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>
<thead>
<tr>
<th>T°C</th>
<th>medium</th>
<th>pK₁</th>
<th>pK₂</th>
<th>10⁻³(ρK₁)</th>
<th>10⁻³(ρK₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.2 (Me₄N)Cl</td>
<td>2.81</td>
<td>3.95</td>
<td>1.1</td>
<td>8.8</td>
</tr>
<tr>
<td>25</td>
<td>0.1 (Me₄N)Cl</td>
<td>2.83</td>
<td>3.97</td>
<td>3.4</td>
<td>2.9</td>
</tr>
<tr>
<td>25</td>
<td>0.4 (Me₄N)Cl</td>
<td>2.83</td>
<td>3.88</td>
<td>0.8</td>
<td>2.1</td>
</tr>
<tr>
<td>15</td>
<td>0 corr</td>
<td>3.04</td>
<td>4.37</td>
<td>8.3</td>
<td>19.9</td>
</tr>
<tr>
<td>25</td>
<td>0 corr</td>
<td>3.06</td>
<td>4.26</td>
<td>2.7</td>
<td>4.9</td>
</tr>
<tr>
<td>35</td>
<td>0 corr</td>
<td>3.08</td>
<td>4.37</td>
<td>3.1</td>
<td>33.7</td>
</tr>
</tbody>
</table>

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>
<thead>
<tr>
<th></th>
<th>10⁻⁴ΔG°</th>
<th>10⁻⁵ΔH°</th>
<th>ΔS°</th>
</tr>
</thead>
<tbody>
<tr>
<td>First dissociation</td>
<td>1.75</td>
<td>-3.23</td>
<td>-69.5</td>
</tr>
<tr>
<td>Second dissociation</td>
<td>2.43</td>
<td>0.65</td>
<td>-79.4</td>
</tr>
</tbody>
</table>

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 (Me₄N)Cl are
\[ K_{\text{NaT}} = \frac{\text{NaTar}}{(\text{Na})(\text{Tar})} = 2.0 \text{ mole}^{-1} \text{ litre} \]
\[ K_{\text{NaHT}} = \frac{\text{NaHTar}}{(\text{Na})(\text{HTar})} = 0.9 \text{ mole}^{-1} \text{ litre}. \]

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 \( 0.6 \leq K_{KT} \leq 1.0 \text{ mole}^{-1} \text{ litre} \) and \( 0.15 \leq K_{KHT} \leq 0.35 \text{ mole}^{-1} \text{ litre} \).

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.

\[ K_{101} = \frac{(\text{MA})}{(\text{M})(\text{A})}, \quad K_{102} = \frac{(\text{MA}_2)}{(\text{M})(\text{A})^2}, \quad K' = \frac{(\text{MHA})}{(\text{M})(\text{HA})}, \]

where \( (\text{M}), (\text{A}) \) etc. represent the various species' concentrations or activities, as appropriate.

<table>
<thead>
<tr>
<th>°C medium</th>
<th>( \log K_{101} )</th>
<th>( \log K_{102} )</th>
<th>( \log K' )</th>
<th>( 10^2 \sigma(\log K_{101}) )</th>
<th>( 10^2 \sigma(\log K_{102}) )</th>
<th>( 10^3 \sigma(\log K') )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 0.2 (Me₄N)Cl</td>
<td>3.410</td>
<td>5.640</td>
<td>2.27</td>
<td>3.4</td>
<td>2.9</td>
<td>1.9</td>
</tr>
<tr>
<td>25 0.1 (Me₄N)Cl</td>
<td>3.676</td>
<td>6.128</td>
<td>2.44</td>
<td>2.2</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>25 0.4 (Me₄N)Cl</td>
<td>3.108</td>
<td>5.559</td>
<td>1.94</td>
<td>1.6</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td>15 0 corr</td>
<td>4.852</td>
<td>7.41</td>
<td>3.10</td>
<td>3</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>25 0 corr</td>
<td>4.604</td>
<td>7.59</td>
<td>2.48</td>
<td>3</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>35 0 corr</td>
<td>4.876</td>
<td>7.93</td>
<td>2.70</td>
<td>4</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^\circ \times 10^{-4}$</th>
<th>$\Delta H^\circ \times 10^{-4}$</th>
<th>$\Delta S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M + A = MA$</td>
<td>2.63</td>
<td>0.0</td>
<td>94.8</td>
</tr>
<tr>
<td>$M + 2A = MA_2$</td>
<td>4.53</td>
<td>4.47</td>
<td>295</td>
</tr>
<tr>
<td>$M + HA = MHA$</td>
<td>1.41</td>
<td>0.56</td>
<td>66</td>
</tr>
</tbody>
</table>

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.

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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.
- **→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 $z_1e$ and $z_2e$, 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

\[ K = (4 \frac{N}{1000})(|z_i z_j| e^2/\varepsilon kT)^3 Q(b) \] ....... (1),

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

\[ x = |z_i z_j| e^2/r \varepsilon kT \text{ and } b = |z_i z_j| e^2/a \varepsilon kT \]

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

\[ \ln K = \ln K^0 + |z_i z_j| e^2/a \varepsilon kT \] ....... (3),
where \( K^0 \) 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

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

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

\[ K_C = \frac{[\text{MA}]}{[\text{M}][\text{A}]} \]

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

The thermodynamic stability constant,

\[ K = \frac{[\text{MA}]}{[\text{M}][\text{A}]} = K_C \cdot \frac{f_{\text{MA}}}{f_M \cdot f_A} \quad \ldots \ldots \ldots \ldots \quad (5), \]

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 mole\(^{-1}\) 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

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

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

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

$K'$ 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(H₂O) displays greater linearity than one of ln K against 1/ε. 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
\[- \log f_\infty = |z_+ z_-| A I^\frac{1}{2} \ldots \ldots \ldots \ldots \ldots (9),\]
where \( I = \frac{1}{2} \sum m_i z_i^2 \) is the ionic strength (10) and \( A \) is a constant. For aqueous solutions at 25°, the activity coefficient of a \( z \)-valent ion is
\[- \log f_z = 0.509 z^2 I^\frac{1}{2} \ldots \ldots \ldots \ldots (9a).\]

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
\[- \log f_z = A z^2 I^\frac{1}{2} / (1 + B a I^\frac{1}{2}) \ldots \ldots (10),\]
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
\[- \log f_z = A z^2 I^\frac{1}{2} / (1 + B a I^\frac{1}{2}) - C' I \ldots (11).\]

A simplified form of Eqn (10), containing no adjustable parameters, has been used by Guntelberg (11)
\[- \log f_z = A z^2 I^\frac{1}{2} / (1 + I^\frac{1}{2}) \ldots \ldots (12).\]

Davies (12) proposed the formula
\[- \log f_z = A z^2 \left( \frac{I^\frac{1}{2}}{1 + I^\frac{1}{2}} \right) - C I \ldots (13),\]
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 \( I^{1/2} \) and extrapolated to infinite dilution, where \( K = K_c \). At higher concentrations, a plot of \( \log K_c + g.A.I^{1/2}/(1 + B.a.I^{1/2}) \) 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 \( g = \sum n_r z_r^2 - \sum n_p z_p^2 \) 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. Ellin(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
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 unrepeatable and ill-defined.

With iterative calculations performed on an 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.

\[ \Delta G = \Delta H - T \Delta S \] ................................ (14).

\[ (\Delta G / \Delta T)_p = - \Delta S \text{ (the Gibbs-Helmholtz equation).} \] ................................ (15).

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

\[ \left[ \frac{\Delta G}{\Delta T} \right]_p = - \frac{\Delta H}{T^2} \] ................................ (16)

or

\[ \left[ \frac{\Delta (AG / T)}{\Delta (1/T)}_p \right] = \Delta H \] ................................ (17).

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

\[ \Delta G^0 = - RT \ln K \] ................................ (18).
References


(9) P. Debye & E. Hückel, Physik.Z., 1923, 24, 305.


(13) E.A. Guggenheim, Phil.Mag., 1935, 19, 58.


(22) E.A. Guggenheim, J.Phys.Chem., 1930, 34, 1758.
(23) E.A. Guggenheim, Phil.Mag., 1936, 22, 983.
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:

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

\[ i^+ \text{ glass solution} + j^+ \text{ glass solution} = j^+ \text{ glass} + i^+ \text{ glass} \]

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
\[ \mu_j + F\psi = \mu_j' + F\psi' , \]
where \( \mu \) represents the chemical potential.

Since \( \mu = \mu^0 + RT \ln(a) \),
\[ F(\psi' - \psi) = \mu_i^0 - \mu_i'^0 + RT \ln(a_i/a_i') , \]
where \( \mu^0 \) and \( \mu^0' \) 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. \( C_i + C_j = \text{constant} = C_0 \).

Assuming that the ionic activity coefficients within the glass are constant and the same for both ions, we can write
\[ K_{ij} = a_i \cdot C_j/(a_j \cdot C_i) = a_i (C_0 - C_i)/(a_j \cdot C_i) \ldots \ldots (1). \]

Hence \( a_i' = f \cdot C_i = a_i \cdot f \cdot C_0/(a_i + K_{ij} \cdot a_j) \), where \( f \) is the activity coefficient of the \( i \) and \( j \) ions in the glass, and
\[ a_i/a_i' = (a_i + K_{ij} \cdot a_j)/(f \cdot C_0). \]

Therefore,
\[ \psi' - \psi = \text{constant} + (RT/F) \ln \left[ (a_i + K_{ij} \cdot a_j)/(f \cdot C_0) \right] . \]

Since \( f \) and \( C_0 \) are constant this can be rewritten,
\[ \mathbb{E} = \mathbb{E}^0 + (RT/F) \ln(a_i + K_{ij} \cdot a_j) \ldots \ldots \ldots \ldots \ldots (2) , \]
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 \( \mathbb{E}^0 \) 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(lb) equation for a cell of type (A). If the electrode responds to more than two ions, we obtain an extended form of Eqn(2),

\[ E = E^0 + (RT/F) \ln(a_{i}^{+} + K_{i,j} a_{j} + K_{i,k} a_{k}^{+} + \ldots) \]

Eisenman et al.\((47)\) introduced the equation,

\[ E = E^0 + n(RT/F) \ln \left[ a_{i}^{1/n} + (K_{i,j} a_{j})^{1/n} \right] \ldots \ldots \ldots \ldots \ldots (3), \]

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 \(n\)th power of the corresponding concentrations, i.e.

\[ \frac{d\ln(a_{i})}{d\ln(C_{i})} = n. \]

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,
\[ J_1 = -D_1(\frac{\partial C_1}{\partial x}) - C_1v_1(\frac{\partial \psi}{\partial x}) \]
and
\[ J_j = -D_j(\frac{\partial C_j}{\partial x}) - C_jv_j(\frac{\partial \psi}{\partial x}) \]
where \( D \)'s, \( C \)'s and \( v \)'s are diffusion coefficients, concentrations and mobilities in a unit field respectively and \( \psi \) is the electric potential.

Now, \( C_i + C_j = C_0 \), a constant, \( J_1 = -J_j \) and \( \psi = D(F/RT) \) for each ion. Hence it can be shown that

\[ \frac{\partial \psi}{\partial x} = \left[ \frac{(RT/F)(D_j-D_1)}{(C_1D_1+C_1D_j)} \right] \frac{\partial C_1}{\partial x} \ldots \ldots \ldots (4) \]
and
\[ J_1 = -\left[ \frac{C_0D_1D_j}{(C_0D_j+C_1D_1-D_j)} \right] \frac{\partial C_1}{\partial x} \]

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

\[ \Delta \psi = \int_{x=0}^{x=\infty} \left( \frac{\partial \psi}{\partial x} \right) dx \]

\[ \Delta \psi = \left( \frac{RT}{F} \right) \int_{C_1'}^{C_0} \frac{(D_j-D_1)}{(C_1D_1+C_1D_j)} dC_1. \] where \( C_1' \) is the concentration of \( i \) at the surface immediately inside the glass. If \( D_1 \) and \( D_j \) are independent of \( C_1 \), the integral becomes,

\[ \Delta \psi = -\left( \frac{RT}{F} \right) \ln \left[ \frac{C_0D_1}{(C_1D_1+C_1D_j)} \right] \ldots \ldots \ldots \ldots \ldots (5). \]

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,
by means of Eqn(1), Eqn(5) becomes,
\[ \Delta \psi = \frac{(RT/F) \ln [(a_i + (D_j/D_1) K_{ij} a_j) / (a_i + K_{ij} a_j)]}{(a_i + K_{ij} a_j)} \ldots \ldots \ldots (6). \]

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

\[ \psi = E^\circ + \frac{(RT/F) \ln (a_i + (D_j/D_1) K_{ij} a_j)}{a_i + K_{ij} a_j} \ldots \ldots \ldots \ldots (7). \]

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,
\[ \psi = E^\circ + n(RT/F) \ln \left[ a_i^{1/n} + (u_j/u_i)^n (K_{ij} a_j)^{1/n} \right]. \ldots \ldots \ldots (8), \]
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,
\[ \psi = E^\circ + n(RT/F) \ln \left[ a_i^{1/n} + (K_{ij} a_j)^{1/n} \right]. \ldots \ldots \ldots (9), \]
where \( K_{ij} = (u_j/u_i)^n K_{ij} \) and can be determined experimentally.

If \( a_i \gg K_{ij} a_j \) (Eqn(3)) or \( a_i \gg K_{ij} a_j \) (Eqn(9)) the cell e.m.f. is of the form,
\[ \psi = E^\circ + (RT/F) \ln a_i \ldots \ldots \ldots \ldots \ldots \ldots \ldots (10a), \]

Conversely, if \( a_i \ll K_{ij} a_j \) or \( a_i \ll K_{ij} a_j \), the cell e.m.f. becomes
\[ \psi = E^\circ + (RT/F) \ln a_j \ldots \ldots \ldots \ldots \ldots \ldots \ldots (10b), \]

where \( E^\circ \) now includes a term \( (RT/F) \ln K_{ij} \) or \( (RT/F) \ln K_{ij}^{\text{pot}} \).

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 $a_i$, $K_{ij}^{pot}$
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 $p_{cH} = -\log c_H$, where $c_H$ is the molarity of the hydrogen ion. As a means of measuring pH Sorensen chose the cell

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

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 $p_{cH}$ 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 $\text{paH} = -\log a_H = -\log c_{H^+}$.

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 $\text{pH}$ has been introduced(9), defined by

$$\text{pH} = -\log c_{H^+},$$

where $f_{H^+}$ is the mean activity coefficient of an univalent electrolyte in the solution.

When the solution contains an unsymmetrical electrolyte or a mixture of electrolytes the assignment of a value to $f_{H^+}$ may be either inadequate or ambiguous and the pH and paH scales become more or less equivalent.

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

$$\text{pH}_g = -\log m_H,$$

where $m_H$ is the molality of the hydrogen ion and $\gamma_{H^+}, \gamma_{\text{Cl}^-}$ 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;H}_2, \text{Soln. X + MCl, AgCl;Ag} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 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The pwH is calculated from the e.m.f. of cell (C) by the expression
\[ \text{pwH} = \frac{F(E - E^0)}{RT \ln 10} + \log m_{\text{Cl}} \]

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
\[ \text{pH}(X) = \text{pH}(S) + \frac{(E_X - E_S)F}{RT \ln 10} \]

In Eqn (13) \( \text{pH}(S) \) 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

$$E = E^0 + E_j - \frac{RT}{F} \log a_H,$$

where $E^0$ 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:

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

where $z_i$ is the ionic charge on $i$.

Eqn(13) can be reformulated

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

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 (3.5 M 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 l/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 supra), 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

\[ y \, \text{M KCl} | y \, \text{M HCl} \]

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

\[ t_i = \frac{\text{concentration of } i}{\text{mobility of } i} \times \text{concentration} \times \text{mobility} \]

then in the layer/composition \( xy\text{M KCl}, (1-x)y \, \text{M HCl} \) we have:

\[
\begin{align*}
t_H &= \frac{(1-x)y \cdot u_H}{(1-x)y \cdot u_H + x \cdot y \cdot u_K + y \cdot v} \\
t_K &= \frac{x \cdot y \cdot u_K}{(1-x)y \cdot u_H + x \cdot y \cdot u_K + y \cdot v} \\
t_C &= \frac{y \cdot v}{(1-x)y \cdot u_H + x \cdot y \cdot u_K + y \cdot v}
\end{align*}
\]

and

\[
\begin{align*}
t_H &= \frac{(1-x)y \cdot u_H}{(1-x)y \cdot u_H + x \cdot y \cdot u_K + y \cdot v} \\
t_K &= \frac{x \cdot y \cdot u_K}{(1-x)y \cdot u_H + x \cdot y \cdot u_K + y \cdot v} \\
t_C &= \frac{y \cdot v}{(1-x)y \cdot u_H + x \cdot y \cdot u_K + y \cdot v}
\end{align*}
\]

In the conditions we have assumed Eqn(4) can be rewritten:
Now \( \frac{\text{d} \ln c_1}{c_1} = \frac{\text{d} \ln c_H}{c_H} = -\frac{\text{d}x}{1-x} \),
\( \frac{\text{d} \ln c_K}{c_K} = \frac{\text{d}x}{x} \) and \( \frac{\text{d} \ln c_{Cl}}{c_{Cl}} = 0 \).

We can now write:

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

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 \( p \) is \( z_p \). We can define the functions, for solution 1,

\[
U_1 = u_i \cdot c_i + u_j \cdot c_j + u_k \cdot c_k + \ldots \ldots ,
\]

\[
V_1 = v_p \cdot a_p + v_q \cdot a_q + v_r \cdot a_r + \ldots \ldots ,
\]

\[
U'_1 = u_i \cdot w_i \cdot c_i + u_j \cdot w_j \cdot c_j + \ldots \ldots ,
\]

and

\[
V'_1 = v_i \cdot z_p \cdot a_p + v_q \cdot z_q \cdot a_q + \ldots \ldots .
\]

Corresponding functions \( U_2, V_2, U'_2 \) and \( V'_2 \) can be defined for solution 2.
Now \( E_j = \frac{RT}{F} \cdot \frac{(U_1-V_1) - (U_2-V_2)}{(U_1'+V_1') - (U_2'+V_2')} \ln \frac{U_1+V_1'}{U_2+V_2'} \) \ldots \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

| reference electrode | mM BA | hM HA, (m-h)M BA | pH electrode ... (D) |

we can simplify the Henderson equation to

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

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

Equation (16) can be transformed to

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

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

\[
E = E^0 + E_j - k \log h, \text{ assuming that the activity coefficients are constant. A plot of } E+k \log h = E^0+E_j \text{ against } h, \text{ when extrapolated to } h = 0, \text{ gives the value of } E^0,
\]
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
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

\[
\text{Ag,AgCl} | \begin{array}{c|c|c|c|c}
& \text{reference} & \text{bridge} & \text{test} & \text{glass} \\
\text{solution} & \text{solution} & \text{solution} & \text{electrode}
\end{array}
\]

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 thermostatic regulator 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 $\pm 0.02^\circ$. The temperature was found to be uniform throughout the bath. All the experimental work was done in a room maintained at $25\pm 0.5^\circ$.

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 the light's reaching them. The laboratory,
Fig. 2  Glass Electrode Y; $T = 25^\circ C$; $0.2M \text{Me}_2\text{NCl}$ 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) pH Measurements in a Constant Ionic Medium

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 pH 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 $\text{Me}_4\text{NCl}$, was added to the titration cell depicted in Fig(3) containing $q\text{M Me}_4\text{NCl}$ solution which had been freed from $\text{CO}_2$ by bubbling nitrogen through it. Cylinder nitrogen (British Oxygen Co. Ltd.) was passed through a series of presaturators

$$q\text{M HCl, qM NaOH, qM Me}_4\text{NCl, qM Me}_4\text{NCl}$$

before it reached the test solution. The presaturator solutions were at the same temperature ($25^\circ\text{C}$) 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
**Graph 5: Extrapolation of liquid junction potential.**

- **Electrode Y**, $E^\circ = 98.65$ mV.
- **Electrode A**, $E^\circ = 79.25$ mV.

**Graph 6: Determination of Biedermann-Sillén d-coefficient.**

$-1 + \text{antilog}\left(\frac{E_j}{k}\right)$
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\textsubscript{4}NCl. In this case an equal volume of (2q)M Me\textsubscript{4}NCl 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\textsubscript{B}-E\textsubscript{X} against -log c\textsubscript{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\textsuperscript{0}+E\textsubscript{j}) against c\textsubscript{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\textsuperscript{0} had been found, plots of L = 10^{-E\textsubscript{j}/kT}-1 against c\textsubscript{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 $Y$; $T=25^\circ$C; $I = 0.2M$; $E^0 = 98.65$ mV

<table>
<thead>
<tr>
<th>$10^3c_H$</th>
<th>$-\log c_H$</th>
<th>$E_B-E_X$</th>
<th>$E^0+E_j-E_j$</th>
<th>$L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>mV</td>
<td>mV</td>
<td>mV</td>
<td></td>
</tr>
<tr>
<td>3.812</td>
<td>2.4189</td>
<td>104.75</td>
<td>97.46</td>
<td>1.19</td>
</tr>
<tr>
<td>7.403</td>
<td>2.1306</td>
<td>120.53</td>
<td>96.19</td>
<td>2.46</td>
</tr>
<tr>
<td>11.79</td>
<td>1.9285</td>
<td>131.05</td>
<td>94.75</td>
<td>3.90</td>
</tr>
<tr>
<td>12.16</td>
<td>1.9152</td>
<td>131.79</td>
<td>94.70</td>
<td>3.95</td>
</tr>
<tr>
<td>7.913</td>
<td>2.1016</td>
<td>122.12</td>
<td>96.06</td>
<td>2.59</td>
</tr>
<tr>
<td>3.995</td>
<td>2.3986</td>
<td>105.79</td>
<td>97.30</td>
<td>1.35</td>
</tr>
<tr>
<td>2.133</td>
<td>2.6711</td>
<td>90.39</td>
<td>98.02</td>
<td>0.63</td>
</tr>
<tr>
<td>1.770</td>
<td>2.7520</td>
<td>85.70</td>
<td>98.12</td>
<td>0.53</td>
</tr>
<tr>
<td>1.410</td>
<td>2.8507</td>
<td>80.07</td>
<td>98.33</td>
<td>0.32</td>
</tr>
<tr>
<td>0.348</td>
<td>3.4583</td>
<td>44.21</td>
<td>98.29</td>
<td>0.36</td>
</tr>
</tbody>
</table>
Table 2

Glass electrode A; \( T=25^\circ \); \( I = 0.2 \); \( \varepsilon^0 = 79.25 \text{mV} \)

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

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 Me₄NCl(43). \( \Lambda^{0.2}_{\text{HCl}} \) was calculated by interpolation.

\[
\frac{d_{\text{lit}}}{d_{\text{lit}}} = \left(\Lambda^{0.2}_{\text{HCl}} - \Lambda^{0.2}_{\text{Me}_4\text{NCl}}\right) / \Lambda^{0.2}_{\text{Me}_4\text{NCl}} = \frac{(388.09 - 92.29)}{92.29} = 3.21
\]
Fig. 7 Corrected Calibration for Glass Electrode Y at 25°C.  
0.2M Mg4NCl Medium
The discrepancy between $d_{\text{obs}}$ and $d_{\text{lit}}$ 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

<table>
<thead>
<tr>
<th>Ionic strength</th>
<th>0.1</th>
<th>0.2</th>
<th>0.2</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode</td>
<td>A</td>
<td>Y</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Number of runs</td>
<td>2</td>
<td>5</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>Number of points</td>
<td>23</td>
<td>54</td>
<td>80</td>
<td>28</td>
</tr>
<tr>
<td>$d_{\text{obs}}$</td>
<td>2.57</td>
<td>2.79</td>
<td>2.79</td>
<td>2.36</td>
</tr>
<tr>
<td>$b$</td>
<td>59.386</td>
<td>59.282</td>
<td>59.180</td>
<td>59.497</td>
</tr>
<tr>
<td>$10^2\sigma_b$</td>
<td>6.38</td>
<td>7.98</td>
<td>8.04</td>
<td>7.84</td>
</tr>
<tr>
<td>$a$</td>
<td>237.94</td>
<td>249.10</td>
<td>247.93</td>
<td>253.06</td>
</tr>
<tr>
<td>$10\sigma_a$</td>
<td>1.68</td>
<td>2.61</td>
<td>2.39</td>
<td>2.31</td>
</tr>
<tr>
<td>$10\sigma_y$</td>
<td>1.34</td>
<td>3.35</td>
<td>4.35</td>
<td>2.24</td>
</tr>
</tbody>
</table>
At each ionic strength the combined calibration data from a number of runs were fitted to an equation

\[ y = E_B - E_X + E_j = a - \log c_H \]

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 \( \text{pH}^1 \) are the values obtained on the first application of the liquid junction correction.
Table 4

Glass Electrode Y at 25°C; I = 0.2

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

The use of \(\text{eqn}(16)\) when the \(\text{Me}_4N^+\) 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)

<table>
<thead>
<tr>
<th>Me₄N</th>
<th>Na</th>
<th>La</th>
<th>Cl</th>
<th>Tartrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.9</td>
<td>50.1</td>
<td>69.7</td>
<td>76.35</td>
<td>83.2</td>
</tr>
</tbody>
</table>

For the case of sodium this was tested experimentally when up to a third of the Me₄N⁺ 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 KNO₃ 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.

