extraction(45). Moeller and Brantley(44) have reported that the presence of HCl or NH_4Cl in light lanthanide chloride solutions up to Cl:Ln ratios of 10:1 has no effect on the absorption spectra, and Freed and Jacobson(46) report no change in the line splitting for $EuCl_3$ solutions over a concentration range 1.5M - 0.0007M, indicating that these systems are free of complexing.

The choice of the anion is also affected by the cation of the background medium, in this case tetramethylammonium ion. Since Diamond's paper(47) much has been written on the effect of quaternary ammonium salts on water structure and the ion-pairing of such salts; the position of tetramethylammonium ion, however, is not clearly defined. Wood and Anderson(48) and Lee and Hyne(49) classify it as a structure breaking, i.e. caesium-like, ion, rather than a structure maker like its higher homologues. Quintin and Justice(50) have found evidence for some form of association between Me_4N^+ and bromide and stability constants have been calculated by Wirth(51) for the bromide complex and by Levien (52) for the bromide and iodide complexes. Fernandez-Prini(53) has calculated a stability constant for the chloride complex. Evans and Kay(54) do not invoke ion-pairing to explain their conductivity data and Azzarri and Kraus(55), also from conductivity measurements, calculate a stability constant for the iodide complex but conclude that tetramethylammonium chloride is probably unassociated in water. Ultrasonic absorption measurements have also been interpreted in terms of ion-pairing(56-58), but more recent and extensive studies(59) contradict this. The larger the anion, the greater the tendency for association, which would favour the selection of chloride rather than perchlorate. As far as lanthanum ion is concerned, the difference between the two is probably marginal and the greater ease of handling of the chlorides is a further advantage. The solubility of tetramethylammonium perchlorate solutions(60) is too low for an effective background medium and Me_4NCl solutions were used.

Experimental

III. Reagents Tetramethylammonium chloride, potassium chloride, potassium nitrate, potassium hydrogen phthalate and constant-boiling hydrochloric acid were prepared as in Section 2.IV and d-tartaric acid and tetramethylammonium hydroxide as in Section 4.V.

Lanthanum chloride solutions were prepared by dissolving lanthanum oxide (Johnson, Matthey & Co., Ltd "specpure") in a small excess of a diluted constant-boiling hydrochloric acid. The oxide dissolved slowly and the solution was left overnight before being either made up to the mark(molar solutions) or diluted and weighed(molal solutions). Before use the oxide was ignited at 1000°C in an electric muffle furnace, in order to decompose any lanthanum carbonate present. The oxide was contained in a porcelain crucible, as recommended by Biedermann and Ciavatta(61), since it was found that the oxide acquired a pink colour when a platinum crucible was used. The chloride content of the solution was checked gravimetrically by precipitation as AgCl, the excess acid by potentiometric titration with standard Me_4NOH and the lanthanum content gravimetrically as the oxalate and as the oxinate. The theoretical composition of the solution was confirmed.

Laboratory reagent grade lanthanum nitrate (B.D.H.Ltd) was used without further purification.

Sodium hydroxide solution was prepared from ampoules of B.D.H. Volumetric reagent.

IV. Apparatus All graduated glassware was of grade A standard and pipettes and burettes were further checked by calibration with distilled water at 25°C. When molal units were used titrations were performed with a weight burette. Glassware was cleaned in chromic acid and/or'pyroneg' (an alkaline detergent) solution rinsed with distilled water and dried in an oven, or, in the case of graduated glassware, with AnalaR acetone.

Weighings of more than 200g were done on a Sartorius chemical balance using Oertling stainless steel weights. A Stanton 'Unimatic' single-pan electric balance was used for smaller weights.

The apparatus for the potentiometric measurements has already been described in Section 2.V.

V. pH Titrations in Constant Background Media

A working solution of lanthanum chloride was prepared by diluting the stock solution, with addition of Me_4NCl to make the total chloride concentration up to the desired level, q M.

The titrations were performed in two ways. (a) Test solutions were made up by pipetting 2q M Me_4NCl, distilled water, tartaric acid solution and lanthanum chloride solution into the cell illustrated in Fig(2.3), such that the chloride concentration was q M. Me_4NOH solution was added from a burette and approximately 2q M Me_4NCl (adjusted for the concentration of chloride in the base) added from a second burette, so that the chloride concentration was constant.

(b) Test solutions were made up by pipetting 2q M Me_4NCl, distilled water and tartaric acid solution into the cell shown in Fig(2.3). The acid was partly neutralised by the addition of Me_4NOH from a burette. The total chloride concentration was q M. Successive volumes of lanthanum chloride solution were added from a burette.

Nitrogen from a cylinder (British Oxygen Co. Ltd) was bubbled through the solution to prevent the absorption of carbon dioxide and to effect mixing. The nitrogen passed through a train of presaturators

q M HCl, q M NaOH, q M Me_4NCl, q M Me_4NCl

before entering the reaction vessel. The details of e.m.f. measurement and the correction for liquid junction potentials have been given in Section 2.Va-c. Measurements were made with phthalate buffer before and after each titration.
The titration cell was maintained at 25°C, which was also the temperature of the room.

The data for the three runs in 0.1M medium (glass electrode A) are given in Tables La.1 - La.3, for the seven runs in 0.2M medium (glass electrode Y) in Tables La.4 - La.10 and for the four runs in 0.4M medium (glass electrode A) in Tables La.11 - La.14. These tables are in Appendix 1d.

VI. pH Titrations in Dilute Solution

Titrations were performed in two ways: (a) test solutions were made up from weighed portions of tartaric acid, distilled water and lanthanum chloride solution and successive additions of tetramethylammonium hydroxide solution made from a weight burette, (b) test solutions were made up from weighed portions of tartaric acid, distilled water and tetramethylammonium hydroxide solution and additions of lanthanum chloride solution made from a weight burette. All weights were corrected for the buoyancy of air. Throughout the titration nitrogen was passed to prevent the absorption of carbon dioxide and to mix the solution. Before entering the titration cell, the nitrogen passed through a series of presaturators

0.1M HCl, 0.1M NaOH, distilled water, distilled water, the last two stages of which were at the same temperature as the cell. The details of e.m.f. measurement and temperature control have been given in Section 2.V.

The data for the runs at 15°, 25° and 35° are given in Tables La.15-La.19, La.20-La.23 and La.24-La.27 respectively in Appendix 1d.

Readings were taken 5 minutes after the addition of the titrant and checked after a further 5 - 10 minutes. Usually there was no difference, but, if there was, readings were taken until constancy was attained. In some cases the readings were checked over a period of 30 - 60 minutes and the drift in the readings found to be negligible.
Březina, Rosický and Pastorek(21) report that the pH is constant over 24 hours in acid cerous tartrate solutions.

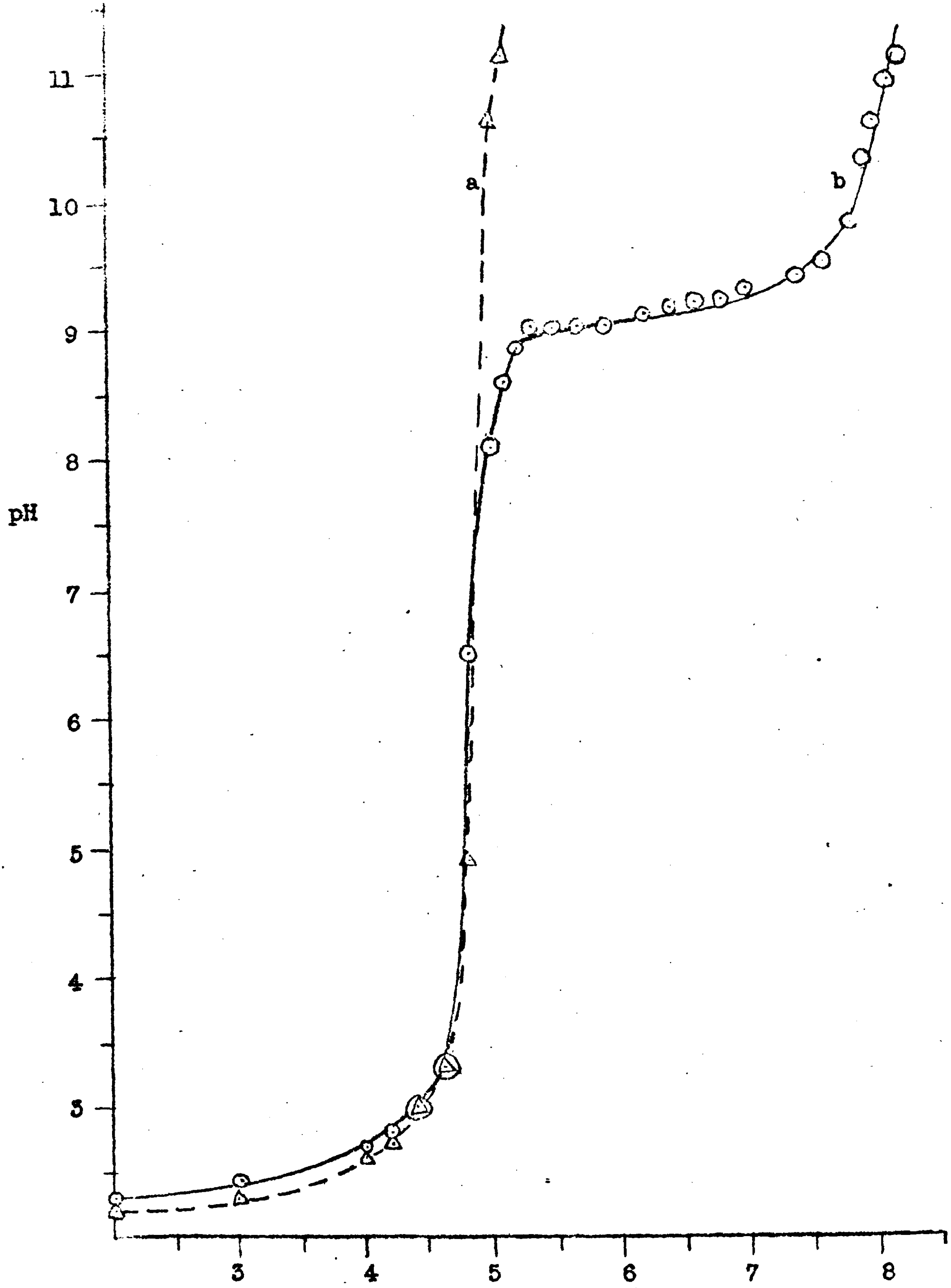

Fig. 1 Titration of a) HCl b) HCl and $La(NO_3)_3$ with NaOH.

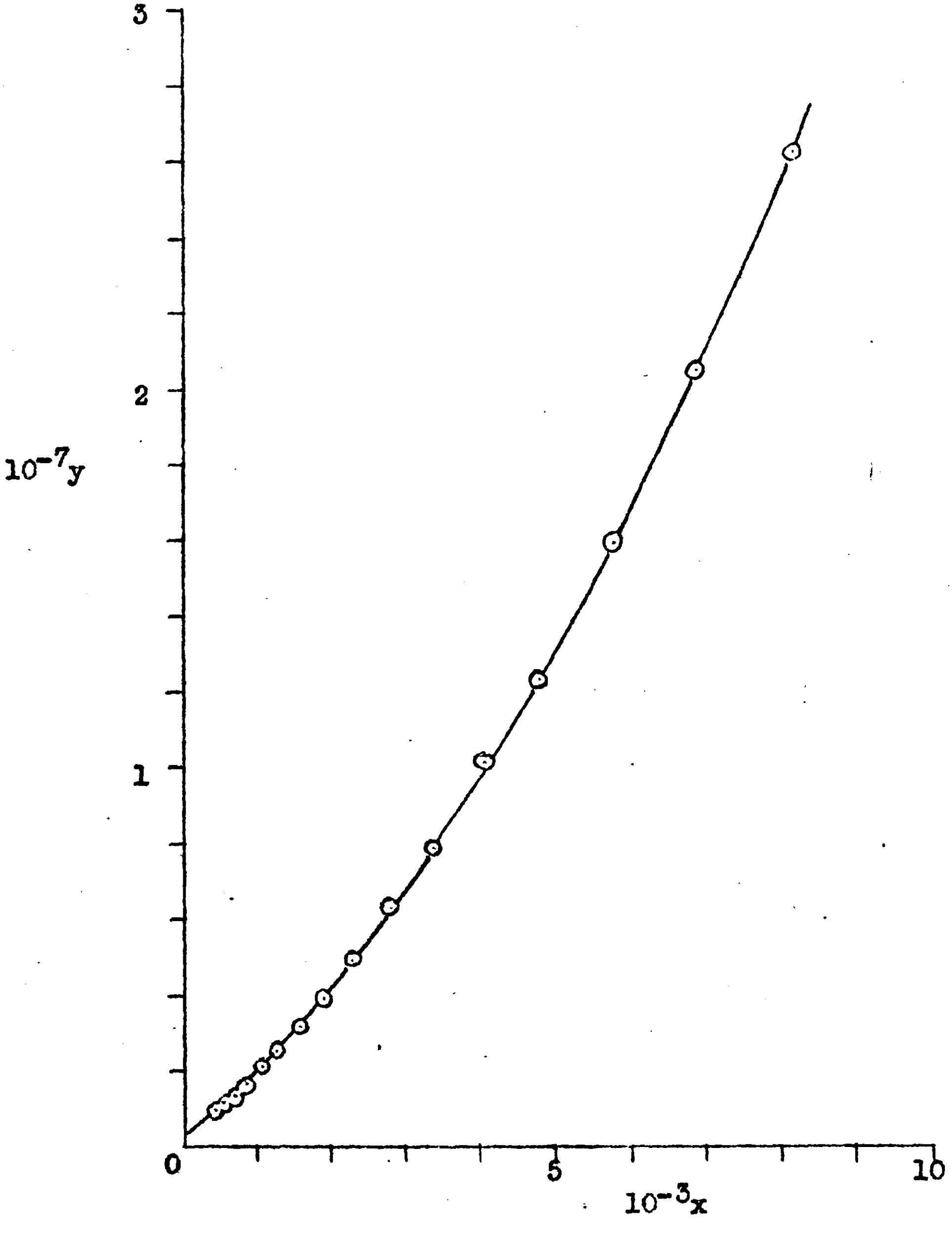

Fig. 2 Gelles - Nancollas Plot for Lanthanum Tartrate at 25°C. in 0.2M Medium. Data from Run La. 4.

Calculation

VII. (a) In order to keep the calculations simple, it is desirable that no hydroxy-complexes are formed. Biedermann and Ciavatta(61) report that hydrolysis of La^{3+} does not occur below pH 6.5 and a check was made by titrating solutions made up from 5 ml 0.98M HCl and either 25ml distilled water or 20ml distilled water and 5ml 0.025M lanthanum nitrate solution with 0.1M NaOH. The two titration curves can be seen in Fig(1). As the titrations in this work rarely reach pH 5, hydrolysis of the metal ion presents no problem.

With the coexistence of both tartrate and hydrogen tartrate ions in appreciable quantities, two distinct series of lanthanum complexes are possible, together with a system of mixed ligand complexes. The identification of the species present is greatly eased by the use of a constant ionic medium, since activity coefficient effects could hinder the resolution of the various equilibria, especially when a highly charged ion like La^{3+} is involved. The calculations were therefore first carried out on data collected in a 0.2M $(Me_4N)Cl$ medium, further data being obtained in 0.1M and 0.4M media.

The data were first treated as an MA-MA_2 system by the method of Gelles and Nancollas(Section 3.I). A typical plot, using the data of Run La.4 is shown in Fig(2). The pronounced upward curvature in the low pH region indicates that protonated complexes are also formed. An estimate of K_{101} was obtained from points in the high pH region and used to calculate K_{111} by the method described in Section 3.IIa, using points in the low pH region. Trial values of K_{101} produced a distinct pattern in the behaviour of the roots $R_1 = (-r + (r^2-4q.s)^{\frac{1}{2}}/2q$ and $R_2 = (-r - (r^2-4q.s)^{\frac{1}{2}})/2q$ of the equation $q.HA^2 + r.HA + s = 0$ as to whether they were physically meaningful("yes") or not ("no"). The pattern is summarised in Table 3.

Table 3

K_{101}(trial)	R_1		R_2	
	low pH	high pH	low pH	high pH
too low	no	no	yes	no
approx. correct	no	yes	yes	no
too high	no	yes	no	no

With a good estimate of K_{101}, at least one physically meaningful root was obtained for each data point, although only rarely did both roots meet this condition. As the trial value of K_{101} deviated more from the true value, there appeared a range of intermediate pH for which neither root was meaningful, and, as the trial constant became even worse, one root never had any meaning. It is not suggested that this behaviour is typical of this method of calculation, since the validity of the roots depends on the stability constants of the complexes,

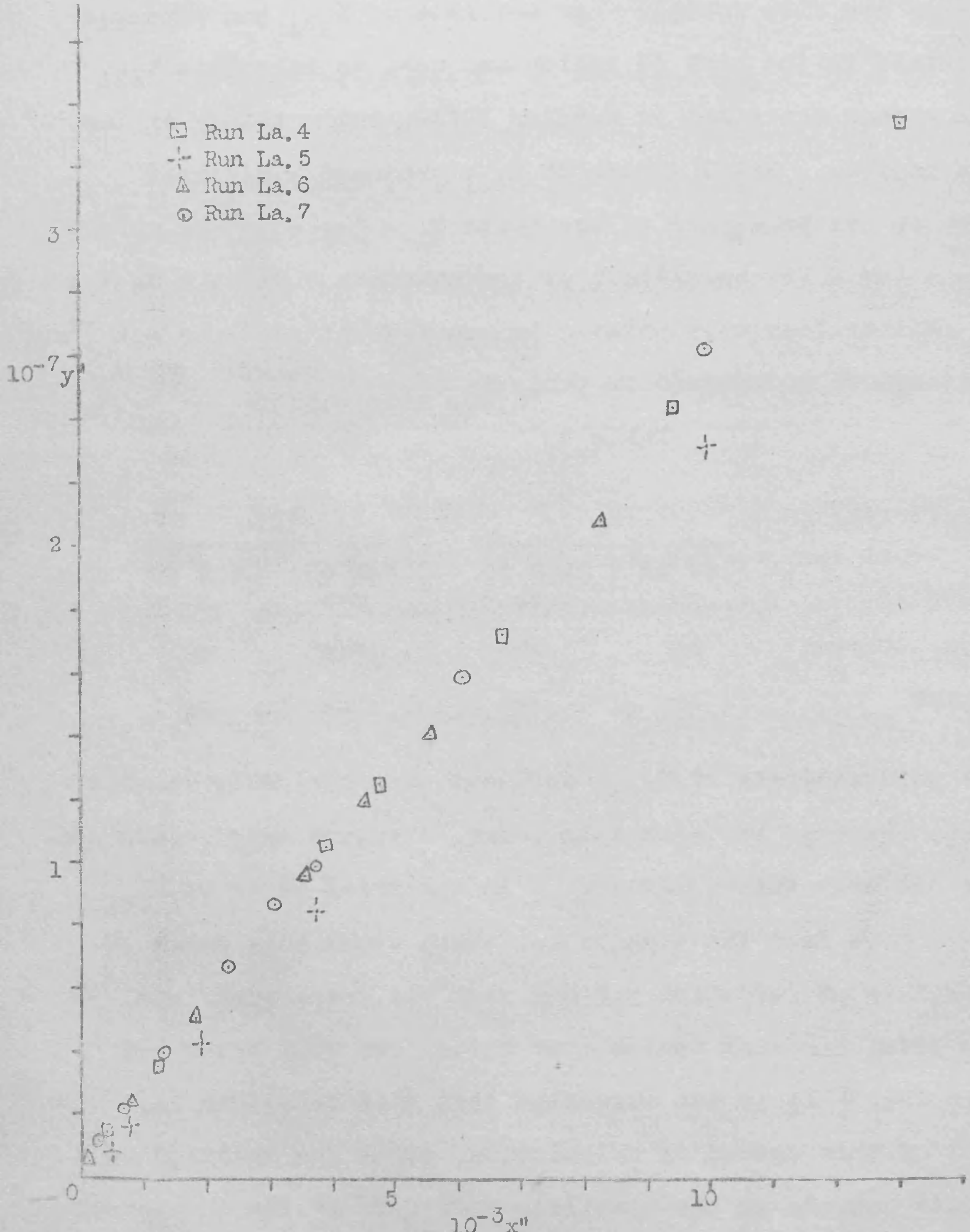

Fig. 3 Lanthanum Tartrate in 0.2M $(Me_4N)Cl$ at 25°C.

the dissociation constants of the acid and the concentrations of the reagents.

The value of K_{111} obtained by the above method was used as a starting value in determining K_{101}, K_{102} and K_{111} by the method of Section 3.III. Linear plots were obtained for all runs and gave good agreement except for Run La.9, in which there was a large ligand-metal ratio. A plot showing points selected at random from the individual runs is shown in Fig(3).

Since the data cover a wide range of pH, metal-ligand ratios and absolute metal and ligand concentrations and good agreement is found between the various runs, with the exception noted above, it is concluded that the system can be treated as consisting of three complexes, MA^+, MA_2^- and MHA^{2+} , in most of the conditions under study. Measurements in 0.1M and 0.4M media lead to the same conclusion. Further checks were made, however, to see if the system could be explained by any other combination of complexes.

The data were tested for the presence of the dimer$(MA)_2$ in addition to the MA complex itself by the method described in Section 3.IV. Plots, corresponding to Eqns 3.26a and 3.26b, are shown in Figs(4a) and (4b) for Run La.4. The curvature is the result of the formation of the protonated

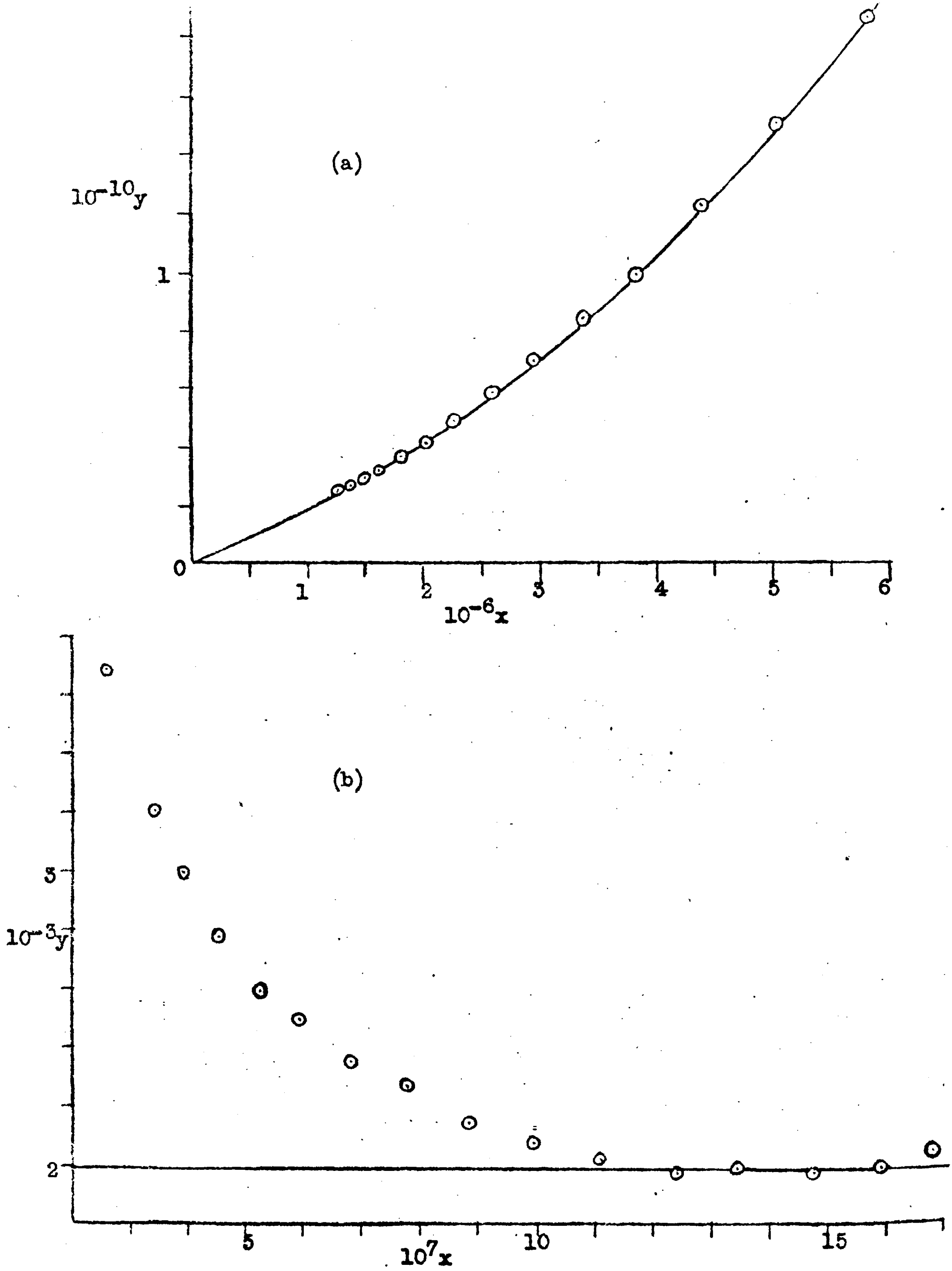

Fig.4 Lanthanum Tartrate in 0.2M $(Me_4N)Cl$ at 25°C.
Plots of (a) Eqn 3.26a (b) Eqn 3.26b for dimer formation

species MHA. Neither Run La.4 nor any other run suggested the presence of the dinuclear species.

The data were also treated as an $MA-MA_2-MHA-M_2A_3$ system by the procedure given in Section 3.VIb. The values of K_{203} obtained were generally negative, unless a deliberately low estimate was made to K_{101}, in which case the values of K_{203} showed a large drift within any given run and very large differences between different runs. Moreover, with such a low approximation to K_{101}, the data requires that more neutral complex be formed at low pH than in the higher pH region, which is the opposite of what would be expected. The neutral species M_2A_3 has, then, also been discounted.

The data were treated as an $MA-MA_2-MA_3$ system using the method of Section 3.V to determine the stability constants, which, however, always turned out negative. MA_3 complexing was assumed to be negligible.

The possible existence of the neutral species MHA_2 was also investigated. Even neglecting the MA_2^- complex by setting K_{102} to zero, the method of Section 3.VIa produced no evidence for the presence of the neutral complex, except for Run La.9, in which the conditions are particularly favourable.

The program GAUSS G (viz. Section 3.VII) was used to refine the stability constants for each run in turn. Three constants, K_{101}· K_{102} and K_{111} were refined simultaneously. When a fourth constant, K_{112}, calculated from the data of Run La.9 was included, neither all four constants, nor any three of them, could ~~not~~ be refined simultaneously, since absurdly large shifts in the constants occurred. The constants could be shifted to very large or negative powers of ten, which, on a subsequent cycle of the program, frequently produced a catastrophic run-time failure. Two, but not any two, of the four could be refined, but the agreement between different runs was relatively poor and the standard error, even with one degree of freedom more, was larger than was obtained with three complexes only. The same was true at all three ionic strengths when an estimate was made to K_{112}. The results for the refinement of three complexes are given in Table 4. The parentheses ( ) in the results for the 0.4M medium indicate that that particular constant was not refined simultaneously with the others, but was given the mean value for the other runs. There is therefore an element of iteration in these results. By "mean" is meant the weighted mean.

Stability constants for some runs calculated by the method of Section 3.III are given in Table 5 for comparison. Refinement could have proceeded further, especially for the 0.1M runs, but was terminated to save computing time. The agreement is nevertheless quite good.

Table 4

The Stability Constants of Lanthanum Tartrate Complexes.

Run	$\log K_{101}$	$10^{3}\sigma_{\log K_{101}}$	$\log K_{102}$	$10^{2}\sigma_{\log K_{102}}$	$\log K_{111}$	$10^{2}\sigma_{\log K_{111}}$		
<u>0.1M medium</u>								
La. 1	3.733	3.9	6.376	4.4	6.533	2.0		
La. 2	3.649	2.9	6.120	0.8	6.380	1.0		
La. 3	3.658	6.5	6.266	7.8	6.395	5.5		
mean	3.676	2.2	6.128	0.7	6.409	0.9		
<u>0.2M medium</u>								
La. 4	3.399	7.8	5.729	10.4	6.240	3.3		
La. 5	3.367	33.8	5.054	69.2	5.923	32.4		
La. 6	3.403	10.4	5.546	5.9	6.139	53.3		
La. 7	3.419	7.2	5.675	6.3	6.203	2.7		
La. 8	3.414	4.9	5.648	4.6	6.149	4.7		
La.10	3.420	108.5	5.716	10.2	6.123	38.4		
mean	3.410	3.4	5.640	2.9	6.206	1.9	/$\log K_{112}$	$10^{2}\sigma_{\log K_{112}}$
La. 9	( )		( )		6.22	5.9	9.0	3.5
<u>0.4M medium</u>								
La.11	3.090	2.4	5.486	2.6	5.848	1.0		
La.12	3.157	6.4	5.764	3.2	6.005	5.5		
La.13	3.119	6.3	5.541	1.4	( )			
La.14	3.116	2.3	( )		5.769	1.3		
mean	3.108	1.6	5.559	1.1	5.820	0.8		

Table 5

Run	$\log K_{101}$	$\log K_{102}$	$\log K_{111}$
La. 1	3.723	6.468	6.557
La. 3	3.652	6.258	6.358
La. 4	3.398	5.697	6.233
La. 7	3.407	5.712	6.204
La.11	3.076	5.580	5.873
La.12	3.153	5.703	5.915

A further check was made on the constants by using them, along with the experimental total acid, total metal and total base, to calculate the pH at each point in the titration. The method has been described in Section 3.XIa. The calculated and observed pHs are listed in Table 6 for Run La.4.

Table 6

pH obs	pH calc	pH obs	pH calc	pH obs	pH calc
2.514	2.515	2.904	2.905	3.393	3.395
2.613	2.614	2.971	2.973	3.510	3.509
2.666	2.666	3.043	3.045	3.645	3.641
2.721	2.721	3.120	3.121	3.813	3.805
2.780	2.779	3.203	3.204	4.026	4.028
2.840	2.841	3.295	3.295		

The agreement for this typical run is very good.

The effects of any possible complexing between lanthanum and the chloride ions of the medium were tested by recalculating the data with various values of K_{LaCl}. A summary of the results of these trials is given in Table 7 for Run La.4.

Table 7

K_{LaCl}	$10^{-3}K_{101}$	$10^{-2}K_{102}$	$10^{-3}\sigma_{K_{101}}$	$10^{-2}\sigma_{K_{102}}$	$10^{-3}\sigma_Y$
0.00	3.493	-2.118	1.15	5.10	1.48
0.08	3.485	-2.444	1.21	5.64	1.55
0.13	3.452	-2.456	1.20	5.69	1.56
0.20	3.407	-2.474	1.18	5.75	1.58

This behaviour is typical of other runs. It can be seen that increasing the trial value of K_{LaCl} increases the standard deviations in K_{102} and Y and has little effect on $\sigma_{K_{101}}$ and the value of K_{102} becomes less realistic (no allowance is made for MHA complexing). The effect of any LaCl complexing was neglected in other calculations.

The results were extrapolated to infinite dilution by plotting

$$E_c = \log K_c + r.\frac{A.I^{\frac{1}{2}}}{1+B.a.I^{\frac{1}{2}}} = \log K^o + r.A.B.I$$

against I(cf Section 4.IX), where K_c and K^o are the stability constants at the particular ionic strength I and at infinite dilution respectively, A and B are the Debye-Hückel parameters, a and b

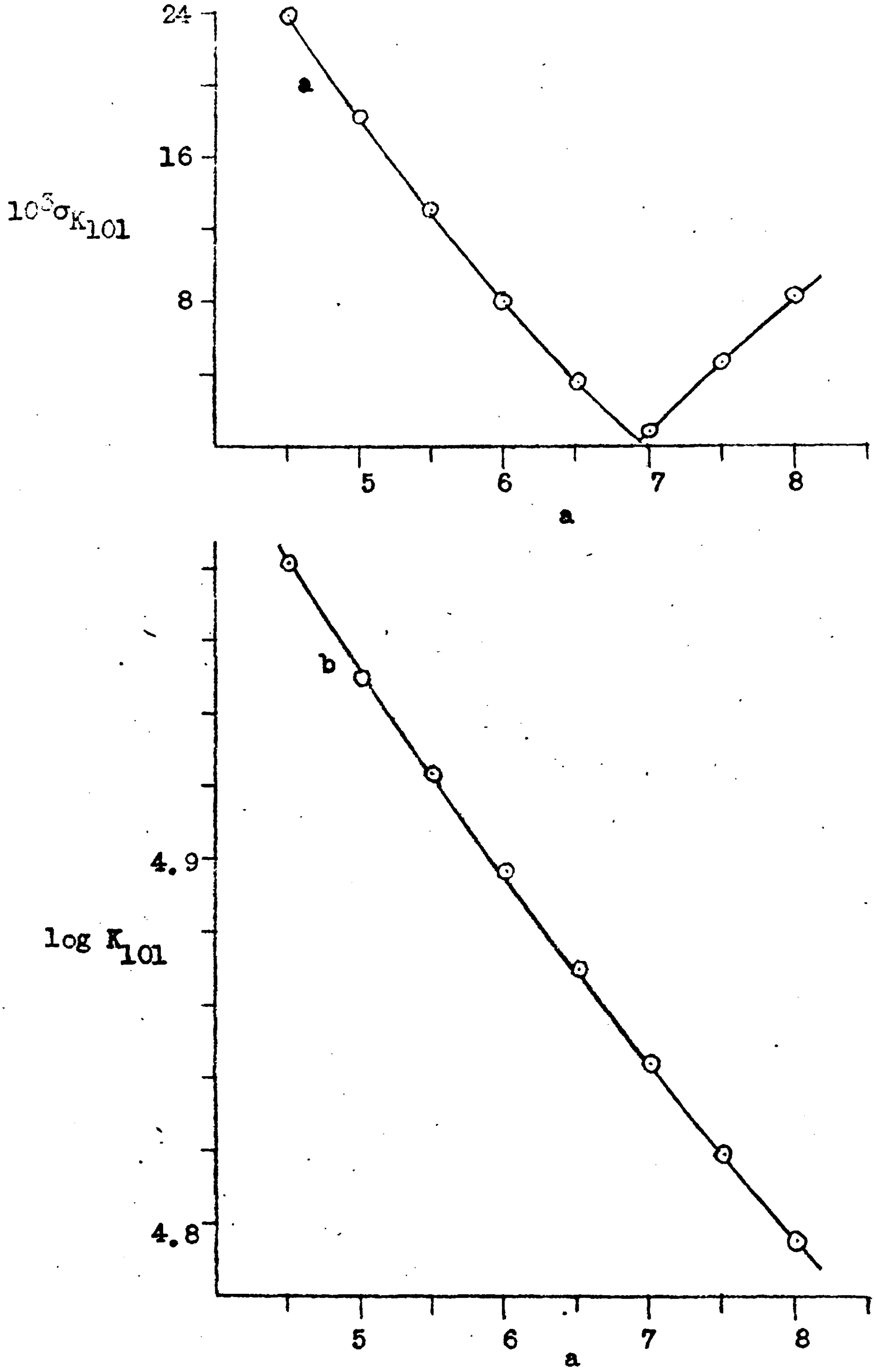

Fig. 5 Effect of parameter a on b) extrapolated value of K_{101} at 25°C for lanthanum tartrate and a) the standard deviation in K_{101}.

are adjustable parameters and r is an integer characteristic of the equilibrium. The values of r for the constants K_{101}, K_{102}, K_{102}/K_{101} and K_{111} are 12, 16, 4 and 10 respectively. Values of E_c are calculated as a is varied systematically and fitted to the equation

$$E_c = p.I + q$$

by the method of least squares. The a-value which leads to the best straight line for the E_c-I plot is assumed to be the correct one. $\log K^o$ is then equal to the corresponding value of q.

Plots of K_{101} and K_{101} against a are shown in Figs 5 a and b respectively. The minimum in the standard deviation occurs at a = 7, which yields a value $\log K^o{}_{101} = 4.844 \pm 0.001$ with the slope b = -0.064. The negative value of b is indicative of some degree of ionic attraction (62) not allowed for in the equilibrium model, most likely a lanthanum - chloride interaction. The standard deviation in K_{102} decreases as a decreases, but does not reach a minimum for positive values of a, which again is an indication of ion association. For K_{111} the minimum in the standard deviation occurs at a = 35, giving $\log K_{111} = 6.946 \pm 0.003$ and b = - 1.81 Such an a-value is unrealistically large and b-value is correspondingly small. In this paragraph, by "standard deviation" is meant the standard deviation in the fit;

no account has been taken of the experimental error in the stability constants. The values of K_{101} are the most accurate of the three sets of constants and it is the extrapolation of these results which is the most significant. If the value a = 7 obtained from K_{101} data is used in the extrapolation of the other constants, we obtain log $K^{o}_{111} = 7.45 \pm 0.06$ with $b = - 0.15$ and log $K^{o}_{102} = 7.5 \pm 0.2$ with $b = 0.03$. These extrapolations would be linear within a 2σ limit, where σ is the standard deviation in the experimental values of the constants at each ionic strength.

(b) Calculations for Runs in Dilute Solution

It is concluded from the results in constant ionic media that only three complexes, of the type MA^{+}, MA_2^{-} and MHA^{2+}, need be considered. Because of the good agreement between the stability constants calculated by the methods of Sections 3.III and 3.VII, it was decided to use only the former, rather than incorporate yet another iterative stage in the already complicated GAUSS G program.

Activity coefficients were calculated using Eqn 1.11, In a mixed electrolyte solution the parameter a has no physical significance (63) and values chosen for a on the basis Bjerrum distance for ion association (21.4 A° for a 3:2

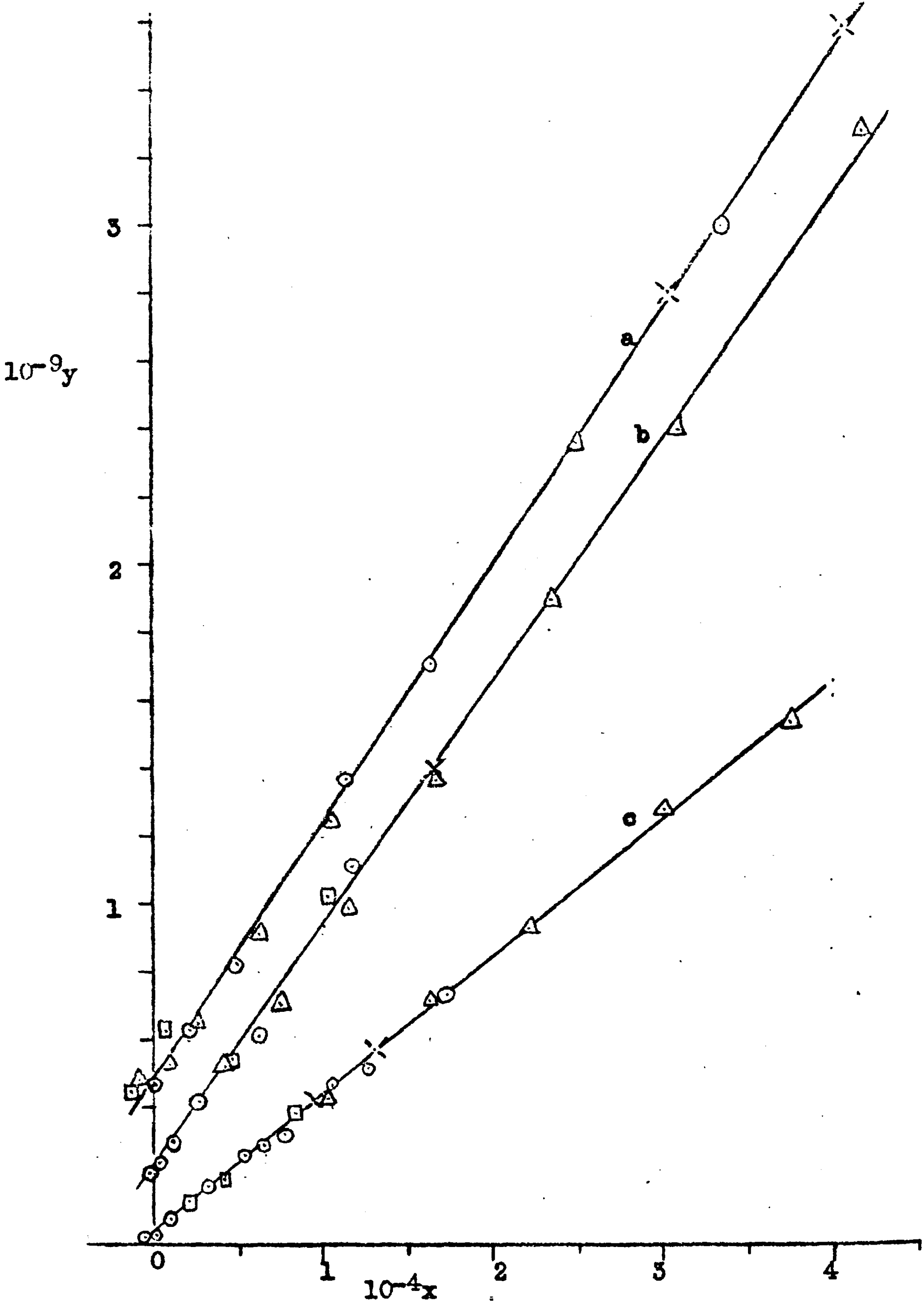

Fig. 6 Thermodynamic Stability Constants of Lanthanum Tartrate

a) 35°C, ordinate displaced 2cm, Runs La. 24 ⊙ , 25 △ , 26 ✕ , 27 ⊡
b) 15°C, ordinate displaced 1cm, Runs La. 15 ✕ , 16 ⊡ , 18 △ , 19 ⊙
c) 25°C, Runs La. 20 ✕ , 21 ⊙ , 22 ⊡ , 23 △
Extreme and alternate points are plotted.

electrolyte in water at 25°) or the sum of the ionic radii plus a number of water molecule radii offer no particular advantage. Fay and Purdie (64) use a = 8.86 and $C' = 0.3Az^2$ in their work on lanthanum sulphate and a = 5.5, C' = 0 have been used to calculate the activity coefficients of lanthanum chloride solutions up to a concentration of 0.03m (35). To conform with the extrapolation of the results in various ionic media, the value 7.0 was used for a. In the absence of of the high background chloride concentration, the conventional Davies (65) value $C' = 0.3Az^2$ was used. The use of these values for a and C' was justified experimentally by the agreement between runs in which the ionic strength covered different ranges, e.g. for the runs at 15°C, I varies from 0.0045 (Run La.17) to 0.013 (Run La.19).

The stability constants were calculated by first obtaining an approximate value of K_{101} by the method of Gelles and Nancollas (Section 3.I) and using it to calculate a rough value of K_{111} (Section 3.II). Individual runs were then treated by the method described in Section 3.III and the average value found for K_{111} at the temperature concerned. This value was used to calculate K_{101} and K_{102} from the combined data at that temperature, including data from runs with too few points for it to be worth calculating K_{111} individually. Random points are plotted in Fig (6).

The stability constants, in molal units, are summarised in Table 8.

Table 8

Thermodynamic Stability Constants of Lanthanum Tartrate Complexes

T^oC	$\log K_{101}$	$\log K_{102}$	$\log K'$
15	4.852 ± 0.003	7.41 ± 0.12	3.10
25	4.604 ± 0.003	7.59 ± 0.04	2.48
35	4.876 ± 0.004	7.93 ± 0.05	2.70

The stability constants were related to the absolute temperature by means of the equation

$$\log K = a + b.T + c.T^2.$$

The coefficients are listed for the three equilibria in Table 9. The coefficients must be viewed with caution as only three points are available for the calculation, but McAuley (66) has tested the coefficients derived from three points in similar circumstances by measurements at additional temperatures and found the fit satisfactory.

Table 9

	a	b	10^3c
K_{101}	235.06	-1.547	2.597
K_{102}	74.39	-0.474	0.840
K'	382.65	-2.530	4.210

The standard entropy change for each reaction was calculated from

$$\Delta S^{o} = R(a + 2bT + 3cT^{2}),$$

whilst the enthalpy and Gibbs energy changes were obtained from Eqns 1.14 and 1.18 respectively. Table 10 summarises these thermodynamic quantities at 25°C

Table 10

Thermodynamic Quantities for Lanthanum - Tartrate Complexing

reaction	$-\Delta G^{o}\times10^{-4}$ j/mole	$\Delta H^{o}\times10^{-4}$ j/mole	ΔS^{o} j/deg/mole
La + A = LaA	2.63(6.28)	0.0(0.0)	94.8(22.6)
La + 2A = LaA_2	4.33(10.4)	4.47(10.7)	295 (70.5)
La + HA = LaHA	1.41(3.38)	0.56(1.3)	66 (16)

The figures in brackets are the corresponding values in c.g.s. units(kcal/mole, kcal/mole and cal/deg/mole respectively).

VIII. Discussion

Comparison of the stability constant of lanthanum tartrate at 25°C and infinite dilution, log K_{101} = 4.604, with that for the succinate in the same conditions (67), log K_{101} = 3.96, shows the increased stability of the tartrate complex caused by the coordination of the α-hydroxyl groups of the tartrate ion. Shevchenko (7) has studied the infra-red absorption spectrum of $La_2(C_4H_4O_6)_3 \cdot 9H_2O$ and found that some of the hydroxyl groups were coordinated and some not.

$PbC_4H_4O_6$, $CdC_4H_4O_6$ and $CoC_4H_4O_6$ exhibit similar behaviour. Grdenic and Kamenar (68) have studied $(NH_4)_2Sb_2(C_4H_4O_6)_2.4H_2O$ by x-ray diffraction and found that both hydroxyl groups coordinate the antimony ion. If the fact of coordination by the hydroxyl group is accepted, the mode of complexing is uncertain. Larsson (69) has studied uranyl glycolate complexes in aqueous solution by infra-red spectrophotometry and reported the coexistence of three types of complexing by glycolate ion:
(a) by the carboxylate group alone, as with acetate
(b) chelation, with the hydroxyl group also complexing the metal ion (c) chelation, with the hydroxyl group hydrogen bonding to a water molecule in the first coordination sphere. It is probable that the coordination in lanthanum-tartrate complexes is similarly varied.

Attempts have been made, e.g. (70,71), to find the denticity of ligands from the formula developed by J. Bjerrum(72), which states that

$$P = S.R.T,$$

where P is the ratio k_n/k_{n+1} of two stepwise thermodynamic stability constants, S is a statistical term depending on the coordination number of the cation and the denticity of the ligand, T is an electrostatic term and R is the "rest effect", a catch-all which includes the effect of such things as quantum-mechanical forces, steric hindrance and ion-dipole interactions. It should be noted that the theory applies only to thermodynamic constants, otherwise an additional factor, which is a function of the ionic strength, must be introduced. The rest effect, R, is commonly taken to equal unity (70), although Bjerrum (72) found that this need not be so in the transition metal ammine complexes. T has been calculated to be about 1.5 for monovalent ligands (70) and 6.5 for divalent ligands (73) in lanthanide complexes. Values of S are summarised in Table 11.

Table 11 - values of the statistical factor S for k_1/k_2

coordination no.	monodentate	bidentate	tridentate	tetradentate
8	2.3	3.5	5.5	4 or 8
9	2.25	3.27	4.9	-

The figures for polydentate ligands are based upon the way coordination sites are occupied in crystals, but in solution the ligand may be able to adapt itself to more awkward situations, with a generally unpredictable effect on S. The situation is further complicated by the possibility that second and subsequent ligands may not use all their coordinating groups, which would diminish S. The value of P found for lanthanum tartrate in this work is 40.7 at 25°, giving $S.R = 6.15$, which is large enough to indicate that tartrate does not act as a bidentate ligand. The evidence is not strong enough to distinguish between the tri- and tetradentate cases. Manning's suggestion (70) that ligands which chelate through coordinated water molecules exhibit a statistical effect which depends only on the number of direct coordinative links is wrong in that a site occupied by a water molecule hydrogen bonded to the ligand is still effectively blocked and the statistics remain the same. Few thermodynamic constants have been obtained for lanthanide complexes and K_{102} has been determined even more rarely. For the lanthanide oxaloacetates at 25°C, P has values in the range 10 - 15(74). At an ionic strength of 0.1 the following P values have been observed (75) for the N-methyl, N-benzyl and C-benzyl derivatives of iminodiacetic acid (IMDA): 20.4, 11.2 and 17 . Also at $I = 0.1$, IMDA itself has $P = 50 - 60$ (76,77) and malic acid (78) has $P = 32.4$. All the data at $I = 0.1$ refer to the lanthanum complexes only. Values of P can be calculated from compilations of stability constants (1,2) for many other ligands in various experimental conditions, but the picture gained thereby is confusing and little weight can be given to conclusions drawn from consideration of P-factors.

Compilations of enthalpy and entropy changes for lanthanide complexing have been published (1,2,79). The data comprise two main bodies: aminopolycarboxylate complexes in 0.1M KNO_3 or

KCl media and monocarboxylic acid complexes in 2M $NaClO_4$ medium. A few thermodynamic quantities have been obtained and these are given in Table 12.

Table 12 - Thermodynamic Properties in 25°C.

Reaction	$-\Delta G^o$ (kcal $mole^{-1}$)	ΔH^o (kcal $mole^{-1}$)	ΔS^o (cal deg $mole^{-1}$)	ref.
La^{3+}+ malonate	6.79	4.8	39	(80)
Gd^{3+}+ malonate	7.32	5.1	42	(80)
Lu^{3+}+ malonate	7.77	5.2	44	(80)
La^{3+}+ $Fe(CN)_6^{3-}$	5.09	2.0	23.9	(81)
La^{3+}+ $Co(CN)_6^{3-}$	5.13	1.33	21.7	(82)

Comparison of figures for lanthanum malonate with those for the tartrate in Table 10 shows that the Gibbs energy changes are quite similar; this is not unusual since Cannan and Kibrick's(83) measurements on the malonates (Mo), succinates (Suc), malates(Ma) and tartrates(Tar) of zinc and alkaline earths show that the order of the stability constants varies with the ionic radius of the metal. For the large barium (1.35A°) and strontium(1.13A°) ions the order is Tar › Ma › Mo › Suc, for calcium(0.99A°) Tar = Ma › Mo › Suc, for zinc(0.74A°) Ma - Mo › Tar › Suc and for magnesium(0.65A°) Mo › Ma › Tar › Suc.

As would be expected, the succinates are always the weakest, but the others occur in any order. It is supposed that the smaller the ion, the more difficult it becomes for the hydroxyl groups on the malate and tartrate ions to participate in coordination, for steric reasons. Any contribution the hydroxyls make to the complexing of such small ions is counteracted by the increased stability of the free anions, due to the interaction between the hydroxyl and carboxylate groups. The ionic radii were taken from Robinson and Stokes (35). Direct comparison between the alkaline and rare earths on the basis of ionic radius or charge density is unlikely to be meaningful because of the change in coordination number.

The similar stabilities of lanthanum malonate and tartrate arise from different causes. The participation of the tartrate hydroxyl groups in the complexing results in a more favourable enthalpy change, balanced by a less favourable entropy change. The same trends in the entropy and enthalpy changes have been observed in the rare earth monocarboxylates and their α-hydroxy derivatives (84-89), where it has been proposed that the more favourable enthalpy changes found with the hydroxyacids arise from the participation of the hydroxyl group in the complexing and that the reason for the smaller entropy changes, contrary to what is expected on chelation,

lies in the coordination of the hydroxyl group via a water molecule in the first coordination sphere of the cation.
In this case the normal entropy gain on chelation, caused by the release of extra particles into the system, does not occur, although the loss of configurational entropy of the ligand still does, resulting in a net lower entropy gain for the hydroxyacid complexes. The above interpretation ignores the contribution to the entropy change made by the release of water molecules from the hydration sphere of the anion.
The compilation by Christensen, Izatt and Hansen (90) shows that the entropy change of dissociation of carboxylic acids is more negative for a monocarboxylic acid than for its α-hydroxy derivative, where hydrogen bonding between the hydroxyl group and the carboxylate group may reduce the number of water molecules entering the anion's cosphere, thus making the entropy change less negative, in spite of any loss of configurational entropy caused by the hydrogen bonding. The same phenomenon is observed in the first dissociation of a dicarboxylic acid when either there is an hydroxyl group available for hydrogen bonding or the second carboxyl group is in a position to do the same. Jaffé (91) has pointed out that in polar solvents intramolecular hydrogen bonds may be observed which have only a fraction of the heat content of the weakest observable intermolecular bonds because of the far more favourable entropy change associated with the former.

The magnitudes of ΔS_1(diss) for various acids are in the order maleic - oxalic > tartaric - malonic > malic > succinic ≈ glutaric = adipic = pimelic = suberic. The values of ΔS_2(diss) are much the same for all the acids except tartaric acid, which has a second hydroxyl group available and a low value of ΔS_2(diss) also. The difference in ΔS_1(diss) for acetic and glycolic acids at infinite dilution, 4.7 cal deg^{-1} mole^{-1}, may be compared with the difference reported by Grenthe (86) between the entropy changes on complexing of lanthanum acetate and glycolate, 6.7 cal deg^{-1} mole^{-1} in a 2M $NaClO_4$ medium.

The evidence from ratios of successive stability constants and from the thermodynamic data is not strong enough to confirm that α-hydroxyacids chelate only indirectly via a bound water molecule, or even that such coordination is the most important of the three types reported by Larsson(69) in his spectroscopic studies.

A minimum occurs at about 25°C. in a plot of log K_{101} against temperature. Such behaviour is uncommon with metal complexes, but is well known in the case of the pKs of weak acids and has been discussed by Gurney (92). The effect of increasing the temperature is to increase the tendency of a bond to break, but in solution the dielectric constant decreases at the same time, enhancing the associative electrostatic forces. These two opposing tendencies result in a minimum, the position of which depends on the relative strengths of the two effects and may not lie within the liquid range of the solvent. This phenomenon has been observed before in the manganese(II), cobalt(II) and nickel(II) oxalates(93) and succinates(94), cadmium acetate(95) and bromide(96), zinc thioglycolate(36) and lanthanum nitrilotriacetate(97). The results of Choppin and Chopoorian(85) for the cerous complexes of α-hydroxymonocarboxylates show minima in logK - T plots which have been ignored by the authors. The temperature variation in log K_{101} for lanthanum tartrate roughly parallels the trend in plots of pKa_2 against T for tartaric acid. A similar comparison can be made for nitrilotriacetic acid, and its lanthanum complex.

The acid dissociation constant, Ka_{111}, for the reaction

$$LaHT^{2+} = LaT^{+} + H^{+}$$

can be obtained from $pKa_{111} = \log K_{111} - \log K_{101}$. Using the results from Table 8, the thermodynamic values of pKa_{111} at 15, 25 and 35°C are 2.51, 2.13 and 2.19 respectively. By fitting the dissociation constant data to the equation $pKa = a + b.T + c.T^2$, we can calculate the standard entropy change from $\Delta S^o = -R(a + 2b.T + 3c.T^2)$. The standard Gibbs energy and enthalpy changes are calculated from Eqns 1.14 and 1.18. At 25°C, the following thermodynamic properties obtain: $\Delta G^o = 1.2x10^4$ j mole^{-1}, $\Delta H^o = -3.0x10^3$ j mole^{-1} and

$\Delta S^o = -51$ j deg^{-1}mole^{-1}. Comparison with the data for the second dissociation of tartaric acid given in Table 4.26 shows that dissociation is much more favoured in the complexed acid, because of both enthalpy and entropy effects. The more favourable enthalpy change arises from the greater ease of removing a proton against the electrostatic field of the positively charged complex than against that of the acid anion. In addition, the newly deprotonated carboxylate group may achieve greater stability by coordinating the metal ion than it could by interaction with the solvent. Inductive effects on the O-H bond in the complexed acid are also possible. The entropy change is more favourable because, apart from the beneficial effects of the carboxylate group's participation in chelation, the acid undergoes a reduction in charge on deprotonation instead of the usual increase, resulting in less ordering of the solvent and hence a less negative entropy change.

It can be seen from Table 10 that the addition of a second tartrate ion to the complex proceeds with a large positive entropy change. While the bis-tartrato complex, being negatively charged, will have a less ordering effect on the solvent structure than the mono-tartrato complex, this is unlikely to account for the observed effect, since the first ligand binds a highly charged lanthanum ion and results in a less charged species. Moreover, diglycolate(98) and iminodiacetate(76), which have the same charge as tartrate, do not have such favourable entropy changes for the second association. A possible explanation is that the coordination number changes on the addition of the second tartrate ion, releasing more water molecules from the hydrated ion than would be expected from the denticity alone. If the tartrate ion is a tetradentate ligand, the bis-tartratolanthanum complex presumably has either a dodecahedral or a square antiprismatic structure, i.e. is 8-coordinate. Since diglycolate and IMDA are tridentate, they would be far less likely to show such an effect. It is likely that the aquo-ion is 9-coordinate (38, 99,). Bridging hydrogen bonds between the two tartrate ligands, as suggested by Manning(10), may reinforce any water exclusive effect by providing an alternative to bonding with the solvent water molecules. Katzin and Barnett(9) report spectral evidence of a change in the coordination number of Pr^{3}, Nd^{3+} and Er^{3+} ions on complexing with tartrate and citrate ions in alkaline solution.

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Chapter 9

Linear Titration Plots

I. Symbols In addition to the symbols already defined, the following will be found throughout this chapter.

Kw	autoprotolysis constant of solvent
Ks	solubility product
m	concentration of titrant
vo	volume of sample
v	volume of titrant added
ve	equivalent volume of titrant

Other symbols are defined in the text.

II. Introduction

The end-point in potentiometric titrations is normally obtained from the point of inflexion of an emf-volume curve, despite the fact that this point does not coincide with the equivalence point(1) and may be difficult to determine graphically, especially in the titration of a weak acid. Moreover, for a non-isovalent precipitation titration i.e. one where the precipitate is of the type A_iB_j, $i \neq j$, the point of inflexion does not coincide even approximately with the equivalence point(2). Linear titration plots yield the equivalence point, allowing for experimental error and innacuracies in calculating activity coefficients, and present no graphical difficulties.

Linear titration plots were proposed by Sørenson(3) and improved by Gran(4), who allowed for volume changes during the titration and extended the procedure to weak acid, complexometric, redox and asymmetric precipitation titrations. Since then the method has been largely ignored - e.g. it is not mentioned in Kolthoff and Elving's "Treatise on Analytical Chemistry" - despite the advantages it offers. Gran's method is, however, inexact in that it takes no account of such effects as the autoprotolysis of water, the dissociation of weak acids and the inherent solubility of precipitates. Exact functions can be derived from the charge and mass balance equations, which has been done by Ingman and Still(5) for a weak monobasic acid in a constant ionic medium. The use of 'conditional' stability constants enables Ingman and Still to treat amino acids as monobasic acids.

The advent of electronic computers removes the need for the approximations in Gran's method and enables functions for more complex systems to be calculated, even in dilute solution since activity corrections can be applied satisfactorily by an iterative procedure. An ALGOL program has been written to deal with the following cases:

1) Gran plots a) strong acid - strong base b) weak acid - strong base
2) Explicit plots a) strong acid - strong base and binary precipitation titrations (b) weak mono- and dibasic acids (including amino-acids) - strong base (c) monobasic weak acid in the presence of the salt of a weak base - strong base (d) weak acid - weak base.

Activity corrections can be applied in all cases. The program is listed in Appendix 2g.

Theoretical

III. Strong acid - strong base and precipitation titrations. For simplicity the Gran treatment will be given for 1:1 reactions only. If vo ml of a strong acid HA of concentration t moles/litre are titrated with a strong base BOH of concentration m moles/litre, the concentration of hydrogen ions after the addition of v ml of base will be, before the end-point

$$H = (txvo - mxv)/(vo + v) \quad \ldots\ldots\ldots\ldots\ldots (1)$$

At the equivalence point $txvo = mxve$ . . . .(2)

Substituting (2) in (1) $H = m(ve - v)/(vo + v)$ . . . . .(3)

A plot of $H(vo + v)$ against v should be linear with an intercept of ve on the v-axis.

After the end-point the hydroxide ion concentration is given by

$$OH = m(v - ve)/(vo + v) \quad \ldots\ldots\ldots\ldots\ldots (4)$$

and since $OH = Kw/H$ . . . .(5)

a plot of $(vo + v)/H$ should be linear with intercept ve on the v-axis.

For a precipitation titration the same equations hold where H is now the indicator ion concentration, OH the counter-ion concentration and Kw = Ks, the solubility product. If the titration is followed potentiometrically the plots become:

a) before the end-point $\mathrm{antilog}(E/k)x(vo + v)$ against v,

b) after the end-point $\mathrm{antilog}(-E/k)x(vo + v)$ against v.

The EXPLICIT function follows from the electroneutrality equation,

$$H + B = OH + A \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Rearranging (6) $H - OH = (\{H\} - Kw/\{H\})/f_H = m(ve - v)/(vo + v)$

$$= A - B.$$

A plot of $F = (vo + v)\ (\{H\} - Kw/\{H\})/f_H = m(ve - v)$ against v should have an intercept of ve on the v-axis and be linear with a slope of -m, so in principle the concentrations of both acid and base can be determined from a single titration.

For a general precipitation reaction,

$$qAP_a + aB_qQ = A_qQ_a + aqB + aqP,$$

$Ks = \{A\}^q\{Q\}^a$, where A, B, P, Q have charges +a, +1, -1, -q respectively.

Electroneutrality gives $aA + B = P + qQ$. Hence,

$$a\{A\}/f_A - q\{Q\}/f_Q = P - B$$

and $$a\{A\}/f_A - q(Ks/\{A\}^q)^{1/a}/f_Q = q.m(ve - v)/(vo + v).$$

A plot of $F = (vo + v)(\{A\}/f_A - \frac{q}{a}(Ks/\{A\}^q)^{1/a}/f_Q$ against v should be linear with slope q.m/a and intercept ve on the v-axis.

IV. Weak Acid - Strong Base

If a weak monobasic acid HA is titrated with a strong monoacid base BOH, the following equations hold:

$$Ka = (HA.f_{HA})/(\{H\}A.f_A) \quad ,$$

$$Ta = HA + A = A(1 + Ka.\{H\}.f_A/f_{HA}) = m.ve/(vo + v),$$

$$Tb = B = m.v/(vo + v)$$

and $H + B = A + OH$ (electroneutrality).

We define a function $Z = Ka\{H\}f_A/f_{HA}$.

Then $H - OH = A - B = Ta/(1 + Z) - Tb$ which can be rearranged to give

$$(H - OH)(1+Z) = Ta - Tb - Z.Tb.$$

If Tb is known, then $Ta - Tb = m(ve - v)/(vo + v)$

$$= (1+Z)(\{H\} - Kw/\{H\})/f_H + Z.m.v/(vo + v)$$

and $Fb = (vo + v)(1 + Z)(\{H\} - Kw/\{H\})/f_H + Z.m.v$.

If Ta is known, then $(H - OH)(1 + Z) + Z.Ta = (Ta - Tb)(1 + Z)$, i.e.

$$Ta - Tb = m(ve - v)/(vo + v) = (\{H\} - Kw/\{H\})/f_H + Z.Ta/(1 + Z).$$

$$Fa = m(ve - v) = (vo + v)(\ (\{H\} - Kw/\{H\})/f_H + Z.Ta/(1 + Z)\ ).$$

A plot of Fa or Fb, as appropriate, against v will be linear with a slope of-m and an intercept ve on the v-axis.

The GRAN treatment assumes $A = Tb$ and $Ha = Ta - Tb$, so, neglecting activity coefficients, $H = Ka(Ta - Tb)/Tb = m.Ka(ve - v)/v$

A plot of $G = v.H$ against v is linear with an intercept ve on the v-axis.

If the titration is carried out in the presence of a known concentration of the salt SHX of a weak base S, then the following additional equations can be written:

$$Kb = (SH.f_{SH})/(S.\{H\}f_S)$$

$$Ts = S + SH = S(1 + Y) = X, \text{ where } Y = Kb.\{H\}f_S/f_{SH}$$

and the electroneutrality equation becomes

$$B + H + SH = OH + A + X.$$

Define the functions $L = Ka.\{H\}f_A/f_{HA}$ and $N = Kb.\{H\}f_S/f_{SH}$.

Now, $H - OH = Ts - Tb + A - SH = Ts - Tb + Ta/(1 + L) - Ts.N/(1 + N)$

$$(H - OH - Ts/(1 + L))(1 + N) = Ta - Tb - N.Tb$$

$$Ta - Tb = (1 + N)(H - OH - Ts/(1 + L)) + N.Tb = m(ve - v)/(vo + v)$$

A plot of

$Fs = (vo + v)((1 + N)((\{H\} - Kw/\{H\})/f_H - Ts/(1 + L)) + N.Tb)$ is linear with slope-m and intercept ve.

V. Weak Dibasic Acid - Strong Base

If vo ml of an acid H_bAX_{b-a}, where a is the negative charge on A, b the number of titrable protons and X a univalent anion, are titrated with a strong base BOH of concentration m moles/litre, then the following equations hold:

$$K_1 = HA.f_{HA}/(A\{H\}f_A),$$

$$K_2 = H_2A.f_{H2A}/(HA\{H\}f_{HA}),$$

$$X = (b - a)Ta \quad ,$$

$$Ta = H_2A + HA + A = A(1 + R + W),$$

where $R = K_1\{H\}f_A/f_{HA}$ and $W = K_1.K_2\{H\}^2f_A/f_{H2A}$,

$$H + B = OH + X + a.A + (a-1)HA + (a-2)H_2A \quad .$$

Combining the above equations we obtain

$$H - OH = b.Ta - Tb - J.Ta,$$

where $J = (R + 2W)/(1 + R + W)$.

If Tb is known $H - OH = b.Ta - Tb - b.J.Ta/b + J.Tb/b - J.Tb/b$,

hence $b.Ta - Tb = (H - OH + J.Tb/b)/(1 - J/b) = m(ve - v)/(vo + v)$.

$$Fb = (vo + v)((\{H\} - Kw/\{H\})/f_H + J.Tb/b)/(1 - J/b) .$$

If Ta is known, $H - OH + J.Ta = b.Ta - Tb = m(ve - v)/(vo + v)$

$$Fa = (vo + v)((\{H\} - Kw/\{H\})/f_H + J.Ta).$$

A plot of Fa or Fb against v will be linear with slope -m and intercept ve. These functions, Fa and Fb, deal comprehensively with dibasic acid titrations; for dicarboxylic acids a = b = 2, for simple amino acids, e.g. glycine, a = b = 1 and for amino acid salts, e.g. glycine hydrochloride, b = 2 and a = 1. If $K_2 = 0$ the functions reduce to those for a monobasic weak acid (b = 1) and if $K_1 = K_2 = 0$ to those for strong acid titrations.

The Gran function for dibasic acids is derived by assuming that the dissociations occur as two distinct steps, i.e. H_2A, HA and A never coexist, and by treating each step as for a monobasic acid. This results in the function $F_1 = (ve_2 - v)H$ for the determination of the first equivalence point(ve_1) and $F_2 = (v - ve_1)H$ for the second equivalence point(ve_2).

VI. Weak Acid - Weak Base

If we consider the titration of vo ml of a weak acid HA with a weak base Na_bB, where b is the negative charge on B, we can write

$$Ka = HA.f_{HA}/(\{H\}A.f_A) \ ,$$

$$Kb = BH.f_{BH}/(\{H\}B.f_B) \ ,$$

$$Ta = HA + A = A(1 + D), \text{ where } D = Ka\{H\}f_A/f_{HA} \ ,$$

$$Tb = BH + B = B(1 + E), \text{ where } E = Kb\{H\}f_B/f_{BH} \ ,$$

$$b.Na + H = OH + A + b.B + (b-1)BH \text{ (electroneutrality).}$$

Therefore $b.Tb + H - OH = Ta + b.Tb - HA - BH$

$$= Ta + b.Tb - Ta/(1 + D^{-1}) - Tb/(1 + E^{-1}).$$

If Tb is known, $H - OH - Tb + E.Tb/(1 + E) + D.Tb/(1 + D)$

$$= (Ta - Tb)(1 - D/(1 + D)\ ) = U.$$

Then $Ta - Tb = U/(1 - D/(1 + D)\ ) = m(ve - v)/(vo + v)$.

$$Fwb = (vo + v)U/(1 - D/(1 + D)\ ).$$

If Ta is known, $H - OH - Ta + D.Ta/(1 + D) + E.Ta/(1 + E)$

$$= (Tb - Ta)(1 - E/(1 + E)\ ) = V.$$

$$Tb - Ta = V/(b - E/(1 + E)\ ) = m(v - ve)/(vo + v).$$

$$Fwa = (vo + v)V/(b - E/(1 + E)\ ).$$

A plot of Fwa or Fwb against v will be linear with intercept ve on the v-axis and slope m. or $-m$

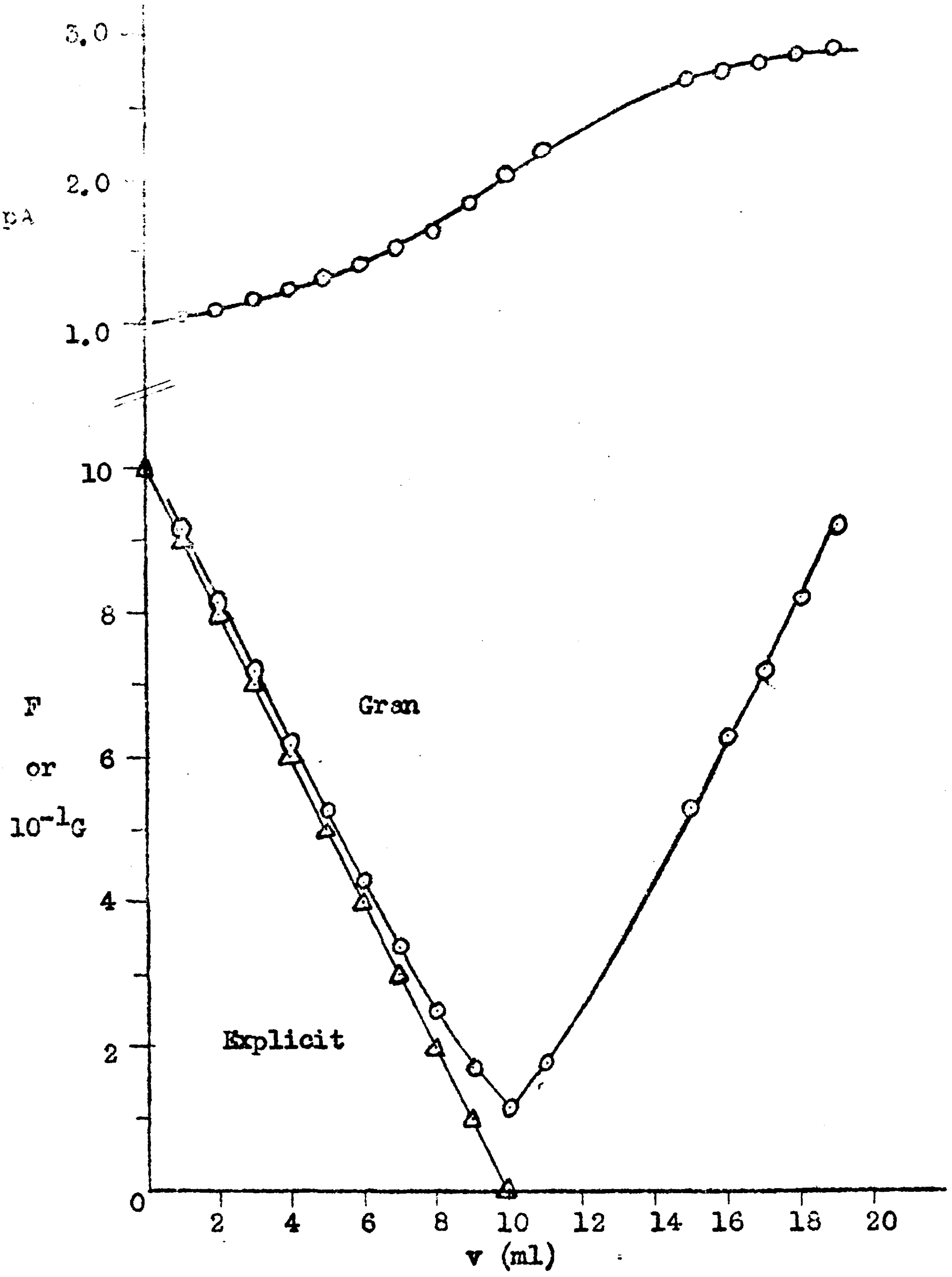

Fig.1 Precipitation Reaction of the type

$A + Q = AQ$

100 ml 0.01M A titrated with 0.1M Q

$K_s = 1.0 \times 10^{-4}$

VII. Discussion

(a) Strong Acid - Strong Base and Precipitation Titrations

The commercial availability of ion-specific electrodes increases the scope of potentiometric titrations, but the accuracy of conventional titration plots and Gran plots is limited by the magnitude of the solubility product and the concentrations of the reactants. The explicit function can be used when the others fail, so long as precipitation has actually started. The behaviour of the three functions is illustrated in Fig.1.