$E_B - E_X (\text{mV})$
A calibration was also performed using the cell without liquid junction

\[ \text{glass electrode, test solution, AgCl,Ag} \ldots \ldots \text{ (F).} \]

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

<table>
<thead>
<tr>
<th>T°C</th>
<th>a</th>
<th>$10^2 b$</th>
<th>$10^5 c$</th>
<th>$10^7 d$</th>
<th>$10^9 e$</th>
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<td>-2.8397</td>
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<td>-1.6834</td>
</tr>
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<td>-4.0462</td>
<td>2.9235</td>
<td>-1.1368</td>
</tr>
<tr>
<td>35</td>
<td>4.0527</td>
<td>-1.4244</td>
<td>-3.0918</td>
<td>0.7121</td>
<td>0.2872</td>
</tr>
</tbody>
</table>
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.

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 G.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 (K₂₇NCl) Medium.

○ △ + □ Represent individual runs.

\[ E_X - E_B \quad (mV) \]

\[ - \log c_{Na} \]
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 Me₄NCl. 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(7) 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 Me₄NCl. Nitrogen from a cylinder (British Oxygen Co.Ltd.), having first passed through a series of presaturators

0.2M HCl, 0.2M NaOH, 0.2M Me₄NCl, 0.2M Me₄NCl

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. 15 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 G\textsuperscript{4+}A\textsubscript{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.
References

   (a) Chapter 4, (b) Chapter 6, (c) Chapter 7.


(14) E.A. Guggenheim: Phil. Mag., 1936, 22, 983.


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, $\text{MY}_m$, a dibasic acid, $\text{H}_2\text{A}$, and a monoacid strong base, $\text{BOH}$. 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:

- $T_a$: Total concentration of ligand
- $T_m$: Total concentration of metal
- $T_b$: 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,
- $K_{a1}$: first dissociation constant of the acid $H_{2}A$,
- $K_{a2}$: second dissociation constant of the acid,
- $I$: the ionic strength,
- $K_w$: 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:
\[ K_{a1} = \frac{[H][HA]}{[H_2A]} = \frac{[H]}{[H_2A]} \cdot f_{HA}/(f_{H_2A}) \quad \ldots \quad (1), \]
\[ K_{a2} = \frac{[H][A]}{[HA]} = \frac{[H]}{[HA]} \cdot f_A/(f_{HA}) \quad \ldots \quad (2), \]
\[ K_w = \frac{[H][OH]}{[H]OH} = \frac{[H]}{[OH]} \cdot f_H \quad \ldots \quad (3) \]

I. The Formation of the Complexes MA and MA2

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

\[ T_m = M + MA + MA_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (4), \]
\[ T_a = H_2A + HA + A + MA + 2MA_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5), \]
\[ mM + (m-a)MA + (m-2a)MA_2 + H + B = Y + OH + aA + (a-1)HA + (a-2)H_2A \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (6). \]

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

\[ a.T_a - m.T_m + Y - T_b + OH - H = HA + 2H_2A, \]

which may be expressed

\[ P - \frac{[H]}{f_H} + K_w/(\{H\}f_H) = HA(1 + 2\{H\}f_{HA}/(K_{a1}f_{H_2A})). \ldots \quad (7), \]

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 \( V = T_a - H_2A - HA - A = MA + 2MA_2 \), then

\[ T_m - V = M - MA_2 = M(1 - K_{102}A^2.f_M.f_{MA}^2/f_{MA_2}) \quad \ldots \quad (8), \]

and \( 2T_m - V = 2M + MA = M(2 + K_{101}A.f_M.f_A/f_{MA}) \quad \ldots \quad (9). \)
Elimination of $M$ from eqns (8) and (9), followed by rearrangement, gives,

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

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

\[ K_{101} = \frac{[MA]}{[M][A]} \quad \text{and} \quad K_{111} = \frac{[MHA]}{[M][H][A]} \].

It is convenient to define a constant

\[ K' = \frac{[MHA]}{[M][HA]} = K_{111} \cdot K_{2} \] .......................... (11).

The mass and charge balance equations are,

\[ T_{m} = M + MA + MHA \] .......................... (12),

\[ T_{a} = H_{2}A + HA + A + MA + MHA \] .......................... (13),

and

\[ mM + (m-a)MA + (m+1-a)MHA + H + B = aA + (a-1)HA + (a-2)H_{2}A + OH + Y \] .......................... (14).

In contrast to the MA-MA₂ case, eqns (12) - (14) cannot be manipulated so as to eliminate all the metal-containing species and 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

\[ Z = (a-1)T_{a} - mT_{m} - T_{b} + Y - H + OH = H_{2}A - A - MA. \]
If an initial estimate \( I = mTm + Tb \) is made to the ionic strength, activity coefficients can be calculated, \( H \) and \( \mathrm{OH} \) 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 = \frac{[H]HA.f_{HA}/(K_1.f_{H_2A}) - K_2.f_{HA}/([H].f_A) - K_{101}.M.A.f_{M}.f_A/f_{MA}.

\]

\[
Z = \frac{[H]HA.f_{HA}}{K_1.f_{H_2A}} - \frac{K_2.f_{HA}}{[H].f_A} - \frac{K_{101}.f_M.f_{HA}.K_2.f_{HA}(Tm - Ta)}{[H].f_{MA}}
\]

\[
- \frac{K_{101}.K_2.HA^2.f_M.f_{HA}(1 + [H].f_{HA}/(K_1.f_{H_2A}) + K_2.f_{HA}/([H].f_A))}{[H].f_{MA}}
\]

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

\[
qHA^2 + rHA + s = 0, \text{ where } s = Z,
\]

\[
r = \frac{K_{101}.f_M.f_{HA}.K_2(Tm - Ta)}{[H].f_{MA}} + \frac{K_2.f_{HA}}{[H].f_A} - \frac{[H].f_{HA}}{K_1.f_{H_2A}}
\]

and

\[
q = \frac{K_{101}.K_2.f_M.f_{HA}}{[H].f_{MA}} \cdot \left( 1 + \frac{[H].f_{HA}}{K_1.f_{H_2A}} + \frac{K_2.f_{HA}}{[H].f_A} \right)
\]

HA can now be obtained as the roots \( \frac{-r \pm \sqrt{r^2 - 4qs}}{2q} \) 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

$$Z' = a \cdot Ta - m \cdot Tm - H - Tb + Y + OH = 2H_{2A} + HA + MHA \ldots (16).$$

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

$$HA^{2} \left( \frac{K' \cdot f_{HA} \cdot f_{M}}{f_{MHA}} \left( 1 + \frac{[H]}{f_{HA}} + \frac{Ka_{2} \cdot f_{HA}}{[H] \cdot f_{A}} \right) \right) + HA \left( 1 + \frac{K' \cdot f_{HA} \cdot f_{M}}{f_{MHA}} \left( Tm - Ta \right) + \frac{2[H] \cdot f_{HA}}{Ka_{1} \cdot f_{H2A}} \right) - Z' = 0 \ldots (17).$$

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

$$ q \cdot H A^2 + r \cdot H A + s = 0 $$

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

$$ R_1 = \left( -r + \sqrt{r^2 - 4qs} \right) / 2q \quad \text{and} \quad R_2 = \left( -r - \sqrt{r^2 - 4qs} \right) / 2q $$

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>
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<th>r</th>
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<th>$R_2$</th>
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<td>-</td>
<td>+,0</td>
<td>yes</td>
<td>no</td>
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<tr>
<td>-,0</td>
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<td>no</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>yes</td>
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</tr>
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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 tendency 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 KDF9 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

$$K' = K_{111} \cdot Ka_2.$$ The mass and charge balance equations are:

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

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

$$nM + (m-a)MA + (m-2a)MA_2 + (m+1-a)MHA + H + B$$

$$= Y + OH + aA + (a-1)HA + (a-2)H_2A \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (20).$$
Combination of equations (3), (18), (19) and (20) yields a function

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

Hence

$$HA = Z''/(1 + \frac{2(H^2f_{HA}}{K_{a1}f_{H2A}} + \frac{K'Mf_{M}f_{HA}}{f_{MHA}}).$$

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

$$V'' = Ta - A - HA - H_2A = MA + 2MA_2 + MHA,$$

is also known, and set up functions

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

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/MA₂/MHA plot for lanthanum tartrate at 25°C in 0.2M (Ma₂N)Cl medium. Data from Run La.4.

△ K' = 150, displaced 1 cm up.
○ K' = 200.
□ K' = 300, displaced 1 cm down.

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 $D_1$, where

$$ D_1 = (\text{area under curve}) - (\text{area under line}) $$

for the $i$th value of $K_{111}$ tried. If $D_1$ 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

$$ K''_{111} = K'_{111}(1 - \frac{D_k}{|D_j - D_k|}), $$

where $K'_{111}$ is the $k$th value of $K_{111}$

$$ \text{(22)} $$

Alternatively $K''_{111}$ may be set equal to the arithmetic or geometric mean of the $j$th and $k$th 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:

$$T_m = M + MA + 2M_2A_2 \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (23),$$

$$T_a = H_2A + HA + A + MA + 2M_2A_2 \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (24),$$

and

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

$$Tm - M = MA + 2M_2A_2$$

$$= K_{101} M A \left( f_M f_A / f_{MA} \right) + 2K_{202} (M A f_M f_A)^2 / f_{M2A2},$$

which can be transformed to

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

or

$$\frac{Tm - M}{M A} \left( \frac{f_{MA}}{f_M f_A} \right) = 2K_{202} M A \left( \frac{f_M f_A}{f_{MA}} \right) + K_{101} \ldots (26b).$$

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 $A_i$, $i = 1, \ldots, N$, we can write,
neglecting activity coefficients,

\[ T_m - M = \sum_{i=1}^{N} iK_{101}M^iA^i, \]

which can be solved for the \( N K_{101} \) 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 \( MA - M_A^2 \) 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

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

The mass and charge balance equations are

\[ T_m = M + MA + MA_2 + MA_3 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (27), \]

\[ T_a = H_2A + HA + A + MA + 2MA_2 + 3MA_3 \quad \ldots \ldots \ldots \ldots \ldots \ldots (28) \]

and \( H + B + mM + (m-a)MA + (m-2a)MA_2 + (m-3a)MA_3 \)

\[ = Y + OH + aA + (a-1)HA + (a-2)H_2A \quad \ldots \ldots \ldots \ldots (29). \]
Combination of Eqns (27), (28) and (29) gives
\[ \text{HA} + 2\text{H}_2\text{A} = \text{Y} + \text{OH} + a\cdot\text{Ta} - m\cdot\text{Tm} - \text{B} - \text{H}, \]
which, together with Eqn (1) gives HA and hence H2A.

Eqn (2) is then used to calculate A. We can now construct a function
\[ V = \text{Ta} - \text{H}_2\text{A} - \text{HA} - A, \]
and hence the functions
\[ \text{Tm} - V = M - MA_2 - 2MA_3, \]
\[ 2\text{Tm} - V = 2M + MA - MA_3 \]
and
\[ 3\text{Tm} - V = 3M + 2MA + MA_2 \]
From the above four functions we derive
\[ \frac{V \cdot f_{MA_3}}{A^3 \cdot f_A^3 \cdot f_M (3\text{Tm} - V)} = K_{103} + K_{102} \cdot \frac{f_{MA_3} (2\text{Tm} - V)}{A \cdot f_A \cdot f_{MA_2} (3\text{Tm} - V)} + K_{101} \cdot \frac{f_{MA_3} (\text{Tm} - V)}{A^2 \cdot f_A^2 \cdot f_{MA} (3\text{Tm} - V)}, \]
which is of the form
\[ x = K_{103} + y \cdot K_{102} + z \cdot K_{101} \] ............ (30a).
Hence
\[ xy = y \cdot K_{103} + y^2 \cdot K_{102} + y \cdot z \cdot K_{101} \] ............ (30b)
and
\[ xz = z \cdot K_{103} + y \cdot z \cdot K_{102} + z^2 \cdot K_{101} \] ............ (30c).

Equations of the types (30a-c) can be set up for each data point and then summed over all n points. Hence
\[ \Sigma x = n \cdot K_{103} + \Sigma y \cdot K_{102} + \Sigma z \cdot K_{101} \] ............ (31a),
\[ \Sigma xy = y \cdot K_{103} + \Sigma y^2 \cdot K_{102} + \Sigma yz \cdot K_{101} \] ............ (31b),
and
\[ \Sigma xz = z \cdot K_{103} + \Sigma yz \cdot K_{102} + \Sigma z^2 \cdot K_{101} \] ............ (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 $T_a$ to $T_m$ is large and the $pH$ is low $MHA_2$ may exist or when the absolute values of $T_m$ and $T_a$ 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:

$$Q = \frac{[H]^f_A}{Ka_2 \cdot f_{HA}} \quad , \quad R = \frac{[H]^2f_A}{Ka_1 \cdot Ka_2 \cdot f_{H_2A}} \quad , \quad F_{ma} = \frac{f_M \cdot f_A}{f_{MA}} \quad ,$$

$$F_{maa} = \frac{f_M \cdot f_A^2}{f_{MA_2}} \quad \text{and} \quad F_{mha} = \frac{f_M \cdot f_A}{f_{MHA}}$$
VI(a) Complexes MA, MA$_2$, MHA, MHA$_2$

The mass and charge balance equations are:

\[ T_m = M + MA + MA_2 + MHA + MHA_2 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (32), \]

\[ T_a = H_2A + HA + A + MA + MHA + 2MHA_2 + 2MA_2 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (33), \]

and \[ mM + (m-a)MA + (m-2a)MA_2 + (m+1-a)MHA + (m+1-2a)MHA_2 + B + H \]

\[ = Y + OH + aA + (a-1)HA + (a-2)H_2A \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (34). \]

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

\[ P = Y + OH + aT_a - mT_m - H - B = MHA + MHA_2 + HA + 2H_2A. \]

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

\[ T_a - 2T_m = A(1 + Q + R) - M(2 + K_{101}A.Fma + K_{111}A.\{H\}.Fmha) \quad (36). \]

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

\[ A^3 K_{102}.Fmaa(1 + Q + R) + A^2 \left[ K_{102}.Fmaa(2T_m-T_a) + K_{101}.Fma(1-R) \right] \]

\[ - K_{111}\{H\}.Fmha(Q+2R) + A \left[ 1 - Q - 3R + K_{101}.Fma(T_m-T_a+P) \right] \]

\[ - K_{111}\{H\}.Fmha(T_m-P) + 2P - T_a = 0, \]

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 \( \text{MA}, \text{MHA}, \text{MA}_2 \) and \( \text{M}_a\text{Am} \)

The mass and charge balance equations are:

\[
\begin{align*}
T_m &= M + MA + MA_2 + \text{MHA} + a.M_a\text{Am} \quad \ldots \ldots \ldots \ldots \ldots \quad (37), \\
T_a &= H_2A + HA + A + MA + \text{MHA} + 2MA_2 + m.M_a\text{Am} \quad \ldots \ldots \ldots \ldots \ldots \quad (38),
\end{align*}
\]

and

\[
\begin{align*}
m.M + (m-a)MA + (m+1-a)\text{MHA} + (m-2a)MA_2 &= Y + \text{OH} + a.A \\
+ (a-1)HA + (a-2)H_2A \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ ld
concentration of the neutral complex and in consequence the stability constant $K_{a\infty}$.

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 $\sum R_i^2$ is a minimum, where $R_i$ is the residual for the $i$th 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 $i$th 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 $\sum R_i^2$ term by term we obtain $n$ equations of
the form

$$2 \sum_{i=1}^{n} R_i \frac{\delta \bar{H}_i}{\delta k_j} = 0$$

Now \( R_i = -\bar{H}_i(\text{obs}) + \bar{H}_i(\text{calc}) = -\bar{H}_i(\text{obs}) + \phi(k_1, \ldots, k_n) \).

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

$$\bar{H}_i = \phi \bar{H}_i + (\frac{\delta \phi}{\delta k_1}) \delta k_1 + (\frac{\delta \phi}{\delta k_2}) \delta k_2 + \ldots \ldots \ldots ,$$

neglecting second and higher order terms and where \( \delta k_j \) is the required shift in the jth stability constant. The best residual can now be expressed

$$\phi R_i = \phi \bar{H}_i + (\frac{\delta \phi}{\delta k_1}) \delta k_1 + (\frac{\delta \phi}{\delta k_2}) \delta k_2 + \ldots \ldots \ldots \ldots .$$

The n normal equations now become

$$\sum_{i=1}^{n} \left( (\frac{\delta \phi}{\delta k_1}) \delta k_1 + (\frac{\delta \phi}{\delta k_2}) \delta k_2 + \ldots \ldots \ldots \right) + \phi R_i \left( \frac{\delta \phi}{\delta k_j} \right) = 0$$

which can be expressed in matrix notation as
Having obtained the requisite mathematical formula we have now to calculate \( H_i \) 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 \( k_{mhr} A_i^m H_i^h \) where \( k_{mhr} \) is the appropriate stability constant and \( h \) is \(-l\) the number of hydroxide ions if it is a hydroxo complex. The procedure adopted depends on whether \( \bar{M}_1 = 0, \bar{A}_1 = 0 \) or neither is zero.

1) \( \bar{M}_1 = 0 \)

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:

\[
F = -\bar{A}_1 + A_1 + \sum_{a} \sum_{h} k_{a\\Theta h} A_i^a H_i^h
\]

\[
G = -\bar{H}_1 + H_1 - Kw/H_i + \sum_{a} \sum_{h} k_{a\\Theta h} A_i^a H_i^h
\]

\( F \) is considered an identity in the experimental data and is used to calculate \( A_1 \) in the following way.
An estimate is made to \( A_1 \), which may be \( \overline{A}_1 \), or any other guess for which there are grounds, and used together with the trial \( k \)'s to calculate

\[
L = A_1 + \sum_a \sum_h a^k_{0ha} A^a_i H^h_i,
\]
which is then compared with \( \overline{A}_1 \). If \( L - \overline{A}_1 \) is within a specified limit the trial value of \( A_1 \) is assumed to be the true one, otherwise a new value is calculated by the Newton-Raphson method i.e.

\[
x_2 = x_1 - x_1 \cdot f(x_1)/f'(x_1)
\]
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

\[
f(x_1)/f'(x_1) = (L - \overline{A}_1)/(A_1 + \sum_a \sum_h a^2_{0ha} A^a_i H^h_i).
\]

The new \( A_1 \) 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,

\[
\begin{align*}
\mathbf{s}_F &= \mathbf{t} \cdot \mathbf{F}_A \cdot \mathbf{s}_A + \mathbf{u} \cdot \mathbf{F}_{H_1} \cdot \mathbf{s}_{H_1} + \mathbf{v} \cdot \mathbf{F}_A \cdot \mathbf{s}_A + \mathbf{w} \cdot \mathbf{F}_{H_1} \cdot \mathbf{s}_{H_1}, \\
\mathbf{s}_G &= \mathbf{t} \cdot \mathbf{G}_A \cdot \mathbf{s}_A + \mathbf{u} \cdot \mathbf{G}_{H_1} \cdot \mathbf{s}_{H_1} + \mathbf{v} \cdot \mathbf{G}_A \cdot \mathbf{s}_A + \mathbf{w} \cdot \mathbf{G}_{H_1} \cdot \mathbf{s}_{H_1},
\end{align*}
\]

where

\[
\begin{align*}
F_{H_1} &= (\partial F/\partial H_1), \\
G_{H_1} &= (\partial G/\partial H_1)
\end{align*}
\]

etc.
Since F is regarded as an identity, \( s_F = 0 \).

Evaluating the derivatives, we find

\[
F_{A_1} = -1, \quad F_{H_1} = 0, \quad G_{A_1} = -1 \quad \text{and} \quad G_{H_1} = 0.
\]

\( F_{A_1}, F_{H_1}, G_{A_1}, \) and \( G_{H_1} \) can be calculated from the equations in \( F \) and \( G \) respectively and \( s_{A_1}, s_{H_1} \) and \( s_{A_1} \) the variances in the experimental data, are known. The equation in \( s_{A_1} \) is used to calculate the unknown \( s_{A_1} \) in terms of known variances.

\[
y \cdot s_{A_1} = \frac{(\bar{t} \cdot s_{A_1} - \bar{w} \cdot F_{A_1} \cdot s_{H_1})}{F_{A_1}}.
\]

Then

\[
s_{G} = -\bar{y} \cdot s_{H_1} + \bar{t} \cdot G_{A_1} \cdot s_{A_1} / F_{A_1} + (G_{H_1} - G_{A_1} \cdot F_{H_1} / F_{A_1}) \cdot \bar{w} \cdot s_{H_1}.
\]

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

\[
s_G^2 = s_{H_1}^2 + G_{A_1}^2 \cdot s_{A_1}^2 / F_{A_1}^2 + (G_{H_1} - G_{A_1} \cdot F_{H_1} / F_{A_1})^2 \cdot s_{H_1}^2.
\]

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

\[ E = -\bar{M}_1 + M_1 + \sum \sum \Sigma m_kM_{m,a}^m A_{l,a}^a H_{l}^h = 0, \]

\[ F = -\bar{A}_1 + A_1 + \sum \sum \Sigma a_kM_{m,a}^m A_{l,a}^a H_{l}^h = 0, \]

\[ G = -\bar{H}_1 + H_1 - Kw/H_1 - \sum \sum \Sigma M_{m,a}^m A_{l,a}^a H_{l}^h. \]

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 \( M_1 \) and \( A_1 \).

Let \( f(M, A) = M_{\text{obs}} - M_{\text{calc}} \) and \( g(M, A) = A_{\text{obs}} - A_{\text{calc}}, \)

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,

\[ f(M, A) = f(M_1, A_1) + f'(M_1, A_1)X_M + f'(M_1, A_1)X_A = 0, \]

\[ g(M, A) = g(M_1, A_1) + g'(M_1, A_1)X_M + g'(M_1, A_1)X_A = 0, \]

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

\[
\begin{bmatrix}
  f'_M & f'_A \\
g'_M & g'_A \\
\end{bmatrix}
\begin{bmatrix}
  x_M \\
x_A \\
\end{bmatrix}
= 
\begin{bmatrix}
  -f \\
  -g \\
\end{bmatrix}
\]

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,

\[
s_E = t_x E_M s_M + u_x E_A s_A + y_x E_H s_H + w_x E_M s_M + x_x E_A s_A + y_x E_H s_H ,
\]

\[
s_F = t_x F_M s_M + u_x F_A s_A + y_x F_H s_H + w_x F_M s_M + x_x F_A s_A + y_x F_H s_H ,
\]

\[
s_G = t_x G_M s_M + u_x G_A s_A + y_x G_H s_H + w_x G_M s_M + x_x G_A s_A + y_x G_H s_H .
\]

\[
E_M = (\lambda E/\lambda M), \quad G_A = (\lambda G/\lambda A) \quad \text{etc. and} \quad t_x, y_x \quad \text{etc. are unit vectors.}
\]

Since both \( E \) and \( F \) are regarded as identities , \( s_E = s_F = 0 \).
Also \( E_A = E_H = F_M = F_h = C_M = C_A = 0 \), \( E_M = F_A = G_H = -1 \)

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 \( s_A \).

\[

\begin{align*}
\gamma \cdot s_M &= \frac{t \cdot F_A \cdot s_M - u \cdot E_A \cdot s_A + (E_A \cdot F_H - E_H \cdot F_A) \cdot y \cdot s_H}{E_M \cdot F_A - F_M \cdot E_A} \\
\chi \cdot s_A &= \frac{t \cdot F_M \cdot s_M - u \cdot E_M \cdot s_A + (E_M \cdot F_H - F_M \cdot E_H) \cdot y \cdot s_H}{F_M \cdot E_A - E_M \cdot F_A}
\end{align*}
\]

we can now express \( s_G \) in terms of known quantities.

\[

s_G = -y \cdot s_H + \frac{t \cdot s_M \cdot (G_M \cdot F_A - F_M \cdot G_A)}{E_M \cdot F_A - F_M \cdot E_A} - \frac{u \cdot s_A \cdot (G_M \cdot E_A - E_M \cdot G_A)}{E_M \cdot F_A - F_M \cdot E_A} \\
+ \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} \cdot y \cdot s_H \cdot G_H
\]

Rearranging and taking the product \( s_G \cdot s_G \) we obtain

\[

s_G^2 = s_H^2 + s_M^2 \left( \frac{(G_M \cdot F_A - F_M \cdot G_A)^2}{E_M \cdot F_A - F_M \cdot E_A} \right) + s_A^2 \left( \frac{(G_M \cdot E_A - E_M \cdot G_A)^2}{E_M \cdot F_A - F_M \cdot E_A} \right) \\
+ s_H^2 \left\{ \frac{E_H \cdot (G_M \cdot F_A - F_M \cdot G_A) + F_H \cdot (G_M \cdot E_A - E_M \cdot G_A)}{F_A \cdot E_M - F_M \cdot E_A} + \frac{G_H}{G_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 ($\lambda f_1/\lambda k_j)$ must be evaluated. This is done by repeating the above procedure with the set of stability constants $k_1, k_2, \ldots, k_j, \ldots, k_n$, where $k'_j = k_j + \Delta k_j$ and so obtaining new values $M'_1, A'_1, \bar{H}'_i(\text{calc})$ and then again with the set containing $k''_j = k_j - \Delta k_j$ and obtaining $M''_1, A''_1$ and $\bar{H}''_i(\text{calc})$. Then $(\lambda f_1/\lambda k_j) = (\bar{H}'_i - \bar{H}''_i)/2\Delta k_j$. 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

$$\frac{\lambda f_1}{\lambda k_j} \left( \frac{\lambda f_1}{\lambda k_k} \right) \text{ or } -\text{OR}_1 \frac{\lambda f_1}{\lambda k_j}$$

a weighting factor $w_i$ may be applied by multiplying each derivative or residual by

$$w_i = 1/\sqrt{s^2}$$

, where $s^2$ 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 $\left( \frac{\Delta f_i}{\Delta k_j} \right)$ 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 $H^+_A$ 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 $K$ 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 $K_{a_2}$ is known. The mass balance equations now become
Ta = HA + A + MA

and

Tm = M + MA.

Then MA = Tm - M and A = \frac{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\(_2\)A

(a) No hydrolysis of the ligand

The mass balance equations are:

\[ Ta = A + MA + M_2A \] ...................................(42),

\[ Tm = M + MA + 2M_2A \] ...................................(43),

Eqs (42) and (43) can be written

\[ Ta = A(1 + K_{101}M + K_{201}M^2) \] .................(44),

\[ Tm - M = A(K_{101}M + 2K_{201}M^2) \] ................(45).

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

\[
\frac{(M - Tm)}{M^2(Tm - 2Ta)} = \frac{(Tm - M - Ta)}{M(Tm - M - 2Ta)} \quad K_{101} + K_{201} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots :: \text{A plot of } y = \frac{(M - Tm)}{M^2(Tm - 2Ta)} \text{ against } x = \frac{(Tm - M - Ta)}{M(Tm - M - 2Ta)} \text{ is a straight line of gradient } K_{101} \text{ 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:
\[ Ta = A + HA + MA + M_2A \] ........................ (47),

\[ Tm = M + MA + 2M_2A \] ........................ (48)

and \[ M + H = a.M + (a-1)HA + (a-m)MA + (a-2m)M_2A + Y + OH \] ........................ (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

$$K_{ijkn} = \frac{M_i H_j A_k X_n}{M_i H_j A_k X^n}.$$  

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:

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

$$T_a = H_2A + HA + A + MA(1 + \Sigma K_{101n}X^n) + 2MA_2(1 + \Sigma K_{102n}X^n) \quad \quad (51),$$
\[ Tx = X + \Sigma n.K_{101n}.M + \Sigma n.K_{101n}.MA + \Sigma n.K_{102n}.MA_2 \ldots \ldots (52), \]
\[ M(m + \Sigma (m-n)K_{100n}.X^n) + MA(m - a + \Sigma (m-a-n)K_{101n}.X^n) \]
\[ + MA_2(m - 2a + \Sigma (m-2a-n)K_{102n}.X^n) + H + B + Tx \]
\[ = Y + OH + a.A + (a-1) + (a-2)H_2A + X \ldots \ldots \ldots \ldots (53). \]

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,
\[ V = MA(1 + \Sigma K_{101n}.X^n) + 2MA_2(1 + \Sigma K_{102n}.X^n), \]
\[ Tm - V = M(1 + \Sigma K_{100n}.X^n) - MA_2(1 + \Sigma K_{102n}.X^n) \ldots \ldots (54) \]
and
\[ 2Tm - B = 2M(1 + \Sigma K_{100n}.X^n) + MA(1 + \Sigma K_{101n}.X^n) \ldots \ldots (55). \]

Elimination of M from Eqns (54) and (55), followed by rearrangement, gives
\[ \frac{V}{A^2(2Tm-V)} = K_{101} \cdot \frac{R_{101}}{R_{100}} \cdot \frac{Tm-V}{A(2Tm-V)} + K_{102} \cdot \frac{R_{102}}{R_{100}}, \]

where \( R_{ijkn} = 1 + \Sigma K_{nijkn}.X^n \).

Since \( Tx \gg Tm, X \) and hence the factors \( R_{ijkn} \) are virtually constant and plot of \( V/(A^2(2Tm-V)) \) against \( (Tm-V)/(A(2Tm-V)) \) will be a straight line of slope \( K_{101} \cdot R_{101}/R_{100} \) and intercept
\[ K_{102} \cdot R_{102}/R_{100} \], 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:

\[
\begin{align*}
M(\text{apparent}) &= R_{100} \cdot M(\text{true}) \\
MA(\text{apparent}) &= R_{101} \cdot MA(\text{true}) \\
MA_2(\text{apparent}) &= R_{102} \cdot MA_2(\text{true})
\end{align*}
\]

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 $\log K(ClO_4^-) - \log K(\text{anion})$.

Table 2

<table>
<thead>
<tr>
<th>metal</th>
<th>anion</th>
<th>dibenz</th>
<th>acac</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>NO$_3^-$</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>Mn</td>
<td>NO$_3^-$</td>
<td>0.37</td>
<td>0.35</td>
</tr>
<tr>
<td>Mn</td>
<td>Cl$^-$</td>
<td>0.74</td>
<td>0.79</td>
</tr>
<tr>
<td>Zn</td>
<td>NO$_3^-$</td>
<td>0.36</td>
<td>0.41</td>
</tr>
<tr>
<td>Zn</td>
<td>Cl$^-$</td>
<td>1.60</td>
<td>1.73</td>
</tr>
<tr>
<td>Co</td>
<td>NO$_3^-$</td>
<td>0.39</td>
<td>0.46</td>
</tr>
<tr>
<td>Co</td>
<td>Cl$^-$</td>
<td>0.77</td>
<td>0.80</td>
</tr>
<tr>
<td>Ni</td>
<td>NO$_3^-$</td>
<td>0.31</td>
<td>0.49</td>
</tr>
<tr>
<td>Ni</td>
<td>Cl$^-$</td>
<td>0.68</td>
<td>0.85</td>
</tr>
<tr>
<td>Fe</td>
<td>Cl$^-$</td>
<td>0.51</td>
<td>0.52</td>
</tr>
<tr>
<td>Pb</td>
<td>NO$_3^-$</td>
<td>0.98</td>
<td>1.13</td>
</tr>
</tbody>
</table>

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 $K_{a1} = 1.5 \times 10^{-3}$ mole litre$^{-1}$ and $K_{a2} = 1.0 \times 10^{-4}$ mole litre$^{-1}$. The complex species $MA^{n-}$ 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.

\[
E = - \bar{M} + \sum_{m \, h \, a} \sum \sum \frac{m}{m \, h \, a} M^m A^a H^h = 0,
\]

\[
F = - \bar{A} + \sum_{m \, h \, a} \sum \sum \frac{a}{m \, h \, a} M^m A^a H^h = 0,
\]

and

\[
G = - \bar{H} + \sum_{m \, h \, a} \sum \sum \frac{h}{m \, h \, a} M^m A^a H^h = 0.
\]
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 $e(M,A,H) = \frac{M}{M_{\text{calc}}}$, $f(M,A,H) = \frac{A}{A_{\text{calc}}}$ and $g(M,A,H) = \frac{H}{H_{\text{calc}}}$. 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

$$e(0) = e(1) + e_M'(1) \cdot X_M + e_A'(1) \cdot X_A + e_H'(1) \cdot X_H = 0,$$
$$f(0) = f(1) + f_M'(1) \cdot X_M + f_A'(1) \cdot X_A + f_H'(1) \cdot X_H = 0,$$
and $$g(0) = g(1) + g_M'(1) \cdot X_M + g_A'(1) \cdot X_A + g_H'(1) \cdot X_H = 0,$$

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 $K_a^1 = 1.5 \times 10^{-5}$ mole litre$^{-1}$, True $K_a^2 = 1.0 \times 10^{-4}$ 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

$$
\begin{bmatrix}
  e_M'(l) & e_A'(l) & e_H'(l) \\
  f_M'(l) & f_A'(l) & f_H'(l) \\
  g_M'(l) & g_A'(l) & g_H'(l)
\end{bmatrix} \begin{bmatrix}
  X_M \\
  X_A \\
  X_H
\end{bmatrix} = \begin{bmatrix}
  -e(l) \\
  -f(l) \\
  -g(l)
\end{bmatrix}.
$$

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**

<table>
<thead>
<tr>
<th></th>
<th>$10^3K_{a1}$</th>
<th>$10^4K_{a2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>actual</td>
<td>1.5000</td>
<td>1.0000</td>
</tr>
<tr>
<td>calculated</td>
<td>1.4999</td>
<td>1.7992</td>
</tr>
</tbody>
</table>

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>
<thead>
<tr>
<th>pH</th>
<th>10M</th>
<th>$10^4 \text{MA}$</th>
<th>$10^4 \text{A}$</th>
<th>$10^3 \text{HA}$</th>
<th>$10^4 \text{H}_2\text{A}$</th>
<th>$10^4 \text{A}$</th>
<th>$10^3 \text{HA}$</th>
<th>$10^4 \text{H}_2\text{A}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7710</td>
<td>1.9990</td>
<td>1.0449</td>
<td>1.3067</td>
<td>2.2142</td>
<td>25.011</td>
<td>2.3512</td>
<td>2.2142</td>
<td>25.012</td>
</tr>
<tr>
<td>2.8369</td>
<td>1.9987</td>
<td>1.2918</td>
<td>1.6156</td>
<td>2.3523</td>
<td>22.831</td>
<td>2.9062</td>
<td>2.3524</td>
<td>22.831</td>
</tr>
<tr>
<td>2.9056</td>
<td>1.9984</td>
<td>1.5979</td>
<td>1.9988</td>
<td>2.4842</td>
<td>20.582</td>
<td>3.5978</td>
<td>2.4840</td>
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<tr>
<td>2.9772</td>
<td>1.9980</td>
<td>1.9747</td>
<td>2.4706</td>
<td>2.6039</td>
<td>18.296</td>
<td>4.4449</td>
<td>2.6039</td>
<td>18.296</td>
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<tr>
<td>3.3781</td>
<td>1.9947</td>
<td>5.3113</td>
<td>6.6562</td>
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<td>7.7802</td>
<td>11.967</td>
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<td>7.802</td>
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<td>3.7715</td>
<td>1.9899</td>
<td>10.109</td>
<td>12.700</td>
<td>2.1495</td>
<td>2.4253</td>
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<td>4.0253</td>
<td>1.9868</td>
<td>13.153</td>
<td>16.549</td>
<td>1.5611</td>
<td>0.9817</td>
<td>29.703</td>
<td>1.5611</td>
<td>0.9819</td>
</tr>
</tbody>
</table>

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,
\[
Ta = A \left( 1 + \frac{H}{K_{a_2}} + \frac{H^2}{K_{a_1}K_{a_2}} + K_{101}M \right) \ldots \ldots (55).
\]

Eliminating \( A \) from Eqns (4.6) and (55) we obtain
\[
H^2 \left( \frac{2Ta}{N} - 1 \right) = H \left( 1 - \frac{Ta}{N} \right) K_{a_1} + K_{a_1}K_{a_2}(1 + K_{101}M) \ldots (56).
\]

Comparison of Eqns (56) and (4.8) shows that treating the data on a simple Speakman basis will result in the correct value for \( K_{a_1} \), and that \( K_{a_2} \) 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 0.2 M 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 \( K_{a_1} \) 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 \( K_{a_2}(\text{apparent}) = r.K_{a_2}(\text{true}) \), then \( A(\text{apparent}) = r.A(\text{true}) \).

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 \( K_{a_1} \). 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

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

or

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

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

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

which results in

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

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

and instead of Eqn (4.6)

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

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

\[ H^2 \left( \frac{2Ta - N}{N} \right) = H \left( \frac{N - Ta}{N} \right) (1 + Ka_2.K_{111}.M)K_a_1 + Ka_1.Ka_2 (1 + K_{102}.M) \ldots (59). \]

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:

\[ HA(\text{apparent}) = HA(\text{true}), \]

\[ H_2A(\text{apparent}) = H_2A(\text{true})/s \]

and \[ A(\text{apparent}) = t \cdot A(\text{true}). \]

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
\[(A + HA + H_2A)_\text{apparent} \approx (A + HA + H_2A + MA + MHA)_\text{true},\]
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
\[
\frac{V}{A^2(2Tm - V)} = \frac{K_{101}(Tm-V)}{A(2Tm-V)} + K_{102} \ldots (60).
\]
The use of \(A\)(apparent) in Eqn (60) results in
\[
K_{101}(\text{apparent}) \approx K_{101}(\text{true})/t \text{ and } K_{102}(\text{apparent}) \approx K_{102}(\text{true})/t^2.
\]
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.
References


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 (Me₄NOH) and background electrolyte (Me₄NCl) 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. $K_{a1} \gg 10^3 K_{a2}$, 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

\begin{align*}
K_{a1} &= \frac{[H][HA]}{[H_2A]} = \frac{HHA f_H f_{HA}}{H_2A f_{H2A}} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1), \\
K_{a2} &= \frac{[H][A]}{[HA]} = \frac{HA f_A f_{HA}}{HA f_{HA}} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2), \\
K_w &= \frac{[H][OH]}{[H_2O]} = \frac{HOH f_H f_{OH}}{H^+ OH} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3), \\
Na + H &= HA + 2A + OH \quad (\text{ electroneutrality }) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4), \\
Ta &= H_2A + HA + A \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5).
\end{align*}
III Speakman's Method

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

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

\[
= 2Ta - Na - \frac{[H]}{f_H} + Kw/(\{H\}.f_{OH}) = N \ldots \ldots (6).
\]

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

\[
Ta = A(1 + \frac{[H]f_A}{Ka_2.f_{HA}} + \frac{[H]^2f_A}{Ka_1.Ka_2.f_{H2A}}) \ldots \ldots \ldots (7).
\]

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

\[
\frac{[H]^2f_A}{f_{H2A}}(\frac{2Ta}{N} - 1) = \frac{[H]f_A}{f_{HA}}(1 - \frac{Ta}{N})Ka_1 + Ka_1.Ka_2 \ldots \ldots (8).
\]

A plot of \(X = \frac{[H]^2f_A}{f_{H2A}}(\frac{2Ta}{N} - 1)\) against \(Y = \frac{[H]}{f_{HA}}(1 - \frac{Ta}{N})\) 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

\[I = Na + H\]

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

\[
I = \frac{1}{2} \left( 3\text{Na} + \frac{3\{\text{H}\}}{f_H} - \frac{2\text{Ta} - \text{Na} - \{\text{H}\}^2/f_H}{1 + 2f_H\{\text{H}\}/K_{a_1}} \right).
\]

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 \(K_{a_2}\) (7, 8)

Measurements made with the cell

\[
\text{Pt} \mid \text{H}_2 \text{O, test solution, AgCl, Ag,}
\]

where the test solution contains the salts \(\text{NaHA, Na}_2\text{A and NaCl}\) in the proportions \(1:q:r\), give rise to the quantity \(\text{pwh}\), defined by

\[
\text{pwh} = - \log m_H - \log f_Hf_{\text{Cl}},
\]

\(m_H\) being the molality of the hydrogen ion.

The equilibria obtaining in the solution are

\[
\text{HA}^- = \text{H}^+ + \text{A}^{2-}
\]

and

\[
2\text{HA}^- = \text{H}_2\text{A} + \text{A}^{2-}.
\]
If \( m \) is the stoichiometric molality of NaHA, we can write the equilibrium concentrations of HA\(^-\) and A\(^2-\) as

\[
\begin{align*}
    m_{\text{HA}} &= m - m_H - 2m_{\text{H}_2A} \quad \ldots \ldots \ldots (9) \\
    m_A &= q_m + m_H + m_{\text{H}_2A} \quad \ldots \ldots \ldots (10).
\end{align*}
\]

The ionic strength \( I = (1+r+3q)m + 2m_H + m_{\text{H}_2A} \quad \ldots \ldots (11)\).

If \( f_H \cdot f_{\text{HA}} \cdot m_H / f_{\text{H}_2A} \) is taken equal to \( f_H \cdot f_{\text{Cl}} \cdot m_H \), i.e. to \( 1/(\text{antilog } p\text{w}H) \), a reasonable assumption in dilute solution, we obtain from Eqs (1) and (9)

\[
m_{\text{H}_2A} = (m - m_H)/(2 + K_{a_1} \text{antilog } p\text{w}H) \quad \ldots \ldots (12).
\]

We can calculate \( m_H \) from the measured p\(\text{w}H \) if a suitable expression is adopted for the activity coefficients, such as

\[
-\log f_z = \frac{A \cdot z^2 \cdot I^\frac{3}{2}}{1 + B \cdot a \cdot I^\frac{3}{2}} - b \cdot I \quad \ldots \ldots \ldots \ldots \ldots (13)
\]

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 Eqs (11) and (12) to constant \( m_H \) and \( m_{\text{H}_2A} \) is followed by calculation of \( m_{\text{HA}} \) and \( m_A \). The value of \( K_{a_1} \) obviously affects the outcome of the above process, but if the conditions are such that \( m_{\text{H}_2A} \) is small, the effect of an inaccuracy in \( K_{a_1} \) will also be small.
Eqn (2) can be written in the form

\[ p_{K_a2} = p_{WH} - \log \frac{m_A}{m_{HA}} + \frac{2A \cdot I^{1/2}}{1 + B \cdot a \cdot I^{1/2}} - 2A \cdot b \cdot I \]  

which can be rearranged to give

\[ p_{K_a2} = p_{K_a2}' + 2A \cdot b \cdot I = p_{WH} - \log \frac{m_A}{m_{HA}} + \frac{2A \cdot I^{1/2}}{1 + B \cdot a \cdot I^{1/2}} \]  

\( p_{K_a2}' \) 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 \( p_{K_a2}' \) against \( I \) will be a straight line of intercept \( p_{K_a2} \) and slope \( 2A \cdot b \).

The thermodynamic value of \( K_a2 \) obtained in this way can be used in conjunction with another set of experimental data to provide an improved estimate of \( K_{a1} \).

IVb. Bate's Method for \( K_{a1} \)

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

\[ \frac{1}{2}\log(K_{a1} \cdot K_{a2})' = \frac{1}{2}\log(K_{a1} \cdot K_{a2}) + A \cdot b \cdot I \]

\[ = p_{WH} - \frac{1}{2}\log \frac{m_A}{m_{H2A}} + \frac{A \cdot I^{1/2}}{1 + B \cdot a \cdot I^{1/2}} \]  

As before we can calculate \( m_{H2A} \) and \( I \) from the measured \( p_{WH} \) and iteration through Eqns (11) - (13). Eqn. (10) then yields \( m_A \). A plot of \( \frac{1}{2}\log(K_{a1} \cdot K_{a2})' \) 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

$$K_{101} = \frac{[NaA^-]}{[Na][A^{2-}]} = \frac{m_{NaA} \cdot f_{NaA}}{m_{Na} \cdot f_{Na} \cdot m_{A} \cdot f_{A}} \ldots \ldots \ldots \ldots (17),$$

$$m_{A} = q \cdot m + m_{H} + m_{H2A} - K_{101} \cdot m_{Na} \cdot m_{A} \cdot f_{A} \quad (\text{cf. Eqn(10)});$$

i.e.

$$m_{A} = (q \cdot m + m_{H} + m_{H2A})/(1 + K_{101} \cdot m_{Na} \cdot f_{A}) \ldots \ldots (18)$$

and

$$m_{Na} = (1 + 2q + r)m/(1 + K_{101} \cdot m_{A} \cdot f_{A}) \ldots \ldots (19).$$

Iteration through Eqns (10), (18), (19) and (13) to constant $m_{A}$, $m_{Na}$ 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) Me₄N⁺ solution prepared by ion-exchange,
b) Na₂CO₃ solution,
c) Me₄N⁺Cl⁻ 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 $\text{Me}_4^+\text{NOH}$ solution was analysed by potentiometric titration against standard hydrochloric acid, the results being treated by Gran's method (Chapter 9). A typical plot for $\text{Me}_4^+\text{NOH}$ 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 $-\text{NMe}_3^+$ groups on the benzene rings of the polystyrene. Baumann (13) reports that at 90$^\circ$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 $\text{Me}_4\text{NOH}$ 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 $\text{Me}_4\text{NOH}$ 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. $\text{Me}_4\text{NOH}$ 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 Me₄NOH 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 Me₄NCl, 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. Me₄NOH solution was added from a burette and -2q M Me₄NCl (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 Me₄NCl, qM Me₄NCl ,

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. \( \text{Me}_4\text{NOH} \) 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. 5 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

<table>
<thead>
<tr>
<th>Run</th>
<th>*Ta (mM)</th>
<th>$10^3K_{a1}$</th>
<th>$10^4K_{a2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T.4</td>
<td>4.56</td>
<td>1.55</td>
<td>1.18</td>
</tr>
<tr>
<td>T.5</td>
<td>10.4</td>
<td>1.53</td>
<td>1.20</td>
</tr>
<tr>
<td>T.6</td>
<td>7.95</td>
<td>1.52</td>
<td>1.19</td>
</tr>
<tr>
<td>T.7</td>
<td>10.1</td>
<td>1.56</td>
<td>1.19</td>
</tr>
<tr>
<td>T.8</td>
<td>5.48</td>
<td>1.54</td>
<td>1.16</td>
</tr>
<tr>
<td>T.9</td>
<td>2.61</td>
<td>1.53</td>
<td>1.15</td>
</tr>
<tr>
<td>T.10</td>
<td>8.64</td>
<td>1.53</td>
<td>1.18</td>
</tr>
<tr>
<td>T.11</td>
<td>4.47</td>
<td>1.55</td>
<td>1.18</td>
</tr>
<tr>
<td>T.12+13**</td>
<td>1.15</td>
<td>1.52</td>
<td>1.10</td>
</tr>
<tr>
<td>T.14</td>
<td>1.84</td>
<td>1.52</td>
<td>1.13</td>
</tr>
</tbody>
</table>
* 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>
<thead>
<tr>
<th>medium</th>
<th>Runs</th>
<th>Points</th>
<th>$10^3K_a_1$</th>
<th>$10^6\sigma K_a_1$</th>
<th>$10^4K_a_2$</th>
<th>$10^7\sigma K_a_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>3</td>
<td>47</td>
<td>1.494</td>
<td>12.3</td>
<td>1.066</td>
<td>6.98</td>
</tr>
<tr>
<td>0.2</td>
<td>11</td>
<td>182</td>
<td>1.540</td>
<td>4.01</td>
<td>1.173</td>
<td>24.0</td>
</tr>
<tr>
<td>0.4</td>
<td>2</td>
<td>52</td>
<td>1.472</td>
<td>2.66</td>
<td>1.308</td>
<td>6.04</td>
</tr>
</tbody>
</table>

The results were extrapolated to infinite dilution by plotting

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

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 $K_a_1$, $r = 2$ and for $K_a_1.K_a_2$, $r = 6$. 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 $pK_{a_1}$ of d-tartaric acid at 25°C.

a) $a = 3.0$  b) $a = 5.0$  c) $a = 5.5$  d) $a = 7.5$. 