Since the Gran function involves less calculation than the explicit one it may be convenient to use in some circumstances and it is therefore desirable to know when the Gran function approximates to the explicit one. If we consider the reaction $xA + yQ = A_xQ_y$ we have the functions

$$F = (vo + v)\left(A - \frac{x}{y}(Ks/A^x)^{1/y}\right)$$

and $G = (vo + v)A$ before the end-point if A is the indicator ion and Q the titrant. If the ratio F/G is to be greater than some agreed discrimination D where $D < 1$, then we can write:

$$F/G = 1 - \frac{x}{y}Ks^{1/y}.A^{-(x/y + 1)} > D$$

$$\text{so } A^{(x/y + 1)} > (\frac{x}{y}.Ks^{1/y})/(1 - D) .$$

After the end-point we can write:

$$F' = (vo + v)\left((Ks/A^x)^{1/y} - \frac{y}{x}A\right)$$

and $G' = (vo + v)Q = (vo + v)(Ks/A^x)^{1/y}$,

$$\text{so } F'/G' = 1 - \frac{y}{x}.A^{(x/y + 1)}/Ks^{1/y} > D$$

and so $A^{(x/y + 1)} < \frac{x}{y}(1 - D)Ks^{1/y}$.
If $x = y$ the conditions become $A^2 > Ks/(1-D)$ and $A^2 < Ks(1-D)$. respectively. The area of applicability of the Gran function can therefore be related to the concentration of the indicator ion and hence to the emf.

Successful use of the explicit function demands an accurate knowledge of Ks. Considering again the reaction $xA + yQ = A_xQ_y$, if an approximation Ls is made to Ks the Gran function may be better than an explicit one if Ls is a poor approximation. When the indicator ion A is in excess the following functions apply:

$$G = (vo + v)A$$
$$F = (vo + v)(A - \frac{x}{y}(Ks/A^x)^{1/y})$$
$$E = (vo + v)(A - \frac{x}{y}(Ls/A^x)^{1/y})$$
$$G - F = \frac{x}{y}(vo + v)(Ks/A^x)^{1/y}$$
$$E - F = \frac{x}{y}(vo + v)(Ls^{1/y} - Ks^{1/y})A^{-x/y}$$
$$\mathrm{mod}(G - F) < \mathrm{mod}(E - F) \text{ if } Ls^{1/y} > 2Ks^{1/y} .$$

When the counter-ion Q is in excess the functions become:

$$G' = (vo + v)/A^{x/y}$$
$$F' = (vo + v)(1/A^{x/y} - \frac{y}{x}A/Ks^{1/y})$$
$$E' = (vo + v)(1/A^{x/y} - \frac{y}{x}A/Ls^{1/y})$$
$$\mathrm{mod}(G' - F') < \mathrm{mod}(E' - F') \text{ if } 1/Ks^{1/y} < \mathrm{mod}(1/Ls^{1/y} - 1/Ks^{1/y}),$$

i.e. if $Ls < Ks/2^y$.

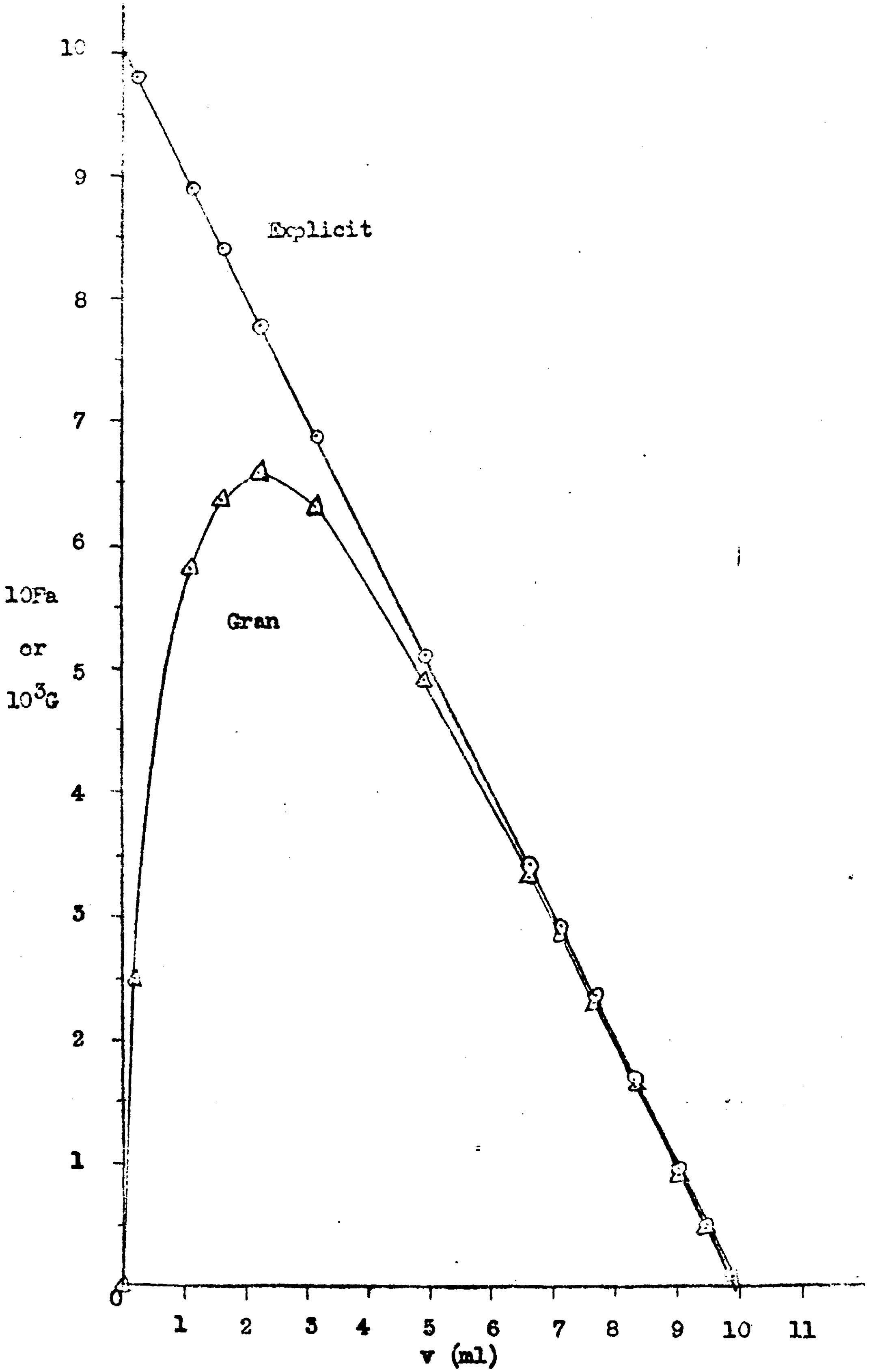

Fig. 2 Titration of 100 ml 0.01M weak acid (pKa = 4.0)

It can be seen that Ls must be very inaccurate before the explicit function breaks down.

(b) Weak Acid - Strong Base Titrations

For monobasic weak acids Gran's method is a good approximation provided that the hydroxide ion concentration and the contribution of the dissociation to the free anion concentration are negligible; the factors affecting the accuracy are the concentration of the acid, its strength and the degree of neutralisation. The two functions are plotted in Fig(2) for a typical case. If we consider the titration of a weak acid before the end-point and term 1/n the degree of neutralisation we can make the approximations

$$A = Ta/n \quad , \quad HA = Ta(n - 1)/n \ , \quad H = (n - 1)Ka \ .$$

Now $Fb/G = 1 + (vo + v)(H - OH)(H + Ka)/(m.v.H)$ and $v = ve/n$. If we define the useful range of G by the condition $Fb/G \leq 1 + D$, where $D > 0$, we get $(vo + v)(H - OH)(H + Ka)/(m.v.H) \leq D$. Substituting for v and H, neglecting OH and rearranging we obtain

$$n.Ka(vo + ve/n) \leq D.m.ve/n \ ,$$

so the limiting value of n is a solution of the quadratic

$$n^2 + r.n - D.m.r/Ka = 0 \ , \text{ where } r = ve/vo.$$

The following table gives examples of limiting n's for various cases when $D = 0.001$.

pKa	r	n(m=0.1)	n(m=0.01)
4	0.1	-	-
	0.5	-	-
	1.0	-	-
5	0.1	-	-
	0.5	2.0	-
	1.0	2.6	-
6	0.1	3.1	-
	0.5	7.0	2.0
	1.0	9.5	2.6

In practice much larger values of D are tolerable since the Gran and explicit functions converge at the end-point, in contrast to the strong acid - strong base functions, and the Gran plot gives a good extrapolation even though the function is a poor approximation to the explicit one. The Gran function has a maximum which occurs at a low degree of neutralisation and it is desirable to keep n less than 1.5 as a precaution.

If the titration is performed in the presence of a salt of a weak base(usually an ammonium salt) a correction should be made to the explicit function. In the acid region this correction would normally be negligible but it may be important at high pH's.

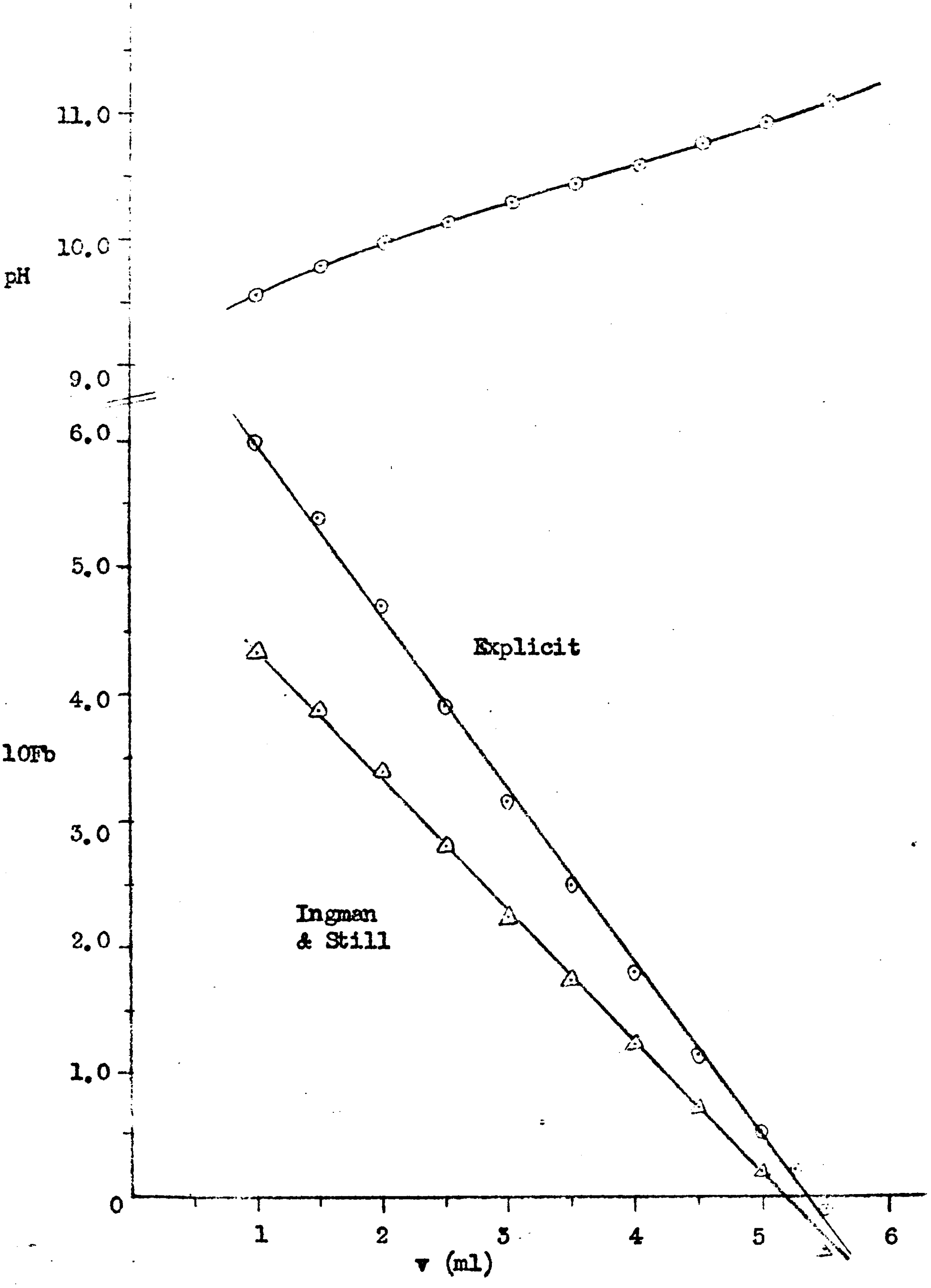

Fig. 3 Titration of 50ml 0.0107M β- alanine with 0.1M NaOH. Equivalent volume = 5.35 ml.

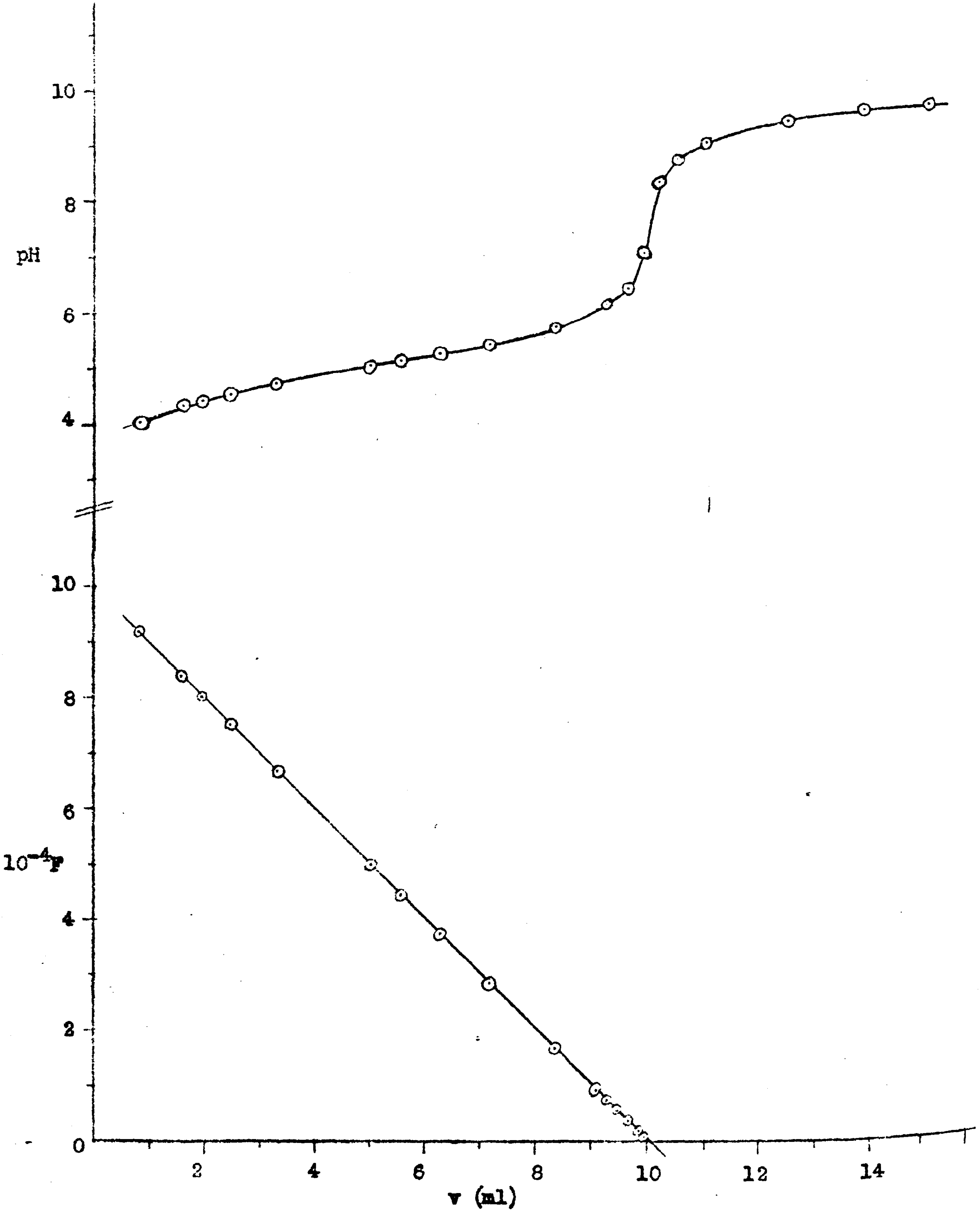

Fig. 4 Titration of 100 ml 0.01M Weak Acid (pKa = 5.0) with 0.1M Weak Base (pKb = 4.0) .

(c) Dibasic Weak Acids

Gran's treatment of dibasic weak acids requires an estimate of one end-point before the other can be calculated, which procedure, apart from the inaccuracies introduced by the approximation, is of little use if the pK's are such that dissociation does not occur in two distinct steps. Ingman and Still(5) have produced a function of monobasic acid form by introducing 'conditional' stability constants(6) but the results they quote for β- alanine in 0.1M $NaClO_4$ are not very accurate (2.4% error). We have reprocessed their data using the values of the dissociation constants obtained by Irving et al(7) in 0.1M KCl and find the error reduced to 0.03% in the opposite direction. The plots are given in Fig(3).

(d) Weak Acid - Weak Base Titrations

Such titrations may be of little practical use but their possibility indicates the versatility of the linear titration plot method.

(e) Activity Coefficients and Titrations in Dilute Solution

Strong acid - strong base titrations

If activity coefficients are neglected in the explicit function for the titration of a monobasic acid with a monoacid base the resulting expression $F' = (H - OH)(vo + v) = f.F$, where f is the activity coefficient for a 1:1 electrolyte and F is the true explicit function, will be linear only if f is constant but may be effectively linear over a range of addition v' if f varies only slightly over this range. Neglecting the effects of autoprotolysis the total number of ions present is constant and f changes solely because of dilution. If we use an extended Debye-Hückel expression for the activity coefficient $-\log f = A.I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ for a univalent ion, the difference in f on dilution from state 1 to state 2 can be calculated and a limit set for the tolerance:

$$0 < -\log(f_1/f_2) = A(I_1^{\frac{1}{2}}/(1 + I_1^{\frac{1}{2}}) - I_2^{\frac{1}{2}}/(1 + I_2^{\frac{1}{2}}) \leq D,$$

$$\text{i.e. } 0 < A(\frac{(m.ve/(vo+v_1))^{\frac{1}{2}}}{1 + (m.ve/(vo+v_1))^{\frac{1}{2}}} - \frac{(m.ve/(vo+v_2))^{\frac{1}{2}}}{1 + (m.ve/(vo+v_2))^{\frac{1}{2}}}) \leq D ,$$

$$0 < A(m.ve)^{\frac{1}{2}}(1/(vx^{\frac{1}{2}} + (m.ve)^{\frac{1}{2}}) - 1/((vx+d)^{\frac{1}{2}} + (m.ve)^{\frac{1}{2}})) \leq D,$$

where $vx = vo + v_1$ and $d = v_2 - v_1$. A change of 0.1% in f means a change of 0.0005 in logf and for ease of calculation can be set equal to $A\text{x}10^{-3}$. Taking a case where $vx = 100$ and $m.ve = 1$,

$$0 < 1/11 - 1/(1 + (100 + d)^{\frac{1}{2}}) \leq 1.0\text{x}10^{-3}.$$

Rearranging $1/11 < 1/(1 + (100+d)^{\frac{1}{2}}) \leq 0.091$.

If d is positive, there is only one condition,

$$1/0.091 > 1 + (100+d)^{\frac{1}{2}} ,$$

$$10.111 > (100+d)^{\frac{1}{2}} ,$$

$$102.23 > 100 + d ,$$

$$d < 2.23,$$

i.e. for the case chosen activity coefficients do not change significantly over a range of addition of 2.2 ml. Experimentally an HCl-Me_4NOH titration gave the same answer whether allowance was made for activity coefficients or not over the range of 1.5 ml studied(vo = 113 ml, m.ve = 1.44).

Weak acid - strong base titrations

In these titrations the total number of ions changes considerably and the variation in f is greater than with strong acids. In the simple Gran function, however, the effect of ignoring the activity coefficient acts in the opposite sense to the error induced by not using the explicit function and the Gran function is more accurate when activity corrections are neglected. The chances of "overcorrection" are in practise small.

Note Figs 1, 2 and 4 were constructed from theoretical "data" calculated on a computer program written by Mr. C.McCallum of this Department. Such "data" was also used to check all parts of the program listed in Appendix 2g.

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(4) G.Gran: Analyst,1952,77,661.

(5) F.Ingman & E.Still: Talanta,1966,13,1431.

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Appendix 1

This appendix contains the data for the potentiometric titrations and is divided into four parts:

(a) Tartaric Acid Runs,

(b) Sodium Tartrate Runs,

(c) A Potassium Tartrate Run,

(d) Lanthanum Tartrate Runs.

The ionic strength and temperature at which each run was performed are stated at the head of each table. The ionic strength was maintained with tetramethylammonium chloride. Runs in dilute solution (indicated by $I \to 0$) were corrected to infinite dilution by means of the Davies equation.

The meanings of the column headings are as follows:

Ta	total concentration of d-tartaric acid,
Tm	total metal concentration (sodium, potassium or lanthanum),
Tb	total base concentration (Me_4NOH or NaOH),
[HCl]	concentration of hydrochloric acid added,
[Na]	free sodium concentration,
[Cl]	concentration of Me_4NCl added, <u>not</u> total chloride,
[NaCl]	concentration of sodium chloride added (to be distinguished from total sodium),
pH	$-\log[H]$ at constant ionic strength and $-\log[H]f_1$ in dilute solution.

Concentrations are in moles per litre for constant ionic strength runs and moles per Kg of solvent for the others. The data are presented as Flexowriter print-outs of stream(10) output from the KDF 9 computer and show more figures than are significant. Concentrations of stock solutions and the delivery volumes of pipettes are known to 0.1 per cent or better. The fourth decimal place cannot be justified in the figures for pH.

In Runs Na.1 and Na.2 sodium hydroxide was the titrant, otherwise tetramethylammonium hydroxide was used. In Runs Na.5 - Na.8 the free sodium concentration was obtained from pNa measurements with a sodium responsive glass electrode.

Appendix 1a

Tartaric Acid Run 1

$I = 0.1$ $T = 25^{\circ}$C.

Ta	Tb	pH
3.8311$_{10}$ -3;	7.7505$_{10}$ -4;	2.8414;
3.7897$_{10}$ -3;	1.1488$_{10}$ -3;	2.9164;
3.7653$_{10}$ -3;	1.3692$_{10}$ -3;	2.9613;
3.7493$_{10}$ -3;	1.5145$_{10}$ -3;	2.9905;
3.7098$_{10}$ -3;	1.8717$_{10}$ -3;	3.0660;
3.6865$_{10}$ -3;	2.0825$_{10}$ -3;	3.1143;
3.6711$_{10}$ -3;	2.2215$_{10}$ -3;	3.1469;
3.6332$_{10}$ -3;	2.5638$_{10}$ -3;	3.2327;
3.5961$_{10}$ -3;	2.8990$_{10}$ -3;	3.3216;
3.5598$_{10}$ -3;	3.2279$_{10}$ -3;	3.4166;
3.5241$_{10}$ -3;	3.5501$_{10}$ -3;	3.5156;
3.4894$_{10}$ -3;	3.8646$_{10}$ -3;	3.6174;
3.4553$_{10}$ -3;	4.1728$_{10}$ -3;	3.7256;
3.4083$_{10}$ -3;	4.5971$_{10}$ -3;	3.8880;
3.3886$_{10}$ -3;	4.7754$_{10}$ -3;	3.9605;
3.3562$_{10}$ -3;	5.0680$_{10}$ -3;	4.0937;
3.3245$_{10}$ -3;	5.3551$_{10}$ -3;	4.2392;
3.2935$_{10}$ -3;	5.6354$_{10}$ -3;	4.4161;
3.2631$_{10}$ -3;	5.9104$_{10}$ -3;	4.6453;

Tartaric Acid Run 2

$I = 0.1$ $T = 25^{\circ}$C.

Ta	Tb	pH
2.8747$_{10}$ -3;	7.7013$_{10}$ -4;	2.9585;
2.8438$_{10}$ -3;	1.1431$_{10}$ -3;	3.0450;
2.8135$_{10}$ -3;	1.5082$_{10}$ -3;	3.1401;
2.7957$_{10}$ -3;	1.7225$_{10}$ -3;	3.2014;
2.7840$_{10}$ -3;	1.8639$_{10}$ -3;	3.2394;
2.7665$_{10}$ -3;	2.0738$_{10}$ -3;	3.3092;
2.7550$_{10}$ -3;	2.2123$_{10}$ -3;	3.3552;
2.7266$_{10}$ -3;	2.5556$_{10}$ -3;	3.4766;
2.6986$_{10}$ -3;	2.8920$_{10}$ -3;	3.5999;
2.6713$_{10}$ -3;	3.2214$_{10}$ -3;	3.7418;
2.6288$_{10}$ -3;	3.7339$_{10}$ -3;	3.9872;
2.6184$_{10}$ -3;	3.8591$_{10}$ -3;	4.0576;
2.6030$_{10}$ -3;	4.0450$_{10}$ -3;	4.1659;
2.5928$_{10}$ -3;	4.1677$_{10}$ -3;	4.2448;
2.5676$_{10}$ -3;	4.4714$_{10}$ -3;	4.4847;

Tartaric Acid Run 3

I = 0.1   T = 25°C.

Ta	Tb	pH
3.8320_{10} -3;	7.7085_{10} -4;	2.8512;
3.7908_{10} -3;	1.1435_{10} -3;	2.9216;
3.7504_{10} -3;	1.5082_{10} -3;	2.9964;
3.6717_{10} -3;	2.2194_{10} -3;	3.1528;
3.6338_{10} -3;	2.5628_{10} -3;	3.2366;
3.5245_{10} -3;	3.5502_{10} -3;	3.5178;
3.4896_{10} -3;	3.8658_{10} -3;	3.6197;
3.4218_{10} -3;	4.4789_{10} -3;	3.8397;
3.3889_{10} -3;	4.7767_{10} -3;	3.9596;
3.3567_{10} -3;	5.0675_{10} -3;	4.0910;
3.3251_{10} -3;	5.3529_{10} -3;	4.2408;
3.2940_{10} -3;	5.6347_{10} -3;	4.4148;
3.2634_{10} -3;	5.9113_{10} -3;	4.6391;

Tartaric Acid Run 4

I = 0.2   T = 25°C.

Ta	Tb	pH
4.7909_{10} -3;	1.8480_{10} -3;	2.9202;
4.7635_{10} -3;	2.1435_{10} -3;	2.9700;
4.7453_{10} -3;	2.3399_{10} -3;	3.0039;
4.7272_{10} -3;	2.5348_{10} -3;	3.0385;
4.7093_{10} -3;	2.7283_{10} -3;	3.0759;
4.6826_{10} -3;	3.0157_{10} -3;	3.1296;
4.4073_{10} -3;	5.9838_{10} -3;	3.8529;
4.3916_{10} -3;	6.1529_{10} -3;	3.9071;
4.3761_{10} -3;	6.3207_{10} -3;	3.9622;
4.3606_{10} -3;	6.4873_{10} -3;	4.0184;
4.3454_{10} -3;	6.6512_{10} -3;	4.0786;
4.3302_{10} -3;	6.8147_{10} -3;	4.1417;

Tartaric Acid Run 5

I = 0.2 T = 25°C.

Ta	Tb	pH
1.1195$_{10}$ -2;	5.1886$_{10}$ -3;	2.8558;
1.1144$_{10}$ -2;	5.4058$_{10}$ -3;	2.8766;
1.1094$_{10}$ -2;	5.6221$_{10}$ -3;	2.8989;
1.0971$_{10}$ -2;	6.1549$_{10}$ -3;	2.9520;
1.0777$_{10}$ -2;	6.9924$_{10}$ -3;	3.0401;
1.0660$_{10}$ -2;	7.4973$_{10}$ -3;	3.0962;
1.0545$_{10}$ -2;	7.9913$_{10}$ -3;	3.1537;
1.0116$_{10}$ -2;	9.8435$_{10}$ -3;	3.3843;
1.0014$_{10}$ -2;	1.0283$_{10}$ -2;	3.4440;
9.9144$_{10}$ -3;	1.0714$_{10}$ -2;	3.5035;
9.8172$_{10}$ -3;	1.1133$_{10}$ -2;	3.5645;
9.7220$_{10}$ -3;	1.1544$_{10}$ -2;	3.6264;
9.6276$_{10}$ -3;	1.1951$_{10}$ -2;	3.6899;
9.5350$_{10}$ -3;	1.2351$_{10}$ -2;	3.7538;

Tartaric Acid Run 6

I = 0.2 T = 25°C.

Ta	Tb	pH
8.8648$_{10}$ -3;	2.5326$_{10}$ -3;	2.7317;
8.7604$_{10}$ -3;	3.1326$_{10}$ -3;	2.7959;
8.6585$_{10}$ -3;	3.7186$_{10}$ -3;	2.8609;
8.5587$_{10}$ -3;	4.2922$_{10}$ -3;	2.9263;
8.4614$_{10}$ -3;	4.8517$_{10}$ -3;	2.9927;
8.3661$_{10}$ -3;	5.3997$_{10}$ -3;	3.0630;
8.2714$_{10}$ -3;	5.9440$_{10}$ -3;	3.1351;
7.5962$_{10}$ -3;	9.8263$_{10}$ -3;	3.7558;
7.4444$_{10}$ -3;	1.0699$_{10}$ -2;	3.9365;
7.3703$_{10}$ -3;	1.1125$_{10}$ -2;	4.0343;
7.2975$_{10}$ -3;	1.1544$_{10}$ -2;	4.1372;
7.2270$_{10}$ -3;	1.1949$_{10}$ -2;	4.2523;
7.1577$_{10}$ -3;	1.2347$_{10}$ -2;	4.3821;

Tartaric Acid Run 7

I = 0.2 T = 25°C.

Ta	Tb	pH
1.1144$_{10}$ -2;	5.4090$_{10}$ -3;	2.8761;
1.1019$_{10}$ -2;	5.9487$_{10}$ -3;	2.9299;
1.0899$_{10}$ -2;	6.4660$_{10}$ -3;	2.9844;
1.0781$_{10}$ -2;	6.9722$_{10}$ -3;	3.0391;
1.0665$_{10}$ -2;	7.4750$_{10}$ -3;	3.0956;
1.0551$_{10}$ -2;	7.9676$_{10}$ -3;	3.1511;
9.5384$_{10}$ -3;	1.2336$_{10}$ -2;	3.7491;
9.4468$_{10}$ -3;	1.2731$_{10}$ -2;	3.8169;
9.3570$_{10}$ -3;	1.3119$_{10}$ -2;	3.8845;
9.2692$_{10}$ -3;	1.3498$_{10}$ -2;	3.9549;
9.1830$_{10}$ -3;	1.3870$_{10}$ -2;	4.0291;
9.0988$_{10}$ -3;	1.4233$_{10}$ -2;	4.1058;
9.0163$_{10}$ -3;	1.4589$_{10}$ -2;	4.1897;
8.9350$_{10}$ -3;	1.4940$_{10}$ -2;	4.2805;
8.8552$_{10}$ -3;	1.5285$_{10}$ -2;	4.3835;

Tartaric Acid Run 8

I = 0.2 T = 25°C.

Ta	Tb	pH
6.0294$_{10}$ -3;	1.4346$_{10}$ -3;	2.7683;
5.9572$_{10}$ -3;	1.8947$_{10}$ -3;	2.8314;
5.8873$_{10}$ -3;	2.3404$_{10}$ -3;	2.8955;
5.8462$_{10}$ -3;	2.6029$_{10}$ -3;	2.9349;
5.8190$_{10}$ -3;	2.7758$_{10}$ -3;	2.9608;
5.7791$_{10}$ -3;	3.0303$_{10}$ -3;	3.0028;
5.7528$_{10}$ -3;	3.1981$_{10}$ -3;	3.0304;
5.7138$_{10}$ -3;	3.4469$_{10}$ -3;	3.0732;
5.6881$_{10}$ -3;	3.6109$_{10}$ -3;	3.1015;
5.6495$_{10}$ -3;	3.8566$_{10}$ -3;	3.1452;
5.6241$_{10}$ -3;	4.0186$_{10}$ -3;	3.1756;
5.5616$_{10}$ -3;	4.4171$_{10}$ -3;	3.2505;
5.2682$_{10}$ -3;	6.2878$_{10}$ -3;	3.6641;
5.2129$_{10}$ -3;	6.6406$_{10}$ -3;	3.7553;
5.1912$_{10}$ -3;	6.7791$_{10}$ -3;	3.7908;
5.1589$_{10}$ -3;	6.9847$_{10}$ -3;	3.8488;
5.1377$_{10}$ -3;	7.1204$_{10}$ -3;	3.8885;
5.1061$_{10}$ -3;	7.3219$_{10}$ -3;	3.9482;
5.0751$_{10}$ -3;	7.5194$_{10}$ -3;	4.0107;
5.0547$_{10}$ -3;	7.6497$_{10}$ -3;	4.0544;
5.0344$_{10}$ -3;	7.7790$_{10}$ -3;	4.1002;
5.0043$_{10}$ -3;	7.9710$_{10}$ -3;	4.1709;
4.9843$_{10}$ -3;	8.0982$_{10}$ -3;	4.2221;
4.9547$_{10}$ -3;	8.2872$_{10}$ -3;	4.3043;
4.9061$_{10}$ -3;	8.5971$_{10}$ -3;	4.4650;

Tartaric Acid Run 9

I = 0.2 T = 25°C.

Ta	Tb	pH
2.7171$_{10}$ -3;	8.7320$_{10}$ -4;	2.9965;
2.7053$_{10}$ -3;	1.0426$_{10}$ -3;	3.0374;
2.6936$_{10}$ -3;	1.2105$_{10}$ -3;	3.0788;
2.6820$_{10}$ -3;	1.3769$_{10}$ -3;	3.1230;
2.6705$_{10}$ -3;	1.5419$_{10}$ -3;	3.1705;
2.6591$_{10}$ -3;	1.7056$_{10}$ -3;	3.2182;
2.6477$_{10}$ -3;	1.8700$_{10}$ -3;	3.2663;
2.6307$_{10}$ -3;	2.1139$_{10}$ -3;	3.3459;
2.5508$_{10}$ -3;	3.2606$_{10}$ -3;	3.7981;
2.5405$_{10}$ -3;	3.4089$_{10}$ -3;	3.8672;
2.5252$_{10}$ -3;	3.6291$_{10}$ -3;	3.9816;
2.5100$_{10}$ -3;	3.8466$_{10}$ -3;	4.1061;
2.5000$_{10}$ -3;	3.9902$_{10}$ -3;	4.2030;
2.4900$_{10}$ -3;	4.1336$_{10}$ -3;	4.3023;
2.4801$_{10}$ -3;	4.2759$_{10}$ -3;	4.4225;
2.4703$_{10}$ -3;	4.4170$_{10}$ -3;	4.5630;

Tartaric Acid Run 10

I = 0.2 T = 25°C.

Ta	Tb	pH
1.0003$_{10}$ -2;	2.6786$_{10}$ -3;	2.6947;
9.8733$_{10}$ -3;	3.1629$_{10}$ -3;	2.7438;
9.7444$_{10}$ -3;	3.6420$_{10}$ -3;	2.7940;
9.6688$_{10}$ -3;	3.9235$_{10}$ -3;	2.8233;
9.6189$_{10}$ -3;	4.1087$_{10}$ -3;	2.8438;
9.5458$_{10}$ -3;	4.3808$_{10}$ -3;	2.8747;
9.4976$_{10}$ -3;	4.5600$_{10}$ -3;	2.8951;
9.4263$_{10}$ -3;	4.8253$_{10}$ -3;	2.9241;
9.3793$_{10}$ -3;	4.9999$_{10}$ -3;	2.9453;
9.3102$_{10}$ -3;	5.2568$_{10}$ -3;	2.9762;
9.2647$_{10}$ -3;	5.4260$_{10}$ -3;	2.9969;
9.1529$_{10}$ -3;	5.8418$_{10}$ -3;	3.0495;
9.0427$_{10}$ -3;	6.2517$_{10}$ -3;	3.1039;
8.9351$_{10}$ -3;	6.6519$_{10}$ -3;	3.1571;
8.8299$_{10}$ -3;	7.0431$_{10}$ -3;	3.2107;
8.0687$_{10}$ -3;	9.8740$_{10}$ -3;	3.6760;
7.9831$_{10}$ -3;	1.0192$_{10}$ -2;	3.7384;
7.8991$_{10}$ -3;	1.0504$_{10}$ -2;	3.8027;
7.8168$_{10}$ -3;	1.0810$_{10}$ -2;	3.8674;
7.7364$_{10}$ -3;	1.1110$_{10}$ -2;	3.9365;
7.6576$_{10}$ -3;	1.1403$_{10}$ -2;	4.0076;
7.5798$_{10}$ -3;	1.1692$_{10}$ -2;	4.0831;
7.5036$_{10}$ -3;	1.1975$_{10}$ -2;	4.1613;
7.4296$_{10}$ -3;	1.2250$_{10}$ -2;	4.2435;
7.3572$_{10}$ -3;	1.2520$_{10}$ -2;	4.3433;
7.2856$_{10}$ -3;	1.2786$_{10}$ -2;	4.4523;

Tartaric Acid Run 11

I = 0.2 T = 25°C.

Ta	Tb	pH
4.8594$_{10}$ -3;	1.1677$_{10}$ -3;	2.8136;
4.8124$_{10}$ -3;	1.5426$_{10}$ -3;	2.8711;
4.7664$_{10}$ -3;	1.9088$_{10}$ -3;	2.9315;
4.7393$_{10}$ -3;	2.1251$_{10}$ -3;	2.9693;
4.7213$_{10}$ -3;	2.2680$_{10}$ -3;	2.9963;
4.6943$_{10}$ -3;	2.4831$_{10}$ -3;	3.0343;
4.6765$_{10}$ -3;	2.6252$_{10}$ -3;	3.0611;
4.6500$_{10}$ -3;	2.8363$_{10}$ -3;	3.1024;
4.6325$_{10}$ -3;	2.9757$_{10}$ -3;	3.1296;
4.6157$_{10}$ -3;	3.1090$_{10}$ -3;	3.1554;
4.5909$_{10}$ -3;	3.3072$_{10}$ -3;	3.1974;
4.5500$_{10}$ -3;	3.6328$_{10}$ -3;	3.2700;
4.3517$_{10}$ -3;	5.2128$_{10}$ -3;	3.6736;
4.3136$_{10}$- 3;	5.5163$_{10}$ -3;	3.7639;
4.2986$_{10}$ -3;	5.6355$_{10}$ -3;	3.7996;
4.2764$_{10}$ -3;	5.8128$_{10}$ -3;	3.8569;
4.2543$_{10}$ -3;	5.9882$_{10}$ -3;	3.9161;
4.2398$_{10}$ -3;	6.1042$_{10}$ -3;	3.9563;
4.2256$_{10}$ -3;	6.2171$_{10}$ -3;	3.9970;
4.2045$_{10}$ -3;	6.3850$_{10}$ -3;	4.0615;
4.1699$_{10}$ -3;	6.6612$_{10}$ -3;	4.1780;
4.1352$_{10}$ -3;	6.9372$_{10}$ -3;	4.3112;
4.1012$_{10}$ -3;	7.2085$_{10}$ -3;	4.4697;

Tartaric Acid Run 12

I = 0.2 T = 25°C.

Ta	Tb	pH
1.1697$_{10}$ -3;	5.6736$_{10}$ -4;	3.2930;
1.1675$_{10}$ -3;	6.4180$_{10}$ -4;	3.3300;
1.1636$_{10}$ -3;	7.7130$_{10}$ -4;	3.3992;
1.1615$_{10}$ -3;	8.4498$_{10}$ -4;	3.4396;
1.1587$_{10}$ -3;	9.3668$_{10}$ -4;	3.4945;
1.1428$_{10}$ -3;	1.4707$_{10}$ -3;	3.8906;
1.1402$_{10}$ -3;	1.5582$_{10}$ -3;	3.9733;
1.1376$_{10}$ -3;	1.6455$_{10}$ -3;	4.0642;
1.1351$_{10}$ -3;	1.7322$_{10}$ -3;	4.1610;
1.1325$_{10}$ -3;	1.8186$_{10}$ -3;	4.2724;
1.1299$_{10}$ -3;	1.9052$_{10}$ -3;	4.4042;

Tartaric Acid Run 13

I = 0.2 T = 25°C.

Ta	Tb	pH
1.1618$_{10}$ -3;	8.3460$_{10}$ -4;	3.43500;
1.1591$_{10}$ -3;	9.2517$_{10}$ -4;	3.4864;
1.1564$_{10}$ -3;	1.0157$_{10}$ -3;	3.5457;
1.1457$_{10}$ -3;	1.3736$_{10}$ -3;	3.8087;
1.1431$_{10}$ -3;	1.4621$_{10}$ -3;	3.8840;
1.1405$_{10}$ -3;	1.5501$_{10}$ -3;	3.9673;
1.1379$_{10}$ -3;	1.6378$_{10}$ -3;	4.0570;
1.1353$_{10}$ -3;	1.7250$_{10}$ -3;	4.1568;
1.1327$_{10}$ -3;	1.8119$_{10}$ -3;	4.2675;
1.1301$_{10}$ -3;	1.8977$_{10}$ -3;	4.3999;
1.1271$_{10}$ -3;	2.0003$_{10}$ -3;	4.6039;

Tartaric Acid Run 14

I = 0.2 T = 25°C.

Ta	Tb	pH
1.8978$_{10}$ -3;	6.0244$_{10}$ -4;	3.0809;
1.8921$_{10}$ -3;	7.2119$_{10}$ -4;	3.1167;
1.8864$_{10}$ -3;	8.3922$_{10}$ -4;	3.1535;
1.8807$_{10}$ -3;	9.5655$_{10}$ -4;	3.1937;
1.8751$_{10}$ -3;	1.0732$_{10}$ -3;	3.2362;
1.8695$_{10}$ -3;	1.1891$_{10}$ -3;	3.2799;
1.8639$_{10}$ -3;	1.3041$_{10}$ -3;	3.3247;
1.8557$_{10}$ -3;	1.4754$_{10}$ -3;	3.3972;
1.8205$_{10}$ -3;	2.2036$_{10}$ -3;	3.7611;
1.8152$_{10}$ -3;	2.3135$_{10}$ -3;	3.8251;
1.8099$_{10}$ -3;	2.4216$_{10}$ -3;	3.8944;
1.8022$_{10}$ -3;	2.5826$_{10}$ -3;	4.0044;
1.7945$_{10}$ -3;	2.7423$_{10}$ -3;	4.1267;
1.7893$_{10}$ -3;	2.8480$_{10}$ -3;	4.2159;
1.7766$_{10}$ -3;	3.1111$_{10}$ -3;	4.5026;
1.7716$_{10}$ -3;	3.2153$_{10}$ -3;	4.7745;

Tartaric Acid Run 15

I = 0.4 T = 25°C.

Ta	Tb	pH
8.0195$_{10}$ -3;	1.2537$_{10}$ -3;	2.6517;
7.9615$_{10}$ -3;	1.4947$_{10}$ -3;	2.6773;
7.9233$_{10}$ -3;	1.6534$_{10}$ -3;	2.6944;
7.8669$_{10}$ -3;	1.8879$_{10}$ -3;	2.7215;
7.8297$_{10}$ -3;	2.0424$_{10}$ -3;	2.7388;
7.7383$_{10}$ -3;	2.4222$_{10}$ -3;	2.7827;
7.6492$_{10}$ -3;	2.7925$_{10}$ -3;	2.8265;
7.5622$_{10}$ -3;	3.1543$_{10}$ -3;	2.8724;
7.4772$_{10}$ -3;	3.5077$_{10}$ -3;	2.9181;
7.3940$_{10}$ -3;	3.8533$_{10}$ -3;	2.9640;
7.3126$_{10}$ -3;	4.1916$_{10}$ -3;	3.0106;
7.2330$_{10}$ -3;	4.5225$_{10}$ -3;	3.0588;
7.1555$_{10}$ -3;	4.8448$_{10}$ -3;	3.1062;
7.0796$_{10}$ -3;	5.1603$_{10}$ -3;	3.1553;
6.9316$_{10}$ -3;	5.7754$_{10}$ -3;	3.2563;
6.8599$_{10}$ -3;	6.0734$_{10}$ -3;	3.3071;
6.7896$_{10}$ -3;	6.3653$_{10}$ -3;	3.3590;
6.7212$_{10}$ -3;	6.6498$_{10}$ -3;	3.4113;
6.6408$_{10}$ -3;	6.9838$_{10}$ -3;	3.4869;
6.5881$_{10}$ -3;	7.2028$_{10}$ -3;	3.5193;
6.5234$_{10}$ -3;	7.4717$_{10}$ -3;	3.5748;
6.4602$_{10}$ -3;	7.7345$_{10}$ -3;	3.6316;
6.3982$_{10}$ -3;	7.9923$_{10}$ -3;	3.6891;
6.3372$_{10}$ -3;	8.2457$_{10}$ -3;	3.7471;
6.2774$_{10}$ -3;	8.4943$_{10}$ -3;	3.8086;
6.2186$_{10}$ -3;	8.7386$_{10}$ -3;	3.8718;
6.1610$_{10}$ -3;	8.9783$_{10}$ -3;	3.9365;
6.1046$_{10}$ -3;	9.2125$_{10}$ -3;	4.0054;
6.0493$_{10}$ -3;	9.4425$_{10}$ -3;	4.0758;
5.9409$_{10}$ -3;	9.8930$_{10}$ -3;	4.2370;

Tartaric Acid Run 16

I = 0.4 T = 25°C.

Ta	Tb	pH
3.8252$_{10}$ -3;	7.9998$_{10}$ -4;	2.8522;
3.7816$_{10}$ -3;	1.1850$_{10}$ -3;	2.9213;
3.7390$_{10}$ -3;	1.5613$_{10}$ -3;	2.9946;
3.7140$_{10}$ -3;	1.7826$_{10}$ -3;	3.0385;
3.6975$_{10}$ -3;	1.9285$_{10}$ -3;	3.0687;
3.6730$_{10}$ -3;	2.1448$_{10}$ -3;	3.1168;
3.6568$_{10}$ -3;	2.2875$_{10}$ -3;	3.1494;
3.6171$_{10}$ -3;	2.6385$_{10}$ -3;	3.2324;
3.5936$_{10}$ -3;	2.8454$_{10}$ -3;	3.2849;
3.5782$_{10}$ -3;	2.9819$_{10}$ -3;	3.3202;
3.5401$_{10}$ -3;	3.3183$_{10}$ -3;	3.4126;
3.5028$_{10}$ -3;	3.6477$_{10}$ -3;	3.5096;
3.4665$_{10}$ -3;	3.9687$_{10}$ -3;	3.6113;
3.4309$_{10}$ -3;	4.2831$_{10}$ -3;	3.7178;
3.4097$_{10}$ -3;	4.4699$_{10}$ -3;	3.7864;
3.3958$_{10}$ -3;	4.5931$_{10}$ -3;	3.8311;
3.3750$_{10}$ -3;	4.7761$_{10}$ -3;	3.9042;
3.3546$_{10}$ -3;	4.9569$_{10}$ -3;	3.9815;
3.3277$_{10}$ -3;	5.1944$_{10}$ -3;	4.0942;
3.2882$_{10}$ -3;	5.5434$_{10}$ -3;	4.2859;
3.2624$_{10}$ -3;	5.7705$_{10}$ -3;	4.4538;
3.2309$_{10}$ -3;	6.0495$_{10}$ -3;	4.7468;

Tartaric Acid Run 17

I = 0.2 T = 25°C.

Ta	Tb	pH
5.0803$_{10}$ -3;	1.9582$_{10}$ -3;	2.9058;
5.0257$_{10}$ -3;	2.3413$_{10}$ -3;	2.9694;
4.9738$_{10}$ -3;	2.7043$_{10}$ -3;	3.0333;
4.9231$_{10}$ -3;	3.0599$_{10}$ -3;	3.0996;
4.8733$_{10}$ -3;	3.4087$_{10}$ -3;	3.1684;
4.8245$_{10}$ -3;	3.7506$_{10}$ -3;	3.2422;
4.7299$_{10}$ -3;	4.4132$_{10}$ -3;	3.3893;
4.6382$_{10}$ -3;	5.0555$_{10}$ -3;	3.5490;
4.5080$_{10}$ -3;	5.9681$_{10}$ -3;	3.8049;
4.4664$_{10}$ -3;	6.2596$_{10}$ -3;	3.8966;
4.4254$_{10}$ -3;	6.5467$_{10}$ -3;	3.9927;
4.3851$_{10}$ -3;	6.8287$_{10}$ -3;	4.0979;
4.3457$_{10}$ -3;	7.1051$_{10}$ -3;	4.2165;
4.3069$_{10}$ -3;	7.3765$_{10}$ -3;	4.3485;
4.2686$_{10}$ -3;	7.6452$_{10}$ -3;	4.5096;
4.2309$_{10}$ -3;	7.9091$_{10}$ -3;	4.7219;

Tartaric Acid Run 18

I = 0.2 T = 25°C.

Ta	Tb	pH
5.1319$_{10}$ -3;	1.6025$_{10}$ -3;	2.8489;
5.0770$_{10}$ -3;	1.9882$_{10}$ -3;	2.9064;
5.0233$_{10}$ -3;	2.3658$_{10}$ -3;	2.9623;
4.9711$_{10}$ -3;	2.7332$_{10}$ -3;	3.0372;
4.9199$_{10}$ -3;	3.0931$_{10}$ -3;	3.1043;
4.8707$_{10}$ -3;	3.4388$_{10}$ -3;	3.1707;
4.8225$_{10}$ -3;	3.7776$_{10}$ -3;	3.2426;
4.7745$_{10}$ -3;	4.1150$_{10}$ -3;	3.3195;
4.7275$_{10}$ -3;	4.4457$_{10}$ -3;	3.3957;
4.6817$_{10}$ -3;	4.7673$_{10}$ -3;	3.4740;
4.6368$_{10}$ -3;	5.0828$_{10}$ -3;	3.5580;
4.5931$_{10}$ -3;	5.3900$_{10}$ -3;	3.6384;
4.5503$_{10}$ -3;	5.6916$_{10}$ -3;	3.7253;
4.5077$_{10}$ -3;	5.9904$_{10}$ -3;	3.8163;
4.4660$_{10}$ -3;	6.2838$_{10}$ -3;	3.9129;
4.4250$_{10}$ -3;	6.5721$_{10}$ -3;	4.0113;
4.3847$_{10}$ -3;	6.8552$_{10}$ -3;	4.1232;
4.3452$_{10}$ -3;	7.1328$_{10}$ -3;	4.2471;
4.3065$_{10}$ -3;	7.4054$_{10}$ -3;	4.3898;
4.2303$_{10}$ -3;	7.9406$_{10}$ -3;	4.8213;

Tartaric Acid Run 19

$I \to 0$ $T = 15^{\circ}$C.

Ta	Tb	pH	[Cl]
1.9738$_{10}$ -3;	8.7302$_{10}$ -5;	3.0303;	7.3526$_{10}$ -5;
1.9673$_{10}$ -3;	2.6583$_{10}$ -4;	3.0792;	2.2388$_{10}$ -4;
1.9591$_{10}$ -3;	4.9595$_{10}$ -4;	3.1504;	4.1769$_{10}$ -4;
1.9522$_{10}$ -3;	6.8693$_{10}$ -4;	3.2069;	5.7853$_{10}$ -4;
1.9451$_{10}$ -3;	8.8592$_{10}$ -4;	3.2841;	7.4612$_{10}$ -4;
1.9374$_{10}$ -3;	1.0983$_{10}$ -3;	3.3819;	9.2501$_{10}$ -4;
1.9331$_{10}$ -3;	1.2199$_{10}$ -3;	3.4363;	1.0274$_{10}$ -3;
1.9286$_{10}$ -3;	1.3429$_{10}$ -3;	3.4893;	1.1310$_{10}$ -3;
1.9236$_{10}$ -3;	1.4821$_{10}$ -3;	3.5610;	1.2483$_{10}$ -3;
1.9170$_{10}$ -3;	1.6662$_{10}$ -3;	3.6558;	1.4033$_{10}$ -3;
1.9111$_{10}$ -3;	1.8299$_{10}$ -3;	3.7497;	1.5411$_{10}$ -3;
1.9063$_{10}$ -3;	1.9635$_{10}$ -3;	3.8280;	1.6536$_{10}$ -3;
1.9008$_{10}$ -3;	2.1158$_{10}$ -3;	3.9062;	1.7819$_{10}$ -3;
1.8950$_{10}$ -3;	2.2785$_{10}$ -3;	4.0049;	1.9190$_{10}$ -3;
1.8870$_{10}$ -3;	2.5006$_{10}$ -3;	4.1482;	2.1060$_{10}$ -3;
1.8822$_{10}$ -3;	2.6344$_{10}$ -3;	4.2368;	2.2187$_{10}$ -3;
1.8765$_{10}$ -3;	2.7924$_{10}$ -3;	4.3440;	2.3518$_{10}$ -3;
1.8717$_{10}$ -3;	2.9271$_{10}$ -3;	4.4382;	2.4652$_{10}$ -3;

Tartaric Acid Run 20

$I \to 0$ $T = 15^{\circ}$C.

Ta	Tb	pH	[Cl]
9.8294$_{10}$ -4;	1.4411$_{10}$ -4;	3.2801;	1.2137$_{10}$ -4;
9.8101$_{10}$ -4;	2.5169$_{10}$ -4;	3.3289;	2.1198$_{10}$ -4;
9.7908$_{10}$ -4;	3.5931$_{10}$ -4;	3.3814;	3.0261$_{10}$ -4;
9.7687$_{10}$ -4;	4.8304$_{10}$ -4;	3.4620;	4.0682$_{10}$ -4;
9.7468$_{10}$ -4;	6.0512$_{10}$ -4;	3.5476;	5.0963$_{10}$ -4;
9.7250$_{10}$ -4;	7.2678$_{10}$ -4;	3.6477;	6.1209$_{10}$ -4;
9.7031$_{10}$ -4;	8.4886$_{10}$ -4;	3.7550;	7.1491$_{10}$ -4;
9.6842$_{10}$ -4;	9.5414$_{10}$ -4;	3.8527;	8.0358$_{10}$ -4;
9.6624$_{10}$ -4;	1.0761$_{10}$ -3;	3.9802;	9.0627$_{10}$ -4;
9.6409$_{10}$ -4;	1.1962$_{10}$ -3;	4.1088;	1.0074$_{10}$ -3;
9.6256$_{10}$ -4;	1.2815$_{10}$ -3;	4.2083;	1.0793$_{10}$ -3;
9.6100$_{10}$ -4;	1.3682$_{10}$ -3;	4.3112;	1.1523$_{10}$ -3;
9.5947$_{10}$ -4;	1.4540$_{10}$ -3;	4.4188;	1.2246$_{10}$ -3;
9.5767$_{10}$ -4;	1.5545$_{10}$ -3;	4.5547;	1.3092$_{10}$ -3;

Tartaric Acid Run 21

I → C T = 25°C.

Ta	Tb	pH	[Cl]
1.4143$_{10}$ -3;	3.6790$_{10}$ -4;	3.2332;	5.6378$_{10}$ -6;
1.4120$_{10}$ -3;	4.8246$_{10}$ -4;	3.2815;	7.3932$_{10}$ -6;
1.4102$_{10}$ -3;	5.7217$_{10}$ -4;	3.3203;	8.7680$_{10}$ -6;
1.4091$_{10}$ -3;	6.2980$_{10}$ -4;	3.3467;	9.6511$_{10}$ -6;
1.4064$_{10}$ -3;	7.6100$_{10}$ -4;	3.4122;	1.1662$_{10}$ -5;
1.4050$_{10}$ -3;	8.3138$_{10}$ -4;	3.4472;	1.2740$_{10}$ -5;
1.4036$_{10}$ -3;	9.0400$_{10}$ -4;	3.4860;	1.3853$_{10}$ -5;
1.4025$_{10}$ -3;	9.5871$_{10}$ -4;	3.5179;	1.4691$_{10}$ -5;
1.4014$_{10}$ -3;	1.0150$_{10}$ -3;	3.5480;	1.5553$_{10}$ -5;
1.4003$_{10}$ -3;	1.0698$_{10}$ -3;	3.5815;	1.6393$_{10}$ -5;
1.3989$_{10}$ -3;	1.1395$_{10}$ -3;	3.6215;	1.7461$_{10}$ -5;

Tartaric Acid Run 22

I → C T = 25°C.

Ta	Tb	pH	[Cl]
2.3259$_{10}$ -3;	6.2716$_{10}$ -4;	3.1239;	9.6107$_{10}$ -6;
2.3211$_{10}$ -3;	7.7313$_{10}$ -4;	3.1659;	1.1848$_{10}$ -5;
2.3155$_{10}$ -3;	9.4601$_{10}$ -4;	3.2204;	1.4497$_{10}$ -5;
2.3098$_{10}$ -3;	1.1199$_{10}$ -3;	3.2773;	1.7162$_{10}$ -5;
2.3027$_{10}$ -3;	1.3349$_{10}$ -3;	3.3522;	2.0457$_{10}$ -5;
2.2973$_{10}$ -3;	1.5006$_{10}$ -3;	3.4027;	2.2995$_{10}$ -5;
2.2923$_{10}$ -3;	1.6510$_{10}$ -3;	3.4603;	2.5300$_{10}$ -5;
2.2870$_{10}$ -3;	1.8121$_{10}$ -3;	3.5255;	2.7769$_{10}$ -5;
2.2821$_{10}$ -3;	1.9632$_{10}$ -3;	3.5900;	3.0084$_{10}$ -5;
2.2763$_{10}$ -3;	2.1413$_{10}$ -3;	3.6710;	3.2813$_{10}$ -5;
2.2710$_{10}$ -3;	2.3011$_{10}$ -3;	3.7416;	3.5263$_{10}$ -5;

Tartaric Acid Run 23

$I \rightarrow 0$ $T = 35^{\circ}C.$

Ta	Tb	pH	[Cl]
1.4010$_{10}$ -3;	2.5852$_{10}$ -4;	3.2104;	2.1769$_{10}$ -4;
1.3951$_{10}$ -3;	4.9021$_{10}$ -4;	3.3105;	4.1278$_{10}$ -4;
1.3913$_{10}$ -3;	6.3795$_{10}$ -4;	3.3810;	5.3718$_{10}$ -4;
1.3863$_{10}$ -3;	8.3433$_{10}$ -4;	3.4844;	7.0255$_{10}$ -4;
1.3835$_{10}$ -3;	9.4380$_{10}$ -4;	3.5520;	7.9473$_{10}$ -4;
1.3784$_{10}$ -3;	1.1418$_{10}$ -3;	3.6752;	9.6145$_{10}$ -4;
1.3727$_{10}$ -3;	1.3648$_{10}$ -3;	3.8246;	1.1492$_{10}$ -3;
1.3700$_{10}$ -3;	1.4722$_{10}$ -3;	3.9010;	1.2397$_{10}$ -3;
1.3676$_{10}$ -3;	1.5636$_{10}$ -3;	3.9677;	1.3166$_{10}$ -3;
1.3662$_{10}$ -3;	1.6178$_{10}$ -3;	4.0090;	1.3622$_{10}$ -3;
1.3629$_{10}$ -3;	1.7485$_{10}$ -3;	4.1043;	1.4723$_{10}$ -3;
1.3596$_{10}$ -3;	1.8760$_{10}$ -3;	4.2080;	1.5797$_{10}$ -3;

Appendix 1b

Sodium Tartrate Run 1

I = 0.2 T = 25°C.

Ta	Tm - Tb	pH	Tb
5.1580$_{10}$ -3;	2.0664$_{10}$ -2;	3.0086;	2.6910$_{10}$ -3;
5.1050$_{10}$ -3;	2.0451$_{10}$ -2;	3.0722;	3.0463$_{10}$ -3;
5.0532$_{10}$ -3;	2.0244$_{10}$ -2;	3.1382;	3.3931$_{10}$ -3;
5.0025$_{10}$ -3;	2.0041$_{10}$ -2;	3.2061;	3.7330$_{10}$ -3;
4.9531$_{10}$ -3;	1.9843$_{10}$ -2;	3.2743;	4.0636$_{10}$ -3;
4.9047$_{10}$ -3;	1.9649$_{10}$ -2;	3.3458;	4.3878$_{10}$ -3;
4.7646$_{10}$ -3;	1.9088$_{10}$ -2;	3.5747;	5.3261$_{10}$ -3;
4.7197$_{10}$ -3;	1.8908$_{10}$ -2;	3.6559;	5.6267$_{10}$ -3;
4.6754$_{10}$ -3;	1.8730$_{10}$ -2;	3.7389;	5.9240$_{10}$ -3;
4.6318$_{10}$ -3;	1.8556$_{10}$ -2;	3.8259;	6.2157$_{10}$ -3;
4.5895$_{10}$ -3;	1.8386$_{10}$ -2;	3.9161;	6.4991$_{10}$ -3;
4.5480$_{10}$ -3;	1.8220$_{10}$ -2;	4.0126;	6.7773$_{10}$ -3;
4.5069$_{10}$ -3;	1.8056$_{10}$ -2;	4.1174;	7.0522$_{10}$ -3;
4.4666$_{10}$ -3;	1.7894$_{10}$ -2;	4.2344;	7.3222$_{10}$ -3;

Sodium Tartrate Run 2

I = 0.2 T = 25°C.

Ta	Tm - Tb	pH	Tb
1.0633$_{10}$ -2;	1.0643$_{10}$ -1;	2.5601;	1.5861$_{10}$ -3;
1.0410$_{10}$ -2;	1.0420$_{10}$ -1;	2.6269;	2.3338$_{10}$ -3;
1.0093$_{10}$ -2;	1.0102$_{10}$ -1;	2.7301;	3.3987$_{10}$ -3;
9.7985$_{10}$ -3;	9.8072$_{10}$ -2;	2.8352;	4.3853$_{10}$ -3;
9.7037$_{10}$ -3;	9.7124$_{10}$ -2;	2.8696;	4.7030$_{10}$ -3;
9.6108$_{10}$ -3;	9.6194$_{10}$ -2;	2.9066;	5.0145$_{10}$ -3;
9.5191$_{10}$ -3;	9.5276$_{10}$ -2;	2.9435;	5.3221$_{10}$ -3;
9.4291$_{10}$ -3;	9.4375$_{10}$ -2;	2.9794;	5.6239$_{10}$ -3;
9.3396$_{10}$ -3;	9.3480$_{10}$ -2;	3.0165;	5.9239$_{10}$ -3;
9.2518$_{10}$ -3;	9.2601$_{10}$ -2;	3.0530;	6.2182$_{10}$ -3;
9.1662$_{10}$ -3;	9.1744$_{10}$ -2;	3.0908;	6.5054$_{10}$ -3;
9.0821$_{10}$ -3;	9.0902$_{10}$ -2;	3.1296;	6.7872$_{10}$ -3;
9.0012$_{10}$ -3;	9.0092$_{10}$ -2;	3.1667;	7.0586$_{10}$ -3;
8.9217$_{10}$ -3;	8.9297$_{10}$ -2;	3.2046;	7.3252$_{10}$ -3;
8.6139$_{10}$ -3;	8.6216$_{10}$ -2;	3.3591;	8.3573$_{10}$ -3;
8.3284$_{10}$ -3;	8.3358$_{10}$ -2;	3.5202;	9.3146$_{10}$ -3;
8.0597$_{10}$ -3;	8.0669$_{10}$ -2;	3.6894;	1.0215$_{10}$ -2;
7.9309$_{10}$ -3;	7.9379$_{10}$ -2;	3.7775;	1.0648$_{10}$ -2;
7.8682$_{10}$ -3;	7.8752$_{10}$ -2;	3.8230;	1.0858$_{10}$ -2;
7.8065$_{10}$ -3;	7.8135$_{10}$ -2;	3.8740;	1.1065$_{10}$ -2;
7.7462$_{10}$ -3;	7.7531$_{10}$ -2;	3.9182;	1.1267$_{10}$ -2;
7.6869$_{10}$ -3;	7.6937$_{10}$ -2;	3.9671;	1.1466$_{10}$ -2;
7.6282$_{10}$ -3;	7.6350$_{10}$ -2;	4.0189;	1.1662$_{10}$ -2;
7.5704$_{10}$ -3;	7.5772$_{10}$ -2;	4.0732;	1.1856$_{10}$ -2;

Sodium Tartrate Run 3

I = 0.2 T = 25°C.

Ta	Tm	pH	Tb
5.0059_{10} -3;	2.0801_{10} -2;	2.9828;	2.4943_{10} -3;
4.9752_{10} -3;	2.0673_{10} -2;	3.0206;	2.7098_{10} -3;
4.9550_{10} -3;	2.0589_{10} -2;	3.0475;	2.8520_{10} -3;
4.9249_{10} -3;	2.0464_{10} -2;	3.0886;	3.0631_{10} -3;
4.8752_{10} -3;	2.0257_{10} -2;	3.1570;	3.4128_{10} -3;
4.8264_{10} -3;	2.0055_{10} -2;	3.2273;	3.7555_{10} -3;
4.7316_{10} -3;	1.9661_{10} -2;	3.3783;	4.4216_{10} -3;
4.6406_{10} -3;	1.9283_{10} -2;	3.5379;	5.0611_{10} -3;
4.5523_{10} -3;	1.8916_{10} -2;	3.7079;	5.6815_{10} -3;
4.5096_{10} -3;	1.8738_{10} -2;	3.7973;	5.9818_{10} -3;
4.4676_{10} -3;	1.8564_{10} -2;	3.8922;	6.2765_{10} -3;
4.4512_{10} -3;	1.8496_{10} -2;	3.9300;	6.3920_{10} -3;
4.4268_{10} -3;	1.8394_{10} -2;	3.9922;	6.5637_{10} -3;
4.3866_{10} -3;	1.8228_{10} -2;	4.1006;	6.8456_{10} -3;
4.3471_{10} -3;	1.8063_{10} -2;	4.2226;	7.1235_{10} -3;
4.3083_{10} -3;	1.7902_{10} -2;	4.3619;	7.3964_{10} -3;

Sodium Tartrate Run 4

I = 0.2 T = 25°C.

Ta	Tm	pH	Tb
3.5432_{10} -3;	2.1272_{10} -2;	2.9860;	1.4771_{10} -3;
3.5058_{10} -3;	2.1047_{10} -2;	3.0619;	1.8269_{10} -3;
3.4691_{10} -3;	2.0827_{10} -2;	3.1418;	2.1693_{10} -3;
3.4333_{10} -3;	2.0612_{10} -2;	3.2270;	2.5039_{10} -3;
3.3982_{10} -3;	2.0402_{10} -2;	3.3154;	2.8317_{10} -3;
3.3639_{10} -3;	2.0195_{10} -2;	3.4067;	3.1526_{10} -3;
3.3302_{10} -3;	1.9993_{10} -2;	3.5063;	3.4670_{10} -3;
3.2972_{10} -3;	1.9795_{10} -2;	3.6065;	3.7756_{10} -3;
3.2648_{10} -3;	1.9601_{10} -2;	3.7145;	4.0781_{10} -3;
3.2332_{10} -3;	1.9411_{10} -2;	3.8279;	4.3733_{10} -3;
3.2022_{10} -3;	1.9225_{10} -2;	3.9468;	4.6629_{10} -3;
3.1716_{10} -3;	1.9041_{10} -2;	4.0815;	4.9488_{10} -3;

Sodium Tartrate Run 5

I = 0.2 T = 25°C.

Ta	Tm	[Na]	pH	[NaCl]
9.5289$_{10}$ -3	1.9058$_{10}$ -2	1.8419$_{10}$ -2	6.7872	0.0000
9.3945$_{10}$ -3	2.1610$_{10}$ -2	2.0996$_{10}$ -2	6.8734	2.8209$_{10}$ -3
9.2633$_{10}$ -3	2.4100$_{10}$ -2	2.3462$_{10}$ -2	6.8396	5.5735$_{10}$ -3
9.0748$_{10}$ -3	2.7681$_{10}$ -2	2.6894$_{10}$ -2	6.7819	9.5312$_{10}$ -3
8.9518$_{10}$ -3	3.0015$_{10}$ -2	2.9158$_{10}$ -2	6.8262	1.2111$_{10}$ -2
8.8333$_{10}$ -3	3.2266$_{10}$ -2	3.1549$_{10}$ -2	6.8218	1.4599$_{10}$ -2
8.7177$_{10}$ -3	3.4461$_{10}$ -2	3.3650$_{10}$ -2	6.8496	1.7026$_{10}$ -2
8.6058$_{10}$ -3	3.6587$_{10}$ -2	3.5934$_{10}$ -2	6.8617	1.9375$_{10}$ -2
8.4961$_{10}$ -3	3.8669$_{10}$ -2	3.7948$_{10}$ -2	6.8514	2.1677$_{10}$ -2
8.3888$_{10}$ -3	4.0708$_{10}$ -2	4.0011$_{10}$ -2	6.8330	2.3930$_{10}$ -2
8.2846$_{10}$ -3	4.2686$_{10}$ -2	4.1818$_{10}$ -2	6.8016	2.6117$_{10}$ -2
8.1827$_{10}$ -3	4.4621$_{10}$ -2	4.3829$_{10}$ -2	6.8009	2.8255$_{10}$ -2
8.0836$_{10}$ -3	4.6502$_{10}$ -2	4.5464$_{10}$ -2	6.8112	3.0334$_{10}$ -2

Sodium Tartrate Run 6

I = 0.2 T = 25°C.