[Graph showing the extrapolation of $pK_{a_1}$ of d-tartaric acid at 25°C with lines labeled a, b, c, and d for different values of a.]
Fig. 5 Standard deviation in the extrapolated value of \( pK_a \) 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, $\sigma_q$, is shown in Fig. 5 for the $K_{a_1}$ case. The corresponding value of $b$ is calculated from $p/(r_A)$.

For $K_{a_1}$, the minimum occurs at $a = 5.25$, giving $-\log K_{a_1} = 3.002$ and $b = 0.34$. The same value of $a$ yields $-\log(K_{a_1}.K_{a_2}) = 7.369$ with $b = 0.23$. The minimum in $\sigma_q$ for $(K_{a_1}.K_{a_2})$ is at $a = 10.15$, for which $-\log(K_{a_1}.K_{a_2}) = 7.250$ and $b = 0.07$. The second dissociation constant is obtained from

$$-\log K_{a_2} = \log(K_{a_1})_{\text{min}} - \log(K_{a_1}.K_{a_2})_{\text{min}},$$

which in this case yields $pK_{a_2} = 4.248$. 
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

\[-\log f_z = A \cdot z^2(I_{1/2}^2/(1 + B \cdot a \cdot I_{1/2}) - b \cdot I),\]

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 \( K_a_1 \) and a 0.6% change in \( \sigma_{K_a_1} \). At constant \( a(2.6) \) a variation in \( b \) from -2.0 to 0.5 changed \( K_a_1 \) by 0.5% and \( \sigma_{K_a_1} \) by 0.6%. There was less than 1% difference in \( K_a_1 \) 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>
<thead>
<tr>
<th>T°C</th>
<th>Runs</th>
<th>Points</th>
<th>(10^4K_a_1) mole Kg(^{-1})</th>
<th>(10^6\sigma_{K_a_1})</th>
<th>(10^5K_a_2) mole Kg(^{-1})</th>
<th>(10^7\sigma_{K_a_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>2</td>
<td>32</td>
<td>9.043</td>
<td>17.4</td>
<td>4.228</td>
<td>19.8</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>22</td>
<td>8.640</td>
<td>5.41</td>
<td>5.447</td>
<td>6.22</td>
</tr>
<tr>
<td>35</td>
<td>1</td>
<td>13</td>
<td>8.284</td>
<td>5.76</td>
<td>4.319</td>
<td>34.9</td>
</tr>
</tbody>
</table>

The values of \( \log K_a_1 \) and \( \log K_a_2 \) were fitted to the equation

\[-\log K = A/T + B + C\cdot T,\]
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

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dissociation</td>
<td>0</td>
<td>2.497</td>
<td>0.0019</td>
</tr>
<tr>
<td>Second</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dissociation</td>
<td>3014</td>
<td>-197.8</td>
<td>0.3387</td>
</tr>
</tbody>
</table>

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.

\[
\Delta G^0 = -2.3026RT \log K
\]

\[
\Delta H^0 = 2.3026R(A - CT^2)
\]

\[
\Delta S^0 = 2.3026R(-B - 2CT)
\]

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.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta G^0$</th>
<th>$\Delta H^0$</th>
<th>$\Delta S^0$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>j mole$^{-1}$</td>
<td>j mole$^{-1}$</td>
<td>j deg$^{-1}$mole$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>First</td>
<td>17500</td>
<td>-3230</td>
<td>-69.5</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>17330</td>
<td>3100</td>
<td>-47.7</td>
<td>Bates &amp; Canham</td>
</tr>
<tr>
<td>Second</td>
<td>24300</td>
<td>650</td>
<td>-79.4</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>24920</td>
<td>990</td>
<td>-80.3</td>
<td>Bates &amp; Canham</td>
</tr>
</tbody>
</table>
References

(9) C. McCallum: private communication.
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 o-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$_2$O 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

<table>
<thead>
<tr>
<th>ligand</th>
<th>T°C. medium</th>
<th>K&lt;sub&gt;101&lt;/sub&gt; method</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EDTA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.2(KCl)</td>
<td>45.7 H;Ag,AgCl</td>
<td>(10)</td>
</tr>
<tr>
<td>25</td>
<td>0.1(Me&lt;sub&gt;4&lt;/sub&gt;NCl)</td>
<td>66 H&lt;sup&gt;+&lt;/sup&gt;-gl</td>
<td>(11)</td>
</tr>
<tr>
<td></td>
<td>0 corr</td>
<td>410 Na&lt;sup&gt;+&lt;/sup&gt;-gl</td>
<td>(12)</td>
</tr>
<tr>
<td><strong>HEEDTA</strong>*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.7-1.0</td>
<td>9.6 Na&lt;sup&gt;23&lt;/sup&gt;n.m.r.</td>
<td>(9)</td>
</tr>
<tr>
<td><strong>NTA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.7-1.0</td>
<td>8.7 Na&lt;sup&gt;23&lt;/sup&gt;n.m.r.</td>
<td>(9)</td>
</tr>
<tr>
<td></td>
<td>20 →0</td>
<td>140 H</td>
<td>(17)</td>
</tr>
<tr>
<td><strong>N-(o-sulphophenyl)-IDA</strong>*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.1 KCl</td>
<td>9.5 H</td>
<td>(18)</td>
</tr>
<tr>
<td><strong>N-(o-carboxyphenyl)-IDA</strong>*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.1 KCl</td>
<td>9.5 H</td>
<td>(18)</td>
</tr>
<tr>
<td><strong>malate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.28(Me&lt;sub&gt;4&lt;/sub&gt;NBr)</td>
<td>2.0 H&lt;sup&gt;+&lt;/sup&gt;-gl</td>
<td>(13)</td>
</tr>
<tr>
<td></td>
<td>30 var</td>
<td>1.1 Na&lt;sup&gt;+&lt;/sup&gt;-gl</td>
<td>(4)</td>
</tr>
<tr>
<td></td>
<td>25 var-0.17</td>
<td>1.9 Na&lt;sup&gt;+&lt;/sup&gt;-gl</td>
<td>(5)</td>
</tr>
<tr>
<td><strong>citrate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>var-0.17</td>
<td>5.0 Na&lt;sup&gt;+&lt;/sup&gt;-gl</td>
<td>(5)</td>
</tr>
<tr>
<td><strong>thiosulphate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>→0</td>
<td>4.8 sol</td>
<td>(19)</td>
</tr>
<tr>
<td>15</td>
<td>0 corr</td>
<td>3.5 sp</td>
<td>(20)</td>
</tr>
<tr>
<td>25</td>
<td>0 corr</td>
<td>3.8 sp</td>
<td>(20)</td>
</tr>
<tr>
<td></td>
<td>35 0 corr</td>
<td>4.0 sp</td>
<td>(20)</td>
</tr>
<tr>
<td><strong>trimetaphosphate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(P&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;9&lt;/sub&gt;&lt;sup&gt;3-&lt;/sup&gt;)</td>
<td>25 →0</td>
<td>25.1 Na&lt;sup&gt;+&lt;/sup&gt;-gl</td>
<td>(14)</td>
</tr>
<tr>
<td></td>
<td>25? 0.56?(Me&lt;sub&gt;4&lt;/sub&gt;NNO&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>0.8 CuHg[K&lt;sub&gt;102&lt;/sub&gt;=1.0]</td>
<td>(22)</td>
</tr>
<tr>
<td><strong>tetrametaphosphate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(P&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;&lt;sup&gt;4-&lt;/sup&gt;)</td>
<td>25 →0</td>
<td>133.3 Na&lt;sup&gt;+&lt;/sup&gt;-gl</td>
<td>(14)</td>
</tr>
<tr>
<td></td>
<td>25 0 corr</td>
<td>550 con</td>
<td>(21)</td>
</tr>
<tr>
<td></td>
<td>25 0 corr</td>
<td>600 H&lt;sup&gt;+&lt;/sup&gt;-gl</td>
<td>(23)</td>
</tr>
</tbody>
</table>
Table 1 (continued)

<table>
<thead>
<tr>
<th>ligand</th>
<th>T°C. medium</th>
<th>K101</th>
<th>method</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrophosphate</td>
<td>25 →0</td>
<td>220</td>
<td>con</td>
<td>(24)</td>
</tr>
<tr>
<td>((P_{2}O_{7}^{4-}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 2.0(KNO₃)</td>
<td>1.6</td>
<td>H⁺-gl</td>
<td>(22)</td>
<td></td>
</tr>
<tr>
<td>25 →0</td>
<td>166</td>
<td>H⁺-gl</td>
<td>(22)</td>
<td></td>
</tr>
<tr>
<td>25 1.0(Me₄NCl)</td>
<td>10</td>
<td>H⁺-gl</td>
<td>(25)</td>
<td></td>
</tr>
<tr>
<td>25 0 corr</td>
<td>200</td>
<td>H⁺-gl</td>
<td>(26)</td>
<td></td>
</tr>
<tr>
<td>40 0 corr</td>
<td>200</td>
<td>H⁺-gl</td>
<td>(26)</td>
<td></td>
</tr>
<tr>
<td>triphosphate</td>
<td>25 0 corr</td>
<td>370</td>
<td>con</td>
<td>(24)</td>
</tr>
<tr>
<td>((P_{3}O_{10}^{5-}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 Na₅L var</td>
<td>6300(K102)</td>
<td>con, tp</td>
<td>(22)</td>
<td></td>
</tr>
<tr>
<td>25 1.0(Me₄NCl)</td>
<td>60</td>
<td>H⁺-gl</td>
<td>(22)</td>
<td></td>
</tr>
<tr>
<td>25 1.0(Me₄NCl)</td>
<td>44</td>
<td>H⁺-gl</td>
<td>(27)</td>
<td></td>
</tr>
<tr>
<td>25-40 0 corr</td>
<td>630(25°,40°)</td>
<td>H⁺-gl</td>
<td>(26)</td>
<td></td>
</tr>
<tr>
<td>orthophosphate</td>
<td>25 0.2 Pr₄NX**</td>
<td>4.0</td>
<td>H⁺-gl</td>
<td>(15)</td>
</tr>
<tr>
<td>AMP*</td>
<td>25 0.2 Pr₄NX**</td>
<td>2.9</td>
<td>H⁺-gl</td>
<td>(15)</td>
</tr>
<tr>
<td>ADP*</td>
<td>25 0.2 Pr₄NX**</td>
<td>6.7</td>
<td>H⁺-gl</td>
<td>(15)</td>
</tr>
<tr>
<td>ATP*</td>
<td>25 0.2 Pr₄NX**</td>
<td>14.3</td>
<td>H⁺-gl</td>
<td>(15)</td>
</tr>
<tr>
<td>30 0.1 buffer</td>
<td>15</td>
<td>sp[buffer = (28)] N-ethylmorpholine</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
* HTEEDTA = N'-\((2\text{-hydroxyethyl})\) 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) $- \log c_H = 2.61$

$I = 0.2$, $T = 25^\circ C$. 
wise to check if a part of the shift in $\Delta \text{EMF}$ 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 $\text{Me}_4\text{NCl}$-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 $\text{Me}_4\text{NCl}$, 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 $\text{Me}_4\text{NOH}$ or NaOH was added from a calibrated burette and $\text{Me}_4\text{NCl}$ 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 $\text{Me}_4\text{NCl}$, 0.2M $\text{Me}_4\text{NCl}$) 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 $\text{Me}_4\text{NOH}$, 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.
all the runs are summarised in Table 2.

Table 2

<table>
<thead>
<tr>
<th>$10^2Na$</th>
<th>$10^3Ka_1$</th>
<th>$10^4Ka_2$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9</td>
<td>1.57</td>
<td>1.20</td>
<td>Run Na.1</td>
</tr>
<tr>
<td>10.4</td>
<td>1.69</td>
<td>1.30</td>
<td>Run Na.2</td>
</tr>
<tr>
<td>2.0</td>
<td>1.72</td>
<td>1.21</td>
<td>Run Na.3</td>
</tr>
<tr>
<td>2.0</td>
<td>1.67</td>
<td>1.30</td>
<td>Run Na.4</td>
</tr>
<tr>
<td>-</td>
<td>1.54</td>
<td>1.17</td>
<td>Chapter 2</td>
</tr>
</tbody>
</table>

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 plot, again for Run 2, is shown in Fig(3). It should be noted that in Runs 1 is and 2 the cation of the base/itself 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 MA₂ 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-MA₂-MHA system (Section 3.III) emphasised the negligibility of the MA₂ 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 $K' = K_{111}K_a^2$ 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

<table>
<thead>
<tr>
<th>Run</th>
<th>$K_{101}$ (mole⁻¹litre)</th>
<th>$K'$ (mole⁻¹litre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na.1</td>
<td>1.7±0.03</td>
<td>0.65</td>
</tr>
<tr>
<td>Na.2</td>
<td>2.0±0.07</td>
<td>0.78</td>
</tr>
<tr>
<td>Na.3</td>
<td>5.9±0.12</td>
<td>2.9</td>
</tr>
<tr>
<td>Na.4</td>
<td>7.6±0.27</td>
<td>1.5</td>
</tr>
</tbody>
</table>
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:

\[ \begin{align*}
K_{a1} &= 1.59 \times 10^{-3} \text{ mole litre}^{-1} \\
K_{a2} &= 1.19 \times 10^{-4} \text{ mole litre}^{-1}
\end{align*} \]

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.

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 $K_{101} = 1.9 \pm 0.03 \text{ mole}^{-1}\text{litre}$ and the mean of Runs Na.1, Na.2 and Na.3a gives $K' = 0.9 \pm 0.3 \text{ mole}^{-1}\text{litre}$. 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 $\Delta \log k$ 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

<table>
<thead>
<tr>
<th>Run</th>
<th>$K_{101}$ (mole$^{-1}$litre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na.5</td>
<td>$3.0 \pm 0.35$</td>
</tr>
<tr>
<td>Na.6</td>
<td>$2.1 \pm 0.36$</td>
</tr>
<tr>
<td>Na.7</td>
<td>$1.4 \pm 0.22$</td>
</tr>
<tr>
<td>Na.8</td>
<td>$5.0 \pm 0.59$</td>
</tr>
</tbody>
</table>
The weighted mean of the above runs is $K_{101} = 2.8 \pm 0.1 \text{ mole}^{-1} \text{ litre}.$

(c) Results The final value of $K_{101}$ was taken as the weighted mean from Runs 1, 2, 3a, 4a and 5 - 8. Hence,

$K_{101} = 2.0 \pm 0.03 \text{ mole}^{-1} \text{ litre}.$ Runs 1, 2 and 3a yield the mean value $K' = 0.9 \pm 0.3 \text{ mole}^{-1} \text{ litre}.$

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

$$(E_1 - E_2)/k = pN_1 - pN_2,$$

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

We can now write

\[
\frac{E_i - E_1}{k} = \text{Constant} + \log T_{\text{NaCl}} - b_{\text{NaCl}} (T_{\text{NaCl}} - 2T_{\text{Ta}}) - b_{\text{NaT}} T_{\text{Ta}}
\]

Since \( E_1 \), \( Tm \) and \( Ta \) are known, the \( b \)-coefficients can be found by solving simultaneous equations. A few points from Run Na.5 yield the values

\[
\begin{align*}
    b_{\text{NaCl}} &= -70 \\
    b_{\text{NaT}} &= -200
\end{align*}
\]

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 value of \( b_{\text{NaCl}} \) 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

\[
\text{citrate} \succ \text{tartrate} \succ \text{malate}.
\]
References


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 D₂O) 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

<table>
<thead>
<tr>
<th>ligand</th>
<th>T°C.</th>
<th>medium</th>
<th>K101</th>
<th>method</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>malate</td>
<td></td>
<td>0.28(Me4NBr)</td>
<td>1.7</td>
<td>H⁺-gl</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>var - 0.17</td>
<td>1.5</td>
<td>K⁺-gl</td>
<td>(4)</td>
</tr>
<tr>
<td>citrate</td>
<td>25</td>
<td>var - 0.17</td>
<td>3.9</td>
<td>K⁺-gl</td>
<td>(4)</td>
</tr>
<tr>
<td>EDTA</td>
<td>25</td>
<td>0.1(Me4NCl)</td>
<td>3.5</td>
<td>H⁺-gl</td>
<td>(5)</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.0(Me4NCl)</td>
<td>4.9</td>
<td>H⁺-gl</td>
<td>(5)</td>
</tr>
<tr>
<td>thiosulphate</td>
<td>25</td>
<td>→0</td>
<td>8.3</td>
<td>sol</td>
<td>(6)</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0 corr</td>
<td>7.1</td>
<td>sp</td>
<td>(7)</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0 corr</td>
<td>10.0</td>
<td>sp</td>
<td>(7)</td>
</tr>
<tr>
<td>orthophosphate</td>
<td>25</td>
<td>0.2**</td>
<td>3.1</td>
<td>H⁺-gl</td>
<td>(8)</td>
</tr>
<tr>
<td>P2O7²⁻</td>
<td>25</td>
<td>1.0(Me4NCl)</td>
<td>6.3</td>
<td>H⁺-gl</td>
<td>(9)</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0 corr</td>
<td>200</td>
<td>H⁺-gl</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0 corr</td>
<td>200</td>
<td>H⁺-gl</td>
<td>(10)</td>
</tr>
<tr>
<td>P3O10⁵⁻</td>
<td>25</td>
<td>1.0(Me4NCl)</td>
<td>24.0</td>
<td>H⁺-gl</td>
<td>(11)</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.0(Me4NCl)</td>
<td>24.5</td>
<td>H⁺-gl</td>
<td>(12)</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0 corr</td>
<td>630</td>
<td>H⁺-gl</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0 corr</td>
<td>630</td>
<td>H⁺-gl</td>
<td>(10)</td>
</tr>
<tr>
<td>AMP*</td>
<td>25</td>
<td>0.2**</td>
<td>1.6</td>
<td>H⁺-gl</td>
<td>(8)</td>
</tr>
<tr>
<td>ADP*</td>
<td>25</td>
<td>0.2**</td>
<td>5.5</td>
<td>H⁺-gl</td>
<td>(8)</td>
</tr>
<tr>
<td>ATP*</td>
<td>25</td>
<td>0.2**</td>
<td>11.5</td>
<td>H⁺-gl</td>
<td>(8)</td>
</tr>
</tbody>
</table>

*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. AnalR 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 Me₄NCl 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 Me₄NCl 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 Me₄NCl 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 Me₄NCl; 0.2M Me₄NCl
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.
Solid line - plot for tartaric acid (electrode A, Chap 5)

broken line - plot for tartaric acid (electrode X, Chap. 4)

Fig. 1 Speakman Plot for Run K.1. O
Calculation

IV. The results were first treated by Speakman's method (Section 4.3), 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 pHs 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>
<thead>
<tr>
<th>electrode</th>
<th>$10^3K_{a1}$</th>
<th>$10^4K_{a1}$</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>1.54</td>
<td>1.173</td>
<td>Chapter 4</td>
</tr>
<tr>
<td>A</td>
<td>1.59</td>
<td>1.19</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>A</td>
<td>1.61</td>
<td>1.20</td>
<td>potassium present</td>
</tr>
</tbody>
</table>

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 Golles - 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 MA₂ 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 $K_{102}$.

$$K_{101} = 0.86 \text{ mole}^{-1}\text{.litre} \quad K_{102} = 0.0 \text{ mole}^{-2}\text{.litre}^2$$

If MA is assumed to be the only complex formed and $K_{101}$ is calculated individually for each point, we obtain the mean $K_{101} = 0.7 \text{ mole}^{-1}\text{.litre}$ with a standard deviation of 0.75. If only the last eleven points are considered the result is

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

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

$$K_{101} = 0.6 \pm 0.15 \text{ mole}^{-1}\text{litre} \text{ and } K' = 0.14 \text{ mole}^{-1}\text{litre},$$
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 \( K' = K a_2 \cdot K_{111} \) and all points are included in the calculation. Omitting points in the lower half of the pH range, the values were

\[
K_{101} = 1.0 \pm 0.1 \text{ mole}^{-1} \text{litre} \quad \text{and} \quad K' = 0.35 \text{ mole}^{-1} \text{litre}.
\]

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

\[
0.6 < K_{101} < 1.0
\]

and

\[
0.15 < K' < 0.35
\]