Ta	Tm	[Na]
7.4026$_{10}$ -3	1.4805$_{10}$ -2	1.4605$_{10}$ -2
7.3209$_{10}$ -3	1.6849$_{10}$ -2	1.6735$_{10}$ -2
7.2410$_{10}$ -3	1.8848$_{10}$ -2	1.8471$_{10}$ -2
7.1485$_{10}$ -3	2.1162$_{10}$ -2	2.1055$_{10}$ -2
7.1182$_{10}$ -3	2.1918$_{10}$ -2	2.1478$_{10}$ -2
7.0882$_{10}$ -3	2.2669$_{10}$ -2	2.2279$_{10}$ -2
7.0136$_{10}$ -3	2.4536$_{10}$ -2	2.4289$_{10}$ -2
6.9407$_{10}$ -3	2.6361$_{10}$ -2	2.6083$_{10}$ -2
6.8691$_{10}$ -3	2.8152$_{10}$ -2	2.7391$_{10}$ -2
6.7990$_{10}$ -3	2.9906$_{10}$ -2	2.9614$_{10}$ -2

Sodium Tartrate Run 7

I = 0.2 T = 25°C.

Ta	Tm	[Na]
7.4026$_{10}$ -3	1.4805$_{10}$ -2	1.4721$_{10}$ -2
7.3861$_{10}$ -3	1.5217$_{10}$ -2	1.5065$_{10}$ -2
7.3697$_{10}$ -3	1.5628$_{10}$ -2	1.5559$_{10}$ -2
7.3534$_{10}$ -3	1.6036$_{10}$ -2	1.5865$_{10}$ -2
7.3209$_{10}$ -3	1.6847$_{10}$ -2	1.6721$_{10}$ -2
7.3048$_{10}$ -3	1.7251$_{10}$ -2	1.7057$_{10}$ -2
7.2888$_{10}$ -3	1.7652$_{10}$ -2	1.7400$_{10}$ -2
7.2411$_{10}$ -3	1.8845$_{10}$ -2	1.8537$_{10}$ -2

Sodium Tartrate Run 8

I = 0.2 T = 25°C.

Ta	Tm	[Na]
2.6380$_{10}$ -3	7.6551$_{10}$ -3	7.5761$_{10}$ -3
2.6338$_{10}$ -3	7.9592$_{10}$ -3	7.8212$_{10}$ -3
2.6276$_{10}$ -3	8.4135$_{10}$ -3	8.3123$_{10}$ -3
2.6173$_{10}$ -3	9.1655$_{10}$ -3	9.0226$_{10}$ -3
2.6071$_{10}$ -3	9.9114$_{10}$ -3	9.8248$_{10}$ -3
2.5969$_{10}$ -3	1.0652$_{10}$ -2	1.0588$_{10}$ -2
2.5670$_{10}$ -3	1.2834$_{10}$ -2	1.2660$_{10}$ -2
2.5473$_{10}$ -3	1.4268$_{10}$ -2	1.4052$_{10}$ -2

Appendix 1c

Potassium Tartrate Run 1

I = 0.2 T = 25^{o}C.

Ta	Tm	pH	Tb
5.2440$_{10}$ -3;	2.1790$_{10}$ -2;	2.7324;	8.2142$_{10}$ -4;
5.1866$_{10}$ -3;	2.1552$_{10}$ -2;	2.7885;	1.2241$_{10}$ -3;
5.1306$_{10}$ -3;	2.1319$_{10}$ -2;	2.8485;	1.6181$_{10}$ -3;
5.0777$_{10}$ -3;	2.1099$_{10}$ -2;	2.9045;	1.9898$_{10}$ -3;
5.0568$_{10}$ -3;	2.1012$_{10}$ -2;	2.9293;	2.1363$_{10}$ -3;
5.0259$_{10}$ -3;	2.0884$_{10}$ -2;	2.9669;	2.3539$_{10}$ -3;
4.9948$_{10}$ -3;	2.0754$_{10}$ -2;	3.0051;	2.5724$_{10}$ -3;
4.9742$_{10}$ -3;	2.0669$_{10}$ -2;	3.0306;	2.7166$_{10}$ -3;
4.9539$_{10}$ -3;	2.0585$_{10}$ -2;	3.0565;	2.8597$_{10}$ -3;
4.9237$_{10}$ -3;	2.0459$_{10}$ -2;	3.0965;	3.0720$_{10}$ -3;
4.8738$_{10}$ -3;	2.0252$_{10}$ -2;	3.1663;	3.4225$_{10}$ -3;
4.8249$_{10}$ -3;	2.0049$_{10}$ -2;	3.2385;	3.7659$_{10}$ -3;
4.7288$_{10}$ -3;	1.9649$_{10}$ -2;	3.3900;	4.4412$_{10}$ -3;
4.6370$_{10}$ -3;	1.9268$_{10}$ -2;	3.5502;	5.0863$_{10}$ -3;
4.5504$_{10}$ -3;	1.8908$_{10}$ -2;	3.7194;	5.6947$_{10}$ -3;
4.5077$_{10}$ -3;	1.8730$_{10}$ -2;	3.8110;	5.9951$_{10}$ -3;
4.4657$_{10}$ -3;	1.8556$_{10}$ -2;	3.9048;	6.2899$_{10}$ -3;
4.4493$_{10}$ -3;	1.8488$_{10}$ -2;	3.9451;	6.4054$_{10}$ -3;
4.4249$_{10}$ -3;	1.8386$_{10}$ -2;	4.0056;	6.5770$_{10}$ -3;
4.4087$_{10}$ -3;	1.8319$_{10}$ -2;	4.0460;	6.6903$_{10}$ -3;
4.3848$_{10}$ -3;	1.8220$_{10}$ -2;	4.1138;	6.8588$_{10}$ -3;
4.3457$_{10}$ -3;	1.8057$_{10}$ -2;	4.2343;	7.1336$_{10}$ -3;
4.3073$_{10}$ -3;	1.7898$_{10}$ -2;	4.3778;	7.4035$_{10}$ -3;

Appendix 1d

Lanthanum Tartrate Run 1

$I = 0.1$ $T = 25^{\circ}C.$

Ta	Tm	pH	Tb	[HCl]
3.9171$_{10}$ -3;	3.4678$_{10}$ -3;	2.5111;	0.0000 ;	5.5426$_{10}$ -4;
3.7904$_{10}$ -3;	3.3556$_{10}$ -3;	2.6452;	1.1456$_{10}$ -3;	5.3633$_{10}$ -4;
3.7501$_{10}$ -3;	3.3199$_{10}$ -3;	2.6904;	1.5106$_{10}$ -3;	5.3062$_{10}$ -4;
3.7106$_{10}$ -3;	3.2849$_{10}$ -3;	2.7395;	1.8677$_{10}$ -3;	5.2503$_{10}$ -4;
3.6719$_{10}$ -3;	3.2507$_{10}$ -3;	2.7885;	2.2173$_{10}$ -3;	5.1956$_{10}$ -4;
3.6340$_{10}$ -3;	3.2171$_{10}$ -3;	2.8414;	2.5600$_{10}$ -3;	5.1420$_{10}$ -4;
3.5968$_{10}$ -3;	3.1842$_{10}$ -3;	2.8951;	2.8957$_{10}$ -3;	5.0894$_{10}$ -4;
3.5606$_{10}$ -3;	3.1522$_{10}$ -3;	2.9531;	3.2231$_{10}$ -3;	5.0382$_{10}$ -4;
3.5251$_{10}$ -3;	3.1208$_{10}$ -3;	3.0133;	3.5441$_{10}$ -3;	4.9880$_{10}$ -4;
3.5040$_{10}$ -3;	3.1021$_{10}$ -3;	3.0494;	3.7348$_{10}$ -3;	4.9581$_{10}$ -4;
3.4901$_{10}$ -3;	3.0898$_{10}$ -3;	3.0768;	3.8606$_{10}$ -3;	4.9384$_{10}$ -4;
3.4558$_{10}$ -3;	3.0594$_{10}$ -3;	3.1455;	4.1710$_{10}$ -3;	4.8898$_{10}$ -4;
3.4355$_{10}$ -3;	3.0414$_{10}$ -3;	3.1896;	4.3542$_{10}$ -3;	4.8611$_{10}$ -4;
3.4221$_{10}$ -3;	3.0296$_{10}$ -3;	3.2208;	4.4752$_{10}$ -3;	4.8422$_{10}$ -4;
3.4023$_{10}$ -3;	3.0120$_{10}$ -3;	3.2683;	4.6549$_{10}$ -3;	4.8141$_{10}$ -4;
3.3891$_{10}$ -3;	3.0004$_{10}$ -3;	3.3011;	4.7736$_{10}$ -3;	4.7955$_{10}$ -4;
3.3697$_{10}$ -3;	2.9832$_{10}$ -3;	3.3537;	4.9490$_{10}$ -3;	4.7681$_{10}$ -4;
3.3569$_{10}$ -3;	2.9718$_{10}$ -3;	3.3961;	5.0647$_{10}$ -3;	4.7499$_{10}$ -4;
3.3253$_{10}$ -3;	2.9439$_{10}$ -3;	3.4900;	5.3504$_{10}$ -3;	4.7052$_{10}$ -4;
3.2942$_{10}$ -3;	2.9163$_{10}$ -3;	3.6039;	5.6318$_{10}$ -3;	4.6612$_{10}$ -4;
3.2637$_{10}$ -3;	2.8893$_{10}$ -3;	3.7393;	5.9079$_{10}$ -3;	4.6180$_{10}$ -4;

Lanthanum Tartrate Run 2

$I = 0.1$ $T = 25^{\circ}C.$

Ta	Tm	pH	Tb	[HCl]
4.1478$_{10}$ -3;	1.8380$_{10}$ -3;	2.5862;	0.0000 ;	2.9378$_{10}$ -4;
4.0527$_{10}$ -3;	1.7959$_{10}$ -3;	2.6859;	8.1143$_{10}$ -4;	2.8704$_{10}$ -4;
4.0066$_{10}$ -3;	1.7755$_{10}$ -3;	2.7396;	1.2052$_{10}$ -3;	2.8378$_{10}$ -4;
3.9615$_{10}$ -3;	1.7555$_{10}$ -3;	2.7941;	1.5901$_{10}$ -3;	2.8058$_{10}$ -4;
3.9175$_{10}$ -3;	1.7360$_{10}$ -3;	2.8515;	1.9661$_{10}$ -3;	2.7747$_{10}$ -4;
3.8744$_{10}$ -3;	1.7169$_{10}$ -3;	2.9108;	2.3338$_{10}$ -3;	2.7442$_{10}$ -4;
3.8320$_{10}$ -3;	1.6981$_{10}$ -3;	2.9746;	2.6959$_{10}$ -3;	2.7141$_{10}$ -4;
3.7905$_{10}$ -3;	1.6797$_{10}$ -3;	3.0423;	3.0501$_{10}$ -3;	2.6847$_{10}$ -4;
3.7501$_{10}$ -3;	1.6618$_{10}$ -3;	3.1143;	3.3956$_{10}$ -3;	2.6561$_{10}$ -4;
3.7104$_{10}$ -3;	1.6442$_{10}$ -3;	3.1883;	3.7339$_{10}$ -3;	2.6280$_{10}$ -4;
3.6717$_{10}$ -3;	1.6271$_{10}$ -3;	3.2701;	4.0643$_{10}$ -3;	2.6006$_{10}$ -4;
3.6338$_{10}$ -3;	1.6103$_{10}$ -3;	3.3570;	4.3879$_{10}$ -3;	2.5738$_{10}$ -4;
3.5967$_{10}$ -3;	1.5939$_{10}$ -3;	3.4520;	4.7046$_{10}$ -3;	2.5475$_{10}$ -4;
3.5604$_{10}$ -3;	1.5777$_{10}$ -3;	3.5574;	5.0149$_{10}$ -3;	2.5217$_{10}$ -4;
3.5248$_{10}$ -3;	1.5619$_{10}$ -3;	3.6712;	5.3193$_{10}$ -3;	2.4965$_{10}$ -4;
3.4898$_{10}$ -3;	1.5465$_{10}$ -3;	3.8014;	5.6177$_{10}$ -3;	2.4717$_{10}$ -4;
3.4557$_{10}$ -3;	1.5314$_{10}$ -3;	3.9568;	5.9089$_{10}$ -3;	2.4476$_{10}$ -4;
3.4223$_{10}$ -3;	1.5165$_{10}$ -3;	4.1378;	6.1944$_{10}$ -3;	2.4239$_{10}$ -4;

Lanthanum Tartrate Run 3

I = 0.1 T = 25°C.

Ta	Tm	pH	Tb	[HCl]
2.0758$_{10}$ -3;	1.8347$_{10}$ -3;	2.7393;	0.0000 ;	2.9325$_{10}$ -4;
2.0516$_{10}$ -3;	1.8133$_{10}$ -3;	2.8151;	4.1337$_{10}$ -4;	2.8983$_{10}$ -4;
2.0279$_{10}$ -3;	1.7924$_{10}$ -3;	2.8919;	8.1719$_{10}$ -4;	2.8648$_{10}$ -4;
2.0140$_{10}$ -3;	1.7801$_{10}$ -3;	2.9438;	1.0545$_{10}$ -3;	2.8452$_{10}$ -4;
2.0048$_{10}$ -3;	1.7720$_{10}$ -3;	2.9796;	1.2109$_{10}$ -3;	2.8322$_{10}$ -4;
1.9822$_{10}$ -3;	1.7521$_{10}$ -3;	3.0748;	1.5958$_{10}$ -3;	2.8003$_{10}$ -4;
1.9690$_{10}$ -3;	1.7403$_{10}$ -3;	3.1385;	1.8224$_{10}$ -3;	2.7816$_{10}$ -4;
1.9602$_{10}$ -3;	1.7326$_{10}$ -3;	3.1873;	1.9718$_{10}$ -3;	2.7692$_{10}$ -4;
1.9387$_{10}$ -3;	1.7135$_{10}$ -3;	3.3110;	2.3395$_{10}$ -3;	2.7388$_{10}$ -4;
1.9259$_{10}$ -3;	1.7023$_{10}$ -3;	3.3963;	2.5565$_{10}$ -3;	2.7208$_{10}$ -4;
1.9175$_{10}$ -3;	1.6949$_{10}$ -3;	3.4591;	2.6996$_{10}$ -3;	2.7089$_{10}$ -4;
1.8969$_{10}$ -3;	1.6766$_{10}$ -3;	3.6440;	3.0519$_{10}$ -3;	2.6798$_{10}$ -4;
1.8848$_{10}$ -3;	1.6659$_{10}$ -3;	3.7827;	3.2588$_{10}$ -3;	2.6626$_{10}$ -4;
1.8768$_{10}$ -3;	1.6588$_{10}$ -3;	3.9087;	3.3952$_{10}$ -3;	2.6513$_{10}$ -4;
1.8649$_{10}$ -3;	1.6483$_{10}$ -3;	4.1001;	3.5977$_{10}$ -3;	2.6346$_{10}$ -4;

Lanthanum Tartrate Run 4

I = 0.2 T = 25°C.

Ta	Tm	pH	Tb	[HCl]
3.7052$_{10}$ -3;	3.6999$_{10}$ -3;	2.5144;	0.0000 ;	9.4441$_{10}$ -4;
3.6239$_{10}$ -3;	3.6187$_{10}$ -3;	2.6134;	8.7530$_{10}$ -4;	9.2368$_{10}$ -4;
3.5853$_{10}$ -3;	3.5802$_{10}$ -3;	2.6662;	1.2904$_{10}$ -3;	9.1385$_{10}$ -4;
3.5475$_{10}$ -3;	3.5425$_{10}$ -3;	2.7213;	1.6968$_{10}$ -3;	9.0423$_{10}$ -4;
3.5100$_{10}$ -3;	3.5050$_{10}$ -3;	2.7802;	2.1009$_{10}$ -3;	8.9466$_{10}$ -4;
3.4732$_{10}$ -3;	3.4683$_{10}$ -3;	2.8396;	2.4966$_{10}$ -3;	8.8529$_{10}$ -4;
3.4375$_{10}$ -3;	3.4326$_{10}$ -3;	2.9040;	2.8809$_{10}$ -3;	8.7619$_{10}$ -4;
3.4026$_{10}$ -3;	3.3977$_{10}$ -3;	2.9708;	3.2573$_{10}$ -3;	8.6727$_{10}$ -4;
3.3685$_{10}$ -3;	3.3637$_{10}$ -3;	3.0434;	3.6236$_{10}$ -3;	8.5860$_{10}$ -4;
3.3352$_{10}$ -3;	3.3304$_{10}$ -3;	3.1196;	3.9826$_{10}$ -3;	8.5010$_{10}$ -4;
3.3022$_{10}$ -3;	3.2974$_{10}$ -3;	3.2028;	4.3381$_{10}$ -3;	8.4168$_{10}$ -4;
3.2698$_{10}$ -3;	3.2651$_{10}$ -3;	3.2944;	4.6865$_{10}$ -3;	8.3343$_{10}$ -4;
3.2380$_{10}$ -3;	3.2333$_{10}$ -3;	3.3929;	5.0287$_{10}$ -3;	8.2533$_{10}$ -4;
3.2068$_{10}$ -3;	3.2022$_{10}$ -3;	3.5099;	5.3643$_{10}$ -3;	8.1738$_{10}$ -4;
3.1763$_{10}$ -3;	3.1717$_{10}$ -3;	3.6454;	5.6930$_{10}$ -3;	8.0960$_{10}$ -4;
3.1463$_{10}$ -3;	3.1418$_{10}$ -3;	3.8129;	6.0155$_{10}$ -3;	8.0196$_{10}$ -4;
3.1167$_{10}$ -3;	3.1122$_{10}$ -3;	4.0258;	6.3345$_{10}$ -3;	7.9440$_{10}$ -4;
3.0876$_{10}$ -3;	3.0831$_{10}$ -3;	4.3061;	6.6476$_{10}$ -3;	7.8699$_{10}$ -4;

Lanthanum Tartrate Run 5

I = 0.2 T = 25°C.

Ta	Tm	pH	Tb	[HCl]
1.7497_{10} -3;	1.7546_{10} -3;	2.7768;	0.0000 ;	4.4788_{10} -4;
1.7136_{10} -3;	1.7185_{10} -3;	2.9568;	8.2219_{10} -4;	4.3864_{10} -4;
1.6960_{10} -3;	1.7008_{10} -3;	3.0611;	1.2239_{10} -3;	4.3413_{10} -4;
1.6856_{10} -3;	1.6903_{10} -3;	3.1294;	1.4610_{10} -3;	4.3147_{10} -4;
1.6787_{10} -3;	1.6835_{10} -3;	3.1756;	1.6175_{10} -3;	4.2971_{10} -4;
1.6685_{10} -3;	1.6733_{10} -3;	3.2621;	1.8489_{10} -3;	4.2711_{10} -4;
1.6618_{10} -3;	1.6666_{10} -3;	3.3215;	2.0017_{10} -3;	4.2540_{10} -4;
1.6519_{10} -3;	1.6566_{10} -3;	3.4200;	2.2286_{10} -3;	4.2285_{10} -4;
1.6453_{10} -3;	1.6500_{10} -3;	3.4911;	2.3783_{10} -3;	4.2117_{10} -4;
1.6356_{10} -3;	1.6403_{10} -3;	3.6122;	2.5991_{10} -3;	4.1869_{10} -4;
1.6292_{10} -3;	1.6339_{10} -3;	3.7063;	2.7448_{10} -3;	4.1705_{10} -4;
1.6197_{10} -3;	1.6243_{10} -3;	3.8802;	2.9612_{10} -3;	4.1462_{10} -4;
1.6135_{10} -3;	1.6181_{10} -3;	4.0244;	3.1041_{10} -3;	4.1302_{10} -4;
1.6041_{10} -3;	1.6087_{10} -3;	4.3400;	3.3172_{10} -3;	4.1062_{10} -4;
1.5979_{10} -3;	1.6025_{10} -3;	4.7532;	3.4579_{10} -3;	4.0904_{10} -4;

Lanthanum Tartrate Run 6

I = 0.2 T = 25°C.

Ta	Tm	pH	Tb	[HCl]
3.9137_{10} -3;	1.9608_{10} -3;	2.5871;	0.0000 ;	5.0050_{10} -4;
3.8238_{10} -3;	1.9157_{10} -3;	2.7033;	9.1666_{10} -4;	4.8900_{10} -4;
3.7803_{10} -3;	1.8939_{10} -3;	2.7645;	1.3599_{10} -3;	4.8344_{10} -4;
3.7377_{10} -3;	1.8726_{10} -3;	2.8312;	1.7932_{10} -3;	4.7800_{10} -4;
3.6921_{10} -3;	1.8498_{10} -3;	2.9155;	2.2581_{10} -3;	4.7216_{10} -4;
3.6556_{10} -3;	1.8315_{10} -3;	2.9756;	2.6301_{10} -3;	4.6750_{10} -4;
3.6156_{10} -3;	1.8114_{10} -3;	3.0523;	3.0382_{10} -3;	4.6237_{10} -4;
3.5764_{10} -3;	1.7918_{10} -3;	3.1373;	3.4374_{10} -3;	4.5736_{10} -4;
3.5382_{10} -3;	1.7727_{10} -3;	3.2260;	3.8267_{10} -3;	4.5248_{10} -4;
3.5008_{10} -3;	1.7539_{10} -3;	3.3244;	4.2077_{10} -3;	4.4770_{10} -4;
3.4645_{10} -3;	1.7357_{10} -3;	3.4298;	4.5780_{10} -3;	4.4305_{10} -4;
3.4289_{10} -3;	1.7179_{10} -3;	3.5484;	4.9407_{10} -3;	4.3850_{10} -4;
3.3939_{10} -3;	1.7003_{10} -3;	3.6837;	5.2973_{10} -3;	4.3402_{10} -4;
3.3596_{10} -3;	1.6832_{10} -3;	3.8426;	5.6467_{10} -3;	4.2964_{10} -4;
3.3260_{10} -3;	1.6664_{10} -3;	4.0352;	5.9885_{10} -3;	4.2535_{10} -4;
3.2932_{10} -3;	1.6499_{10} -3;	4.2802;	6.3235_{10} -3;	4.2114_{10} -4;

Lanthanum Tartrate Run 7

I = 0.2 T = 25°C.

Ta	Tm	pH	Tb	[HCl]
7.3906$_{10}$ -3;	3.7015$_{10}$ -3;	2.3792;	0.0000 ;	9.4482$_{10}$ -4;
7.1555$_{10}$ -3;	3.5838$_{10}$ -3;	2.4819;	1.2683$_{10}$ -3;	9.1477$_{10}$ -4;
7.0796$_{10}$ -3;	3.5457$_{10}$ -3;	2.5186;	1.6779$_{10}$ -3;	9.0507$_{10}$ -4;
7.0048$_{10}$ -3;	3.5083$_{10}$ -3;	2.5556;	2.0815$_{10}$ -3;	8.9551$_{10}$ -4;
6.9316$_{10}$ -3;	3.4716$_{10}$ -3;	2.5923;	2.4767$_{10}$ -3;	8.8614$_{10}$ -4;
6.8589$_{10}$ -3;	3.4352$_{10}$ -3;	2.6311;	2.8687$_{10}$ -3;	8.7686$_{10}$ -4;
6.7878$_{10}$ -3;	3.3996$_{10}$ -3;	2.6702;	3.2526$_{10}$ -3;	8.6776$_{10}$ -4;
6.7199$_{10}$ -3;	3.3656$_{10}$ -3;	2.7099;	3.6190$_{10}$ -3;	8.5908$_{10}$ -4;
6.6533$_{10}$ -3;	3.3322$_{10}$ -3;	2.7506;	3.9783$_{10}$ -3;	8.5057$_{10}$ -4;
6.5880$_{10}$ -3;	3.2995$_{10}$ -3;	2.7906;	4.3304$_{10}$ -3;	8.4223$_{10}$ -4;
6.5240$_{10}$ -3;	3.2675$_{10}$ -3;	2.8332;	4.6758$_{10}$ -3;	8.3405$_{10}$ -4;
6.4603$_{10}$ -3;	3.2356$_{10}$ -3;	2.8760;	5.0197$_{10}$ -3;	8.2590$_{10}$ -4;
6.3978$_{10}$ -3;	3.2043$_{10}$ -3;	2.9197;	5.3570$_{10}$ -3;	8.1791$_{10}$ -4;
6.3370$_{10}$ -3;	3.1738$_{10}$ -3;	2.9637;	5.6851$_{10}$ -3;	8.1013$_{10}$ -4;
6.2773$_{10}$ -3;	3.1439$_{10}$ -3;	3.0093;	6.0071$_{10}$ -3;	8.0250$_{10}$ -4;
6.2192$_{10}$ -3;	3.1148$_{10}$ -3;	3.0562;	6.3208$_{10}$ -3;	7.9507$_{10}$ -4;
6.1621$_{10}$ -3;	3.0862$_{10}$ -3;	3.1043;	6.6287$_{10}$ -3;	7.8778$_{10}$ -4;
6.1055$_{10}$ -3;	3.0579$_{10}$ -3;	3.1549;	6.9340$_{10}$ -3;	7.8054$_{10}$ -4;
6.0500$_{10}$ -3;	3.0301$_{10}$ -3;	3.2065;	7.2338$_{10}$ -3;	7.7344$_{10}$ -4;
5.9954$_{10}$ -3;	3.0027$_{10}$ -3;	3.2775;	7.5285$_{10}$ -3;	7.6646$_{10}$ -4;
5.9417$_{10}$ -3;	2.9758$_{10}$ -3;	3.3198;	7.8180$_{10}$ -3;	7.5960$_{10}$ -4;
5.8891$_{10}$ -3;	2.9495$_{10}$ -3;	3.3758;	8.1020$_{10}$ -3;	7.5287$_{10}$ -4;
5.8374$_{10}$ -3;	2.9236$_{10}$ -3;	3.4302;	8.3809$_{10}$ -3;	7.4626$_{10}$ -4;

Lanthanum Tartrate Run 8

I = 0.2 T = 25°C.

Ta	Tm	pH	Tb	[HCl]
5.7348_{10} -3;	1.9160_{10} -3;	2.5545;	5.0968_{10} -4;	4.8906_{10} -4;
5.6698_{10} -3;	1.8943_{10} -3;	2.5808;	7.5381_{10} -4;	4.8352_{10} -4;
5.6063_{10} -3;	1.8730_{10} -3;	2.6085;	9.9246_{10} -4;	4.7810_{10} -4;
5.5446_{10} -3;	1.8524_{10} -3;	2.6357;	1.2242_{10} -3;	4.7284_{10} -4;
5.4842_{10} -3;	1.8323_{10} -3;	2.6640;	1.4508_{10} -3;	4.6769_{10} -4;
5.4246_{10} -3;	1.8123_{10} -3;	2.6920;	1.6748_{10} -3;	4.6261_{10} -4;
5.3663_{10} -3;	1.7928_{10} -3;	2.7207;	1.8939_{10} -3;	4.5763_{10} -4;
5.3091_{10} -3;	1.7737_{10} -3;	2.7492;	2.1087_{10} -3;	4.5276_{10} -4;
5.2531_{10} -3;	1.7550_{10} -3;	2.7800;	2.3189_{10} -3;	4.4798_{10} -4;
5.1984_{10} -3;	1.7368_{10} -3;	2.8096;	2.5245_{10} -3;	4.4332_{10} -4;
5.1448_{10} -3;	1.7189_{10} -3;	2.8403;	2.7258_{10} -3;	4.3875_{10} -4;
5.0918_{10} -3;	1.7012_{10} -3;	2.8713;	2.9246_{10} -3;	4.3423_{10} -4;
5.0400_{10} -3;	1.6838_{10} -3;	2.9022;	3.1194_{10} -3;	4.2981_{10} -4;
4.9894_{10} -3;	1.6669_{10} -3;	2.9332;	3.3095_{10} -3;	4.2549_{10} -4;
4.9398_{10} -3;	1.6504_{10} -3;	2.9658;	3.4959_{10} -3;	4.2126_{10} -4;
4.8915_{10} -3;	1.6342_{10} -3;	2.9983;	3.6772_{10} -3;	4.1714_{10} -4;
4.8441_{10} -3;	1.6184_{10} -3;	3.0324;	3.8550_{10} -3;	4.1311_{10} -4;
4.7975_{10} -3;	1.6028_{10} -3;	3.0665;	4.0301_{10} -3;	4.0913_{10} -4;
4.7518_{10} -3;	1.5876_{10} -3;	3.1024;	4.2018_{10} -3;	4.0523_{10} -4;
4.7070_{10} -3;	1.5726_{10} -3;	3.1382;	4.3700_{10} -3;	4.0142_{10} -4;
4.6631_{10} -3;	1.5579_{10} -3;	3.1756;	4.5350_{10} -3;	3.9767_{10} -4;
4.6196_{10} -3;	1.5434_{10} -3;	3.2119;	4.6982_{10} -3;	3.9396_{10} -4;
4.5770_{10} -3;	1.5292_{10} -3;	3.2503;	4.8584_{10} -3;	3.9033_{10} -4;
4.5356_{10} -3;	1.5153_{10} -3;	3.2876;	5.0141_{10} -3;	3.8679_{10} -4;
4.4949_{10} -3;	1.5017_{10} -3;	3.3305;	5.1669_{10} -3;	3.8332_{10} -4;
4.4547_{10} -3;	1.4883_{10} -3;	3.3720;	5.3180_{10} -3;	3.7989_{10} -4;
4.4071_{10} -3;	1.4724_{10} -3;	3.4256;	5.4966_{10} -3;	3.7584_{10} -4;
4.3686_{10} -3;	1.4595_{10} -3;	3.4695;	5.6411_{10} -3;	3.7256_{10} -4;
4.3311_{10} -3;	1.4470_{10} -3;	3.5152;	5.7821_{10} -3;	3.6935_{10} -4;
4.2942_{10} -3;	1.4347_{10} -3;	3.5641;	5.9208_{10} -3;	3.6621_{10} -4;
4.2575_{10} -3;	1.4224_{10} -3;	3.6135;	6.0584_{10} -3;	3.6308_{10} -4;
4.2215_{10} -3;	1.4104_{10} -3;	3.6645;	6.1937_{10} -3;	3.6001_{10} -4;
4.1860_{10} -3;	1.3985_{10} -3;	3.7186;	6.3269_{10} -3;	3.5698_{10} -4;
4.1512_{10} -3;	1.3869_{10} -3;	3.7766;	6.4579_{10} -3;	3.5401_{10} -4;
4.1169_{10} -3;	1.3754_{10} -3;	3.8365;	6.5865_{10} -3;	3.5109_{10} -4;
4.0832_{10} -3;	1.3642_{10} -3;	3.9010;	6.7131_{10} -3;	3.4822_{10} -4;
4.0498_{10} -3;	1.3530_{10} -3;	3.9671;	6.8386_{10} -3;	3.4537_{10} -4;
4.0169_{10} -3;	1.3420_{10} -3;	4.0411;	6.9621_{10} -3;	3.4256_{10} -4;
3.9847_{10} -3;	1.3313_{10} -3;	4.1196;	7.0831_{10} -3;	3.3982_{10} -4;
3.9530_{10} -3;	1.3207_{10} -3;	4.2083;	7.2022_{10} -3;	3.3711_{10} -4;
3.9220_{10} -3;	1.3103_{10} -3;	4.3043;	7.3185_{10} -3;	3.3447_{10} -4;
3.8915_{10} -3;	1.3001_{10} -3;	4.4214;	7.4331_{10} -3;	3.3187_{10} -4;

Lanthanum Tartrate Run 9

I = 0.2 T = 25°C.

Ta	Tm	pH	Tb	[HCl]
3.6545$_{10}$ -3;	3.7162$_{10}$ -4;	3.0206;	9.7374$_{10}$ -4;	9.4859$_{10}$ -5;
3.6344$_{10}$ -3;	5.5325$_{10}$ -4;	2.9973;	9.6837$_{10}$ -4;	1.4122$_{10}$ -4;
3.6144$_{10}$ -3;	7.3289$_{10}$ -4;	2.9761;	9.6306$_{10}$ -4;	1.8707$_{10}$ -4;
3.5951$_{10}$ -3;	9.0710$_{10}$ -4;	2.9563;	9.5791$_{10}$ -4;	2.3154$_{10}$ -4;
3.5760$_{10}$ -3;	1.0794$_{10}$ -3;	2.9381;	9.5281$_{10}$ -4;	2.7553$_{10}$ -4;
3.5568$_{10}$ -3;	1.2526$_{10}$ -3;	2.9197;	9.4769$_{10}$ -4;	3.1973$_{10}$ -4;
3.5377$_{10}$ -3;	1.4239$_{10}$ -3;	2.9040;	9.4262$_{10}$ -4;	3.6346$_{10}$ -4;
3.5191$_{10}$ -3;	1.5920$_{10}$ -3;	2.8885;	9.3765$_{10}$ -4;	4.0637$_{10}$ -4;
3.5006$_{10}$ -3;	1.7584$_{10}$ -3;	2.8745;	9.3273$_{10}$ -4;	4.4884$_{10}$ -4;
3.4825$_{10}$ -3;	1.9218$_{10}$ -3;	2.8605;	9.2790$_{10}$ -4;	4.9056$_{10}$ -4;
3.4645$_{10}$ -3;	2.0836$_{10}$ -3;	2.8472;	9.2312$_{10}$ -4;	5.3185$_{10}$ -4;
3.4466$_{10}$ -3;	2.2453$_{10}$ -3;	2.8349;	9.1833$_{10}$ -4;	5.7312$_{10}$ -4;
3.4288$_{10}$ -3;	2.4053$_{10}$ -3;	2.8232;	9.1360$_{10}$ -4;	6.1396$_{10}$ -4;
3.4112$_{10}$ -3;	2.5639$_{10}$ -3;	2.8128;	9.0891$_{10}$ -4;	6.5444$_{10}$ -4;
3.3938$_{10}$ -3;	2.7208$_{10}$ -3;	2.8013;	9.0427$_{10}$ -4;	6.9451$_{10}$ -4;
3.3766$_{10}$ -3;	2.8760$_{10}$ -3;	2.7908;	8.9968$_{10}$ -4;	7.3411$_{10}$ -4;
3.3595$_{10}$ -3;	3.0296$_{10}$ -3;	2.7807;	8.9514$_{10}$ -4;	7.7332$_{10}$ -4;
3.3425$_{10}$ -3;	3.1829$_{10}$ -3;	2.7713;	8.9061$_{10}$ -4;	8.1244$_{10}$ -4;
3.3257$_{10}$ -3;	3.3346$_{10}$ -3;	2.7627;	8.8612$_{10}$ -4;	8.5118$_{10}$ -4;
3.3091$_{10}$ -3;	3.4843$_{10}$ -3;	2.7527;	8.8170$_{10}$ -4;	8.8938$_{10}$ -4;
3.2926$_{10}$ -3;	3.6325$_{10}$ -3;	2.7441;	8.7731$_{10}$ -4;	9.2721$_{10}$ -4;
3.2765$_{10}$ -3;	3.7781$_{10}$ -3;	2.7369;	8.7301$_{10}$ -4;	9.6438$_{10}$ -4;
3.2605$_{10}$ -3;	3.9223$_{10}$ -3;	2.7286;	8.6874$_{10}$ -4;	1.0012$_{10}$ -3;
3.2446$_{10}$ -3;	4.0656$_{10}$ -3;	2.7212;	8.6450$_{10}$ -4;	1.0378$_{10}$ -3;
3.2288$_{10}$ -3;	4.2076$_{10}$ -3;	2.7132;	8.6031$_{10}$ -4;	1.0740$_{10}$ -3;
3.2132$_{10}$ -3;	4.3479$_{10}$ -3;	2.7060;	8.5616$_{10}$ -4;	1.1098$_{10}$ -3;
3.1978$_{10}$ -3;	4.4868$_{10}$ -3;	2.6989;	8.5205$_{10}$ -4;	1.1453$_{10}$ -3;
3.1824$_{10}$ -3;	4.6255$_{10}$ -3;	2.6920;	8.4795$_{10}$ -4;	1.1807$_{10}$ -3;
3.1672$_{10}$ -3;	4.7629$_{10}$ -3;	2.6849;	8.4389$_{10}$ -4;	1.2157$_{10}$ -3;
3.1522$_{10}$ -3;	4.8975$_{10}$ -3;	2.6782;	8.3991$_{10}$ -4;	1.2501$_{10}$ -3;
3.1374$_{10}$ -3;	5.0309$_{10}$ -3;	2.6721;	8.3596$_{10}$ -4;	1.2842$_{10}$ -3;
3.1024$_{10}$ -3;	5.3469$_{10}$ -3;	2.6577;	8.2662$_{10}$ -4;	1.3648$_{10}$ -3;
3.0735$_{10}$ -3;	5.6067$_{10}$ -3;	2.6459;	8.1893$_{10}$ -4;	1.4312$_{10}$ -3;
3.0455$_{10}$ -3;	5.8592$_{10}$ -3;	2.6348;	8.1147$_{10}$ -4;	1.4956$_{10}$ -3;
3.0178$_{10}$ -3;	6.1086$_{10}$ -3;	2.6238;	8.0409$_{10}$ -4;	1.5592$_{10}$ -3;
2.9934$_{10}$ -3;	6.0592$_{10}$ -3;	2.6680;	9.7576$_{10}$ -4;	1.5466$_{10}$ -3;

Lanthanum Tartrate Run 10

I = 0.2 T = 25°C.