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.
References


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

<table>
<thead>
<tr>
<th>T°C</th>
<th>medium</th>
<th>pKₐ₁</th>
<th>pKₐ₂</th>
<th>-log(Kₐ₁Kₐ₂)</th>
<th>method</th>
<th>date</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>-&gt;0</td>
<td>3.057</td>
<td>4.381</td>
<td>7.438</td>
<td>H;Ag,AgCl</td>
<td>1951</td>
<td>(1)</td>
</tr>
<tr>
<td>15</td>
<td>0 corr</td>
<td>3.04</td>
<td>4.37</td>
<td>7.41</td>
<td>H⁺-gl</td>
<td>1969</td>
<td>(2)</td>
</tr>
<tr>
<td>16.8</td>
<td>0 corr</td>
<td>2.93</td>
<td>-</td>
<td>-</td>
<td>qh</td>
<td>1928</td>
<td>(3)</td>
</tr>
<tr>
<td>17.6</td>
<td>0 corr</td>
<td>-</td>
<td>4.23</td>
<td>-</td>
<td>qh</td>
<td>1928</td>
<td>(3)</td>
</tr>
<tr>
<td>18</td>
<td>0 corr</td>
<td>3.02</td>
<td>4.55</td>
<td>7.57</td>
<td>emf</td>
<td>1928</td>
<td>(4)</td>
</tr>
<tr>
<td>20</td>
<td>0 corr</td>
<td>2.98</td>
<td>4.39</td>
<td>7.37</td>
<td>qh</td>
<td>1938</td>
<td>(5)</td>
</tr>
<tr>
<td>20</td>
<td>-&gt;0</td>
<td>3.044</td>
<td>4.372</td>
<td>7.416</td>
<td>H;Ag,AgCl</td>
<td>1951</td>
<td>(1)</td>
</tr>
<tr>
<td>20</td>
<td>0 corr</td>
<td>2.89</td>
<td>4.52</td>
<td>7.41</td>
<td>H</td>
<td>1965</td>
<td>(6)</td>
</tr>
<tr>
<td>25</td>
<td>0 corr</td>
<td>-</td>
<td>4.29</td>
<td>-</td>
<td>sol</td>
<td>1926</td>
<td>(7)</td>
</tr>
<tr>
<td>25</td>
<td>0 corr</td>
<td>2.98</td>
<td>4.34</td>
<td>7.32</td>
<td>H;Ag,AgCl</td>
<td>1934</td>
<td>(8)</td>
</tr>
<tr>
<td>25</td>
<td>-&gt;0</td>
<td>2.52</td>
<td>4.16</td>
<td>6.68</td>
<td>con</td>
<td>1940</td>
<td>(9)</td>
</tr>
<tr>
<td>25</td>
<td>-&gt;0</td>
<td>3.036</td>
<td>4.366</td>
<td>7.402</td>
<td>H;Ag,AgCl</td>
<td>1951</td>
<td>(1)</td>
</tr>
<tr>
<td>25</td>
<td>-&gt;0</td>
<td>2.95</td>
<td>4.44</td>
<td>7.39</td>
<td>H⁺-gl</td>
<td>1951</td>
<td>(10)</td>
</tr>
<tr>
<td>25</td>
<td>0 corr</td>
<td>3.03</td>
<td>4.45</td>
<td>7.48</td>
<td>H⁺-gl</td>
<td>1959</td>
<td>(11)</td>
</tr>
<tr>
<td>25</td>
<td>0 corr</td>
<td>3.036</td>
<td>-</td>
<td>-</td>
<td>con</td>
<td>1959</td>
<td>(11)</td>
</tr>
<tr>
<td>25</td>
<td>0 corr</td>
<td>3.11</td>
<td>4.26</td>
<td>7.37</td>
<td>H⁺-gl</td>
<td>1961</td>
<td>(12)</td>
</tr>
<tr>
<td>25</td>
<td>0 corr</td>
<td>3.01</td>
<td>4.55</td>
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<td>H⁺-gl</td>
<td>1964</td>
<td>(13)</td>
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<td>T°C</td>
<td>medium</td>
<td>pKa₁</td>
<td>pKa₂</td>
<td>-log(Kₐ₁Kₐ₂)</td>
<td>method</td>
<td>date</td>
<td>ref.</td>
</tr>
<tr>
<td>-------</td>
<td>----------------</td>
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<td>------</td>
<td>--------------</td>
<td>---------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>25</td>
<td>→0</td>
<td>3.00</td>
<td>4.25</td>
<td>7.25</td>
<td>H⁺-gl</td>
<td>1969</td>
<td>(2)</td>
</tr>
<tr>
<td>25</td>
<td>0 corr</td>
<td>3.06</td>
<td>4.26</td>
<td>7.32</td>
<td>H⁺-gl</td>
<td>1969</td>
<td>(2)</td>
</tr>
<tr>
<td>35</td>
<td>→0</td>
<td>3.019</td>
<td>4.367</td>
<td>7.386</td>
<td>H; Ag, AgCl</td>
<td>1951</td>
<td>(1)</td>
</tr>
<tr>
<td>35</td>
<td>0 corr</td>
<td>3.08</td>
<td>4.37</td>
<td>7.45</td>
<td>H⁺-gl</td>
<td>1969</td>
<td>(2)</td>
</tr>
<tr>
<td>50</td>
<td>0 corr</td>
<td>2.94</td>
<td>4.39</td>
<td>7.33</td>
<td>H; Ag, AgCl</td>
<td>1934</td>
<td>(8)</td>
</tr>
<tr>
<td>50</td>
<td>→0</td>
<td>3.021</td>
<td>4.391</td>
<td>7.412</td>
<td>H; Ag, AgCl</td>
<td>1951</td>
<td>(1)</td>
</tr>
<tr>
<td>74</td>
<td>0 corr</td>
<td>3.01</td>
<td>4.51</td>
<td>7.52</td>
<td>H; Ag, AgCl</td>
<td>1934</td>
<td>(8)</td>
</tr>
<tr>
<td>20</td>
<td>0.1(NaClO₄)</td>
<td>2.80</td>
<td>3.96</td>
<td>6.76</td>
<td>H⁺-gl</td>
<td>1964</td>
<td>(14)</td>
</tr>
<tr>
<td>25</td>
<td>0.1 Me₄NCl</td>
<td>2.83</td>
<td>3.97</td>
<td>6.80</td>
<td>H⁺-gl</td>
<td>1969</td>
<td>(2)</td>
</tr>
<tr>
<td>25</td>
<td>0.136(KNO₃)</td>
<td>2.81</td>
<td>3.95</td>
<td>6.76</td>
<td>H⁺-gl</td>
<td>1960</td>
<td>(15)</td>
</tr>
<tr>
<td>25</td>
<td>0.2(KCl)</td>
<td>2.88</td>
<td>3.94</td>
<td>6.82</td>
<td>H</td>
<td>1938</td>
<td>(16)</td>
</tr>
<tr>
<td>25</td>
<td>0.2 Me₄NBr</td>
<td>2.95</td>
<td>3.98</td>
<td>6.93</td>
<td>H⁺-gl</td>
<td>1963</td>
<td>(17)</td>
</tr>
<tr>
<td>25</td>
<td>0.2 Me₄NCl</td>
<td>2.81</td>
<td>3.93</td>
<td>6.74</td>
<td>H⁺-gl</td>
<td>1969</td>
<td>(2)</td>
</tr>
<tr>
<td>25</td>
<td>0.4 Me₄NCl</td>
<td>2.83</td>
<td>3.88</td>
<td>6.71</td>
<td>H⁺-gl</td>
<td>1969</td>
<td>(2)</td>
</tr>
<tr>
<td>20</td>
<td>1.0 NaClO₄</td>
<td>2.37</td>
<td>3.41</td>
<td>5.78</td>
<td>H⁺-gl</td>
<td>1957</td>
<td>(18)</td>
</tr>
<tr>
<td>20</td>
<td>1.0 NaNO₃</td>
<td>2.66</td>
<td>3.61</td>
<td>6.27</td>
<td>H⁺-gl</td>
<td>1969</td>
<td>(19)</td>
</tr>
<tr>
<td>25</td>
<td>1.0(KNO₃)</td>
<td>2.60</td>
<td>3.77</td>
<td>6.37</td>
<td>H⁺-gl</td>
<td>1964</td>
<td>(20)</td>
</tr>
<tr>
<td>25</td>
<td>1.0 Na(ClO₄)</td>
<td>2.59</td>
<td>3.84</td>
<td>6.43</td>
<td>H⁺-gl</td>
<td>1968</td>
<td>(21)</td>
</tr>
<tr>
<td>18</td>
<td>var</td>
<td>3.01</td>
<td>4.55</td>
<td>7.56</td>
<td>con, kin</td>
<td>1924</td>
<td>(22)</td>
</tr>
<tr>
<td>20</td>
<td>var</td>
<td>3.05</td>
<td>4.13</td>
<td>7.18</td>
<td>qh</td>
<td>1924</td>
<td>(23)</td>
</tr>
<tr>
<td>18</td>
<td>var</td>
<td>2.90</td>
<td>4.02</td>
<td>6.92</td>
<td>H</td>
<td>1925</td>
<td>(24)</td>
</tr>
<tr>
<td>25</td>
<td>var</td>
<td>-</td>
<td>4.40</td>
<td>-</td>
<td>kin</td>
<td>1927</td>
<td>(25)</td>
</tr>
<tr>
<td>18</td>
<td>var</td>
<td>2.93</td>
<td>3.99</td>
<td>6.92</td>
<td>H</td>
<td>1934</td>
<td>(26)</td>
</tr>
<tr>
<td>?</td>
<td>var</td>
<td>2.75</td>
<td>3.99</td>
<td>6.74</td>
<td>H⁺-gl+pol</td>
<td>1960</td>
<td>(27)</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>°C</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>30</th>
<th>40</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKα₁</td>
<td>3.118</td>
<td>3.095</td>
<td>3.075</td>
<td>3.025</td>
<td>3.018</td>
<td>3.020</td>
</tr>
</tbody>
</table>

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) $K_{101} = 0.0$. 
Series la of the Bates and Canham data was recalculated according to the method for $K_{a_2}$ 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 $K_{a_1}$ values from this work (8.64x10$^{-4}$ mole Kg$^{-1}$) and Bates and Canham's own (9.1x10$^{-4}$ 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 $K_{a_1} = 8.6x10^{-4}$ 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 $K_{a_1}$ had little effect on the results, which are summarised in Table 3.

Table 3

<table>
<thead>
<tr>
<th>$10^4K_{a_1}$</th>
<th>8.64</th>
<th>8.64</th>
<th>8.64</th>
<th>9.10</th>
<th>9.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{101}$</td>
<td>0.0</td>
<td>6.45</td>
<td>13.0</td>
<td>0.0</td>
<td>6.45</td>
</tr>
<tr>
<td>$10A.b.$</td>
<td>-0.18</td>
<td>1.42</td>
<td>2.67</td>
<td>-0.17</td>
<td>1.43</td>
</tr>
</tbody>
</table>

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 Me₄NOH 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.

<table>
<thead>
<tr>
<th></th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>NH₄⁺</th>
<th>Cs⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>- log K₁₀₁</td>
<td>0.76</td>
<td>0.56</td>
<td>0.40</td>
<td>0.36</td>
<td>0.32</td>
<td>0.30</td>
</tr>
<tr>
<td>- log K'</td>
<td>0.42</td>
<td>0.20</td>
<td>0.04</td>
<td>0.08</td>
<td>-0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

K' = Ka₂·K₁₁₁

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: $K_{101} = 96.2 \text{ mole}^{-1} \text{ litre}$ and $K' = 29.2 \text{ mole}^{-1} \text{ litre}$. 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 $K(K^0$ at infinite dilution) or degree of dissociation $\alpha$. $K$ having been obtained by an approximate method, $K^0$ is
determined by extrapolation to zero ionic strength and the activity coefficients calculated from the relation (for symmetrical electrolytes)

\[ K^0 = K \cdot f^2. \]

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 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 $pK_a = 3.04$, which is in better agreement with literature values (Table 1) than Frei's figure. Although the

Table 5

<table>
<thead>
<tr>
<th>M</th>
<th>pH</th>
<th>$10^3$</th>
<th>$f$</th>
<th>$10^3K_a$</th>
<th>$10^3$</th>
<th>$f$</th>
<th>$10^4K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>2.77</td>
<td>2.65</td>
<td>0.644</td>
<td>1.23</td>
<td>1.78</td>
<td>0.954</td>
<td>8.95</td>
</tr>
<tr>
<td>0.010</td>
<td>2.59</td>
<td>4.76</td>
<td>0.541</td>
<td>1.26</td>
<td>2.72</td>
<td>0.944</td>
<td>9.08</td>
</tr>
<tr>
<td>0.015</td>
<td>2.49</td>
<td>6.54</td>
<td>0.496</td>
<td>1.24</td>
<td>3.45</td>
<td>0.938</td>
<td>9.07</td>
</tr>
<tr>
<td>0.020</td>
<td>2.42</td>
<td>8.02</td>
<td>0.473</td>
<td>1.21</td>
<td>4.08</td>
<td>0.933</td>
<td>9.07</td>
</tr>
<tr>
<td>0.025</td>
<td>2.36</td>
<td>9.62</td>
<td>0.455</td>
<td>1.24</td>
<td>4.70</td>
<td>0.929</td>
<td>9.39</td>
</tr>
</tbody>
</table>

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 $K_a^2$ ($4.3x10^{-5}$ 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.
Fig. 5 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 ($K' = K_a^2K_{111}$) and one half ($K_{101}$) neutralised acid. Frei calculated activity coefficients as described above and obtained the results $K_{101} = 96.2 \text{ mole}^{-1} \text{ litre}$ and $K' = 29.2 \text{ mole}^{-1} \text{ litre}$. 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

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

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 $25^\circ\text{C}$ in 0.2M medium (Chapter 5) to infinite dilution by means of the Davies(31) Equation ($b = 0.3$) yields the values

$K' = 1.6 \text{ mole}^{-1} \text{ litre}$ and $K_{101} = 6.5 \text{ mole}^{-1} \text{ litre}$,
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

<table>
<thead>
<tr>
<th>T°C</th>
<th>medium</th>
<th>K'(mole⁻¹l.)</th>
<th>K₁₀₁(mole⁻¹l.)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0 corr.</td>
<td>29.2</td>
<td>96.2</td>
<td>(6)</td>
</tr>
<tr>
<td>20</td>
<td>0 corr.</td>
<td>1.7</td>
<td>8.4</td>
<td>(6)+(2)</td>
</tr>
<tr>
<td>25</td>
<td>0 corr</td>
<td>1.6</td>
<td>6.5</td>
<td>(2)</td>
</tr>
<tr>
<td>25</td>
<td>0.2M Me₄NCl</td>
<td>0.9</td>
<td>2.0</td>
<td>(2)</td>
</tr>
<tr>
<td>25</td>
<td>0.2M Me₄NBr</td>
<td>1.6</td>
<td>3.6</td>
<td>(17)</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Run</th>
<th>Ion</th>
<th>$10^2 Tm(M)$</th>
<th>$pK_1$(calc)</th>
<th>$pK_1$(obs)</th>
<th>$pK_2$(calc)</th>
<th>$pK_2$(obs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na.1</td>
<td>Na⁺</td>
<td>2.9</td>
<td>2.80</td>
<td>2.80</td>
<td>3.92</td>
<td>3.92</td>
</tr>
<tr>
<td>Na.2</td>
<td>Na⁺</td>
<td>10.4</td>
<td>2.78</td>
<td>2.77</td>
<td>3.89</td>
<td>3.89</td>
</tr>
<tr>
<td>Na.3</td>
<td>Na⁺</td>
<td>2.0</td>
<td>2.80</td>
<td>2.77</td>
<td>3.92</td>
<td>3.92</td>
</tr>
<tr>
<td>Na.4</td>
<td>Na⁺</td>
<td>2.0</td>
<td>2.80</td>
<td>2.78</td>
<td>3.92</td>
<td>3.88</td>
</tr>
<tr>
<td>K.1</td>
<td>K⁺</td>
<td>2.0</td>
<td>2.81</td>
<td>2.79</td>
<td>3.93</td>
<td>3.92</td>
</tr>
</tbody>
</table>

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.
References

(2) This work
(3) R.Kuhn & T.Wagner-Jauregg: Ber., 1928, 61, 483.
References (continued)


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: \( \text{LaT'} \cdot 4\text{H}_2\text{O}, \text{La}_4\text{T}_3 \cdot 14\text{H}_2\text{O}, \text{KLaT}'' \cdot 3\text{H}_2\text{O}, \text{K}_2\text{LaT}''\text{OH} \cdot 4\text{H}_2\text{O}, \text{K}_2\text{LaTT}'. \text{H}_2\text{O}, \text{K}_3\text{LaT}_2'. \text{H}_2\text{O}, \text{K}_4\text{LaT}'' \cdot 5\text{H}_2\text{O}, \)

where \( T = \text{C}_4\text{H}_4\text{O}_6^{2-}, T' = \text{C}_4\text{H}_3\text{O}_6^{3-} \) and \( T'' = \text{C}_4\text{H}_2\text{O}_6^{4-} \).

Davidenko (6) reports the solid compounds \( \text{LaT'} \cdot 3\text{H}_2\text{O} \) and \( \text{La}_2\text{T}_3 \cdot 9\text{H}_2\text{O} \) and also the following species: \( \text{LaT}^+, \text{LaT}_2^-, \text{LaT'}\text{T}^2^- \) and \( \text{LaT}_2^3^- \). From solubility measurements Davidenko postulates the complexes \( \text{La(OH)}\text{T}_2 \cdot 2^- \) and \( \text{La(OH)}_2\text{T}_2 \cdot 3^- \). Shevchenko (7) has recorded the infrared spectrum of \( \text{La}_2\text{T}_3 \cdot 9\text{H}_2\text{O} \). 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 Paris (100) have studied cerous and dysprosium tartrate by means of thermometric titrations and found three complexes of the type \( \text{LnT}, \text{Ln}_2\text{T}_3 \) and \( \text{LnT}_2 \).
Work on lanthanide Tartrates in acid solution is summarised in Table 1.

Table 1 - Stability Constants of Lanthanide Tartrate Complexes

<table>
<thead>
<tr>
<th>Metal Ligand Method</th>
<th>T°C Medium</th>
<th>$\log K_{101}$</th>
<th>$\log K_{102}$</th>
<th>$\log K'$</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^1$ dl dis 25 0.0597(NaClO$_4$)</td>
<td>3.75</td>
<td>6.02</td>
<td>(10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$^2$ dl $H^+$-gl 20 0.1(KNO$_3$)</td>
<td>3.46 ± 0.45</td>
<td>5.52 ± 0.45</td>
<td>(11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La dl 25 1(NaClO$_4$)</td>
<td>2.08</td>
<td>(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La d? H 25 var</td>
<td></td>
<td>2.5</td>
<td>(13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$^3$ d? H 25 var</td>
<td>3.68</td>
<td>6.37</td>
<td>6.32</td>
<td>(K$_{201}$)</td>
<td>(14)</td>
</tr>
<tr>
<td>La emf</td>
<td>3.06</td>
<td>4.25</td>
<td>(15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$^4$ ? $H^+$-gl 23 0.2(KCl)</td>
<td>3.10</td>
<td>(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La ? sol -25</td>
<td>2.36</td>
<td>6.10</td>
<td>(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La d $H^+$-gl 25 0.2</td>
<td>3.06</td>
<td>1.19</td>
<td>(17)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr $H^+$-gl 20 var</td>
<td>4.77</td>
<td>(18)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu dis 20 0.1 NH$_4$Cl</td>
<td></td>
<td>6.79</td>
<td>(19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu$^5$ d tp 25 0.1(NaNO$_3$)</td>
<td>6.11</td>
<td>9.34</td>
<td>(20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce d H 25 0.3</td>
<td></td>
<td>2.45</td>
<td>(21)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y d? H 25 var</td>
<td>4.07</td>
<td>6.89</td>
<td>2.82</td>
<td>(22)</td>
<td></td>
</tr>
<tr>
<td>Eu$^6$ dl dis 25 0.0597(NaClO$_4$)</td>
<td>4.07</td>
<td>7.18</td>
<td>(23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d dis 25 0.0597(NaClO$_4$)</td>
<td>4.07</td>
<td>7.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>meso dis 25 0.0597(NaClO$_4$)</td>
<td>4.78</td>
<td>7.94</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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. III B. The constants quoted are fairly scattered, particularly the second consecutive constant $k_{102} = \frac{k_{102}}{k_{101}}$.

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 $\text{LaNO}_2^+$ 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

<table>
<thead>
<tr>
<th>°C medium</th>
<th>K LnCl</th>
<th>K LnNO₃</th>
<th>K LnClO₄</th>
<th>method</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mole⁻¹l.</td>
<td>mole⁻¹l.</td>
<td>mole⁻¹l.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lanthanum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22 1.0(HClO₄)</td>
<td>0.9</td>
<td>1.3</td>
<td>-</td>
<td>dis</td>
<td>(26)</td>
</tr>
<tr>
<td>25 4.0 NaClO₄</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
<td>dis</td>
<td>(27)</td>
</tr>
<tr>
<td>? 1.0</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>?</td>
<td>(28)</td>
</tr>
<tr>
<td>? 0.1(KCl)</td>
<td>-</td>
<td>29</td>
<td>-</td>
<td>NO₃⁻ sél</td>
<td>(24)</td>
</tr>
<tr>
<td>25 1.0(NaClO₄)</td>
<td>0.75</td>
<td>0.55</td>
<td>0.51(LaClO₃)</td>
<td>dis</td>
<td>(12)</td>
</tr>
<tr>
<td>Cerous</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22 1.0(HClO₄)</td>
<td>0.9</td>
<td>1.3</td>
<td>-</td>
<td>dis</td>
<td>(26)</td>
</tr>
<tr>
<td>25 5.11(ClO₄)</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>sp</td>
<td>(29)</td>
</tr>
<tr>
<td>30 1.0(NaClO₄)</td>
<td>-</td>
<td>2.9</td>
<td>-</td>
<td>dil</td>
<td>(30)</td>
</tr>
<tr>
<td>25 0 corr</td>
<td>-</td>
<td>-</td>
<td>4.4</td>
<td>sp</td>
<td>(31)</td>
</tr>
<tr>
<td>25</td>
<td>1.5</td>
<td>2.6</td>
<td>-</td>
<td>act/cix</td>
<td>(32)</td>
</tr>
<tr>
<td>25</td>
<td>1 H(ClO₄)</td>
<td>0.8</td>
<td>1.63</td>
<td>-</td>
<td>dis</td>
</tr>
</tbody>
</table>

for the NdNO₂⁺ and GdNO₂⁺ 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 obey 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 with a number of other metal ions. Krumholtz has interpreted the uv absorption spectra of Nd\(^{3+}\) in HClO\(_4\) solutions in terms of ion pairing, but Karraker 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 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. This difference between the two groups of ions has been used to effect group separation by ion exchange and solvent extraction. Moeller and Brantley have reported that the presence of HCl or NH\(_4\)Cl in light lanthanide chloride solutions up to Cl:Ln ratios of 10:1 has no effect on the absorption spectra, and Freed and Jacobson 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 Me₄N⁺ 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 Me₄NCl 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 Me₄NOH 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 Me₄NCl 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 $\text{Me}_4\text{NCl}$, 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. $\text{Me}_4\text{NOH}$ solution was added from a burette and approximately 2q M $\text{Me}_4\text{NCl}$ (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 $\text{Me}_4\text{NCl}$, distilled water and tartaric acid solution into the cell shown in Fig(2.3). The acid was partly neutralised by the addition of $\text{Me}_4\text{NOH}$ 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 $\text{Me}_4\text{NCl}$, q M $\text{Me}_4\text{NCl}$

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(NO₃)₃ with NaOH.
Fig. 2 Celles - Nancollas Plot for Lanthanum Tartrate at 25°C. in 0.2M Medium. Data from Run La, 4.
VII. (a) In order to keep the calculations simple, it is desirable that no hydroxy-complexes are formed. Biedermann and Diavatta(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$_4$N)$^+$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 3.1). 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 $R_1 = (-r + (r^2 - 4q.s)^{1/2})/2q$ and $R_2 = (-r - (r^2 - 4q.s)^{1/2})/2q$ 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

<table>
<thead>
<tr>
<th>$K_{101}$ (trial)</th>
<th>$R_1$</th>
<th>$R_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>low pH</td>
<td>high pH</td>
</tr>
<tr>
<td>too low</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>approx. correct</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>too high</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

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 (Na₂N)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, $MA^+$, $MA^-$ 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 (Me₄N)Cl at 25°C. Plots of (a) Eqn 3.26a (b) Eqn 3.26b for dimer formation
Run species MHA. Neither/La.4 nor any other run suggested the presence of the dinuclear species.

The data were also treated as an $\text{MA-MA}_2^*-\text{MHA}-\text{M}_2\text{A}_3$ system by the procedure given in Section 3.VIb. The values of $K_{2\theta_3}$ obtained were generally negative, unless a deliberately low estimate was made to $K_{101}$, in which case the values of $K_{2\theta_3}$ 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 $\text{M}_2\text{A}_3$ has, then, also been discounted.

The data were treated as an $\text{MA-MA}_2^*-\text{MA}_3$ system using the method of Section 3.V to determine the stability constants, which, however, always turned out negative. $\text{MA}_3$ complexing was assumed to be negligible.

The possible existence of the neutral species $\text{MHA}_2$ was also investigated. Even neglecting the $\text{MA}_2^-$ 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 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.

<table>
<thead>
<tr>
<th>Run</th>
<th>( \log K_{101} )</th>
<th>( 10^{3 \log K_{101}} )</th>
<th>( \log K_{102} )</th>
<th>( 10^{3 \log K_{102}} )</th>
<th>( \log K_{111} )</th>
<th>( 10^{3 \log K_{111}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0.1M medium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La. 1</td>
<td>3.733</td>
<td>3.9</td>
<td>6.376</td>
<td>4.4</td>
<td>6.533</td>
<td>2.0</td>
</tr>
<tr>
<td>La. 2</td>
<td>3.649</td>
<td>2.9</td>
<td>6.120</td>
<td>0.8</td>
<td>6.380</td>
<td>1.0</td>
</tr>
<tr>
<td>La. 3</td>
<td>3.658</td>
<td>6.5</td>
<td>6.266</td>
<td>7.8</td>
<td>6.395</td>
<td>5.5</td>
</tr>
<tr>
<td>mean</td>
<td>3.676</td>
<td>2.2</td>
<td>6.128</td>
<td>0.7</td>
<td>6.409</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>0.2M medium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La. 4</td>
<td>3.399</td>
<td>7.8</td>
<td>5.729</td>
<td>10.4</td>
<td>6.240</td>
<td>3.3</td>
</tr>
<tr>
<td>La. 5</td>
<td>3.367</td>
<td>33.8</td>
<td>5.054</td>
<td>69.2</td>
<td>5.923</td>
<td>32.4</td>
</tr>
<tr>
<td>La. 6</td>
<td>3.403</td>
<td>10.4</td>
<td>5.546</td>
<td>5.9</td>
<td>6.139</td>
<td>53.3</td>
</tr>
<tr>
<td>La. 7</td>
<td>3.419</td>
<td>7.2</td>
<td>5.675</td>
<td>6.3</td>
<td>6.203</td>
<td>2.7</td>
</tr>
<tr>
<td>La. 8</td>
<td>3.414</td>
<td>4.9</td>
<td>5.648</td>
<td>4.6</td>
<td>6.149</td>
<td>4.7</td>
</tr>
<tr>
<td>La. 10</td>
<td>3.420</td>
<td>108.5</td>
<td>5.716</td>
<td>10.2</td>
<td>6.123</td>
<td>38.4</td>
</tr>
<tr>
<td>mean</td>
<td>3.410</td>
<td>3.4</td>
<td>5.640</td>
<td>2.9</td>
<td>6.206</td>
<td>1.9</td>
</tr>
<tr>
<td>La. 9 ( )</td>
<td>( )</td>
<td>6.22</td>
<td>5.9</td>
<td>9.0</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td><strong>0.4M medium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La. 11</td>
<td>3.090</td>
<td>2.4</td>
<td>5.486</td>
<td>2.6</td>
<td>5.848</td>
<td>1.0</td>
</tr>
<tr>
<td>La. 12</td>
<td>3.157</td>
<td>6.4</td>
<td>5.764</td>
<td>3.2</td>
<td>6.005</td>
<td>5.5</td>
</tr>
<tr>
<td>La. 13</td>
<td>3.119</td>
<td>6.3</td>
<td>5.541</td>
<td>1.4</td>
<td>( )</td>
<td></td>
</tr>
<tr>
<td>La. 14</td>
<td>3.116</td>
<td>2.3</td>
<td>( )</td>
<td>5.769</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td>3.108</td>
<td>1.6</td>
<td>5.559</td>
<td>1.1</td>
<td>5.820</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Table 5

<table>
<thead>
<tr>
<th>Run</th>
<th>logK_{101}</th>
<th>logK_{102}</th>
<th>logK_{111}</th>
</tr>
</thead>
<tbody>
<tr>
<td>La. 1</td>
<td>3.723</td>
<td>6.468</td>
<td>6.557</td>
</tr>
<tr>
<td>La. 3</td>
<td>3.652</td>
<td>6.258</td>
<td>6.358</td>
</tr>
<tr>
<td>La. 4</td>
<td>3.398</td>
<td>5.697</td>
<td>6.233</td>
</tr>
<tr>
<td>La. 7</td>
<td>3.407</td>
<td>5.712</td>
<td>6.204</td>
</tr>
<tr>
<td>La.11</td>
<td>3.076</td>
<td>5.580</td>
<td>5.873</td>
</tr>
<tr>
<td>La.12</td>
<td>3.153</td>
<td>5.703</td>
<td>5.915</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>pH obs</th>
<th>pH calc</th>
<th>pH obs</th>
<th>pH calc</th>
<th>pH obs</th>
<th>pH calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.514</td>
<td>2.515</td>
<td>2.904</td>
<td>2.905</td>
<td>3.393</td>
<td>3.395</td>
</tr>
<tr>
<td>2.613</td>
<td>2.614</td>
<td>2.971</td>
<td>2.973</td>
<td>3.510</td>
<td>3.509</td>
</tr>
<tr>
<td>2.666</td>
<td>2.666</td>
<td>3.043</td>
<td>3.045</td>
<td>3.645</td>
<td>3.641</td>
</tr>
<tr>
<td>2.721</td>
<td>2.721</td>
<td>3.120</td>
<td>3.121</td>
<td>3.813</td>
<td>3.805</td>
</tr>
<tr>
<td>2.780</td>
<td>2.779</td>
<td>3.203</td>
<td>3.204</td>
<td>4.026</td>
<td>4.028</td>
</tr>
<tr>
<td>2.840</td>
<td>2.841</td>
<td>3.295</td>
<td>3.295</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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>
<thead>
<tr>
<th>$K_{LaCl}$</th>
<th>$10^{-3}K_{101}$</th>
<th>$10^{-2}K_{102}$</th>
<th>$10^{-3}K_{101}$</th>
<th>$10^{-2}K_{102}$</th>
<th>$10^{-3}Y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>3.493</td>
<td>-2.118</td>
<td>1.15</td>
<td>5.10</td>
<td>1.48</td>
</tr>
<tr>
<td>0.08</td>
<td>3.485</td>
<td>-2.444</td>
<td>1.21</td>
<td>5.64</td>
<td>1.55</td>
</tr>
<tr>
<td>0.13</td>
<td>3.452</td>
<td>-2.456</td>
<td>1.20</td>
<td>5.69</td>
<td>1.56</td>
</tr>
<tr>
<td>0.20</td>
<td>3.407</td>
<td>-2.474</td>
<td>1.18</td>
<td>5.75</td>
<td>1.58</td>
</tr>
</tbody>
</table>

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

$$E_c = \log K_c + r.\frac{A.I^{1/2}}{1+B.a.I^{1/2}} = \log K^o + r.A.B.I$$

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

\[ E_c = p \cdot I + q \]

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. \( \log K^0 \) is then equal to the corresponding value of \( q \).

Plots of \( K_{101} \) and \( K_{101} \) against \( a \) are shown in Figs 5a and b respectively. The minimum in the standard deviation occurs at \( a = 7 \), which yields a value \( \log K^0_{101} = 4.844 \pm 0.001 \) 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 $\log K_{111}^0 = 7.45 \pm 0.06$ with
$b = -0.15$ and $\log K_{102}^0 = 7.5 \pm 0.2$ 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 $\text{M}^+, \text{M}^-\text{A}^-$ and
$\text{MHA}^{2+}$, 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 Å 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 ×, 15 △, 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 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 3.1) and using it to calculate a rough value of $K_{111}$ (Section 3.2). Individual runs were then treated by the method described in Section 3.3 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

<table>
<thead>
<tr>
<th>T°C</th>
<th>logK_{101}</th>
<th>logK_{102}</th>
<th>logK'</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>4.852±0.003</td>
<td>7.41±0.12</td>
<td>3.10</td>
</tr>
<tr>
<td>25</td>
<td>4.604±0.003</td>
<td>7.59±0.04</td>
<td>2.48</td>
</tr>
<tr>
<td>35</td>
<td>4.876±0.004</td>
<td>7.93±0.05</td>
<td>2.70</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>10^3c</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_{101}</td>
<td>235.06</td>
<td>-1.547</td>
<td>2.597</td>
</tr>
<tr>
<td>K_{102}</td>
<td>74.39</td>
<td>-0.474</td>
<td>0.840</td>
</tr>
<tr>
<td>K'</td>
<td>382.65</td>
<td>-2.530</td>
<td>4.210</td>
</tr>
</tbody>
</table>

The standard entropy change for each reaction was calculated from
\[ \Delta S^0 = R(a + 2bT + 3cT^2), \]

whilst the enthalpy and Gibbs energy changes were obtained from Eqs 1.14 and 1.18 respectively. Table 10 summarises these thermodynamic quantities at 25°C.

Table 10

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(-\Delta G^0\times 10^{-4}) j/mole</th>
<th>(\Delta H^0\times 10^{-4}) j/mole</th>
<th>(\Delta S^0) j/deg/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>La + A = LaA</td>
<td>2.63(6.28)</td>
<td>0.0(0.0)</td>
<td>94.8(22.6)</td>
</tr>
<tr>
<td>La + 2A = LaA₂</td>
<td>4.33(10.4)</td>
<td>4.47(10.7)</td>
<td>295 (70.5)</td>
</tr>
<tr>
<td>La + HA = LaHA</td>
<td>1.41(3.38)</td>
<td>0.56(1.3)</td>
<td>66 (16)</td>
</tr>
</tbody>
</table>

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 \(\alpha\)-hydroxyl groups of the tartrate ion. Shevchenko (7) has studied the infra-red absorption spectrum of \(La_2(C_4H_4O_6)_3\cdot9H_2O\) 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

\[
P = S \cdot R \cdot T,
\]

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>
<thead>
<tr>
<th>Coordination No.</th>
<th>Monodentate</th>
<th>Bidentate</th>
<th>Tridentate</th>
<th>Tetradeinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>2.3</td>
<td>3.5</td>
<td>5.5</td>
<td>4 or 8</td>
</tr>
<tr>
<td>9</td>
<td>2.25</td>
<td>3.27</td>
<td>4.9</td>
<td></td>
</tr>
</tbody>
</table>

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 tetradeutate 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 $25^\circ$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 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 $0.1M \text{KNO}_3$ or
KCl media and monocarboxylic acid complexes in 2M NaClO₄ medium. A few thermodynamic quantities have been obtained and these are given in Table 12.

Table 12 - Thermodynamic Properties in 25°C.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>-ΔG° (kcal mole⁻¹)</th>
<th>ΔH° (kcal mole⁻¹)</th>
<th>ΔS° (cal deg mole⁻¹)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La³⁺ malonate</td>
<td>6.79</td>
<td>4.8</td>
<td>39</td>
<td>(80)</td>
</tr>
<tr>
<td>Gd³⁺ malonate</td>
<td>7.32</td>
<td>5.1</td>
<td>42</td>
<td>(80)</td>
</tr>
<tr>
<td>Lu³⁺ malonate</td>
<td>7.77</td>
<td>5.2</td>
<td>44</td>
<td>(80)</td>
</tr>
<tr>
<td>La³⁺ Fe(CN)₆³⁻</td>
<td>5.09</td>
<td>2.0</td>
<td>23.9</td>
<td>(81)</td>
</tr>
<tr>
<td>La³⁺ Co(CN)₆³⁻</td>
<td>5.13</td>
<td>1.33</td>
<td>21.7</td>
<td>(82)</td>
</tr>
</tbody>
</table>

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 (1.35Å°) and strontium (1.13Å°) ions the order is Tar > Ma > Mo > Suc, for calcium (0.99Å°) Tar = Ma > Mo > Suc, for zinc (0.74Å°) Ma > Mo > Tar > Suc and for magnesium (0.65Å°) 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 $\Delta S_1(\text{diss})$ for various acids are in the order maleic - oxalic > tartaric - malonic > malic > succinic * glutaric = adipic = pimelic = suberic. The values of $\Delta S_2(\text{diss})$ are much the same for all the acids except tartaric acid, which has a second hydroxyl group available and a low value of $\Delta S_2(\text{diss})$ also. The difference in $\Delta S_1(\text{diss})$ 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 $\alpha$-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 $K_1$ 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 \(\alpha\)-hydroxy monocarboxylates show minima in log\(K - T\) 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, \(K_{a111}\), for the reaction

\[
\text{LaHT}^{2+} = \text{LaT}^+ + \text{H}^+
\]

can be obtained from \(pK_{a111} = \log K_{111} - \log K_{101}\). Using the results from Table 8, the thermodynamic values of \(pK_{a111}\) at 15, 25 and 35\(^\circ\)C are 2.51, 2.13 and 2.19 respectively. By fitting the dissociation constant data to the equation \(pK_a = a + b.T + c.T^2\), we can calculate the standard entropy change from \(\Delta S^0 = -R(a + 2b.T + 3c.T^2)\). The standard Gibbs energy and enthalpy changes are calculated from Eqs. 1.14 and 1.18. At 25\(^\circ\)C, the following thermodynamic properties obtain:

\[
\Delta G^0 = 1.2\times10^4 \text{J mole}^{-1}, \quad \Delta H^0 = -3.0\times10^3 \text{J mole}^{-1}
\]
\[ \Delta S^0 = -51 \text{ J deg}^{-1}\text{mole}^{-1}. \] 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 Sm\(^3+\) 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.

- $K_w$: autoprotolysis constant of solvent
- $K_b$: solubility product
- $m$: concentration of titrant
- $v_0$: volume of sample
- $v$: volume of titrant added
- $v_e$: 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
innaccuracies 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

$$H = \frac{(txvo - mxv)}{(vo + v)} \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

At the equivalence point $$txvo = mxve \ldots \ldots \ldots \ldots \ldots \ldots (2)$$

Substituting (2) in (1) $$H = \frac{m(ve - v)}{(vo + v)} \ldots \ldots \ldots \ldots (3)$$

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

$$OH = \frac{m(v - ve)}{(vo + v)} \ldots \ldots \ldots \ldots \ldots \ldots (4)$$

and since $$OH = \frac{Kw}{H} \ldots \ldots \ldots \ldots \ldots \ldots (5)$$

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 antilog($$\frac{E}{k}x(vo + v)$$) against v,

b) after the end-point antilog($$-\frac{E}{k}x(vo + v)$$) against v.
The EXPLICIT function follows from the electroneutrality equation,

\[ H + B = OH + A \] \hspace{1cm} (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,

\[ qAP_a + aB_q Q = A_q Q_a + aQ + aP, \]

\[ K_s = \{A\}^q \{Q\}^a, \text{ where } A, B, P, Q \text{ have charges } +a, +1, -1, -q \text{ respectively.} \]

Electroneutrality gives \( aA + B = P + qQ. \) Hence,

\[ a\{A\}/f_A - q\{Q\}/f_Q = P - B \]

and

\[ a\{A\}/f_A - q(K_s/\{A\}^q)^{1/a}/f_Q = q.m(ve - v)/(vo + v). \]

A plot of \( F = (vo + v)(\{A\}/f_A - q_a \left(\frac{K_s}{\{A\}^q}\right)^{1/a}/f_Q \) 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:

\[ Ka = (HA.f_{HA})/(\{H\}A.f_A), \]

\[ Ta = HA + A = A(1 + Ka.\{H\}A.f_A/f_{HA}) = m.ve/(vo + v), \]

\[ Tb = B = m.v/(vo + v) \]
and \( H + B = A + OH \) (electroneutrality).

We define a function \( Z = \frac{Ka}{f_H} \frac{f_A}{f_{HA}} \).

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, \( H = \frac{Ka(Ta - Tb)}{Tb} = m.Ka(ve - v)/v \)

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:
\[ Kb = \frac{(SH \cdot f_{SH})}{(S \cdot \{H^+ f_S\})} \]

\[ Ts = S + SH = S(1 + Y) = X, \text{ where } Y = Kb \cdot \frac{\{H^+ f_S\}}{f_{SH}} \]

and the electroneutrality equation becomes

\[ B + H + SH = OH + A + X. \]

Define the functions \( L = Ka \cdot \frac{\{H^+ f_A\}}{f_{HA}} \) and \( N = Kb \cdot \frac{\{H^+ f_S\}}{f_{SH}} \).

Now, \( H - OH = Ts - Tb + A - SH = Ts - Tb + Ta/(1 + L) - Ts \cdot N/(1 + N) \)

\[ (H - OH - Ts/(1 + L))(1 + N) = Ta - Tb - N \cdot Tb \]

\[ Ta - Tb = (1 + N)(H - OH - Ts/(1 + L)) + N \cdot Tb = m(ve - v)/(vo + v) \]

A plot of

\[ Fs = (vo + v)((1 + N)((\{H^+\} - Kw/\{H^+\})/f_H - Ts/(1 + L)) + N \cdot Tb) \]

is linear with slope \(-m\) and intercept \(ve\).

V. Weak Dibasic Acid - Strong Base

If \( vo \) ml of an acid \( H_b A X_{b-a} \), 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:

\[ K_1 = \frac{HA \cdot f_{HA}}{(A \cdot \{H^+ f_A\})}, \]

\[ K_2 = \frac{H_2A \cdot f_{H_2A}}{(HA \cdot \{H^+ f_H\})}, \]

\[ X = (b - a)Ta, \]

\[ Ta = H_2A + HA + A = A(1 + R + W), \]

where \( R = K_1 \cdot \{H^+ f_A\}/f_{HA} \) and \( W = K_1 \cdot K_2 \cdot \{H^+\}^2 f_A / f_{H_2A} \).

\[ H + B = OH + X + a \cdot A + (a-1)HA + (a-2)H_2A. \]
Combining the above equations we obtain

\[ H - OH = b \cdot Ta - Tb - J \cdot Ta, \]

where \( J = \frac{(R + 2W)}{(1 + R + W)}. \)

If \( Tb \) is known \( H - OH = b \cdot Ta - Tb - b \cdot J \cdot Ta/b + J \cdot Tb/b, \)
hence \( b \cdot Ta - Tb = \frac{(H - OH + J \cdot Tb/b)}{(1 - J/b)} = \frac{m(ve - v)}{(vo + v)}. \)

\[ Fb = (vo + v)\left( \frac{[H]}{Kw/[H]} f_H + J \cdot Tb/b \right) / (1 - J/b). \]

If \( Ta \) is known, \( H - OH + J \cdot Ta = b \cdot Ta - Tb = m(ve - v)/(vo + v) \)

\[ Fa = (vo + v)\left( \frac{[H]}{Kw/[H]} f_H + J \cdot Ta \right). \]

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 \( v_0 \) ml of a weak acid HA with a weak base \( \text{Na}_bB \), where \( b \) is the negative charge on B, we can write

\[
K_a = \frac{[\text{HA}]}{[\text{H}][\text{A}]} ,
\]

\[
K_b = \frac{[\text{BH}]}{[\text{B}][\text{H}]} ,
\]

\[
T_a = \text{HA} + A = A(1 + D) , \quad \text{where} \quad D = \frac{K_a[A]}{[\text{HA}]},
\]

\[
T_b = \text{BH} + B = B(1 + \epsilon) , \quad \text{where} \quad \epsilon = \frac{K_b[B]}{[\text{BH}]},
\]

\[
b \cdot \text{Na} + H = OH + A + b \cdot B + (b-1)BH \ \text{(electroneutrality)}.
\]

Therefore \( b \cdot T_b + H = OH = Ta + b \cdot T_b - HA - BH \)

\[
= Ta + b \cdot T_b - Ta/(1 + D^{-1}) - T_b/(1 + \epsilon^{-1}).
\]

If \( T_b \) is known, \( H = OH = T_b + \epsilon \cdot T_b/(1 + \epsilon) + D \cdot T_b/(1 + D) \)

\[
= (T_a - T_b)(1 - D/(1 + D)) = U.
\]

Then \( T_a - T_b = U/(1 - D/(1 + D)) = m(v_e - v)/(v_0 + v) \).

\[
F_{wb} = (v_0 + v)U/(1 - D/(1 + D)).
\]

If \( T_a \) is known, \( H = OH = T_a + D \cdot T_a/(1 + D) + \epsilon \cdot T_a/(1 + \epsilon) \)

\[
= (T_b - T_a)(1 - \epsilon/(1 + \epsilon)) = V.
\]

\[
T_b - T_a = V/(b - \epsilon/(1 + \epsilon)) = m(v - v_e)/(v_0 + v).
\]

\[
F_{wa} = (v_0 + v)V/(b - \epsilon/(1 + \epsilon)).
\]

A plot of \( F_{wa} \) or \( F_{wb} \) against \( v \) will be linear with intercept \( v_e \) on the \( v \)-axis and slope \( m. \)
Precipitation Reaction of the type

\[ A + Q \rightarrow AQ \]

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 $xA + yQ = A^y Q_x$ we have the functions

$$F = (v_0 + v) \left( A - \frac{x}{y} \frac{K_s}{A^x} \right)^{1/y}$$

and

$$G = (v_0 + v)A$$

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:

$$\frac{F}{G} = 1 - \frac{K_s}{y} A^{-\left(\frac{x}{y} + 1\right)} > D$$

so

$$A^{\left(\frac{x}{y} + 1\right)} > \left(\frac{x}{y} \frac{K_s}{y}\right)/(1 - D).$$

After the end-point we can write:

$$F' = (v_0 + v) \left( \frac{K_s}{A^x} \right)^{1/y} - \frac{y}{x} A$$

and

$$G' = (v_0 + v)Q = (v_0 + v) \left( \frac{K_s}{A^x} \right)^{1/y},$$

so

$$\frac{F'}{G'} = 1 - \frac{y}{x} A^{\left(\frac{x}{y} + 1\right)} \frac{1}{K_s^{1/y}} > D.$$
and so \( A^{(x/y + 1)} < \frac{K_s}{l} (1 - D) K_s^{1/y} \).

If \( x = y \) the conditions become \( A^2 > K_s/(l-D) \) and \( A^2 < K_s(l-D) \) 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 \( K_s \). Considering again the reaction \( xA + yQ = A_x Q_y \), if an approximation \( L_s \) is made to \( K_s \) the Gran function may be better than an explicit one if \( L_s \) is a poor approximation. When the indicator ion \( A \) is in excess the following functions apply:

\[
G = (v_0 + v)A \\
F = (v_0 + v)(A - \frac{K_s}{A^{x/y}}) \\
E = (v_0 + v)(A - \frac{L_s}{A^{x/y}}) \\
G - F = \frac{K_s}{A^{x/y}} (v_0 + v) \left( 1 - \frac{K_s}{A^{x/y}} \right) \\
E - F = \frac{L_s}{A^{x/y}} (v_0 + v) \left( 1 - \frac{L_s}{A^{x/y}} \right) \\
\text{mod}(G - F) < \text{mod}(E - F) \text{ if } L_s^{1/y} > 2K_s^{1/y}.
\]

When the counter-ion \( Q \) is in excess the functions become:

\[
G' = \frac{(v_0 + v)}{A^{x/y}} \\
F' = (v_0 + v) \left( 1/A^{x/y} - \frac{K_s}{A^{x/y}} \right) \\
E' = (v_0 + v) \left( 1/A^{x/y} - \frac{L_s}{A^{x/y}} \right) \\
\text{mod}(G' - F') < \text{mod}(E' - F') \text{ if } 1/K_s^{1/y} < \text{mod}(1/L_s^{1/y} - 1/K_s^{1/y}),
\]

i.e. if \( L_s < K_s/2^y \).
Fig. 2  Titration of 100 ml 0.01M weak acid (pKa = 4.0)
It can be seen that $L_s$ 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

$$A = Ta/n, \quad HA = Ta(n - 1)/n, \quad H = (n - 1)Ka.$$  

Now $F_b/G = 1 + (vo + v)(H - OH)(H + Ka)/(m \cdot v \cdot H)$ and $v = ve/n$. If we define the useful range of $G$ by the condition $F_b/G \leq 1 + D$, where $D > 0$, we get $(vo + v)(H - OH)(H + Ka)/(m \cdot v \cdot H) \leq D$. Substituting for $v$ and $H$, neglecting $OH$ and rearranging we obtain

$$n \cdot Ka(vo + ve/n) \leq D \cdot m \cdot ve/n,$$

so the limiting value of $n$ is a solution of the quadratic

$$n^2 + r \cdot n - D \cdot m \cdot r/Ka = 0,$$  

where $r = ve/vo$.

The following table gives examples of limiting $n$'s for various cases when $D = 0.001$. 
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.

<table>
<thead>
<tr>
<th>pKa</th>
<th>$r$</th>
<th>$n(m=0.1)$</th>
<th>$n(m=0.01)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.6</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>3.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>7.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>9.5</td>
<td>2.6</td>
</tr>
</tbody>
</table>
Fig. 3 Titration of 50ml 0.0107% β-alanine with 0.1% NaOH. Equivalent volume = 5.35 ml.
Fig. 4 Titrination 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 NaClO₄ 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 $F' = (H - OH)(V_0 + V) = f.F$, where $f$ is the activity coefficient for a 1:1 electrolyte
and $P$ 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 $-\log f = A_1^{1/2}/(1 + I_1^{1/2})$ 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:

$$0 < -\log(f_1/f_2) = A_1^{1/2}/(1 + I_1^{1/2}) - I_2^{1/2}/(1 + I_2^{1/2}) \leq D,$$

i.e. $0 < A_1\left(\frac{(m \cdot ve/(vo+v_1))^{1/2}}{1 + (m \cdot ve/(vo+v_1))^{1/2}} - \frac{(m \cdot ve/(vo+v_2))^{1/2}}{1 + (m \cdot ve/(vo+v_2))^{1/2}}\right) \leq D,$

$$0 < A(m \cdot ve)^{1/2}(1/(vx^{1/2} + (m \cdot ve)^{1/2}) - 1/((vx+d)^{1/2} + (m \cdot ve)^{1/2}) ) \leq D,$$

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 $\log f$. and for ease of calculation can be
set equal to $A_110^{-3}$. Taking a case where $vx = 100$ and $m \cdot ve = 1,$

$$0 < 1/11 - 1/(1 + (100 + d)^{1/2}) \leq 1.0\times10^{-3}.$$  

Rearranging $1/11 < 1/(1 + (100+d)^{1/2}) \leq 0.091$.

If $d$ is positive, there is only one condition,

$$1/0.091 > 1 + (100+d)^{1/2},$$

$$10.111 > (100+d)^{1/2},$$

$$102.23 > 100 + d,$$

$$d < 2.23,$$
i.e. for the case chosen activity coefficients do not change significantly over a range of addition of 2.2 ml.