Ta	Tm	pH	Tb	[HCl]
4.0077$_{10}$ -3;	4.0333$_{10}$ -4;	3.8799;	5.8578$_{10}$ -3;	1.0295$_{10}$ -4;
3.9838$_{10}$ -3;	5.9975$_{10}$ -4;	3.8301;	5.8228$_{10}$ -3;	1.5309$_{10}$ -4;
3.9602$_{10}$ -3;	7.9383$_{10}$ -4;	3.7834;	5.7883$_{10}$ -3;	2.0263$_{10}$ -4;
3.9370$_{10}$ -3;	9.8425$_{10}$ -4;	3.7377;	5.7543$_{10}$ -3;	2.5124$_{10}$ -4;
3.9140$_{10}$ -3;	1.1725$_{10}$ -3;	3.6923;	5.7208$_{10}$ -3;	2.9927$_{10}$ -4;
3.8912$_{10}$ -3;	1.3603$_{10}$ -3;	3.6511;	5.6874$_{10}$ -3;	3.4723$_{10}$ -4;
3.8685$_{10}$ -3;	1.5460$_{10}$ -3;	3.6090;	5.6543$_{10}$ -3;	3.9463$_{10}$ -4;
3.8461$_{10}$ -3;	1.7298$_{10}$ -3;	3.5703;	5.6216$_{10}$ -3;	4.4154$_{10}$ -4;
3.8240$_{10}$ -3;	1.9114$_{10}$ -3;	3.5339;	5.5892$_{10}$ -3;	4.8791$_{10}$ -4;
3.8022$_{10}$ -3;	2.0908$_{10}$ -3;	3.5007;	5.5573$_{10}$ -3;	5.3368$_{10}$ -4;
3.7806$_{10}$ -3;	2.2681$_{10}$ -3;	3.4686;	5.5257$_{10}$ -3;	5.7894$_{10}$ -4;
3.7590$_{10}$ -3;	2.4448$_{10}$ -3;	3.4381;	5.4943$_{10}$ -3;	6.2405$_{10}$ -4;
3.5963$_{10}$ -3;	2.3390$_{10}$ -3;	3.7382;	6.2109$_{10}$ -3;	5.9704$_{10}$ -4;
3.5768$_{10}$ -3;	2.5068$_{10}$ -3;	3.7044;	6.1772$_{10}$ -3;	6.3986$_{10}$ -4;
3.5576$_{10}$ -3;	2.6721$_{10}$ -3;	3.6700;	6.1440$_{10}$ -3;	6.8208$_{10}$ -4;
3.5386$_{10}$ -3;	2.8357$_{10}$ -3;	3.6375;	6.1112$_{10}$ -3;	7.2383$_{10}$ -4;
3.5200$_{10}$ -3;	2.9964$_{10}$ -3;	3.6058;	6.0790$_{10}$ -3;	7.6484$_{10}$ -4;
3.5015$_{10}$ -3;	3.1553$_{10}$ -3;	3.5754;	6.0471$_{10}$ -3;	8.0541$_{10}$ -4;
3.4832$_{10}$ -3;	3.3132$_{10}$ -3;	3.5482;	6.0154$_{10}$ -3;	8.4571$_{10}$ -4;
3.4650$_{10}$ -3;	3.4695$_{10}$ -3;	3.5211;	5.9841$_{10}$ -3;	8.8560$_{10}$ -4;
3.4471$_{10}$ -3;	3.6238$_{10}$ -3;	3.4956;	5.9531$_{10}$ -3;	9.2499$_{10}$ -4;
3.4293$_{10}$ -3;	3.7765$_{10}$ -3;	3.4718;	5.9225$_{10}$ -3;	9.6398$_{10}$ -4;
3.4116$_{10}$ -3;	3.9289$_{10}$ -3;	3.4487;	5.8919$_{10}$ -3;	1.0029$_{10}$ -3;
3.3941$_{10}$ -3;	4.0796$_{10}$ -3;	3.4278;	5.8617$_{10}$ -3;	1.0413$_{10}$ -3;
3.3600$_{10}$ -3;	4.3735$_{10}$ -3;	3.4064;	5.8027$_{10}$ -3;	1.1164$_{10}$ -3;
3.3431$_{10}$ -3;	4.5191$_{10}$ -3;	3.3681;	5.7735$_{10}$ -3;	1.1535$_{10}$ -3;
3.3263$_{10}$ -3;	4.6633$_{10}$ -3;	3.3499;	5.7446$_{10}$ -3;	1.1903$_{10}$ -3;

Lanthanum Tartrate Run 11

I = 0.4   T = 25°C.

Ta	Tm	pH	Tb	[HCl]
3.4971$_{10}$ -3;	4.5909$_{10}$ -3;	2.5497;	0.0000 ;	9.2510$_{10}$ -4;
3.4250$_{10}$ -3;	4.4962$_{10}$ -3;	2.6373;	7.1360$_{10}$ -4;	9.0601$_{10}$ -4;
3.3900$_{10}$ -3;	4.4503$_{10}$ -3;	2.6816;	1.0592$_{10}$ -3;	8.9677$_{10}$ -4;
3.3558$_{10}$ -3;	4.4053$_{10}$ -3;	2.7284;	1.3977$_{10}$ -3;	8.8771$_{10}$ -4;
3.3354$_{10}$ -3;	4.3786$_{10}$ -3;	2.7580;	1.5990$_{10}$ -3;	8.8233$_{10}$ -4;
3.3220$_{10}$ -3;	4.3610$_{10}$ -3;	2.7778;	1.7317$_{10}$ -3;	8.7878$_{10}$ -4;
3.2889$_{10}$ -3;	4.3176$_{10}$ -3;	2.8284;	2.0590$_{10}$ -3;	8.7002$_{10}$ -4;
3.2694$_{10}$ -3;	4.2920$_{10}$ -3;	2.8603;	2.2517$_{10}$ -3;	8.6487$_{10}$ -4;
3.2566$_{10}$ -3;	4.2751$_{10}$ -3;	2.8810;	2.3789$_{10}$ -3;	8.6147$_{10}$ -4;
3.2249$_{10}$ -3;	4.2335$_{10}$ -3;	2.9353;	2.6925$_{10}$ -3;	8.5308$_{10}$ -4;
3.2062$_{10}$ -3;	4.2089$_{10}$ -3;	2.9692;	2.8773$_{10}$ -3;	8.4813$_{10}$ -4;
3.1938$_{10}$ -3;	4.1927$_{10}$ -3;	2.9928;	2.9993$_{10}$ -3;	8.4487$_{10}$ -4;
3.1634$_{10}$ -3;	4.1528$_{10}$ -3;	3.0534;	3.3003$_{10}$ -3;	8.3682$_{10}$ -4;
3.1454$_{10}$ -3;	4.1292$_{10}$ -3;	3.0892;	3.4780$_{10}$ -3;	8.3207$_{10}$ -4;
3.1336$_{10}$ -3;	4.1136$_{10}$ -3;	3.1158;	3.5954$_{10}$ -3;	8.2893$_{10}$ -4;
3.1043$_{10}$ -3;	4.0752$_{10}$ -3;	3.1818;	3.8850$_{10}$ -3;	8.2118$_{10}$ -4;
3.0755$_{10}$ -3;	4.0374$_{10}$ -3;	3.2523;	4.1695$_{10}$ -3;	8.1357$_{10}$ -4;
3.0473$_{10}$ -3;	4.0004$_{10}$ -3;	3.3299;	4.4487$_{10}$ -3;	8.0610$_{10}$ -4;
3.0197$_{10}$ -3;	3.9641$_{10}$ -3;	3.4126;	4.7217$_{10}$ -3;	7.9880$_{10}$ -4;
2.9926$_{10}$ -3;	3.9285$_{10}$ -3;	3.5047;	4.9897$_{10}$ -3;	7.9163$_{10}$ -4;
2.9658$_{10}$ -3;	3.8934$_{10}$ -3;	3.6106;	5.2547$_{10}$ -3;	7.8454$_{10}$ -4;
2.9395$_{10}$ -3;	3.8588$_{10}$ -3;	3.7328;	5.5149$_{10}$ -3;	7.7758$_{10}$ -4;

Lanthanum Tartrate Run 12

I = 0.4   T = 25°C.

Ta	Tm	pH	Tb	[HCl]
7.8264$_{10}$ -3;	2.5693$_{10}$ -3;	2.7783;	4.0675$_{10}$ -3;	5.1773$_{10}$ -4;
7.7351$_{10}$ -3;	2.5393$_{10}$ -3;	2.8159;	4.4235$_{10}$ -3;	5.1169$_{10}$ -4;
7.6460$_{10}$ -3;	2.5101$_{10}$ -3;	2.8564;	4.7706$_{10}$ -3;	5.0580$_{10}$ -4;
7.5591$_{10}$ -3;	2.4815$_{10}$ -3;	2.8951;	5.1096$_{10}$ -3;	5.0005$_{10}$ -4;
7.4741$_{10}$ -3;	2.4536$_{10}$ -3;	2.9356;	5.4410$_{10}$ -3;	4.9443$_{10}$ -4;
7.3911$_{10}$ -3;	2.4264$_{10}$ -3;	2.9758;	5.7648$_{10}$ -3;	4.8893$_{10}$ -4;
7.3098$_{10}$ -3;	2.3997$_{10}$ -3;	3.0153;	6.0815$_{10}$ -3;	4.8356$_{10}$ -4;
7.2303$_{10}$ -3;	2.3736$_{10}$ -3;	3.0578;	6.3918$_{10}$ -3;	4.7830$_{10}$ -4;
7.1524$_{10}$ -3;	2.3480$_{10}$ -3;	3.1008;	6.6953$_{10}$ -3;	4.7315$_{10}$ -4;
7.0767$_{10}$ -3;	2.3232$_{10}$ -3;	3.1439;	6.9907$_{10}$ -3;	4.6813$_{10}$ -4;
7.0025$_{10}$ -3;	2.2988$_{10}$ -3;	3.1877;	7.2799$_{10}$ -3;	4.6323$_{10}$ -4;
6.8594$_{10}$ -3;	2.2518$_{10}$ -3;	3.2771;	7.8380$_{10}$ -3;	4.5376$_{10}$ -4;
6.7213$_{10}$ -3;	2.2065$_{10}$ -3;	3.3733;	8.3765$_{10}$ -3;	4.4462$_{10}$ -4;
6.5880$_{10}$ -3;	2.1627$_{10}$ -3;	3.4728;	8.8962$_{10}$ -3;	4.3581$_{10}$ -4;
6.4600$_{10}$ -3;	2.1207$_{10}$ -3;	3.5797;	9.3952$_{10}$ -3;	4.2734$_{10}$ -4;

Lanthanum Tartrate Run 13

I = 0.4   T = 25°C.

Ta	Tm	pH	Tb	[HCl]
3.8724$_{10}$ -3;	1.0175$_{10}$ -3;	3.7289;	5.6382$_{10}$ -3;	2.0503$_{10}$ -4;
3.8500$_{10}$ -3;	1.2640$_{10}$ -3;	3.6846;	5.6056$_{10}$ -3;	2.5471$_{10}$ -4;
3.8278$_{10}$ -3;	1.5077$_{10}$ -3;	3.6442;	5.5734$_{10}$ -3;	3.0382$_{10}$ -4;
3.8059$_{10}$ -3;	1.7489$_{10}$ -3;	3.6061;	5.5415$_{10}$ -3;	3.5241$_{10}$ -4;
3.7843$_{10}$ -3;	1.9873$_{10}$ -3;	3.5713;	5.5100$_{10}$ -3;	4.0045$_{10}$ -4;
3.7630$_{10}$ -3;	2.2219$_{10}$ -3;	3.5366;	5.4789$_{10}$ -3;	4.4773$_{10}$ -4;
3.7419$_{10}$ -3;	2.4539$_{10}$ -3;	3.5059;	5.4482$_{10}$ -3;	4.9448$_{10}$ -4;
3.6961$_{10}$ -3;	2.9584$_{10}$ -3;	3.4447;	5.3815$_{10}$ -3;	5.9614$_{10}$ -4;
3.6797$_{10}$ -3;	3.1388$_{10}$ -3;	3.4232;	5.3577$_{10}$ -3;	6.3249$_{10}$ -4;
3.6594$_{10}$ -3;	3.3620$_{10}$ -3;	3.3985;	5.3281$_{10}$ -3;	6.7747$_{10}$ -4;
3.6197$_{10}$ -3;	3.7990$_{10}$ -3;	3.3543;	5.2703$_{10}$ -3;	7.6552$_{10}$ -4;

Lanthanum Tartrate Run 14

I = 0.4   T = 25°C.

Ta	Tm	pH	Tb	[HCl]
1.1607$_{10}$ -2;	1.0138$_{10}$ -2;	2.4279;	4.4235$_{10}$ -3;	2.0429$_{10}$ -3;
1.1473$_{10}$ -2;	1.0021$_{10}$ -2;	2.4519;	4.7706$_{10}$ -3;	2.0194$_{10}$ -3;
1.1343$_{10}$ -2;	9.9074$_{10}$ -3;	2.4753;	5.1096$_{10}$ -3;	1.9964$_{10}$ -3;
1.1215$_{10}$ -2;	9.7961$_{10}$ -3;	2.5001;	5.4410$_{10}$ -3;	1.9740$_{10}$ -3;
1.1091$_{10}$ -2;	9.6872$_{10}$ -3;	2.5274;	5.7648$_{10}$ -3;	1.9520$_{10}$ -3;
1.0969$_{10}$ -2;	9.5808$_{10}$ -3;	2.5474;	6.0815$_{10}$ -3;	1.9306$_{10}$ -3;
1.0849$_{10}$ -2;	9.4765$_{10}$ -3;	2.5719;	6.3918$_{10}$ -3;	1.9096$_{10}$ -3;
1.0508$_{10}$ -2;	9.1779$_{10}$ -3;	2.6462;	7.2799$_{10}$ -3;	1.8494$_{10}$ -3;
1.0399$_{10}$ -2;	9.0832$_{10}$ -3;	2.6706;	7.5618$_{10}$ -3;	1.8303$_{10}$ -3;
1.0293$_{10}$ -2;	8.9904$_{10}$ -3;	2.6939;	7.8380$_{10}$ -3;	1.8116$_{10}$ -3;
1.0188$_{10}$ -2;	8.8989$_{10}$ -3;	2.7198;	8.1100$_{10}$ -3;	1.7932$_{10}$ -3;
1.0086$_{10}$ -2;	8.8093$_{10}$ -3;	2.7440;	8.3765$_{10}$ -3;	1.7752$_{10}$ -3;
9.9847$_{10}$ -3;	8.7211$_{10}$ -3;	2.7694;	8.6389$_{10}$ -3;	1.7574$_{10}$ -3;

Lanthanum Tartrate Run 15

I → C T = 15°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
9.4952$_{10}$ -4;	2.0028$_{10}$ -3;	3.7829;	2.1635$_{10}$ -3;	6.1922$_{10}$ -4;	1.8221$_{10}$ -3;
9.4704$_{10}$ -4;	1.9975$_{10}$ -3;	4.0263;	2.3016$_{10}$ -3;	6.1760$_{10}$ -4;	1.9384$_{10}$ -3;

Lanthanum Tartrate Run 16

I → C T = 15°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
1.3240$_{10}$ -3;	1.4497$_{10}$ -3;	3.4108;	1.9932$_{10}$ -3;	4.4821$_{10}$ -4;	1.6787$_{10}$ -3;
1.3185$_{10}$ -3;	1.4436$_{10}$ -3;	3.5397;	2.2133$_{10}$ -3;	4.4635$_{10}$ -4;	1.8641$_{10}$ -3;
1.3138$_{10}$ -3;	1.4386$_{10}$ -3;	3.6798;	2.3997$_{10}$ -3;	4.4478$_{10}$ -4;	2.0210$_{10}$ -3;
1.3102$_{10}$ -3;	1.4346$_{10}$ -3;	3.8155;	2.5443$_{10}$ -3;	4.4355$_{10}$ -4;	2.1428$_{10}$ -3;

Lanthanum Tartrate Run 17

I → C T = 15°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
5.3745$_{10}$ -4;	2.1987$_{10}$ -3;	3.4227;	1.1466$_{10}$ -3;	6.7980$_{10}$ -4;	9.6567$_{10}$ -4;

Lanthanum Tartrate Run 18

I → 0 T = 15°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
8.4818$_{10}$ -4;	1.0150$_{10}$ -3;	3.0397;	2.2839$_{10}$ -4;	3.1383$_{10}$ -4;	1.9235$_{10}$ -4;
8.4504$_{10}$ -4;	1.0113$_{10}$ -3;	3.1050;	4.3111$_{10}$ -4;	3.1266$_{10}$ -4;	3.6308$_{10}$ -4;
8.4318$_{10}$ -4;	1.0090$_{10}$ -3;	3.1504;	5.5138$_{10}$ -4;	3.1198$_{10}$ -4;	4.6437$_{10}$ -4;
8.4151$_{10}$ -4;	1.0070$_{10}$ -3;	3.1934;	6.5934$_{10}$ -4;	3.1136$_{10}$ -4;	5.5529$_{10}$ -4;
8.3942$_{10}$ -4;	1.0045$_{10}$ -3;	3.2540;	7.9424$_{10}$ -4;	3.1058$_{10}$ -4;	6.6890$_{10}$ -4;
8.3781$_{10}$ -4;	1.0026$_{10}$ -3;	3.3041;	8.9858$_{10}$ -4;	3.0999$_{10}$ -4;	7.5681$_{10}$ -4;
8.3520$_{10}$ -4;	9.9948$_{10}$ -4;	3.3968;	1.0666$_{10}$ -3;	3.0902$_{10}$ -4;	8.9824$_{10}$ -4;
8.3319$_{10}$ -4;	9.9707$_{10}$ -4;	3.4758;	1.1966$_{10}$ -3;	3.0828$_{10}$ -4;	1.0077$_{10}$ -3;
8.3156$_{10}$ -4;	9.9513$_{10}$ -4;	3.5572;	1.3016$_{10}$ -3;	3.0768$_{10}$ -4;	1.0963$_{10}$ -3;
8.2962$_{10}$ -4;	9.9280$_{10}$ -4;	3.6617;	1.4273$_{10}$ -3;	3.0696$_{10}$ -4;	1.2021$_{10}$ -3;
8.2749$_{10}$ -4;	9.9025$_{10}$ -4;	3.8268;	1.5647$_{10}$ -3;	3.0617$_{10}$ -4;	1.3178$_{10}$ -3;
8.2556$_{10}$ -4;	9.8794$_{10}$ -4;	4.0172;	1.6891$_{10}$ -3;	3.0546$_{10}$ -4;	1.4225$_{10}$ -3;
8.2431$_{10}$ -4;	9.8645$_{10}$ -4;	4.1952;	1.7697$_{10}$ -3;	3.0499$_{10}$ -4;	1.4904$_{10}$ -3;
8.2334$_{10}$ -4;	9.8529$_{10}$ -4;	4.3870;	1.8325$_{10}$ -3;	3.0463$_{10}$ -4;	1.5433$_{10}$ -3;

Lanthanum Tartrate Run 19

I → 0 T = 15°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
1.6629$_{10}$ -3;	1.3717$_{10}$ -4;	3.9643;	2.0761$_{10}$ -3;	4.2412$_{10}$ -5;	1.7486$_{10}$ -3;
1.6567$_{10}$ -3;	2.0951$_{10}$ -4;	3.9106;	2.0685$_{10}$ -3;	6.4777$_{10}$ -5;	1.7420$_{10}$ -3;
1.6485$_{10}$ -3;	3.0593$_{10}$ -4;	3.8396;	2.0582$_{10}$ -3;	9.4587$_{10}$ -5;	1.7334$_{10}$ -3;
1.6410$_{10}$ -3;	3.9434$_{10}$ -4;	3.7733;	2.0488$_{10}$ -3;	1.2192$_{10}$ -4;	1.7255$_{10}$ -3;
1.6315$_{10}$ -3;	5.0564$_{10}$ -4;	3.6946;	2.0370$_{10}$ -3;	1.5633$_{10}$ -4;	1.7155$_{10}$ -3;
1.6200$_{10}$ -3;	6.4124$_{10}$ -4;	3.6065;	2.0226$_{10}$ -3;	1.9826$_{10}$ -4;	1.7034$_{10}$ -3;
1.6108$_{10}$ -3;	7.4884$_{10}$ -4;	3.5442;	2.0112$_{10}$ -3;	2.3153$_{10}$ -4;	1.6938$_{10}$ -3;
1.5992$_{10}$ 3;	8.8557$_{10}$ -4;	3.4776;	1.9966$_{10}$ -3;	2.7380$_{10}$ -4;	1.6816$_{10}$ -3;
1.5873$_{10}$ -3;	1.0249$_{10}$ -3;	3.4191;	1.9818$_{10}$ -3;	3.1688$_{10}$ -4;	1.6691$_{10}$ -3;
1.5741$_{10}$ -3;	1.1811$_{10}$ -3;	3.3623;	1.9652$_{10}$ -3;	3.6518$_{10}$ -4;	1.6552$_{10}$ -3;
1.5609$_{10}$ -3;	1.3358$_{10}$ -3;	3.3190;	1.9488$_{10}$ -3;	4.1300$_{10}$ -4;	1.6413$_{10}$ -3;
1.5429$_{10}$ -3;	1.5471$_{10}$ -3;	3.2598;	1.9264$_{10}$ -3;	4.7834$_{10}$ -4;	1.6224$_{10}$ -3;

Lanthanum Tartrate Run 20

I → 0 T = 25°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
2.4280$_{10}$ -3;	6.4192$_{10}$ -4;	2.8331;	6.8967$_{10}$ -5;	1.9847$_{10}$ -4;	1.0569$_{10}$ -6;
2.4251$_{10}$ -3;	6.4114$_{10}$ -4;	2.8485;	1.5588$_{10}$ -4;	1.9823$_{10}$ -4;	2.3888$_{10}$ -6;
2.4203$_{10}$ -3;	6.3987$_{10}$ -4;	2.8733;	2.9634$_{10}$ -4;	1.9784$_{10}$ -4;	4.5419$_{10}$ -6;
2.4156$_{10}$ -3;	6.3862$_{10}$ -4;	2.9009;	4.3557$_{10}$ -4;	1.9745$_{10}$ -4;	6.6748$_{10}$ -6;

Lanthanum Tartrate Run 21

I → 0 T = 25°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
1.9049$_{10}$ -3;	7.6980$_{10}$ -4;	2.8558;	0.0000 ;	2.3801$_{10}$ -4;	0.0000 ;
1.8977$_{10}$ -3;	7.6686$_{10}$ -4;	2.9111;	2.7289$_{10}$ -4;	2.3710$_{10}$ -4;	4.1817$_{10}$ -6;
1.8950$_{10}$ -3;	7.6579$_{10}$ -4;	2.9339;	3.7222$_{10}$ -4;	2.3677$_{10}$ -4;	5.7036$_{10}$ -6;
1.8919$_{10}$ -3;	7.6454$_{10}$ -4;	2.9566;	4.8874$_{10}$ -4;	2.3638$_{10}$ -4;	7.4896$_{10}$ -6;
1.8893$_{10}$ -3;	7.6348$_{10}$ -4;	2.9768;	5.8747$_{10}$ -4;	2.3605$_{10}$ -4;	9.0027$_{10}$ -6;
1.8862$_{10}$ -3;	7.6224$_{10}$ -4;	3.0039;	7.0285$_{10}$ -4;	2.3567$_{10}$ -4;	1.0770$_{10}$ -5;
1.8804$_{10}$ -3;	7.5988$_{10}$ -4;	3.0538;	9.2151$_{10}$ -4;	2.3494$_{10}$ -4;	1.4121$_{10}$ -5;
1.8777$_{10}$ -3;	7.5880$_{10}$ -4;	3.0810;	1.0217$_{10}$ -3;	2.3461$_{10}$ -4;	1.5656$_{10}$ -5;
1.8762$_{10}$ -3;	7.5820$_{10}$ -4;	3.0978;	1.0779$_{10}$ -3;	2.3442$_{10}$ -4;	1.6517$_{10}$ -5;
1.8744$_{10}$ -3;	7.5747$_{10}$ -4;	3.1138;	1.1459$_{10}$ -3;	2.3420$_{10}$ -4;	1.7560$_{10}$ -5;
1.8714$_{10}$ -3;	7.5623$_{10}$ -4;	3.1453;	1.2609$_{10}$ -3;	2.3381$_{10}$ -4;	1.9322$_{10}$ -5;
1.8683$_{10}$ -3;	7.5499$_{10}$ -4;	3.1800;	1.3759$_{10}$ -3;	2.3343$_{10}$ -4;	2.1085$_{10}$ -5;
1.8612$_{10}$ -3;	7.5212$_{10}$ -4;	3.2645;	1.6426$_{10}$ -3;	2.3254$_{10}$ -4;	2.5170$_{10}$ -5;
1.8485$_{10}$ -3;	7.4700$_{10}$ -4;	3.4450;	2.1184$_{10}$ -3;	2.3096$_{10}$ -4;	3.2462$_{10}$ -5;
1.8437$_{10}$ -3;	7.4506$_{10}$ -4;	3.5281;	2.2993$_{10}$ -3;	2.3036$_{10}$ -4;	3.5234$_{10}$ -5;
1.8346$_{10}$ -3;	7.4137$_{10}$ -4;	3.7129;	2.6418$_{10}$ -3;	2.2922$_{10}$ -4;	4.0484$_{10}$ -5;
1.8310$_{10}$ -3;	7.3991$_{10}$ -4;	3.7953;	2.7771$_{10}$ -3;	2.2877$_{10}$ -4;	4.2557$_{10}$ -5;
1.8270$_{10}$ -3;	7.3831$_{10}$ -4;	3.8959;	2.9263$_{10}$ -3;	2.2827$_{10}$ -4;	4.4841$_{10}$ -5;
1.8238$_{10}$ -3;	7.3700$_{10}$ -4;	3.9843;	3.0481$_{10}$ -3;	2.2787$_{10}$ -4;	4.6710$_{10}$ -5;
1.8209$_{10}$ -3;	7.3583$_{10}$ -4;	4.0669;	3.1568$_{10}$ -3;	2.2751$_{10}$ -4;	4.8376$_{10}$ -5;

Lanthanum Tartrate Run 22

I → C T = 25°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
8.6718$_{10}$ -4;	1.8552$_{10}$ -4;	3.4847;	6.2736$_{10}$ -4;	5.7360$_{10}$ -5;	9.6136$_{10}$ -6;
8.6588$_{10}$ -4;	2.1490$_{10}$ -4;	3.4652;	6.2642$_{10}$ -4;	6.6443$_{10}$ -5;	9.5993$_{10}$ -6;
8.6380$_{10}$ -4;	2.6150$_{10}$ -4;	3.4339;	6.2492$_{10}$ -4;	8.0852$_{10}$ -5;	9.5762$_{10}$ -6;
8.6011$_{10}$ -4;	3.4467$_{10}$ -4;	3.3864;	6.2224$_{10}$ -4;	1.0657$_{10}$ -4;	9.5353$_{10}$ -6;
8.5747$_{10}$ -4;	4.0398$_{10}$ -4;	3.3551;	6.2033$_{10}$ -4;	1.2490$_{10}$ -4;	9.5060$_{10}$ -6;
8.5396$_{10}$ -4;	4.8278$_{10}$ -4;	3.3231;	6.1780$_{10}$ -4;	1.4927$_{10}$ -4;	9.4671$_{10}$ -6;

Lanthanum Tartrate Run 23

I → C T = 25°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
6.9716$_{10}$ -4;	1.0254$_{10}$ -3;	3.0268;	0.0000 ;	3.1702$_{10}$ -4;	0.0000 ;
6.9594$_{10}$ -4;	1.0236$_{10}$ -3;	3.0677;	1.2577$_{10}$ -4;	3.1647$_{10}$ -4;	1.9273$_{10}$ -6;
6.9456$_{10}$ -4;	1.0215$_{10}$ -3;	3.1136;	2.6741$_{10}$ -4;	3.1584$_{10}$ -4;	4.0979$_{10}$ -6;
6.9260$_{10}$ -4;	1.0186$_{10}$ -3;	3.1930;	4.6811$_{10}$ -4;	3.1495$_{10}$ -4;	7.1733$_{10}$ -6;
6.9150$_{10}$ -4;	1.0170$_{10}$ -3;	3.2420;	5.8139$_{10}$ -4;	3.1445$_{10}$ -4;	8.9092$_{10}$ -6;
6.9025$_{10}$ -4;	1.0152$_{10}$ -3;	3.3005;	7.0910$_{10}$ -4;	3.1388$_{10}$ -4;	1.0866$_{10}$ -5;
6.8891$_{10}$ -4;	1.0132$_{10}$ -3;	3.3770;	8.4710$_{10}$ -4;	3.1327$_{10}$ -4;	1.2981$_{10}$ -5;
6.8654$_{10}$ -4;	1.0097$_{10}$ -3;	3.5462;	1.0904$_{10}$ -3;	3.1219$_{10}$ -4;	1.6709$_{10}$ -5;
6.8529$_{10}$ -4;	1.0079$_{10}$ -3;	3.6650;	1.2179$_{10}$ -3;	3.1162$_{10}$ -4;	1.8664$_{10}$ -5;
6.8339$_{10}$ -4;	1.0051$_{10}$ -3;	3.9233;	1.4129$_{10}$ -3;	3.1076$_{10}$ -4;	2.1651$_{10}$ -5;

Lanthanum Tartrate Run 24

I → 0 T = 35°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
1.6759$_{10}$ -3;	1.1518$_{10}$ -3;	2.8219;	0.0000 ;	3.5611$_{10}$ -4;	0.0000 ;
1.6535$_{10}$ -3;	1.1364$_{10}$ -3;	2.9762;	7.3506$_{10}$ -4;	3.5135$_{10}$ -4;	6.1908$_{10}$ -4;
1.6472$_{10}$ -3;	1.1321$_{10}$ -3;	3.0207;	9.4068$_{10}$ -4;	3.5002$_{10}$ -4;	7.9222$_{10}$ -4;
1.6417$_{10}$ -3;	1.1282$_{10}$ -3;	3.0674;	1.1241$_{10}$ -3;	3.4883$_{10}$ -4;	9.4673$_{10}$ -4;
1.6351$_{10}$ -3;	1.1237$_{10}$ -3;	3.1235;	1.3379$_{10}$ -3;	3.4744$_{10}$ -4;	1.1267$_{10}$ -3;
1.6269$_{10}$ -3;	1.1181$_{10}$ -3;	3.2116;	1.6095$_{10}$ -3;	3.4569$_{10}$ -4;	1.3556$_{10}$ -3;
1.6140$_{10}$ -3;	1.1092$_{10}$ -3;	3.3693;	2.0322$_{10}$ -3;	3.4295$_{10}$ -4;	1.7116$_{10}$ -3;
1.6068$_{10}$ -3;	1.1043$_{10}$ -3;	3.4776;	2.2672$_{10}$ -3;	3.4143$_{10}$ -4;	1.9094$_{10}$ -3;
1.5993$_{10}$ -3;	1.0991$_{10}$ -3;	3.6130;	2.5137$_{10}$ -3;	3.3983$_{10}$ -4;	2.1170$_{10}$ -3;
1.5945$_{10}$ -3;	1.0958$_{10}$ -3;	3.7160;	2.6704$_{10}$ -3;	3.3882$_{10}$ -4;	2.2489$_{10}$ -3;
1.5845$_{10}$ -3;	1.0890$_{10}$ -3;	4.0534;	2.9980$_{10}$ -3;	3.3669$_{10}$ -4;	2.5249$_{10}$ -3;

Lanthanum Tartrate Run 25

I → 0 T = 35°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
1.6182$_{10}$ -3;	9.4227$_{10}$ -4;	2.8924;	1.9776$_{10}$ -4;	2.9133$_{10}$ -4;	1.6655$_{10}$ -4;
1.5959$_{10}$ -3;	9.2929$_{10}$ -4;	3.0755;	9.5218$_{10}$ -4;	2.8732$_{10}$ -4;	8.0194$_{10}$ -4;
1.5907$_{10}$ -3;	9.2629$_{10}$ -4;	3.1246;	1.1266$_{10}$ -3;	2.8639$_{10}$ -4;	9.4881$_{10}$ -4;
1.5837$_{10}$ -3;	9.2218$_{10}$ -4;	3.2006;	1.3660$_{10}$ -3;	2.8512$_{10}$ -4;	1.1505$_{10}$ -3;
1.5778$_{10}$ -3;	9.1875$_{10}$ -4;	3.2694;	1.5650$_{10}$ -3;	2.8406$_{10}$ -4;	1.3181$_{10}$ -3;
1.5699$_{10}$ -3;	9.1419$_{10}$ -4;	3.3769;	1.8307$_{10}$ -3;	2.8265$_{10}$ -4;	1.5418$_{10}$ -3;
1.5622$_{10}$ -3;	9.0967$_{10}$ -4;	3.5048;	2.0934$_{10}$ -3;	2.8125$_{10}$ -4;	1.7631$_{10}$ -3;
1.5569$_{10}$ -3;	9.0659$_{10}$ -4;	3.6053;	2.2725$_{10}$ -3;	2.8030$_{10}$ -4;	1.9139$_{10}$ -3;
1.5514$_{10}$ -3;	9.0337$_{10}$ -4;	3.7326;	2.4595$_{10}$ -3;	2.7931$_{10}$ -4;	2.0714$_{10}$ -3;
1.5449$_{10}$ -3;	8.9961$_{10}$ -4;	3.9061;	2.6781$_{10}$ -3;	2.7815$_{10}$ -4;	2.2555$_{10}$ -3;
1.5354$_{10}$ -3;	8.9410$_{10}$ -4;	4.2565;	2.9986$_{10}$ -3;	2.7644$_{10}$ -4;	2.5254$_{10}$ -3;

Lanthanum Tartrate Run 26

I → C T = 35°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
8.5445$_{10}$ -4;	1.6933$_{10}$ -3;	3.1510;	9.1773$_{10}$ -4;	5.2354$_{10}$ -4;	7.7294$_{10}$ -4;
8.4832$_{10}$ -4;	1.6811$_{10}$ -3;	3.3188;	1.3059$_{10}$ -3;	5.1978$_{10}$ -4;	1.0998$_{10}$ -3;
8.4489$_{10}$ -4;	1.6743$_{10}$ -3;	3.4453;	1.5228$_{10}$ -3;	5.1768$_{10}$ -4;	1.2826$_{10}$ -3;
8.4118$_{10}$ -4;	1.6670$_{10}$ -3;	3.6328;	1.7577$_{10}$ -3;	5.1541$_{10}$ -4;	1.4004$_{10}$ -3;

Lanthanum Tartrate Run 27

I → C T = 35°C.