Experimentally an HCl-Me₄NOH 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.
References


(3) P. Sørensen: Kem. Maanedssbl., 1951, 32, 73. ref. in (4).


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 \( I \to C \)) were corrected to infinite dilution by means of the Davies equation.

The meanings of the column headings are as follows:

- \( T_a \) total concentration of d-tartaric acid,
- \( T_m \) total metal concentration (sodium, potassium or lanthanum),
- \( T_b \) total base concentration (Me\(_4\)NOH or NaOH),
- \([HCl]\) concentration of hydrochloric acid added,
- \([Na]\) free sodium concentration,
- \([Cl]\) concentration of Me\(_4\)NCl added, not 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(1C) 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 C.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

\[ I = C.1 \quad T = 25^\circ C. \]

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Tartaric Acid Run 2

\[ I = C.1 \quad T = 25^\circ C. \]

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Tartaric Acid Run 4

\[ I = C \cdot 2 \quad T = 25^\circ C. \]

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## Tartaric Acid Run 5

\[ I = C.2 \quad T = 25^\circ C. \]

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## Tartaric Acid Run 6

\[ I = C.2 \quad T = 25^\circ C. \]

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$T = 25^\circ \text{C.}$

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### Tartaric Acid Run 8

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Tartaric Acid Run 9

\( I = 0.2 \quad T = 25^\circ C \)

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Tartaric Acid Run 1C

\( I = 0.2 \quad T = 25^\circ C \)

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### Tartaric Acid Run 11

**I = 0.2**  
**T = 25°C.**

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### Tartaric Acid Run 12

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**T = 25°C.**

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## Tartaric Acid Run 13

\( I = 0.2 \) \hspace{1cm} \( T = 25^\circ C \)

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## Tartaric Acid Run 14

\( I = 0.2 \) \hspace{1cm} \( T = 25^\circ C \)

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**Tartaric Acid Run 15**

\[ I = 0.4 \quad T = 25^\circ C. \]

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### Tartaric Acid Run 16

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**T = 25°C.**

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## Tartaric Acid Run 17

$I = 0.2\quad T = 25^\circ\mathrm{C}$

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## Tartaric Acid Run 18

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### Tartaric Acid Run 19

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### Tartaric Acid Run 20

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### Tartaric Acid Run 21

I → C  \hspace{1cm} T = 25^\circ \text{C.}

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### Tartaric Acid Run 22

I → C  \hspace{1cm} T = 25^\circ \text{C.}

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### Appendix 1b

#### Sodium Tartrate Run 1

$I = 0.2 \quad T = 25^\circ C.$

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#### Sodium Tartrate Run 2

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### Sodium Tartrate Run 3

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### Sodium Tartrate Run 4

$$\text{I} = C.2 \quad T = 25^\circ\text{C.}$$

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### Sodium Tartrate Run 5

I = C.2  \[ T = 25^\circ C. \]

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### Sodium Tartrate Run 6

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### Sodium Tartrate Run 7

\[ I = 0.2 \quad T = 25^\circ C. \]

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### Sodium Tartrate Run 8

\[ I = 0.2 \quad T = 25^\circ C. \]

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Appendix 1c

Potassium Tartrate Run 1

I = C.2  
T = 25°C.

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## Appendix 1d

**Lanthanum Tartrate Run 1**

\[ I = C.1 \quad T = 25^\circ C. \]

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Lanthanum Tartrate Run 3

\[ I = 0.1 \quad T = 25^\circ C. \]

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Lanthanum Tartrate Run 4

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Lanthanum Tartrate Run 5

\[ I = 0.2 \quad T = 25^\circ C. \]

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Lanthanum Tartrate Run 7

I = 0.2
T = 25°C.

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## Lanthanum Tartrate Run 11

**I = 0.4 \quad T = 25^\circ C.**

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## Lanthanum Tartrate Run 12

**I = 0.4 \quad T = 25^\circ C.**

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### Lanthanum Tartrate Run 13

I = 0.4  \quad T = 25°C.

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### Lanthanum Tartrate Run 14

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Lanthanum Tartrate Run 15

\[ \text{I} \rightarrow \text{C} \quad T = 15^\circ \mathrm{C.} \]

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Lanthanum Tartrate Run 16

\[ \text{I} \rightarrow \text{C} \quad T = 15^\circ \mathrm{C.} \]

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Lanthanum Tartrate Run 17

\[ \text{I} \rightarrow \text{C} \quad T = 15^\circ \mathrm{C.} \]

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**Lanthanum Tartrate Run 19**

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### Lanthanum Tartrate Run 2C

\[ I \rightarrow C \quad T = 25^\circ C \]

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### Lanthanum Tartrate Run 21

\[ I \rightarrow C \quad T = 25^\circ C \]

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### Lanthanum Tartrate Run 22

I → C  \quad T = 25^\circ C.

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### Lanthanum Tartrate Run 23

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$I \rightarrow C  \quad T = 35^\circ C.$

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<td>1.3379 &amp; -3;</td>
<td>3.4744 &amp; -4;</td>
<td>1.1267 &amp; -3;</td>
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<td>1.1181 &amp; -3;</td>
<td>3.2116;</td>
<td>1.6C95 &amp; -3;</td>
<td>3.4569 &amp; -4;</td>
<td>1.3556 &amp; -3;</td>
</tr>
<tr>
<td>1.6146 &amp; -3;</td>
<td>1.1292 &amp; -3;</td>
<td>3.3693;</td>
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<td>3.4295 &amp; -4;</td>
<td>1.7116 &amp; -3;</td>
</tr>
<tr>
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<td>3.4776;</td>
<td>2.2672 &amp; -3;</td>
<td>3.4143 &amp; -4;</td>
<td>1.9C94 &amp; -3;</td>
</tr>
<tr>
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<td>1.1C91 &amp; -3;</td>
<td>3.613C;</td>
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<td>1.1C89 &amp; -3;</td>
<td>4.5C34;</td>
<td>2.998C &amp; -3;</td>
<td>3.3669 &amp; -4;</td>
<td>2.5249 &amp; -3;</td>
</tr>
</tbody>
</table>

### Lanthanum Tartrate Run 25

$I \rightarrow C \quad T = 35^\circ C.$

<table>
<thead>
<tr>
<th>$Ta$</th>
<th>$Tm$</th>
<th>$pH$</th>
<th>$Tb$</th>
<th>$[HCl]$</th>
<th>$[Cl]$</th>
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<tr>
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<td>2.8924;</td>
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<td>1.6655 &amp; -4;</td>
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<tr>
<td>1.5959 &amp; -3;</td>
<td>9.2929 &amp; -4;</td>
<td>3.7555;</td>
<td>9.5218 &amp; -4;</td>
<td>2.8732 &amp; -4;</td>
<td>8.19C4 &amp; -4;</td>
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<td>9.2218 &amp; -4;</td>
<td>3.2C6;</td>
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<td>2.8512 &amp; -4;</td>
<td>1.15C5 &amp; -3;</td>
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<td>1.3C81 &amp; -3;</td>
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<td>9.C67 &amp; -4;</td>
<td>3.5C48;</td>
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<td>9.C659 &amp; -4;</td>
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<td>1.5514 &amp; -3;</td>
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</tbody>
</table>
## Lanthanum Tartrate Run 26

$I \to C \quad T = 35^\circ C.$

<table>
<thead>
<tr>
<th>Ta</th>
<th>Tm</th>
<th>pH</th>
<th>Tb</th>
<th>[HCl]</th>
<th>[Cl]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.5445(_{10}^{-4})</td>
<td>1.6933(_{10}^{-3})</td>
<td>3.151c</td>
<td>9.1773(_{10}^{-4})</td>
<td>5.2354(_{10}^{-4})</td>
<td>7.7294(_{10}^{-4})</td>
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<tr>
<td>8.4832(_{10}^{-4})</td>
<td>1.6811(_{10}^{-3})</td>
<td>3.3188</td>
<td>1.3059(_{10}^{-3})</td>
<td>5.1978(_{10}^{-4})</td>
<td>1.8998(_{10}^{-3})</td>
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<td>8.4489(_{10}^{-4})</td>
<td>1.6743(_{10}^{-3})</td>
<td>3.4453</td>
<td>1.5228(_{10}^{-3})</td>
<td>5.1768(_{10}^{-4})</td>
<td>1.2826(_{10}^{-3})</td>
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<td>8.4118(_{10}^{-4})</td>
<td>1.6670(_{10}^{-3})</td>
<td>3.6328</td>
<td>1.7577(_{10}^{-3})</td>
<td>5.1541(_{10}^{-4})</td>
<td>1.4004(_{10}^{-3})</td>
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</tbody>
</table>

## Lanthanum Tartrate Run 27

$I \to C \quad T = 35^\circ C.$

<table>
<thead>
<tr>
<th>Ta</th>
<th>Tm</th>
<th>pH</th>
<th>Tb</th>
<th>[HCl]</th>
<th>[Cl]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8648(_{10}^{-3})</td>
<td>6.5689(_{10}^{-4})</td>
<td>3.4272</td>
<td>2.0167(_{10}^{-3})</td>
<td>2.0125(_{10}^{-4})</td>
<td>1.6948(_{10}^{-3})</td>
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<tr>
<td>1.8577(_{10}^{-3})</td>
<td>6.4843(_{10}^{-4})</td>
<td>3.5217</td>
<td>2.2174(_{10}^{-3})</td>
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<tr>
<td>1.8433(_{10}^{-3})</td>
<td>6.4341(_{10}^{-4})</td>
<td>3.7518</td>
<td>2.6256(_{10}^{-3})</td>
<td>1.9893(_{10}^{-4})</td>
<td>2.2073(_{10}^{-3})</td>
</tr>
<tr>
<td>1.8326(_{10}^{-3})</td>
<td>6.3946(_{10}^{-4})</td>
<td>3.9717</td>
<td>2.9471(_{10}^{-3})</td>
<td>1.9771(_{10}^{-4})</td>
<td>2.4753(_{10}^{-3})</td>
</tr>
</tbody>
</table>
Appendix 2

This appendix includes seven ALGOL programs written for the English Electric - Leo - Marconi KDF 9 computer. The programs 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 $K = Ka_2 \cdot K_{111}$ 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 6C, with certain restrictions on the complete language. The representation used here is the 8-channel (Flexowriter) version.
Appendix 2a

DDC44C1CCWPU+WC3CC34BPST→

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(2C); open(7C);
again : copy text (2C,7C,[;] );

n := read(2C);
d := read(2C);
c := read(2C);
b := d/c;
e := ln(1C.C);
k := read(2C);

begin array t[1:6], g, v, m, sw, h, w[1:n];

for i := 1 step 1 until 6 do t[1] := read(2C);
for i := 1 step 1 until n do
begin
v[i] := read(2C);
w[i] := c.C;
write(7C, format ([ssss-nddddd]), h[i]);
repeat : sw[i] := w[i];
g[i] := exp(-exh[i]);
m[i] := k/e x ln(1 + b x g[i]);
w[i] := v[i] - m[i];
if abs(sw[i] - w[i]) x 1CC > 1 then goto repeat;

write(7C, format ([ssss-ndddddd]), m[i]);
write(7C, format ([ssss-nndddd.dd]), w[i]);
write(7C, format ([ssss-nndddd.d]), h[i]);
end;
end;
p := read(2C);
if p = 2 then goto again;
close(7C);
close(2C);
Appendix 2b

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 (2C);
open (7C);
F1 := format ([-d.dddd,-nd]);
F2 := format ([s-d.dddd,-nd]);

again: copy text (2C, 7C, []);
c := read (2C);
if c = C then begin
  T := read (2C);
  D := read (2C);
for i := 1 step 1 until 3 do
  begin AC[i] := read(2C);
    BE[i] := read(2C)
  end;
DHA := 1.8249b6 / sqrt((D * T)^3);
DHB := 5.0293b1 / sqrt(D * T)
end;

m := read (2C);
a := read (2C);
KA1 := read (2C);
KA2 := read (2C);
KW := read (2C);
n := read (2C);
e := ln(1C.C);

begin integer F3;
array ta, tm, ha, na, sh, cl [1 : n];
boolean array bo [1 : n];
k := C;
F3 := format ([,s-d.dddd,-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] := m * tm[i] + cl[i];
    end else cl[i] := m * tm[i];
  if q = 2 then
begin
    tm[i][1] := tm[i] + na[i];
    na[i] := c.c
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, sxx, r, s, t, P, Q, R, S, T,
      dl, delta, dc, cc, syy, 1, 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 bool[n];

  for i := 1 step 1 until n do
    begin
      if c = c 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] := axta[i] - m * tm[i] - na[i] + cl[i];
      na[i] := v[i];
      if c = 1 then
        fh[i] := fhha[i] := fha[i] :=
        fmaa[i] := i.c;
      MHA[i] := c.c
    end;

new kg:  
kg := read(20);
f := read(20);
g := read(20);
w := read(20);
DD := read(20);
l := c;
writetext(7C,[[2c6s]KMHA*GIVEN*==**]);
write(7C,F1,kG);
writetext(7C,[[c6s]DISCRIMINATION*==**]);
write(7C,F1,g);

K1 := K2 := SI := C.C;
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 = C then begin
    fh[i] := ACTCO (1, I[i], AC[1], BE[1]);
    fha[i] := ACTCO (1 - a, I[i], AC[1], BE[1]);
    fa[i] := ACTCO (a, I[i], AC[1], BE[1]);
    fm[i] := ACTCO (m, I[i], AC[m], BE[m]);
    fma[i] := ACTCO (m - a + 1, I[i], AC[m+a-1], BE[m+a-1]);
    fmaa[i] := ACTCO (m - 2 + a, I[i], AC[2x-ma], BE[2x-ma])
  end;
  if bo[i] then ha[i] := exp(-ex(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] := (c[l]-h[i]+OH[i])/(1+2×ha[i]×fha[i]/
  (KA1×fha[i])+kg×M[i]×fma[i]/fmaa[i]);
  H2A[i] := ha[i] × HA[i] × fha[i]/(fha[i] × KA1);
  A[i] := KA2 × fha[i] × HA[i]/(ha[i] × fa[i]);
  y[i] := (v[i] - MHA[i])×fma[i]/(A[i]+2 × fm[i]
  × fa[i]+2 × (2 × tm[i] - v[i] - MHA[i]));
  x[i] := (tm[i] - v[i]) × fma[i]/(A[i] × fa[i] ×
  (2 × tm[i] - v[i] - MHA[i]) × fma[i])
end;

j := k := C;

for i := 1 step 1 until n do
  if x[i] > ay then ay := x[i] else ay := ay;
if minus := if ay = C.C then true else false;
if minus and once then begin once:= false;
write text (7C, [[2c]Note.*All*x*values*are*negative.[c]]);
end;

try: for i :=1 step 1 until n do begin
  if x[i] > C.C 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;
\[
\text{boo}[1] := \begin{cases} 
\text{true} & \text{if } x[1] < C.C \text{ or } x[1] < ay/1c \text{ or } \text{minus} \\
\text{false} & \text{otherwise}
\end{cases}
\]

\[
\text{if } j = 1 \text{ then begin } \\
\text{minus} := \text{true}; \\
sx := sy := sxy := sxx := C.C; \\
j := C; \\
\text{end;}
\]

\[
\text{write text (7C, [[2c]Note. **One*positive*value*of*nx.[c]])} \\
\text{once} := \text{false}; \\
\text{goto try end;}
\]

\[
u := j \times sxx - sx^2; \\
K1 := (j \times sxy - sx \times sy)/u; \\
\text{if } K1 < C.C \text{ then begin } \\
\text{write text (7C, [[2c]KMA*is*negative]);} \\
\text{bool} := \text{true}; \\
\text{goto emerg end} \\
\text{else } \text{bool} := \text{false};
\]

\[
\text{for } i := 1 \text{ step 1 until } n \text{ do begin } \\
\text{M}[i] := (2 \times \text{tm}[i] - v[i] - \text{MHA}[i]) \times \text{fma}[i]/ \\
(K1 \times A[i] \times \text{fm}[i] \times \text{fa}[i] + 2 \times \text{fma}[i]); \\
\text{if } \text{M}[i] < C.C \text{ then } \text{M}[i] := C.C; \\
\text{MHA}[i] := \text{kg} \times \text{M}[i] \times \text{HA}[i] \times \text{fm}[i] \times \text{fha}[i]/\text{fmha}[i]; \\
\text{if } \text{MHA}[i] < C.C \text{ then } \text{MHA}[i] := C.C \\
\text{end;}
\]

\[
\text{comp: goto if } \text{1CCG} \times \text{abs(K1 - K11)} - 6 \leq \text{abs(K1)} \text{ then strength else cycle;}
\]

\[
\text{strength: SI := C.C; } \\
\text{for } i := 1 \text{ step 1 until } n \text{ do begin } \\
\text{MA}[i] := 2 \times \text{tm}[i] - v[i] - \text{MHA}[i] - 2 \times \text{M}[i]; \\
\text{if } \text{MA}[i] < C.C \text{ then } \text{MA}[i] := C.C; \\
\text{MA2}[i] := \text{M}[i] - \text{tm}[i] + v[i]; \\
\text{if } \text{MA2}[i] < C.C \text{ then } \text{MA2}[i] := C.C; \\
\text{IF } c = C \text{ then } I[1] := (m \times 2 \times \text{M}[i] + (m - a) \times 2 \times \text{MA}[i] + \\
(m-2x) \times 2 \times \text{MA2}[i] + (m-a+1) \times 2 \times \text{MHA}[i] + \\
\text{+ na}[i] + h[i] + (a-2) \times 2 \times \text{H2A}[i] + \\
\text{+ (a-1) \times 2 \times \text{HA}[i] + a \times 2 \times A[i] + OH[i])/2; \\
\text{SI := SI + I[1] end;}
\text{if } \text{1CCG \times abs(SI - IS) > abs(IS) then goto recalcul;}
\]

\[
\text{refine: for } i := 1 \text{ step 1 until } n \text{ do begin if } x[i] > C.C \\
\text{or } \text{minus then } \\
\text{begin } \text{sx} := \text{sx} + x[i] \times 3; \\
\text{sx} := \text{sx} + x[i] \times 4; \\
\text{sxy} := \text{sxy} + x[i] \times 2 \times y[i]; \\
\text{sy} := \text{sy} + y[i] \times 2 \text{ end end;}
\]

\[
\text{cc} := (\text{sxxsy} - \text{sxxsxy})/u; \\
\text{dl} := \text{sy} + j \times \text{cc} \times 2 + K1 \times 2 \times \text{sx} - 2 \times (\text{cc} \times \text{sy} \\
\text{+ K1} \times \text{sx} \times K1 \times \text{cc} \times \text{sx}); \\
\text{writetext(7C,[[c]kg*]=)}; \\
\text{write(7C,F1,kg}); \\
\text{writetext(7C,[[s]std*deviation*in*slope*]=)}; \\
\text{write(7C,F1,\sqrt{(jxd/(j-2)xu))});}
\]
P := \frac{sxx^2}{sxx} - j;
Q := \frac{sxx - jxsx^3}{sxx};
R := \frac{(jxsxy - sxxsy)}{sxx};
S := \frac{sxx}{j} - jxsx^4/sxx;
T := \frac{jxsxy}{sxx} - sy;
s := \frac{(Rxs - Qxt)/(Qs^2 - Psx)}{QxT/(Qs^2 - Psx)};

\text{dc} := sy + jxr^2 + s^2xsxx + t^2xsx^4 + 2x(rsxsxx + rxtxsxx +
txsx^2xsx^3) - rxsy - sxx^2xsx - txsxxy;
\text{delta} := rx(s + t(x[n] + x[1]))x(x[n] - x[1]) + s/2x((r + sxx[n] +
txx[n]x^2 - (r + sxx[1] + txx[1]x^2))x^2 + t/3x((r + sxx[n] +
txx[n]x^2x^3 - (r + sxx[1] + txx[1]x^2x^2))x^3) - (x[n] - x[1])/2x(rx^2 + sxx(x[n] + x[1]) + tx(x[n]x^2 + x[1]x^2));
l := l + 1;
\text{if } dl < gx \text{dc or } l = DD \text{ then goto jump;}
\text{ if first then begin first := false;}
\text{ if delta} < C.C \text{ then begin k1 := kg;}
\quad \text{kg} := kg + kgwx;
\quad \text{less} := true;
\quad \text{del} := \text{delta}
\text{ end;}
\text{ if delta} > C.C \text{ then begin k2 := kg;}
\quad \text{kg} := kg - wxkg;
\quad \text{less} := false;
\quad \text{del} := \text{delta}
\text{ end;}
\text{ goto cycle}
\text{ end;}
\text{ if not two then begin}
\text{ if delta} < C.C \text{ and less then begin k1 := kg;}
\text{ if delta} < \text{del} \text{ then w := -w;}
\quad \text{kg} := kg + wxkg;
\quad \text{del} := \text{delta;}
\text{ goto cycle}
\text{ end;}
\text{ if delta} > C.C \text{ and not less then begin k2 := kg;}
\text{ if delta} > \text{del} \text{ then w := -w;}
\quad \text{kg} := kg - wxkg;
\quad \text{del} := \text{delta;}
\text{ goto cycle}
\text{ end;}
\text{ end;
if delta < C.C then begin k1 := kg; 
   del1 := delta; 
   kg := kg - (k2-kg)*del1/(del2-del1) 
end;

if delta > C.C 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 bool[i] then k := k + 1; 
if k = C then begin 
   K2 := ((sxx x sy - sx x sxy)/u)/K1; 
   indiv := false 
else indiv := true; 
if indiv then begin 
   sx := C.C; 
   for i := 1 step 1 until n do 
      begin if bool[i] then begin 
         if MA[i] > C.C and A[i] > C.C then 
            K[i] := fmaa[i] x MA2[i]/(MA[i] x fma[i] x A[i] x fa[i]) 
         else K[i] := C.C; 
            sx := sx + K[i] 
      end; 
   K2 := sx /k 
end;

f := sqrt(jxdl/(j-2)/u); 
g := sqrt(dlxsxx/(j-2)/u); 
test(C);

print: write text (7C, [[4c] K1*=*=]); 
write (7C,F1, K1); 
if not indiv then write text (7C, [[4s] K2*=*=]) 
else write text (7C, [[4s] Av.*K2*=*]); 
write (7C, F1, K2); 
writeln(7C,[[4s]KMHA**]); 
write(7C,F1,kg); 
writeln(7C,[[2c]K1K2**]); 
write(7C,F1,cc); 
writeln(7C,[[6s]STANDARD*ERROR*IN*K1K2**]); 
write(7C,F1,g); 
writeln(7C,[[c23s]STANDARD*ERROR*IN*K1*]); 
write(7C,F1,f);
emerg: write text (7C, [[2c3s]abscissa[7s]ordinate[c]]); for i := 1 step 1 until n do begin write (7C, F1, x[i]); write (7C, format ([ssss-d.dddd-n dc]), y[i]) end; fin: p := read(2c); 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 (7C, [[2c5s]M[11s]MA[9s]MA2[9s]MHA[9s]HA[1Cs]A]); if c = C then write text (7C, [[11s] I]); if indiv then write text (7C, [[11s] K]); for i := 1 step 1 until n do begin write text (7C, [[c]]); write (7C, F1, M[i]); write (7C, F2, MA[i]); write (7C, F2, MA2[i]); write (7C, F2, MHA[i]); write (7C, F2, HA[i]); if c = C then write (7C, F2, I[i]); if indiv then write (7C, F2, K[i]) end; escape: writetext(7C,[[3c4s]NUMBER*OF*CYCLES*==**]); write(7C,format([nddd]),l); writetext(7C,[[2c4s]DEVIATION*FROM*LINE*==**]); write(7C,F1,d1); writetext(7C,[[c4s]DEVIATION*FROM*CURVE*==**]); write(7C,F1,dc); writetext(7C,[[2c4s]UPPER*LIMIT*IN*KMHA*==**]); write(7C,F1,k2); writetext(7C,[[c4s]LOWER*LIMIT*IN*KMHA*==**]); write(7C,F1,k1); writetext(7C,[[3c5s]A[11s]B[11s]C[c]]); write(7C,F2,r); write(7C,F2,s); write(7C,F2,t); write(7C,F2,t); p := read (2c) end; if p = 3 then goto new kg end end; if p = 2 then goto again; close (7C); close (2c) end →
Appendix 2c