Ta	Tm	pH	Tb	[HCl]	[Cl]
1.8648$_{10}$ -3;	6.5089$_{10}$ -4;	3.4272;	2.0167$_{10}$ -3;	2.0125$_{10}$ -4;	1.6904$_{10}$ -3;
1.8577$_{10}$ -3;	6.4843$_{10}$ -4;	3.5217;	2.2174$_{10}$ -3;	2.0048$_{10}$ -4;	1.8587$_{10}$ -3;
1.8433$_{10}$ -3;	6.4341$_{10}$ -4;	3.7518;	2.6256$_{10}$ -3;	1.9893$_{10}$ -4;	2.2007$_{10}$ -3;
1.8320$_{10}$ -3;	6.3946$_{10}$ -4;	3.9717;	2.9471$_{10}$ -3;	1.9771$_{10}$ -4;	2.4703$_{10}$ -3;

Appendix 2

This appendix includes seven ALGOL programs written for the English Electric - Leo - Marconi KDF 9 computer. The proframs were written for the following purposes:

(a) application of the Biedermann-Sillen liquid junction potential correction to e.m.f. data,

(b) determination of stability constants K_{1C1}, K_{1C2} and $K = Ka_2.K_{111}$ from pH data,

(c) determination of stability constants K_{1C1} and K_{2C2} from pH data,

(d) refinement of stability constants (GAUSS G),

(e) determination of the stability constant K_{1C1} from pM data,

(f) determination of stability constants K_{1C1} and K_{2C1} from pM data,

(g) analysis by potentiometric titration using the linear titration plot method.

The version of ALGOL used may be found in the KDF 9 manual or, more conveniently, in the book KDF 9 ALGOL Programming by J.S. Green, published by English Electric - Leo - Marconi Computers Ltd, Kidsgrove, Staffordshire. KDF 9 ALGOL is a proper subset of ALGOL 60, with certain restrictions on the complete language. The representation used here is the 8 - channel (Flexowriter) version.

Appendix 2a

```
DD0440100WPU+W0300034BPST→

begin integer i, p, n;
      real    d, c, k, b, e;
      comment Program applies Biedermann-Sillen
              liquid junction correction to e.m.f. data
              and iterates until consistency is achieved;

              open(20);             open(70);
again :    copy text (20,70,[;] );
n := read(20);
d := read(20);
c := read(20);
b := d/c;
e := ln(10.0);
k := read(20);

begin array t[1:6], g, v, m, sw, h, w[1:n];

for i := 1 step 1 until 6 do t[i] := read(20);
for i := 1 step 1 until n do
begin    v[i] := read(20);
         w[i] := 0.0;
         h[i] := t[1] + (t[4] - (t[3] - v[i] )) / t[2];
         write (70, format ([ -nd.dddd]), h[i] );
repeat :    sw[i] :=w[i];
g[i] := exp(-e×h[i]);
m[i] := k/e × ln(1 + b × g[i]);
w[i] := v[i] - m[i];
h[i] := t[1] + (t[6] - (t[3] - w[i])) / t[5];
if abs(sw[i] - w[i]) × 100 > 1 then goto repeat;

write(70, format ([ssss-ndd.ddd]),  m[i]);
write(70, format ([ssss-nddd.dd]),  w[i]);
write(70, format ([ssss-nd.ddddc]), h[i]);

end
end;

p := read(20);
if p = 2 then goto again ;
close(70);
close(20);
end →
```

Appendix 2b

```
DD0441400WPU+W030034APST→


begin comment Program ,given KMHA,calculates KMA and KMA2
              by an iterative method,refining KMHA;
       integer  c, p, n, i, m, a, q, DD, j, F1, F2, k;
       real w, e, K1, K2, KA1, KA2, KW,  DHA, DHB, T, D, K11;
       array    AC,BE[1:3];

    real procedure  ACTCO (z, I, AC, BE);
        value  I, z, AC, BE;
        real  I, AC, BE;
        integer  z;
        begin  ACTCO :=exp(-e × DHA × z↑2 × (sqrt(I)/
               (1 + DHB × AC × sqrt(I)) - BE × I))
          end  ACTCO;


open (20);
open (70);
F1 := format ([-d.dddd₁₀-nd]);
F2 := format ([s-d.dddd₁₀-nd]);

again:  copy text (20, 70, [;]);
        c := read (20);
        if c = 0 then begin
            T := read (20);
            D := read (20);
for i:= 1 step 1 until 3 do
      begin AC[i]:= read(20);
            BE[i]:= read(20)
      end;
          DHA := 1.8249₁₀6 / sqrt((D × T)↑3);
          DHB := 5.0293₁₀1 / sqrt(D × T)
          end;

  m := read (20);
  a := read (20);
KA1 := read (20);
KA2 := read (20);
 KW := read (20);
  n := read (20);
  e := ln(10.0);

begin  integer  F3;
       array  ta, tm, ha, na, sh, cl [1 : n];
       boolean array  bo [1 : n];

 k := 0;
F3 := format ([ss-d.dddd₁₀-nd;]);
```

```
repeat :  q := read (20);
          p := read(20);
          j := read (20);


proc :  for i := k + 1 step 1 until k + j do
       begin  ta[i] := read (20);
              tm[i] := read (20);
              ha[i] := read (20);
              na[i] := read (20);
              bo[i] := false;
              if p = 2 or p= 4 then
              begin  cl[i] := read (20);
                     cl[i] := m × tm[i] + cl[i]
              end else  cl[i] := m × tm[i]    ;
          if q = 2 then begin tm[i]:= tm[i] + na[i];
                              na[i]:= 0.0 end;
           end;
        k := k + j;
        goto if k = n then main else repeat;


emf:  p := p;

Harned:  p := p;

main:    test(0);

     begin  real  sx, sy, ay, sxy, sxx, u, kg, IS, SI,
                     k1,k2,sx3,sx4,sxxy,r,s,t,P,Q,R,S,T,
                     dl,delta,dc,cc,syy,l,f,g,del1,del2;
         boolean  indiv, minus, once, bool,first,two,less;
            array  H2A, HA, A, x, y, K, I, v, fh, fha, fhha,
                   fa, h, M, MA, MA2, OH, fm, fmha, fma,
                   fmaa, MHA [1 : n];
              boolean array  boo[1 : n];

              for i := 1 step 1 until n do begin
               if c = 0 then  I[i] := m × tm[i] + na[i];
               if not bo[i] then  ha[i] := exp(-e × ha[i]);
                 v[i] := na[i] + cl[i];
                cl[i] := a×ta[i] - m×tm[i] - na[i] + cl[i];
                na[i] := v[i];
               if c = 1 then fh[i] := fhha[i] := fha[i] :=
                fa[i] := fm[i] := fmha[i] := fma[i] :=
                fmaa[i] := 1.0;
                 MHA[i] := 0.0     end;

new kg:  kg:= read(20);
          f:=read(20);
          g:=read(20);
          w:=read(20);
         DD:=read(20);
          l:=0;
```

```
    writetext(70,[[2c6s]KMHA*GIVEN*=**]);
    write(70,F1,kg);
    writetext(70,[[c6s]DISCRIMINATION*=**]);
    write(70,F1,g);

              K1 := K2 := SI :=  0.0;
              once := true;    first:= true;    two:= false;
for i:= 1 step 1 until n do M[i]:= f;

recalc :  IS := SI;
          for i := 1 step 1 until n do begin
             if c = 0 then begin
           fh[i] := ACTCO (1, I[i], AC[1], BE[1]);
         fhha[i] := ACTCO (2 - a, I[i], AC[1], BE[1]);
          fha[i] := ACTCO (1 - a, I[i],AC[1], BE[1]);
           fa[i] := ACTCO (a, I[i], AC[a], BE[a]);
           fm[i] := ACTCO (m, I[i], AC[m], BE[m]);
         fmha[i] := ACTCO (m - a + 1, I[i], AC[m+1-a], BE[m+1-a]);
          fma[i] := ACTCO (m - a, I[i], AC[m-a], BE[m-a]);
          fmaa[i] := ACTCO (m - 2 × a,I[i],AC[2×a-m],BE[2×a-m])
         end;
  if bo[i] then ha[i] := exp(-e×(sh[i] + ln(fh[i])/e));
              h[i] := ha[i]/fh[i];
             OH[i] := exp(-e × KW)/(fh[i] × ha[i])   end;

cycle:  K11 := K1;
         for i := 1 step 1 until n do  begin
          HA[i] := (cl[i]-h[i]+OH[i])/(1+2×ha[i]×fha[i]/
                   (KA1×fhha[i])+kg×M[i]×fm[i]×fha[i]/fmha[i]);
         H2A[i] := ha[i] × HA[i] × fha[i]/(fhha[i] × KA1);
           A[i] := KA2 × fha[i] × HA[i]/(ha[i] × fa[i]);
           v[i] := ta[i] - H2A[i] - HA[i] - A[i];
           y[i] := (v[i] - MHA[i])× fmaa[i]/(A[i]↑2 × fm[i]
                    × fa[i]↑2 × (2 × tm[i] - v[i] - MHA[i]));
           x[i] := (tm[i] - v[i]) × fmaa[i]/(A[i] × fa[i] ×
                  (2 × tm[i] - v[i] - MHA[i]) × fma[i])   end;

sx := sy := sxy := sxx := syy:= sx3:= sx4:= sxxy:=  ay := 0.0;
j := k := 0;

for i := 1 step 1 until n do
if x[i] > ay then ay := x[i] else  ay := ay;
minus := if ay = 0.0 then true else false;
if minus and once then  begin once:= false;
write text (70, [[2c]Note.**All*x*values*are*negative.[c]]);
                            end;

try:  for i :=1 step 1 until n do  begin
       if x[i] > 0.0 or minus then  begin
       sx := sx + x[i];
       sy := sy + y[i];
      sxy := sxy + x[i] × y[i];
      sxx := sxx + x[i]↑2;
j := j + 1  end;
```

```
boo[i] := if x[i] < 0.0 or x[i] < ay/10 or minus
          then true else false  end;
if j = 1 then  begin  minus := true;
                      sx:=sy:=sxy:=sxx:= 0.0;
                        j:= 0;
write text (70, [[2c]Note. **One*positive*value*of*nx.[c]]);
          once := false;
          goto try   end;

 u := j × sxx - sx↑2;
K1 := (j × sxy - sx × sy)/u;
if K1 < 0.0 then  begin
                  write text (70, [[2c]KMA*is*negative]);
                  bool := true;
                  goto emerg  end
           else bool := false;

for i := 1 step 1 until n do  begin
   M[i] := (2 × tm[i] - v[i] - MHA[i]) × fma[i]/
           (K1 × A[i] × fm[i] × fa[i] + 2× fma[i]);
if M[i] < 0.0 then M[i] := 0.0;
   MHA[i] := kg × M[i] × HA[i] × fm[i] × fha[i]/fmha[i];
if MHA[i] < 0.0 then MHA[i] := 0.0    end;

comp:  goto  if 1000 × abs(K1 - K11) - ₁₀-6 ≤ abs(K1) then
       strength else cycle;

strength:  SI := 0.0;
for i := 1 step 1 until n do begin
   MA[i] := 2 × tm[i] - v[i] - MHA[i] - 2 ×M[i];
if MA[i] < 0.0 then MA[i] := 0.0;
   MA2[i] := M[i] - tm[i] + v[i];
if MA2[i] < 0.0 then MA2[i] := 0.0;
if c = 0 then  I[i] := (m↑2 × M[i] +(m - a)↑2 × MA[i] +
                  (m-2×a)↑2 × MA2[i] + (m-a+1)↑2 × MHA[i]
                  + na[i] + h[i] + (a-2)↑2 × H2A[i] +
                  (a - 1)↑2 × HA[i] + a↑2 × A[i] + OH[i])/2;
SI := SI + I[i]   end;
if 1000 × abs(SI - IS) > abs(IS) then goto recalc;


refine:  for i:= 1 step 1 until n do begin if x[i]>0.0
               or minus then
      begin  sx3:= sx3 + x[i]↑3;
             sx4:= sx4 + x[i]↑4;
            sxxy:= sxxy + x[i]↑2×y[i];
             syy:= syy + y[i]↑2 end end;
    cc:= (sxx×sy - sx×sxy)/u;
    dl:= syy + j×cc↑2 + K1↑2×sxx - 2×(cc×sy
           + K1×sxy - K1×cc×sx);
    writetext(70,[[c]kg*=]);
    write(70,F1,kg);
    writetext(70,[[sssss]std*deviation*in*slope*=]);
    write(70,F1,sqrt(j×dl/((j-2)×u)));
```

```
P:= sx↑2/sxx - j;
Q:= sx - j×sx3/sxx;
R:= (j×sxy - sx×sy)/sxx;
S:= sxx - j×sx4/sxx;
T:= j×sxxy/sxx - sy;
s:= (R×S - Q×T)/(Q↑2 - P×S);
t:= (R×Q - P×T)/(P×S - Q↑2);
r:= (sy - t×sxx - s×sx)/j;

dc:= syy + j×r↑2 + s↑2×sxx + t↑2×sx4 + 2×(r×s×sx + r×t×sxx +
      t×s×sx3 - r×sy  -s×sxy - t×sxxy);
delta:= r×(s + t×(x[n] + x[1]))×(x[n]-x[1]) + s/2×((r+s×x[n]
        + t×x[n]↑2)↑2 - (r + s×x[1] + t×x[1]↑2)↑2) + t/3×((r
        + s×x[n] + t×x[n]↑2)↑3 - (r + s×x[1] + t×x[1]↑2)↑3)
        -(x[n]-x[1])/2×(r×2+s×(x[n]+x[1])+t×(x[n]↑2+x[1]↑2));
l:= l+1;
if dl < g×dc or l= DD then goto jump;

if first then begin first:= false;
                    if delta < 0.0 then
                    begin k1:= kg;
                          kg:= kg + kg×w;
                        less:= true;
                        del1:= delta
                    end;
                    if delta > 0.0 then
                    begin k2:= kg;
                          kg:= kg - w×kg;
                        less:= false;
                        del2:= delta
                    end  ;
                    goto cycle
                    end;

if not two then begin
                       if delta < 0.0 and less then
                       begin k1:= kg;
                             if delta < del1 then w:= -w;
                             kg:= kg + w×kg;
                           del1:= delta;
                           goto cycle
                       end;
                       if delta > 0.0 and not less then
                       begin k2:= kg;
                             if delta > del2 then w:= -w;
                             kg:= kg - w×kg;
                           del2:= delta;
                           goto cycle
                       end
                       end;
```

```
if delta < 0.0 then begin k1:= kg;
                    del1:= delta;
                      kg:= kg - (k2-kg)×del1/(del2-del1)
                 end;

if delta > 0.0 then begin k2:= kg;
                    del2:= delta;
                      kg:= kg + (k1-kg)×del2/(del2-del1)
                end;

       two:= true;
       goto cycle;

jump:  for i := 1 step 1 until n do
       if boo[i] then k := k + 1;
       if k = 0 then  begin
       K2 := ((sxx × sy - sx × sxy)/u)/K1;
            indiv := false  end
       else   indiv := true;
if indiv then  begin
   sx := 0.0;
   for i := 1 step 1 until n do
   begin  if boo[i] then  begin
           if MA[i] > 0.0 and A[i] > 0.0 then
           K[i] := fmaa[i] × MA2[i]/(MA[i]×fma[i]×A[i]×fa[i])
               else K[i] := 0.0;
             sx := sx + K[i]  end  end;
             K2 := sx /k  end;

f:= sqrt(j×dl/(j-2)/u);
g:= sqrt(dl×sxx/(j-2)/u);
test(0);

print:  write text (70, [[4c] K1*=*]);
write (70,F1, K1);
if not indiv then  write text (70, [[4s] K2*=*])
             else  write text (70, [[4s] Av.*K2*=*]);
write (70, F1, K2);
writetext(70,[[4s]KMHA*=**]);
write(70,F1,kg);
writetext(70,[[2c]K1K2*=**]);
write(70,F1,cc);
writetext(70,[[6s]STANDARD*ERROR*IN*K1K2*=*]);
write(70,F1,g);
writetext(70,[[c23s]STANDARD*ERROR*IN*K1*=*]);
write(70,F1,f);
```

```
emerg:  write text (70, [[2c3s]abscissa[7s]ordinate[c]]);
for i := 1 step 1 until n do begin
write (70, F1, x[i]);
write (70, format ([ssss-d.dddd₁₀-ndc]), y[i])  end;
fin: p:=read(20);
if l=DD then goto escape;
 if bool then  begin  bool := false;
                      if p = 1 then goto fin
                end;
if p = 1 then begin
write text (70, [[2c5s]M[11s]MA[9s]MA2[9s]MHA[9s]HA[10s]A]);

if c = 0 then write text (70, [[11s] I]);
if indiv then write text (70, [[11s] K]);

for i := 1 step 1 until n do begin
write text (70,[[c]]);
write (70, F1, M[i]);
write (70, F2, MA[i]);
write (70, F2, MA2[i]);
write (70, F2, MHA[i]);
write (70, F2, HA[i]);
write (70, F2, A[i]);
if c = 0 then write (70, F2, I[i]);
if indiv then write (70, F2, K[i])  end;

escape: writetext(70,[[3c4s]NUMBER*OF*CYCLES*=**]);
        write(70,format([nddd]),l);
        writetext(70,[[2c4s]DEVIATION*FROM*LINE*=**]);
        write(70,F1,dl);
        writetext(70,[[c4s]DEVIATION*FROM*CURVE*=**]);
        write(70,F1,dc);
        writetext(70,[[2c4s]UPPER*LIMIT*IN*KMHA*=**]);
        write(70,F1,k2);
        writetext(70,[[c4s]LOWER*LIMIT*IN*KMHA*=**]);
        write(70,F1,k1);

        writetext(70,[[3c5s]A[11s]B[11s]C[c]]);
        write(70,F2,r);
        write(70,F2,s);
        write(70,F2,t);


    p := read (20)  end;
if p = 3 then goto new kg     end  end;

if p = 2 then goto again;
close (70);
close (20)  end →
```

Appendix 2c

```
DD044040 0WPU+W030034DPST→

begin   integer  c, p, n, i, m, a, b, j, F1, F2, k, FS;
        real     e,K1,K2,KA1,KA2,DHA,DHB,AC,BE,T,D,K11,K22;
        boolean  bool;

        real procedure  ACTCO (z, I);
        comment  activity coefficient calculated by Davies
                 equation;
         value  I, z;
         real  I;
         integer  z;
         begin  ACTCO :=exp(-e × DHA × z↑2 × (sqrt(I)/
                          (1 + DHB × AC × sqrt(I)) - BE × I))
         end  ACTCO;


open (20);
open (10);
open (70);
F1 := format ([-d.dddd₁₀-nd]);
F2 := format ([s-d.dddd₁₀-nd]);
FS := format ([ssss-d.dddd₁₀-ndc]);

comment  data tape starts with 0 if activity corrections
valid, 1 if I constant.  If 0 is punched, it is followed by
the values of the temperature and dielectric constant, distance
of closest approach of the ions and beta for the Davies
equation;

again:  copy text (20, 70, [;]);
        c := read (20);
        if c = 0 then begin
            T := read (20);
            D := read (20);
           AC := read (20);
           BE := read (20);
          DHA := 1.8249₁₀6 / sqrt((D × T)↑3);
          DHB := 5.0293₁₀1 / sqrt(D × T)
          end;

comment  m is the valency of the metal ion, a is the valency
of the anion, b is the number of acid constants which are
valid, KA1 is the first dissociation constant of the acid, KA2
is the second constant for the acid (= 0 if b = 1), and n is the
total number of points in the calculation;

  m := read (20);
  a := read (20);
  b := read (20);
KA1 := read (20);
KA2 := read (20);
  n := read (20);
```

```
comment  now follows any number of sections of input data each
starting with a parameter, p, which is 1 or 2 if data already
processed, 1 if no HCl present, 2 if HCl present, 3 if pHs
given directly and 4 if emf readings given.  Original data
sections will be output as processed data for further use;

e := ln(10.0);
begin  integer  F3, F4;
       array  ta, tm, ha, na, sh, cl [1 : n];
       boolean array  bo [1 : n];
 k := 0;
F3 := format ([ss-d.dddd₁₀-nd;]);
F4 := format ([ ss-nd.dddd; ]);
repeat :  p := read (20);
          j := read (20);
          goto if p < 3 then proc else
               if p = 3 then Harned else emf;

comment  processed data starts with j = no. of points, and
then j sets of total acid, total metal, minus log H activity,
[Na], and [HCl] if necessary;

proc :  for i := k + 1 step 1 until k + j do
       begin  ta[i] := read (20);
              tm[i] := read (20);
              ha[i] := read (20);
              na[i] := read (20);
              bo[i] := false;
              if p = 2 then  begin  cl[i] := read (20);
                                    cl[i] := m×tm[i] + cl[i]
                             end
                        else        cl[i] := m × tm[i]
       end;
       k := k + j;
        goto if k = n then main else repeat;


emf:  begin  real  u;
             real array  t[1 :10],  ca,me,em,hcl [1 : j];
    for i:= 1 step 1 until 10 do  t[i] := read (20);
    t[3] := t[3] + t[4];
    for i := 1 step 1 until j do
     begin  ca[i] := read (20);
            me[i] := read (20);
            em[i] := read (20);
            u := t[3] + ca[i] + me[i];
            ta[k + i] := t[1] × t[4]/u;
            na[k + i] := t[2] × ca[i]/u;
            tm[k + i] := t[9] ×me[i]/u;
            ha[k + i] := if c = 1 then t[5] + (t[8] - (t[7]
             - em[i]))/t[6] else
             t[5] + (t[5] - t[6]) × (em[i] - t[7])/(t[7] - t[8]);
               hcl[i] := t[10] × me[i]/u;
            cl[k + i] := hcl[i] + m × tm[i];
            bo[k + i] := false   end;
```

```
gap(10, 20);
if t[10] > ⏨-7 then write text (10, [[c] 2;[c]])
                else write text (10, [[c] 1;[c]]);
                     write (10, format ([-nddd;c]), j);
for i:=1 step 1 until j do  begin
  write text (10, [[c]]);
  write (10, F3, ta[k + i]);
  write (10, F3, tm[k + i]);
  write (10, F4, ha[k + i]);
  write (10, F3, na[k + i]);
  if t [10] > ⏨-7 then write (10, F3, hcl[i])  end;
  gap(10, 20);
k := k + j;
goto if k = n then main else repeat  end;

Harned:    p:= p;


main:     begin  real  sx, sy, ay, sxy, sxx, syy, d, dm, KD, u;
                 boolean  indiv, minus, plot, once;
                 array  H2A, HA, A, x, y, K, I, v, fh, fha,
                        fhha, fa, h, M, MA,MA2, OH [1 : n];
                 boolean array  boo[1 : n];

          p:= read(20);
  plot:= if p=0 then false else true;

                for i := 1 step 1 until n do begin
                  if c = 0 then  I[i] :=
                (m↑2× tm[i]+a↑2× ta[i] + cl[i] + na[i])/2;
                  if not bo[i] then  ha[i] := exp(-e × ha[i]);
                  v[i] := na[i] + cl[i];
                 cl[i] := a×ta[i] - m×tm[i] - na[i] + cl[i];
                 na[i] := v[i];
                 if c = 1 then fh[i] := fhha[i] := fha[i] :=
                                 fa[i] := 1.0   end;
                K1  := K2 := 0.0;
                once := true;

recalc :  K11 := K1;
          K22 := K2;
         for i := 1 step 1 until n do begin
         if c = 0 then begin  fh[i] := ACTCO (1, I[i]);
                             fhha[i] := ACTCO (2 - a, I[i]);
                              fha[i] := ACTCO (1 - a, I[i]);
                               fa[i] := ACTCO (a, I[i]) end;
         if bo[i] then ha[i] := exp(-e × (sh[i] + ln(fh[i])/e));
           h[i] := ha[i]/fh[i];
          OH[i]:= exp(-e × 14.008)/(fh[i] × ha[i]);
         H2A[i]:= (cl[i] - h[i] + OH[i])/(b + (b - 1) ×KA1
                    × fhha[i]/(ha[i] × fha[i]));
          HA[i]:=KA1 × fhha[i] × H2A[i]/(ha[i] × fha[i]);
           A[i]:= KA2 × fha[i] × HA[i]/(ha[i] × fa[i]);
           M[i]:= tm[i] - ta[i] + H2A[i] + HA[i] + A[i];
```

```
          if c = 0 then begin
             fh[i] := ACTCO (m, I[i]);
              if b = 1 then begin
            fha[i] := ACTCO (m - (a - 1), I[i]);
           fhha[i] := ACTCO (m ×2 - 2 × (a - 1), I[i])end
                else  begin
            fha[i] := ACTCO (m - a, I[i]);
           fhha[i] := ACTCO (m ×2 - a × 2 , I[i])end   end;
          if b = 1 then A[i] := HA[i];
      end;

graph: for i:= 1 step 1 until n do
       begin if plot then begin
           y[i] := (tm[i] - M[i])×fhha[i]/(M[i] × A[i]×fh[i]
                      ×fa[i])↑2;
           x[i] := fhha[i]/(M[i]×A[i]×fh[i]×fa[i]×fha[i])
           end else begin
           y[i] :=  (tm[i]-M[i])×fha[i]×fhha[i]/
                        (M[i]×A[i]×fh[i]×fa[i]);
           x[i] :=  fh[i]×fa[i]×fha[i]×M[i]×A[i]×2/fhha[i]  end;
       end;

sx := sy := sxy := sxx := ay := syy  := 0.0;
j := k := 0;

for i := 1 step 1 until n do
if x[i] > ay then ay := x[i] else  ay := ay;
minus := if ay = 0.0 then true else false;
if minus and once then
begin writetext(70, [[2c]* All*x*values*are*negative.[c]]);
      once := false   end;

try:  for i :=1 step 1 until n do  begin
      if x[i] > 0.0 or minus then  begin
       sx := sx + x[i];
       sy := sy + y[i];
      sxy := sxy + x[i] × y[i];
      sxx := sxx + x[i]↑2;
      syy := syy + y[i]↑2;
        j := j + 1  end;
boo[i] := if x[i] < 0.0 or x[i] < ay/10 or minus
          then true else false  end;

if j = 1 then  begin  minus := true;
                             j := 0;
          sx:= sy:= sxx:= syy:= sxy:= 0.0;
          write text ( 70, [[2c]**One*positive*value*of*x.[c]]);
          once := false;
          goto try   end;

u := j × sxx - sx↑2;
D := (j × sxy - sx × sy)/u;
T := (sxx×sy - sx×sxy)/u;
```

```
if plot then begin K1:= D;
                   KD:= 0.5×T/D↑2 end
        else begin K1:= T;
                   KD:= D/T↑2 end;
if K1 < 0.0 then  begin writetext(70,[[2c]KMA*is*negative]);
                           bool := true;
                           goto emerg  end
            else bool := false;
for i := 1 step 1 until n do
if boo[i] then k := k + 1;

if k = 0 then  begin K2 := KD;
                   indiv := false  end
   else  begin   indiv := true;
                  goto metal  end;

comp:  if 1000 × abs(K1 - K11) - ⏨-6 ≤ abs(K1) and 1000 ×
       abs(K2 - K22) - ⏨-6 ≤ abs(K2) then goto print;
  if indiv then goto recalc;

metal:  for i := 1 step 1 until n do begin
   MA[i] := M[i]×A[i]×fh[i]×fa[i]×K1/fha[i];
if MA[i] < 0.0 then MA[i] := 0.0;
   MA2[i] :=( tm[i]- M[i]- MA[i])/2;
if MA2[i] < 0.0 then MA2[i] := 0.0;
if b = 1 then  A[i] := 0.0;
if c = 0 then  I[i] := (m↑2 × M[i] +(m - a)↑2 × MA[i] +
                 ((m - a)×  2)↑2 × MA2[i] + na[i] + h[i] +
                 (a - 2)↑2 × H2A[i] + (a - 1)↑2 × HA[i] +
                  a↑2 × A[i] + OH[i])/2;
if b = 1 then A[i] := HA[i]   end;

if indiv then  begin
    ay := 0.0;
    k  := 0;
    for i := 1 step 1 until n do  begin
    if boo[i] then  begin  if MA[i] > 0.0 and A[i] > 0.0 then
    K[i] := fhha[i] × MA2[i]/((MA[i] × fha[i])↑2) else
    K[i] := 0.0;
    ay   := ay + K[i];
    if K[i] > 0.0 then k := k + 1  end  else  K[i] := 0.0 end;
    if k = 0 then K2 := 0.0 else  K2 := ay /k;
    goto comp  end;
goto recalc;


print:  gap(70, 20);
comment  all programs output K1, K2, x and y;

emerg: ay:= syy + j×T↑2 + D↑2×sxx - 2×(T×sy + D×sxy - D×T×sx);
```

```
      dm:= sqrt(j×ay/(j-2)/u);
      d := sqrt(ay×sxx/(j-2)/u);

write text (70, [[c] K1*=*]);
write (70,F1, K1);
write text (70, [[6s]standard*deviation*in*K1*=*]);
write (70,F1, (if plot then dm else d));
write text (70, [[c] KD*=*]);
write (70,F1, KD);
write text (70, [[6s]standard*deviation*in*K1K1KD*=*]);
write(70,F1,(if plot then d else dm));
if indiv then begin
write text (70, [[c]AV*K2*=*]);
write (70,F1, K2)    end;

write text (70, [[2c3s] ABSCISSA[9s] ORDINATE[c]]);
for i := 1 step 1 until n do begin
write (70, F1, x[i]);
write (70, FS, y[i])  end;
comment  if concentrations of all species desired punch 1.  If
another data tape follows punch 2 otherwise punch 0;

fin:  p := read (20);
      if bool then  begin  bool := false;
                           if p = 1 then goto fin    end;
if p = 1 then begin
writetext(70,[[2c5s]M[11s]MA[9s]MA2[10s]HA[10s]A[10s]H2A ]);
if c = 0 then write text (70, [[11s] I]);
if indiv then write text (70, [[11s] K]);

for i := 1 step 1 until n do begin
write text ( 70,[[c]]);
write (70, F1, M[i]);
write (70, F2, MA[i]);
write (70, F2, MA2[i]);
write (70, F2, HA[i]);
write (70, F2, A[i]);
write (70, F2, H2A[i]);
if c = 0 then write (70, F2, I[i]);
if indivthen write (70, F2, K[i])  end;

p := read (20);
if p= 100 then begin plot:= false;
                     K1:= K2:= K11:= K22:= 0.0;
                     goto graph end;
  end  end  end;

if p = 2 then goto again;
close (10);
close (20);
close (70)
  end →
```

Appendix 2d

```
DD04417 00WPU+W030034APST→

begin real ckwl, EX1, EX2, hx, sqr, sqro, sqru, Y1, Y2, Y3, Y4,
           vx, tx, anv, ade, ro, D, bo, ho, aha, chc, sr, uxl,
           bhb, temp, r, ruw, wt, HO1, HO2, HO3, wto, X1, alo;

      integer p, f, fa, fc, a, iws, n, mt, ncd, ncc, k, l, j,
              m, l1, l2, i, nit, icc, zj, nn, nncv, ncv, ihs,
              ivx, itx, stop;

                hx:=ln(10.0);
                 f:=format([ss-nddd]);
                fa:=format([ss-d.dddd⏨-nd]);
                fc:=format([ss-ndd.dddd]);
               open(20);   open(70);

again:         copytext(20, 70, [;]);
                  p:= read(20);
                  n:= read(20);
                 nn:= n×2;
                 mt:= read(20);
                 l1:= read(20);
                 l2:= read(20);
                EX1:= read(20);
                EX2:= read(20);
                iws:= read(20);
                ihs:= read(20);
                  a:= read(20);
               ckwl:= read(20);
                ncv:= read(20);
                ivx:= read(20);
                itx:= read(20);
begin array e, ck, b, term[1:n], h, x, de[1:n],sem[1:2,1:2],
            sev, shft[1:2], cc[1:n,1:nn], c[1:n,1:mt], cl, bb,
            ch, u, hcl, scl, sch, sbb, sph, shcl, tvx,ttx[1:mt];
      integer array ml, mm, mn[1:n];

      procedure invert(j,l,a);
      value     j,l;
      integer   j,l;
      array     a;
      begin real in;
             in:= a[j];
           a[j]:= a[l];
           a[l]:= in
      end invert;
```

```
    procedure swap(j,l,a);
      value    j,l;
      integer  j,l;
      integer array    a;
      begin real in;
            in:= a[j];
          a[j]:= a[l];
          a[l]:= in
      end swap;

for i:=1 step 1 until n do begin ml[i]:= read(20);
                                 mm[i]:= read(20);
                                 mn[i]:= read(20);
                                  e[i]:= read(20) end;

for i:=1 step 1 until mt do
begin cl[i]:=if p=7 then 0.0 else read(20);
        ifp=6 then begin ch[i]:=read(20);
                          u[i]:=read(20) end
              else begin bb[i]:=read(20);
                          u[i]:=read(20);
                         ch[i]:=read(20) end;
                       hcl[i]:=if ihs=2 then read(20)
                                         else 0.0;
                         ch[i]:=a×cl[i]+hcl[i]-ch[i]
end;

if iws=0 then writetext(70, [[2c]UNIT*WEIGHTS*TO*BE*SET*
                                         BY*PROGRAM])
         else for i:=1 step 1 until mt do
         begin scl[i]:=if p=7 then 0.0 else read(20);
               if p=6 then begin sch[i]:=read(20);
                                 sph[i]:=read(20) end
                      else begin sbb[i]:=read(20);
                                 sph[i]:=read(20);
                                 sch[i]:=read(20) end;
shcl[i]:=sqrt(shcl[i]↑2+(a×scl[i])↑2+sch[i]↑2) end;

                stop:= read(20);
                 ncd:= read(20);
                nncv:= ncv×2;
writetext(70, [[2c]number*of*cycles*=*]);
write(70, f, ncd);

for i:=1 step 1 until ncv do h[i]:=read(20);
ncc:=0;
icc:=0;
for i:= 1 step 1 until mt do u[i]:= exp(hx×u[i]);
if iws=1 then for i:=1 step 1 until mt do
      sph[i]:=sph[i]×hx/u[i];
for i:= 1 step 1 until mt do
begin tvx[i]:= if ivx=0 then bb[i] else read(20);
      ttx[i]:= if itx=0 then cl[i] else read(20)
end;
```

```
L11:   ncc:= ncc+1;
        sqr:= 0.0;
       sqro:= 0.0;
       sqru:= 0.0;
test(0);

for i:=1 step 1 until n do
begin ck[i]:= 0.0;
      for j:=1 step 1 until n do cc[i, j]:= 0.0
end;
      l:= 0;

L37:  for k:= 11 step 1 until 12 do
begin zj:= 0;
       m:= 0;
      Y1:= EX1×bb[k];
      Y3:= EX2×cl[k];
      vx:= tvx[k];
      tx:= ttx[k];

L16:test(0);
     for i:= 1 step 1 until n do b[i]:= exp(hx×e[i]);
if p=5 then goto CONC5;
if p=6 then goto CONC6;

CONC 7: nit:= 0;

CONC 6: nit:= 0;

CONC 5: nit:=0;
for j:=1 step 1 until n do term[j]:= b[j]×u[k]↑mn[j];

test(0);
L502:   for j:= 1 step 1 until n do
        c[j,k]:= term[j]×tx↑ml[j]×vx↑mm[j];
           nit:= nit+1;

bo:=vx;
alo:=tx;
for j:= 1 step 1 until n do
begin alo:= alo+ml[j]×c[j,k];
       bo:= bo+mm[j]×c[j,k] end;
       Y2:= abs(bo-bb[k]);
       Y4:= abs(alo-cl[k]);
if nit>100 then goto L516;
if Y1-Y2≥0.0 and Y3-Y4≥0.0 then goto L509;

sev[1]:= bo-bb[k];
sev[2]:= alo-cl[k];
sem[1,1]:= -vx;
sem[1,2]:= 0.0;
sem[2,2]:= -tx;
```

```
for j:=1 step 1 until n do
    begin sem[1,1]:= sem[1,1]-c[j,k]×mm[j]↑2;
          sem[1,2]:= sem[1,2]-c[j,k]×mm[j]×ml[j];
          sem[2,2]:= sem[2,2]-c[j,k]×ml[j]↑2 end;
             aha := sem[1,2]↑2-sem[1,1]×sem[2,2];
           shft[1]:=(sev[2]×sem[1,2]-sev[1]×sem[2,2])/aha;
           shft[2]:=(sev[1]×sem[1,2]-sem[1,1]×sev[2])/aha;
if shft[1]<-0.9999 then shft[1]:= -0.9999;
if shft[2]<-0.9999 then shft[2]:= -0.9999;
vx:= vx+vx×shft[1];
tx:= tx+tx×shft[2];
    goto L502;

L509:   ho:= 1.0/u[k]-ckwl×u[k];
     for j:= 1 step 1 until n do ho:= ho-mn[j]×c[j,k];
     if iws≠1 then goto L18;
    aha:= bhb:= 0.0;
    chc:= 1.0/u[k]+ckwl×u[k];
for i:= 1 step 1 until n do
begin aha:= aha+mm[i]×mn[i]×c[i,k];
      bhb:= bhb+ml[i]×mn[i]×c[i,k];
      chc:= chc+mn[i]↑2×c[i,k] end;

temp:= 1.0/(sem[1,1]×sem[2,2]-sem[1,2]×sem[2,1]);

  sr:= sch[k]↑2+(sbb[k]×temp×(aha×sem[2,2]-sem[1,2]×bhb))↑2
     + (scl[k]×temp×(aha×sem[2,1]-sem[1,1]×bhb))↑2
     + (sph[k]×u[k]×(chc+temp×(aha×(sem[1,2]×bhb
     - sem[2,2]×aha)-bhb×(sem[1,1]×bhb-sem[2,1]×aha))))↑2;
     goto L18;

L516:   ho:= ch[k];
      uxl:= ln(u[k])/hx;
      newline(70,1);
      write(70, fa, bb[k]);
      write(70, fa, cl[k]);
      write(70, fc, uxl);
writetext(70, [[2c4s]  iteration*does*not*converge]);
L18:  if stop = 0 then test(10);
      if icc=0 then begin tvx[k]:= vx;
                          ttx[k]:= tx end;

    if m=0 or l>0 then begin
    if iws=0 then sr:= 1.0;
                  wt:= 1.0/sqrt(sr);
                 ruw:= (ho-ch[k]);
                   r:= wt×ruw end;

if l>0 then goto L31;
  m:= m+1;
if m=2 then goto L251;
if m=3 then goto L252;
```

```
L250:  sqro:= sqro+r↑2;
      wto  := wt;
        HO1:= ho;
         ro:= r;
         zj:= zj+1;
      e[zj]:= e[zj]+h[zj];
        icc:= icc+1;
goto L16;


L251:   HO2:= ho;
      e[zj]:= e[zj]-2×h[zj];
      goto L16;

L252:   HO3:= ho;
      e[zj]:= e[zj]+h[zj];
     de[zj]:= wto×(HO2-HO3)/2/h[zj];

if de[zj]=0.0 then begin newline(70,1);
                         write   (70,f,k);
                         write   (70,f,zj);
                         writetext(70,[[sss]zero])
                   end;

if zj=ncv then goto L50;

        zj:= zj+1;
         m:= 1;
     e[zj]:= e[zj]+h[zj];
    goto L16;

L50: for i:=1 step 1 until ncv do
     begin ck[i]:= ck[i]-ro×de[i];
           for j:=1 step 1 until ncv do
           cc[i,j]:= cc[i,j]+de[i]×de[j];
           for j:=ncv+1 step 1 until nncv do
           cc[i,j]:= if j=ncv+i then 1.0 else 0.0 end;
               icc:= 0;
          if l=0 then goto skip;


L31:  sqr:= sqr+r↑2;
     sqru:= sqru+ruw↑2;
skip:  test(0);

end;
      if l>0 then goto L43;

       k:= 0;
ROUND: k:= k+1;
      if ck[k]= 0.0 then goto exit;
      goto if k = ncv then MATRIN else ROUND;
```

```
MATRIN: if stop=0 then test(10);

         a:= ncv;
        if a = 1 then begin cc[1,2]:= 1/cc[1,1];
                            goto vault
                      end;
cycle:   for i:= 1 step 1 until a do
         begin D:= if cc[i,a]≠0.0 then cc[i,a] else 1.0;
         for j:= 1 step 1 until nncv do cc[i,j]:= cc[i,j]/D
         end;

if a=1 then goto leap;
for i:= 1 step 1 until a-1 do
for j:= 1 step 1 until nncv do cc[i,j]:= cc[i,j]-cc[a,j];
a:= a-1;
goto cycle;

leap:   i:= ncv;
hop :   a:= i-1;
jump:   D:= cc[i,a];
        for j:= 1 step 1 until nncv do
        cc[i,j]:= cc[i,j]-cc[a,j]×D;
             a := a-1;
            if a>0 then goto jump;
             i := i-1;
        if i>1 then goto hop;

vault: for i:= 1 step 1 until ncv do
       for j:= 1 step 1 until ncv do cc[i,j]:= cc[i,j+ncv];

       for i:= 1 step 1 until ncv do x[i]:= 0.0;
       for i:= 1 step 1 until ncv do
       for j:= 1 step 1 until ncv do x[i]:= x[i]+cc[i,j]×ck[j];
test(0);

for i:=1 step 1 until ncv do if abs(x[i])>0.5 then
     begin newline(70,1);
           write  (70, f, i);
           writetext(70, [[2c4s]overshifted]);
           x[i]:= 0.5×x[i]
     end;

          sqro:= sqro/(mt - ncv);
if ncc=1 then begin
writetext(70, [[2c]Weighted*variance*with*input*constants*=]);
write(70, fa, sqro) end;
for i:=1 step 1 until ncv do e[i]:= e[i]+x[i];

L153:  i:= i+1;
     icc:= 1;
        goto L37;
```

```
L43:   sqr:= sqr/(mt-ncv);
       writetext(70, [[2c]weighted*variance*is]);
       write(70, fa, sqr);
       writetext(70, [[c]unweighted*sum*of*squares*of
                          *deviations*=]);
       write(70, fa, sqru);
    for i:= 1 step 1 until ncv do
    begin X1:= cc[i,i]×sqr;
          newline(70,1);
          write  (70, f, i);
          write  (70, fa, e[i]);
          write  (70, fa, sqrt(abs(X1)));
          if X1<0.0 then writetext(70, [[4s]negative])
    end;

if sqr>sqro then begin for i:= 1 step 1 until ncv do
begin x[i]:= 0.5×x[i];
      e[i]:= e[i]-x[i] end;

writetext(70, [[2c]half*shifts*applied*for*next*cycle])
end;
          if ncc<ncd then goto L11;

if in basic symbol(20) = 185 then
begin ncc:= read(20);
      ncv:= read(20);
      if in basic symbol(20) = 142 then
      begin  l1:= read(20);
             l2:= read(20);
            icc:= 0
      end;
      if in basic symbol(20) = 142 then
      for i:= 1 step 1 until ncc do
      begin j:= read(20);
          if in basic symbol(20) = 142 then e[j]:= read(20);
          if in basic symbol(20) = 142 then
           begin l:= read(20);
                 if sqr>sqro then icc:= -1;
                 invert(j,l,e);
                 swap  (j,l,ml);
                 swap  (j,l,mm);
                 swap  (j,l,mn);
          end;
      end;
      for i:= 1 step 1 until ncv do h[i]:= read(20);
      if icc = -1 then goto exit;
      writetext(70,[[8c]new*run[4c]]);
      ncc:= 0;
      goto L11;
end;
exit: writetext(70,[[4c]escape*route*taken]);
      if in basic symbol(20) = 142 then goto again;
         close(20);    close(70);
end ; end→
```

Appendix 2e

```
DD0441000WPU+W0300340PST→

begin integer n,i,s,p,q,a,b,dev,F1,F2,F3,F4;
      real    e,kw,KA2,KMA,vo,svo,svc,vm,pvv,
              SSK,sv;
      boolean error,pr;
      comment Calculates K101 from pM measurements. If
              q = 1, a hydrolysis correction is applied.
              If error is true, experimental errors are
              read in and used to weight the calculations;

      F2:= format([ss-d.dddd₁₀-nd]);
      F3:= format([ssss-ndd.dddd;]);
      F4:= format([-d.dddd₁₀-nd]);
       e:= ln(10.0);

       open(20);        open(70);

     dev:= read(20);
     if dev = 10 then open(10);

again:    copytext(20,70,[;;]);
      error:= read boolean(20);
          n:= read(20);
          q:= read(20);
          b:= 0;
         pr:= false;

     if q = 1 then begin  kw:= exp(-e×(read(20)));
                         KA2:= read(20);
                           a:= read(20)
                   end;

begin array t[1:23],v,em,ta,tm,u,h,cl,M,MA,
            K,sta,stm,sM,SK,pM,A[1:n];

plus:      p:= read(20);
         goto if p = 1 then proc else emf;

proc:    s:= read(20);
         b:= b + s;
        for i:= b+1-s step 1 until b do
        begin  ta[i]:= read(20);
               tm[i]:= read(20);
                M[i]:= read(20);
              if q = 1 then begin  h[i]:= read(20);
                                  cl[i]:= read(20)
                            end;
```

```
                if error then begin sta[i]:= read(20);
                                    stm[i]:= read(20);
                                     sM[i]:= read(20)
                                end;
           end;
           goto if b = n then main else plus;


emf :      s:= read(20);
           b:= b + s;
          F1:= format([ssss-d.dddd₁₀-nd]);
          for i:= 1 step 1 until 9 do t[i]:= read(20);
          if q = 1 then for i:= 10 step 1 until 13 do
          t[i]:= read(20);
          if error then for i:= 14 step 1 until 23 do
          t[i]:= read(20);

comment The subscripted variables t[i] represent,
          1 - vol of solvent,2 - vol of acid,3 - vol of
          metal,4 - conc of acid,5 - conc of metal,6 -
          conc of metal in titrant,7 - glass electrode
          slope,8 - glass electrode intercept,9 -
          reference emf,10 - reference pH,11 - pH
          electrode slope,12 - pH buffer emf,13 -
          reference pH emf.
          14 - rel error in initial vol,15 - rel error
          in t[2],16 - rel error in t[4],17 - rel error
          in t[3],18 - rel error in t[5],19 - abs error
          in vol of titrant,20 - rel error in conc of
          titrant t[6],21 - abs error in pM electrode
          slope,22 - abs error in intercept t[8],
          23 - abs error in pM;

            vo:= t[1] + t[2] + t[3];
           t[2]:= t[2]xt[4];
           t[3]:= t[3]xt[5];
          for i:= b+1-s step 1 until b do
          begin  v[i]:= read(20);
               em[i]:= read(20);
               if q = 1 then h[i]:= read(20);
                vm  := v[i]xt[6];
                u[i]:= vo + v[i];
               ta[i]:= t[2]/u[i];
               tm[i]:= (t[3] + vm)/u[i];
               pM[i]:= (em[i] - t[9] - t[8])/t[7];
                M[i]:= exp(-expM[i]);
               if q = 1 then begin h[i]:= t[10]+(t[13]-
                                        (t[12]-h[i]))/t[11];
                                  cl[i]:= vm/u[i]
                             end;
```

```
           if error then
           begin pvv:= v[i]×t[19];
                 svo:= t[14]×vo;
                 svc:= t[3]↑2×(t[17]↑2 + t[18]↑2);
               sM[i]:= (pM[i]×e×M[i])↑2×((t[23]↑2 +
                        t[22]↑2)/(em[i]-t[9]-t[8])↑2
                        + (t[21]/t[7])↑2);
                 sv := (svo↑2 + (if v[i]=0.0 then 0.0
                        else t[19]↑2))/u[i]↑2;
              sta[i]:= ta[i]↑2×(t[15]↑2 + t[16]↑2 + sv);
              stm[i]:= tm[i]↑2×((svc + vm↑2×(t[20]↑2 +
                        (if v[i]=0.0 then 0.0 else (t[19]/
                        v[i])↑2)))/(t[3]+vm)↑2 + sv);
           end;
           end;

           gap(10,250);
           writetext(10,[[c]1;[c]]);
           write(10,format([nddd;c]),s);

print:      for i:= b+1-s step 1 until b do
            begin newline(10,1);
                  write(10,F1,ta[i]);
                  write(10,F1,tm[i]);
                  write(10,F1, M[i]);
                  if q = 1 then begin write(10,F3,h[i]);
                                      write(10,F1,cl[i])
                                end;
             end;

            if error then
            begin gap(10,50);
                  newline(10,10);
                  for i:= b+1-s step 1 until b do
                  begin newline(10,1);
                        write(10,F1,sta[i]);
                        write(10,F1,stm[i]);
                        write(10,F1, sM[i])
                  end;
             end;

             if pr then goto skip;
             if b ≠ n then goto plus;

main:       KMA:= SSK:= 0.0;
            for i:= 1 step 1 until n do
            begin MA[i]:= tm[i] - M[i];
                  if q = 1 then h[i]:= exp(-e×h[i]);
                   A[i]:= if q = 0 then ta[i] - MA[i]
                          else (h[i]+tm[i]-a×A[i]-cl[i] -
                          kw/h[i])/(a + (a - 1)/KA2×h[i]);
                   K[i]:= MA[i]/(M[i]×A[i]);
```

```
         if error then SK[i]:= K[i]↑2×(sM[i]/M[i]↑2 +
                               (stm[i] + sM[i])/MA[i]↑2
                               + (stm[i] + sta[i]
                               + sM[i])/A[i]↑2)
                   else SK[i]:= 1.0;
                SSK:= SSK + 1.0/SK[i];
                KMA:= KMA + K[i]/SK[i];
           end;

        writetext(70,[[cc6s]KMA*=]);
        write(70,F4,KMA/SSK);

         if error then
         begin writetext(70,[[cc6s]error*in*KMA*=]);
                write(70,F4,sqrt(1.0/SSK))
         end else
                writetext(70,[[cc6s]unit*weights*applied]);
        writetext(70,[[6c6s]M[12s]MA[13s]A[13s]K]);
        if error then writetext(70,[[13s]SIGK]);
        newline(70,2);

        for i:= 1 step 1 until n do
        begin write(70,F2,M[i]);
              write(70,F2,MA[i]);
              write(70,F2,A[i]);
              write(70,F2,K[i]);
              if error then write(70,F2,sqrt(SK[i]));
              newline(70,1);
        end;

        if in basic symbol(20) = 185 then
        begin pr:= true;
              F1:= format([ssss-d.dddd10-nd]);
              gap(10,150);
              goto print
        end;

skip :  if in basic symbol(20) = 142 then goto again;

         close(20);    close(70);
       if dev = 10 then close(10);

end
end→
```

Appendix 2f

```
DD0441300WPU+W030034XPST→

begin comment This program calculates KMA = MA/(M×A) and
      KM2A = M2A/(MA×M) from pM measurements by a least
      squares procedure and if pH data are available
      also calculates KMA and KM2A for each data point;
      real    kw,e,sx,sy,sxy,sx2,KA2,K1,K2;
      integer a,n,i,s,b,p,F1,F2,F3,F4;
      boolean INDIV1,INDIV2;

F1:= format([ssss-d.dddd₁₀-nd;]);
F2:= format([ssss-ndd.dddd;]);
F3:= format([ss-d.dddd₁₀-nd]);
F4:= format([ssss-d.dddd₁₀-nd]);
 e:= ln(10.0);
open(20);   open(70);

again:  copytext(20,70,[;]);
        comment n= total no of points,p= 1 for pM only and
         2 for pM and pH(proc data)  p=3 for pM only and 4
         for pM and pH(original data).s= no of points in
         section,kw = ion product of solvent,KA2 = 2nd
         dissociation constant of acid,a is charge on acid
         anion;
         a:= read(20);
         n:= read(20);
         b:= 0;
         INDIV1:= false;    INDIV2:= false;


begin array h,cl,tm,ta,v,em,x,y,u,M,MA,M2A,A,HA,K,KK[1:n],
            t[1:13];

plus: p:=read(20);
       goto if p<3 then proc else emf;

proc: s:=read(20);
     if p=2 then begin kw:=read(20);KA2:=read(20)end;
      b:= b+s;
      for i:= b-s+1 step 1 until b do
      begin comment  Data columns are total acid,total metal,
                     free metal,pH,total salt added;
            ta[i]:=read(20);
            tm[i]:=read(20);
             M[i]:=read(20);
      if p=2 then begin h[i]:=read(20);
                       cl[i]:=read(20) end end;
          goto if b=n then main else plus;
```

```
comment t[1-9] are,resp,vol of solvent,vol of acid,vol of
        salt,conc of acid,conc of salt,conc of titrant,
        slope of Na electrode calibration,intercept of Na
        electrode calibration,reference emf.t[10-13] are
        reference pH,slope of pH response,buffer emf,ref
        emf on calibration graph;
emf:
        s:= read(20);
        b:= b+s;
    if p=4 then begin kw:=read(20);   KA2:=read(20) end;
    for i:= 1 step 1 until 9 do t[i]:=read(20);
    if p=4 then for i:=10 step 1 until 13 do t[i]:=read(20);

    for i:= b-s+1 step 1 until b do
    begin  v[i]:=read(20);
          em[i]:=read(20);
           M[i]:=exp(-ex((em[i]-t[9]-t[8])/t[7]));
           u[i]:= t[1] + t[2] + t[3] + v[i];
          ta[i]:=t[2]×t[4]/u[i];
          tm[i]:=(t[3]×t[5] + v[i]×t[6])/u[i];
           if p=4 then begin h[i]:=read(20);
                             h[i]:=t[10]+ (t[13] - (t[12]
                                    - h[i]))/t[11];
                            cl[i]:=v[i]×t[6]/u[i] end end;
open(10);
gap(10,250);
write(10,format([d;c]),p-2);
write(10,format([nddd;c]),s);
for i:= b-s+1 step 1 until b do
begin  writetext(10,[[c]]);
       write(10,F1,ta[i]);
       write(10,F1,tm[i]);
       write(10,F1,M[i]);
if p=4 then begin write(10,F2,h[i]);
                  write(10,F1,cl[i]) end end;
p:=p-2;
close(10);
goto if b=n then main else plus;

main: sx:=sy:=sxy:=sx2:=0.0;
      K2:= 0.0;
       b:= 0;

for i:=1 step 1 until n do begin
 h[i]:= exp(-e×h[i]);
HA[i]:= if p=2 then a×ta[i] - tm[i] + cl[i] - h[i] + kw/h[i]
                else 0.0;
 y[i]:=(M[i] - tm[i])/M[i]↑2/(tm[i] - M[i] - 2×ta[i] + 2×HA[i]);
 x[i]:= (tm[i] - M[i] - ta[i] + HA[i])/M[i]/(tm[i] - M[i]
          - 2×ta[i] + HA[i]×2);
```

```
if x[i]>0.0 then begin    b:=b+1;
                         sx:=sx+x[i];
                         sy:=sy+y[i];
                        sxy:=sxy + x[i]×y[i];
                        sx2:=sx2 + x[i]↑2  end end;
if b<2 then begin sx:=sy:=sxy:=sx2:=0.0;
         for i:= 1 step 1 until n do begin
             sx:=sx + x[i];
             sy:=sy + y[i];
            sxy:=sxy + x[i]×y[i];
            sx2:=sx2 + x[i]↑2 end end;

K1:= if b<2 then (sx×sy - n×sxy)/(sx↑2 -n×sx2)
            else (sx×sy - b×sxy)/(sx↑2 - b×sx2);
for i:= 1 step 1 until n do begin
if x[i]<0.0 then begin K[i]:= (y[i] - K1×x[i])/K1;
                         K2:= K2 + K[i] end end;
K2:= if b=n then (sy - K1×sx)/K1/n else K2/(n - b);
     if b≠n then INDIV2:= true;

out: writetext(70,[[3c6s]ABSCISSA[6s]ORDINATE]);
      for i:= 1 step 1 until n do
      begin newline(70,1);
            write(70,F4,x[i]);
            write(70,F4,y[i]) end;

for i:= 1 step 1 until n do
begin A[i]:= (ta[i] - HA[i])/(1 + K1×M[i] + K1×M[i]↑2×K2);
     MA[i]:= 2×ta[i] - tm[i] - 2×A[i] - 2×HA[i] + M[i];
    M2A[i]:= (tm[i] - M[i] - MA[i])/2;
end;

print:   writetext(70,[[3c4s]K1*=*]);
         write(70,F3,K1);
         writetext(70,[[6s]K2*=*]);
         write(70,F3,K2);
         writetext(70,[[3c6s]M[12s]MA[11s]M2A[10s]A]);
if p=2 then writetext(70,[[11s]HA]);
if INDIV1 then writetext(70,[[11s]K1]);
if INDIV2 then writetext(70,[[11s]K2]);
```

```
for i:= 1 step 1 until n do
begin newline(70,1);
      write(70,F3,M[i]);
      write(70,F3,MA[i]);
      write(70,F3,M2A[i]);
      write(70,F3,A[i]);
  if p=2 then write(70,F3,HA[i]);
  if INDIV1 then write(70,F3,KK[i]);
  if INDIV1 or x[i]<0.0 then write(70,F3,K[i]) end;
  if p=1 or INDIV1 then goto emerg;

pH only:if p=2 then begin
comment This section calculates KMA and KM2A for each
        individual point if pH data are available;

K1:=K2:=0.0;
          for i:=1 step 1 until n do
        begin A[i]:= KA2xHA[i]/h[i];
            M2A[i]:= tm[i] - ta[i] - M[i] + A[i] + HA[i];
             MA[i]:=tm[i] - M[i] - 2xM2A[i];
             KK[i]:=MA[i]/M[i]/A[i];
              K1  := K1 + KK[i];
              K[i]:= M2A[i]/M[i]/MA[i];
              K2  := K2 + K[i];
        end;

INDIV1:=true;   INDIV2:= true;
            K1:= K1/n;       K2:= K2/n;
writetext(70,[[6c3s]INDIVIDUAL*CALCULATIONS]);
            goto print end;

emerg: p:= read(20);
       if p=2 then goto again;
       close(20);    close(70);
end end→
```

Appendix 2g

```
DD0440600WPU+W030034RPST→

begin real e, k, es, vo, v, t, kw, pm, ts, K1,
           K2, T, dha, dhb, D, s, u, ao, be;
      integer p, q, r, i, n, F1, F2, a, b, pp, g, l;
      real procedure ACTCO (z, I);
      value I, z;
      real  I;
      integer  z;
      begin
      ACTCO:=exp(-e×dha×z↑2×(sqrt(I)/(1+dhb×ao×sqrt(I))
                 - be×I))
      end activity coefficients from Davies equation;

           e:= ln(10.0);
          F1:=format([-d.dddd⏨-nd]);
          F2:=format([3s-d.dddd⏨-nd]);
           open(20);   open(70);
again:   copytext(20, 70, [;]);

comment   pp = 0 for emfs, 1 for direct pH readings.
  q = 0 if activity coefficients are  to be calculated else 1.
          Gran plots : r= 1,2 or 3
  1 for strong acid - strong base with indicator ion in excess,
  2 for strong acid - strong base with counter-ion in excess,
  3 for weak acid - strong base.
           Explicit plots: r = 4,5,6 or 7
  4 for strong acid - strong base and precipitation titrations,
  5 for weak(dibasic) acid - strong base,
  6 for weak monobasic acid - strong base in presence
    of a salt of a weak base,
  7 for weak acid - weak base;

          pp:=read(20);
           q:=read(20);


if q=0 then begin  T:=read(20);
                   D:=read(20);
                  ao:=read(20);
                  be:=read(20);
                   s:=read(20);
                   u:=read(20);
                dha:=1.8249⏨6/sqrt((D×T)↑3);
                dhb:=5.0293⏨1/sqrt(D×T)
        end T is abs temp D dielectric const
            ao distance of closest approach be empirical
            coefficient  s conc of salt present
            u estimated conc of sample;

     r:=read(20);
     n:=read(20);
```

```
      vo:=read(20);
       v:=read(20);
       t:=read(20);
       k:= if pp=1 then 1.0 else read(20);

if r<4 then begin  a:=  b:= 1;
                  es:= pm:= 0.0 end;
if r>3 then begin es:= if pp=1 then 0.0 else read(20);
                  pm:= if pp=1 then 0.0 else read(20);
                  kw:= read(20);
                   b:= read(20);
                   a:= read(20) end;
if r>4 then begin K1:= read(20);
                  K2:= read(20) end;
if r=6 then       ts:= read(20);

comment  n = no. of points,
        vo = volume of diluting solution,
         v = volume of sample,
         t = concentration of standard solution,
         k = slope of emf response,
        es = emf of reference solution,
        pm = -log10(activity in reference solution),
        kw = solubility product or autoprotolysis constant,
        ts = concentration of salt of weak base in sample,
        K1,K2,b and a are different for different values of r:
 r          K1            K2                 b                a

 4          -             -              charge on        charge on
                                       indicator ion    counter-ion
 5       H2A/(HxHA)     HA/(HxA)      no of titrable    charge on A
                                            protons
6or7     HA/(HxA)       BH/(HxB)      charge on B       charge on A
        For a monobasic weak acid r=5 and K1 = 0.0;

             g:= 0;
            vo:= vo+v;
if q=0 then u:= s+u;

readings:  begin real    sx, sy, sxy, sx2, sy2, m, c, d,
                         dy, dm, c1, c2;
                 array   f, x, y, h, fh, fha, fa, fhha, fb,
                         fbh, I, vx[1:n];
                 comment x is vol of titrant added, y is emf
                   or pH. Except when r=4,if p=1 titrant is
                   standard solution,if p=2 titrant is
                   unknown.When r=4,if titrant is the
                   standard solution p>0,if abs(p)=1 then
                   soln of indicator ion is standard else
                   abs(p)=2;
```

```
                switch  sr:= R1,R2,R3,R4,R5,R6,R7;
                switch  si:= I1,I2,I3,I4,I5,I6,I7;
                boolean array bo[1:n];

            for i:=1 step 1 until n do begin x[i]:=read(20);
                                             y[i]:=read(20);
                                            vx[i]:= vo+x[i];
                                            bo[i]:=true
                                        end;
            p:=read(20);
           c2:=0.0;
            for i:= 1 step 1 until n do
            begin if q=1 then
            fh[i]:=fha[i]:=fa[i]:=fhha[i]:=fb[i]:=fbh[i]:=1.0
                          else I[i]:=u×v/vx[i]
            end;
            if r>3 then for i:= 1 step 1 until n do
            h[i]:= exp(e×((es-y[i])/k - pm));

recalc:    c1:= c2;
            if q=0 and r<5 then for i:= 1 step 1 until n do
            begin  fh[i]:= ACTCO( b , I[i]);
                  fha[i]:= ACTCO(b-a, I[i]);
                   fa[i]:= ACTCO( a , I[i])
            end;

            if q=0 and r>4 then for i:= 1 step 1 until n do
            begin  fh[i]:= ACTCO( 1 ,I[i]);
                   fa[i]:= ACTCO( a ,I[i]);
                  fha[i]:= ACTCO(a-1,I[i]);
            end;

            goto sr[r];


R1:     for i:= 1 step 1 until n do
        f[i]:= vx[i]×exp(-e×y[i]/k)/fh[i];
        goto fit;

R2:     for i:= 1 step 1 until n do
        f[i]:= vx[i]×exp(e×y[i]/k)/fh[i];
        goto fit;

R3:     for i:=1 step 1 until n do
        f[i]:= x[i]×exp(-e×y[i]/k)×fha[i]/fh[i]/fa[i];
        goto fit;

R4:     for i:=1 step 1 until n do
        f[i]:= vx[i]×(b×h[i]/fh[i]-a×(kw/h[i]↑a)↑(1/b)/fa[i]);
        goto fit;
```

```
R5:     for i:= 1 step 1 until n do
        begin if q=0 then fhha[i]:= ACTCO(a-2,I[i]);
               fb[i]:= h[i]×K1/fhha[i];
              fbh[i]:= h[i]×K2×fa[i];
        if p=1 then f[i]:= vx[i]×(b×(h[i] - kw/h[i])/fh[i]
                    ×(1 + fbh[i]×(1/fha[i]+fb[i])) + t×x[i]/
                    vx[i]×fbh[i]×(1/fha[i]+2×fb[i]))/
                    (b + fbh[i]×((b-1)/fha[i] + (b-2)×fb[i]));
        if p=2 then f[i]:= vx[i]×((h[i]-kw/h[i])/fh[i] +
                      t×v/vx[i]×fbh[i]×(1/fha[i] + 2×fb[i])
                      /(1 + fbh[i]×(1/fha[i] + fb[i])))
        end;
        goto fit;

R6:     for i:= 1 step 1 until n do
        begin if q=0 then begin fb[i]:= ACTCO( b ,I[i]);
                               fbh[i]:= ACTCO(b-1,I[i])
                          end;
               fhha[i]:= h[i]×K1×fa[i];
                  f[i]:= ((h[i]-kw/h[i])/fh[i]×vx[i] - ts×
                         v/(1 + K2×h[i]/fbh[i]))
                         × (1 + fhha[i]) + t×x[i]×fhha[i]
        end;
        goto fit;

R7:     for i:= 1 step 1 until n do
        begin if q=0 then begin  fb[i]:= ACTCO( b ,I[i]);
                                fbh[i]:= ACTCO(b-1,I[i])
                          end;
                               fhha[i]:= h[i]×K1×fa[i];
                                  I[i]:= h[i]×K2×fb[i];
        if p = 1 then f[i]:= (vx[i]×(h[i]-kw/h[i])/fh[i]
                             - t×x[i]×(a- fhha[i]/(fha[i]
                             +fhha[i]) - I[i]/(fbh[i] +
                             I[i])))/(a - fhha[i]/(fha[i]
                             + fhha[i]));
        if p = 2 then f[i]:= (vx[i]×(h[i]-kw/h[i])/fh[i]
                        - t×v×(a - fhha[i]/(fha[i]+fhha[i])
                        - I[i]/(fbh[i] + I[i])))
                        /(b - I[i]/(fbh[i] + I[i]))
        end;
        goto fit;


fit:   l:= g;
       g:= 0;
       sx:=sy:=sxy:=sx2:=sy2:=0.0;
```

```
    for i:=1 step 1 until n do
    begin if bo[i] then begin sx:= sx + x[i];
                              sy:= sy + f[i];
                             sxy:= sxy+ x[i]×f[i];
                             sy2:= sy2+ f[i]↑2;
                             sx2:= sx2+ x[i]↑2
                         end
    end;
    d:= (n-1)×sx2-sx↑2;
    m:= ((n-1)×sxy-sx×sy)/d;
    c:= (sx2×sy-sx×sxy)/d;

if r<5 then c2:= if p>0 then -c/m×t/v×(if p=1 then b/a else a/b)
                 else -t×v×m/c×(if p=-1 then b/a else a/b);
if r=5 then c2:= if p=1 then -c/m×t/v/b else -v×t×b×m/c;
if r>5 then c2:= if p=1 then -c/m×t/v   else -v×t×m/c;

if r=4 then begin for i:= 1 step 1 until n do
                begin if (kw/h[i]↑a)↑(1/b) > (if abs(p)=1 then c2
                      else t)×(if p>0 then v else x[i])/(vo+x[i])
                      then begin bo[i]:= false;
                                 g:= g + 1
                           end
                end;
                if g≠1 and g>0 then goto fit
                end;

      goto if q=1 or abs(c2- c1) ≤ c2×₁₀-4 then OUT
                                            else si[r];

I1:I2:      for i:= 1 step 1 until n do
            I[i]:=(s×v+t×(ifp=1 then -c/m else v))/v×[i];
            goto recalc;

I3    :     if pp = 1 then for i:=1 step 1 until n do
            I[i]:=(s×v+x[i]×(if p=1 then t else c2 ))/
                     vx[i]+exp(-e×y[i]);
            goto recalc;

I4    :     for i:= 1 step 1 until n do
            I[i]:= s×v/vx[i] + 0.5×(b↑2×h[i]/fh[i] + a↑2×
                   (kw/h[i]↑a)↑(1/b)/fa[i] + (if p>0 then (t×
                   x[i]×(if p=1 then b else a) + c2×v×(if p=1
                   then a else b))/vx[i] else (t×v×(if p= -1
                   then b else a) + c2×x[i]×(if p= -1 then a
                   else b))/vx[i]));
            goto recalc;
```

```
I5    :     if p = 1 then for i:= 1 step 1 until n do
            I[i]:= s×v/vx[i] + 0.5×((h[i] + kw/h[i])/fh[i] +
                   (x[i]×t + c2×v×(b - a + a↑2 - fbh[i]×(fb[i]
                   ×4×(a-1) + (a×2 - 1)/fha[i])/(1 + fbh[i]×
                   (1/fha[i] + fb[i]))))/vx[i]);
            if p = 2 then for i:= 1 step 1 until n do
            I[i]:=s×v/vx[i] + 0.5×((h[i] + kw/h[i])/fh[i] +
                   (c2×x[i] + t×v×((b-a) + (a↑2 - fbh[i]×((a×2
                   - 1)/fha[i] + 4×(a-1)×fb[i])/(1 + fbh[i]×
                   fa[i]×(1/fha[i] + fb[i]))))))/vx[i]);
            goto recalc;

I6    :     for i:= 1 step 1 until n do
            I[i]:= h[i]/fh[i] + (t×x[i] + ts×v/(1 + fbh[i]/
                   K2/h[i]))/vx[i];
            goto recalc;

I7    :     if p = 1 then for i:= 1 step 1 until n do
            I[i]:= (s×v + t×((b-0.5)×x[i]/(1 + I[i]/fbh[i])
                   - (a-0.5)× c/m/(1 + fhha[i]/fha[i])))/vx[i]
                   + 0.5×((h[i] + kw/h[i])/fh[i] + (((b-1)↑2
                   + b)×x[i] - (a-1)↑2×c/m)×t/vx[i]);
            if p = 2 then for i:= 1 step 1 until n do
            I[i]:= (s×v + (b-0.5)×x[i]×c2/(1 + I[i]/fbh[i])
                   + (a-0.5)×v×t/(1 + fhha[i]/fha[i]))/vx[i]
                   + 0.5×((h[i] + kw/h[i])/fh[i] + (((b-1)↑2 +
                   b)×x[i]×c2 + (a-1)↑2×v×t)/vx[i]);
            goto recalc;



OUT:       dy:= sy2 + (n-g)×c↑2 + m↑2×sx2
                   -2×(c×sy + m×sxy - m×c×sx);
        if dy < 0.0 then dy:= 0.0;
           dm:= sqrt((n-g)×dy/(n-g-2)/d);
            d:= sqrt(dy×sx2/d/(n-2-g));

writetext(70, [[4c]  M*=*]);
write(70, F1, m);
writetext(70, [[3s] STANDARD*ERROR*IN*M*=*]);
write(70, F1, dm);
writetext(70, [[4c] C*=*]);
write(70, F1, c);
writetext(70, [[3s]STANDARD*ERROR*IN*C*=*]);
write(70, F1, d);
writetext(70, [[2c]STANDARD*DEVIATION*IN*Y*=*]);
write(70, F1, sqrt(dy/(n-2-g)));
```

```
writetext(70, [[3c9s] v[8s] f*obs[8s] f*calc[7s]
                                    deviation[2c]]);
        for i:= 1 step 1 until n do
                 begin newline(70, 1);
                       y[i]:= m×x[i] + c;
                       write  (70, F2, x[i]);
                       write  (70, F2, f[i]);
                       write  (70, F2, y[i]);
                       write  (70, F2, f[i]-y[i]);
                 if not bo[i] then out basic symbol(70,205)
                 end;

writetext(70, [[3c3s]VE*=*]);
write(70, F1, -c/m);
writetext(70, [[3s]STANDARD*ERROR*IN*VE*=*]);
write(70, F1, -sqrt((d/c)↑2+(dm/m)↑2)×c/m);
writetext(70, [[2c]CONCENTRATION*=*]);
write(70, F1, c2);

if in basic symbol(20) = 142 then goto again;

      close(20);      close(70);
end end→
```