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 X DHA X zT2 X (sqrt(I)/
(1 + DHB X AC X sqrt(I)) - BE X I))
end  ACTCO;

open (2C);
open (1C);
open (7C);
F1 := format ([d.ddddB-nd2]5)
F2 := format ([s-d.ddddB-nddJ])
FS := format (ssss-d.ddddB-ndcJ);

comment  data tape starts with C if activity corrections valid, 1 if I constant. If C 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 (2C, 7C, ]]);
c := read (2C);
if c = C then begin
   T := read (2C);
   D := read (2C);
   AC := read (2C);
   BE := read (2C);
   DHA := 1.8249b6 / sqrt((D X T)t3);
   DHB := 5.293b1 / sqrt(D X 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 (= C if b = 1), and n is the total number of points in the calculation;

m := read (2C);
a := read (2C);
b := read (2C);
KA1 := read (2C);
KA2 := read (2C);
n := read (2C);
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(1C.C);
begin integer F3, F4;
array ta, tm, ha, na, sh, cl [1 : n];
boolean array bo [1 : n];
k := 0;
F3 := format ([ss-d.ddd0-nd;]);
F4 := format ([ss-nd.ddd; ]); 
repeat : p := read (2C);
j := read (2C);
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 (2C);
tm[i] := read (2C);
ha[i] := read (2C);
na[i] := read (2C);
bo[i] := false;
if p = 2 then begin cl[i] := read (2C);
c1[i] := mxtm[i] + c1[i]
end
else cl[i] := m x tm[i]

k := k + j;
goto if k = n then main else repeat;

emf: begin real u;
real array t[1 :1C], ca,me,em,hcl [1 : j];
for i:= 1 step 1 until 1C do t[i] := read (2C);
for i := 1 step 1 until j do
begin ca[i] := read (2C);
me[i] := read (2C);
em[i] := read (2C);
u := t[3] + ca[i] + me[i];
ta[k + i] := t[1] x t[4]/u;
na[k + i] := t[2] x ca[i]/u;
tm[k + i] := t[93 xme[i]/u;
ha[k + i] := if c = 1 then t[5] + (t[8] - (t[7]
hcl[i] := t[1C] x me[i]/u;
c1[k + i] := hcl[i] + m x tm[i];
bo[k + i] := false
end;

gap(1C, 2C);
if t[1C] > \gamma - 7 then write text (1C, [[c] 2;[c]]);
else write text (1C, [[c] 1;[c]]);
write (1C, format ([_nddd;c]), j);

for i:=1 step 1 until j do begin
    write text (1C, [[c]]);
    write (1C, F3, ta[k + i]);
    write (1C, F3, tm[k + i]);
    write (1C, F4, ha[k + i]);
    write (1C, F3, na[k + i]);
    if t[1C] > \gamma - 7 then write (1C, F3, hcl[1]) end;

    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(2C);
    plot:= if p=0 then false else true;

    for i := 1 step 1 until n do begin
        if c = C then I[i] :=
            (m+a \times tm[1]+a \times ta[1] + cl[1] + na[1])/2;
        if not bo[i] then ha[i] := exp(-e \times ha[i]);
        v[i] := na[i] + cl[i];
        cl[i] := axta[i] - mxtm[i] - na[i] + cl[i];
        na[i] := v[i];
        if c = 1 then fh[i] := fha[i] := fha[0] :=
            fa[i] := 1.C end;

        K1 := K2 := 0.0;
        once := true;

    recalc : K11 := K1;
    K22 := K2;
    for i := 1 step 1 until n do begin
        if c = C then begin
            fh[i] := ACTCC (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 \times (sh[i] + ln(fh[i])/e));
        h[i] := ha[i]/fh[i];
        OH[i] := exp(-e \times 14.008)/(fh[i] \times ha[i]);
        H2A[i] := (cl[i] - h[i] + OH[i])/(b + (b - 1) \times KA1
            \times fhha[i]/(ha[i] \times fha[i]));
        HA[i] := KA1 \times fhha[i] \times H2A[i]/(ha[i] \times fha[i]);
        A[i] := KA2 \times fha[i] \times HA[i]/(ha[i] \times fa[i]);
if c = C then begin
\[ f_{ni} := ACTCO (m, I[i]); \]
if b = 1 then begin
\[ f_{ha[i]} := ACTCO (m - (a - 1), I[i]); \]
\[ f_{hha[i]} := ACTCO (m \times 2 - 2 \times (a - 1), I[i]) \] end
else begin
\[ f_{ha[i]} := ACTCO (m - a, I[i]); \]
\[ f_{hha[i]} := ACTCO (m \times 2 - a \times 2, I[i]) \] end end;
if b = 1 then \[ A[i] := HAti; \] end;
graph: for i := 1 step 1 until n do
begin if plot then begin
\[ y[i] := \frac{(tm[i] - M[i]) \times fhha[i]}{(M[i] \times A[i] \times fh[i]} \times \frac{fa[i]}{2}; \]
\[ x[i] := \frac{f_{hha[i]}(M[i] \times A[i] \times fh[i]}{M[i] \times A[i] \times xfa[i] \times fh[i]} \] end else begin
\[ y[i] := \frac{(tm[i] - M[i]) \times fh[i]}{(M[i] \times A[i] \times fh[i]} \times \frac{fa[i]}{2}; \]
\[ x[i] := f_{hha[i]} \times xfa[i] \times fh[i]}{(M[i] \times A[i] \times fh[i]} \times xfa[i] \times fh[i]} \] end;
j := k := C;
for i := 1 step 1 until n do
if x[i] > ay then ay := x[i] else ay := ay;
minus := if ay = C.C then true else false;
if minus and once then
begin writetext(7C, [[2c]* All*x*values*are*negative.[c]])
one := false end;
try: for i := 1 step 1 until n do
begin if x[i] > C.C or minus then begin
\[ sx := sx + x[i]; \]
\[ sy := sy + y[i]; \]
\[ sxy := sxy + x[i] \times y[i]; \]
\[ sxx := sxx + x[i]^2; \]
\[ syy := syy + y[i]^2; \]
\[ j := j + 1 \] end;
boo[i] := if x[i] < C.C or x[i] < ay/1C or minus
then true else false end;
if j = 1 then begin minus := true;
\[ j := C; \]
write text (7C, [[2c]*One*positive*value*of*x.[c]])
one := false;
goto try end;
u := j \times sxx - sx^2;
D := (j \times sxy - sx \times sy)/u;
T := (sxxysy - sxsxy)/u;
if plot then begin Kl := D; KD := C \times \text{T/D}^2 \end
else begin Kl := T; KD := D/T^2 \end;

if Kl < C.C then begin writetext(7C,[[2c]KMA*is*negative]);
    bool := true;
    goto emerg \end
else bool := \text{false};

for i := 1 step 1 until n do
    if boo[i] then k := k + 1;

if k = C then begin K2 := KD;
    indiv := \text{false} \end
else begin indiv := \text{true};
goto metal \end;

comp: if 1CCC \times \text{abs(K1 - K11)} - \mu - 6 < \text{abs(K1)} and 1CCC \times 
       \text{abs(K2 - K22)} - \mu - 6 < \text{abs(K2)} then goto print;
if indiv then goto recalc;

metal: for i := 1 step 1 until n do begin
    if MA[i] < C.C then MA[i] := C.C;
    if MA2[i] < C.C then MA2[i] := C.C;
    if b = 1 then A[i] := C.C;
    if c = C then I[1] := (m^2 \times M[1] + (m - a)^2 \times MA[1] +
                      ((m - a) \times 2)^2 \times MA2[1] + na[1] + h[1] +
                      (a - 2)^2 \times H2A[1] + (a - 1)^2 \times HA[1] +
                      a^2 \times A[1] + OH[1])/2;
    if b = 1 then A[i] := HA[1] \end;

if indiv then begin
    ay := C.C;
    k := C;
    for i := 1 step 1 until n do begin
        if boo[i] then begin if MA[i] > C.C and A[i] > C.C then
                         K[1] := f\text{hha}[i] \times MA2[1]/((MA[i] \times f\text{ha}[1])^2) \else
                         K[1] := C.C;
                         ay := ay + K[1];
                         if K[1] > C.C then k := k + 1 \end
                        else K[1] := C.C end;
        if k = C then K2 := C.C else K2 := ay / k;
        goto comp \end;
goto recalc;

print: \text{gap}(7C, 2C);
\text{comment all programs output K1, K2, x and y;}

emerg: ay := syy + j\times T^2 + D^2\times sxx - 2\times(Txsy + Dxsxy - D\times Txsx);
\[ dm := \sqrt{\frac{jXay}{(j-2)/u}}; \]
\[ d := \sqrt{\frac{ayxss}{(j-2)/u}}; \]

\[
\text{write text \((7C, c K1 =\ast\))};
\]

\[
\text{write \((7C, F1, K1)\)};
\]

\[
\text{write \((7C, c 6s2standard\_deviation\_in\_K1 =\ast\))};
\]

\[
\text{write \((7C, F1, \text{if plot then } dm \text{ else } d))};
\]

\[
\text{write \((7C, F1, \text{K}D =\ast\))};
\]

\[
\text{write \((7C, c 6s2standard\_deviation\_in\_K1KD =\ast\))};
\]

\[
\text{write}(7C, F1, \text{if plot then } d \text{ else } dm));
\]

\[
\text{if indiv then begin}
\]

\[
\text{write text \((7C, c AV\_K2 =\ast\))};
\]

\[
\text{write \((7C, F1, K2)\)} \text{ end};
\]

\[
\text{write text \((7C, c 2c3s\_ABSCISSA[9s\_ORDINATE[c]])\)};
\]

\[
\text{for } i := 1 \text{ step } 1 \text{ until } n \text{ do begin}
\]

\[
\text{write \((7C, F1, x[i])\)};
\]

\[
\text{write \((7C, F2, y[i])\)} \text{ end;}
\]

\[
\text{comment \underline{if concentrations of all species desired punch 1. If another data tape follows punch 2 otherwise punch C;}}
\]

\[
\text{fin: } p := \text{read (2C)};
\]

\[
\text{if bool then begin } \text{bool} := \text{false};
\]

\[
\text{if } p = 1 \text{ then goto fin } \text{ end;}
\]

\[
\text{if } p = 1 \text{ then begin}
\]

\[
\text{write text \((7C, c 2c5s\_M[11s]\_MA[1Cs]\_MA2[1Cs]\_HA[1Cs]\_A[1Cs]\_H2A )\)};
\]

\[
\text{if } c = 0 \text{ then write text \((7C, c I[1])\)};
\]

\[
\text{if indiv then write text \((7C, c 11s\_K)\)};
\]

\[
\text{for } i := 1 \text{ step } 1 \text{ until } n \text{ do begin}
\]

\[
\text{write text \((7C, c 1c)\)};
\]

\[
\text{write \((7C, F1, M[i])\)};
\]

\[
\text{write \((7C, F2, MA[i])\)};
\]

\[
\text{write \((7C, F2, MA2[i])\)};
\]

\[
\text{write \((7C, F2, HA[i])\)};
\]

\[
\text{write \((7C, F2, A[i])\)};
\]

\[
\text{write \((7C, F2, H2A[i])\)};
\]

\[
\text{if } c = 0 \text{ then write } (7C, F2, I[1]);
\]

\[
\text{if indiv then write } (7C, F2, K[i]) \text{ end;}
\]

\[
p := \text{read (2C)};
\]

\[
\text{if } p = 1 \text{ then begin } \text{plot} := \text{false};
\]

\[
\text{K1 := K2 := K11 := K22 := C.C;}
\]

\[
\text{goto graph end;}
\]

\[
\text{if } p = 2 \text{ then goto again;}
\]

\[
\text{close \((1C)\)};
\]

\[
\text{close \((2C)\)};
\]

\[
\text{close \((7C)\)} \text{ end} \rightarrow
Appendix 2d

```plaintext
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, H01, H02, H03, wto, X1, alo;

integer p, f, fa, fc, a, iws, n, mt, ncd, ncc, k, l, j, m, l1, l2, i, nlt, icc, zj, nn, nncv, ncv, 1hs, ivx, itx, stop;

hx:=ln(1C.C);
f:=format([ss-nddd]);
fa:=format([ss-d.ddd-d]);
f:=format([ss-nddd-d]);
open(20); open(70);
copytext(20, 70, i;2 again:
P again:
copytext(20, 70, [j]);
p:= read(20);
n:= read(20);
mm:= n×2;
mt:= read(20);
l1:= read(20);
l2:= read(20);
EX1:= read(20);
EX2:= read(20);
iws:= read(20);
1hs:= 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;
    ln:= 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(2C);
mm[i] := read(2C); mn[i] := read(2C);
e[i] := read(2C) end;

for i := 1 step 1 until mt do begin cl[i] := if p = 7 then C.C else read(2C); ch[i] := read(2C); u[i] := read(2C) end
else begin bb[i] := read(2C); u[i] := read(2C); ch[i] := read(2C) end;

hcl[i] := if iws = 2 then read(2C) else C.C;
ch[i] := axcl[i] + hcl[i] - ch[i]

if iws = C then writetext(7C, [[2c]UNIT*WEIGHTS*TO*BE*SET*
BY*PROGRAM]]
else for i := 1 step 1 until mt do
begin scl[i] := if p = 7 then C.C else read(2C); sph[i] := read(2C) end
else begin sph[i] := read(2C); sph[i] := read(2C); sch[i] := read(2C) end;

shcl[i] := sqrt(scl[i]^2 + (axscl[i])^2 + sch[i]^2) end;

stop := read(2C);
ncd := read(2C);
nccv := ncv * 2;
writetext(7C, [[2c]number*of*cycles*]);
write(7C, f, ncc);

for i := 1 step 1 until ncv do h[i] := read(2C);
ncc := 0;
icc := 0;
for i := 1 step 1 until mt do u[i] := exp(hxxu[i]);
if iws = 1 then for i := 1 step 1 until mt do sph[i] := sph[i] * hxx / u[i];
for i := 1 step 1 until mt do
begin tvx[i] := if tvx = C then bb[i] else read(2C);
ttx[i] := if ttx = C then cl[i] else read(2C)
end;
L11: ncc := ncc+1;
sqr := C.C;
sqro := C.C;
sqru := C.C;
test(c);

for i := 1 step 1 until n do
begin
  c[i] := C.C;
end;
L37: for k := 11 step 1 until 12 do
begin
  z[j] := C;
m := C;
y1 := EX1xbb[k];
y3 := EX2xcl[k];
vx := tvx[k];
tx := ttx[k];
end;
L16: test(c);
    for i := 1 step 1 until n do b[i] := exp(hxxe[i]);
if p=5 then goto CONC5;
if p=6 then goto CONC6;
CONC 7: nit := C;
CONC 6: nit := C;
CONC 5: nit := C;
for j := 1 step 1 until n do term[j] := b[j]xu[k]tmn[j];
test(c);
L5C2: for j := 1 step 1 until n do
begin
nit := nit+1;
end;
bo := vx;
alo := tx;
for j := 1 step 1 until n do
begin
  alo := alo+ml[j]xc[j,k];
  bo := bo+mm[j]xc[j,k]
end;
y2 := abs(bo-bb[k]);
y4 := abs(alo-cl[k]);
if nit>100 then goto L516;
if y1-y2>C.C and y3-y4>C.C then goto L5C9;
sev[1] := bo-bb[k];
sev[2] := alo-cl[k];
sem[1,1] := -vx;
sem[1,2] := C.C;
sem[2,2] := -tx;
for j:=1 step 1 until n do
    begin
        sem[1,1]:= sem[1,1]-c[j,k]*xm[j]xmn[j]T2;
        sem[1,2]:= sem[1,2]-c[j,k]*xm[j]xml[j];
        sem[2,2]:= sem[2,2]-c[j,k]*xm[j]xml[j]T2 end;
        aha := sem[1,2]T2-sem[1,1]xsem[2,2];
        end:
        aha := (semi[1,2]xsemi[2,2]-semi[1,1]xsemi[2,2])/aha;
        vx := vx+vxxshft[1];
        tx := tx+txxshft[2];
        goto L5C2;
L5C9:
    ho := 1.0/u[k]-ckwlxu[k];
    for j:=1 step 1 until n do ho := ho-mn[j]xc[j,k];
    if lws/=1 then goto L18;
    aha := bhb := C.C;
    chc := 1.0/u[k]+ckwlxu[k];
    for i:=1 step 1 until n do
        begin
            aha := aha+mm[1]xmn[1,k];
            bhb := bhb+ml[1]xmn[1,k];
            chc := chc+mn[1]T2xc[1,k] end;
    temp := 1.0/(sem[1,1]xsem[2,2]-sem[1,2]xsem[2,1]);
    sr := sch[k]T2+(sbb[k]xtempx(ahaxsem[2,2]-sem[1,2]xbhb))T2
        + (sc1[k]xtempx(ahaxsem[2,1]-sem[1,1]xbhb))T2
        + (sph[k]xu[k]x(chc+tempx(ahaxsem[1,2]xbhb
        - sem[2,2]xaha)-bhbx(sem[1,1]xbhb-sem[2,1]xaha))))T2;
    goto L18;
L18:
    if stop = C then test(1C);
    if icc=C then begin tvx[k] := vx;
        ttx[k] := tx end;
        if m=C or l>C then begin
            if lws=C then begin
                sr := 1.0/
sqrt(sr);
                wt := 1.0/sqrt(sr);
                ruw := (ho-ch[k]);
                r := wt+ruw end;
            if l>C then goto L31;
            m := m+1;
            if m=2 then goto L251;
            if m=3 then goto L252;
L25C:  \[sqro := sqro + r^2\];
       \[wto := wt;\]
       \[HO1 := ho;\]
       \[ro := r;\]
       \[z_j := z_j + 1;\]
       \[e[z_j] := e[z_j] + h[z_j];\]
       \[icc := icc + 1;\]
       \[goto L16;\]

L251:  \[HO2 := ho;\]
       \[e[z_j] := e[z_j] - 2 \times h[z_j];\]
       \[goto L16;\]

L252:  \[HO3 := ho;\]
       \[e[z_j] := e[z_j] + h[z_j];\]
       \[de[z_j] := \frac{wto(x(HO2 - HO3))/2}{h[z_j]};\]

\[\textbf{if} \ \text{de[z_j]} = C.C \ \textbf{then begin}\]
\[\text{newline(7C,1);}\]
\[\text{write (7C,f,k);}\]
\[\text{write (7C,f,z);}\]
\[\text{writetext(7C,[[ss]zer0]);}\]
\[\textbf{end};\]

\[\textbf{if} \ \text{z_j} = ncv \ \textbf{then goto L5C;}\]

\[\text{z_j := z_j + 1;}\]
\[m := 1;\]
\[e[z_j] := e[z_j] + h[z_j];\]
\[\textbf{goto L16;}\]

L5C:  \textbf{for} \ i := 1 \ \textbf{step} \ 1 \ \textbf{until} \ ncv \ \textbf{do} \begin{align*}
&\textbf{begin} \\
&\text{ck[i]} := \text{ck[i] - roxde[i];} \\
&\textbf{for} \ j := 1 \ \textbf{step} \ 1 \ \textbf{until} \ ncv \ \textbf{do} \\
&\text{cc[i,j]} := \text{cc[i,j] + de[i]xd}[j]; \\
&\textbf{for} \ j := ncv + 1 \ \textbf{step} \ 1 \ \textbf{until} \ nncv \ \textbf{do} \\
&\text{cc[i,j]} := \text{if}\ j = ncv + 1 \ \textbf{then} \ 1.C \ \textbf{else} \ C.C \ \textbf{end}; \\
&\text{icc := C;} \\
&\text{if} \ l = C \ \textbf{then goto skip;} \\
\end{align*}\]

L31:  \[\text{sqr := s} + r^2;\]
       \[\text{sqr := s} + r^2;\]
       \[\text{skip := test(C);}\]
       \[\text{end; if} \ l > C \ \textbf{then goto L43;}\]

ROUND:  \[k := C;\]
         \[\text{if} \ ck[k] = C.C \ \textbf{then goto exit;}\]
         \[\textbf{goto if} \ k = ncv \ \textbf{then} \text{MATRIN} \ \textbf{else} \text{ROUND;}\]
MATRIN: if stop=C then test(1C);

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[1,a]≠C.C then cc[1,a] else 1.C;
for j := 1 step 1 until nncv do cc[1,j] := cc[1,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[1,j] := cc[1,j]-cc[a,j];
a := a-1;
goto cycle;
leap: i := ncv;
hop: a := i-1;
jump: D := cc[1,a];
for j := 1 step 1 until nncv do
cc[1,j] := cc[1,j]-cc[a,j]*D;
a := a-1;
if a>C 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[1,j] := cc[1,j+ncv];
for i := 1 step 1 until ncv do x[1] := C.C;
for i := 1 step 1 until ncv do
for j := 1 step 1 until ncv do x[1] := x[1]+cc[1,j]*xck[j];
test(C);
for i := 1 step 1 until ncv do if abs(x[1])>C.5 then
begin newline(7C,1);
write (7C, f, i);
writetext(7C, [[2c4s]overshifted]);
x[1] := C.5*x[1]
end;

sqro := sqro/(mt - ncv);
if ncc=1 then begin
writetext(7C, [[2c]Weighted*variance*with*input*constants*]=);
write(7C, 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(7C, [2c]weighted*variance*is]
    write(7C, fa, sqr);
    writetext(7C, [c]unweighted*sum*of*squares*of
    *deviations*=
    write(7C, fa, sqru);
    for i:= 1 step 1 until ncv do
    begin X1 := cc[1,1]x$sqr;
       newline(7C, 1);
       write (7C, f, 1);
       write (7C, fa, e[1]);
       write (7C, fa, sqrt(abs(X1)));
       if X1<1.1 then writetext(7C, [[4s]negative])
    end;
    if sqr>sqro then begin for i:= 1 step 1 until ncv do
    begin x[i] := 0.5x[i];
       e[i] := e[i]-x[i] end;
    writetext(7C, [2c]half*shifts*applied*for*next*cycle)
    end;
    if ncc<ncl then goto L11;
    if in basic symbol(2C) = 185 then
    begin ncc := read(2C);
       ncv := read(2C);
       if in basic symbol(2C) = 142 then
    begin l1 := read(2C);
       l2 := read(2C);
       icc := C
    end;
    if in basic symbol(2C) = 142 then
    for i:= 1 step 1 until ncc do
    begin j := read(2C);
       if in basic symbol(2C) = 142 then e[j] := read(2C);
       if in basic symbol(2C) = 142 then
    begin l := read(2C);
       if sqr>sqro then icc := -1;
       invert(j,l,e);
       swap (j,l,ml);
       swap (j,l,mm);
    end;
    end;
    for i:= 1 step 1 until ncv do h[i] := read(2C);
    if icc = -1 then goto exit;
    writetext(7C, [8c][new*run[4c]]
    ncc := C;
    goto L11;
end;
exit: writetext(7C, [[4c]escape*route*taken]);
    if in basic symbol(2C) = 142 then goto again;
    close(2C); goto(7C);
Appendix 2e

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 KIC1 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.dddd,nd]);
F3:= format([ssss-ndd.dddd,2]);
F4:= format([-d.dddd,nd]);
e:= ln(1C.C);

open(2C);        open(7C);

dev:= read(2C);
if dev = 1C then open(1C);
again:    copytext(2C,7C,[;]);
    error:= read boolean(2C);
    n:= read(2C);
    q:= read(2C);
    b:= C;
    pr:= false;

if q = 1 then begin kw:= exp(-ex(read(2C)));
                  KA2:= read(2C);
                  a:= read(2C)
            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(2C);
        goto if p = 1 then proc else emf;

    proc:
        s:= read(2C);
        b:= b + s;
        for i:= b+1-s step 1 until b do
          begin ta[i]:= read(2C);
                        tm[i]:= read(2C);
                        M[i]:= read(2C);
        if q = 1 then begin h[i]:= read(2C);
                          cl[i]:= read(2C)
                         end;
          end;

if error then begin sta[1]:= read(2C);
    stm[1]:= read(2C);
    sM[1]:= read(2C)
end;
goto if b = n then main else plus;

emf :
    s:= read(2C);
    b:= b + s;
    F1:= format([ssss-d.dddd-dn-dn]);
for i:= 1 step 1 until 9 do t[i]:= read(2C);
if q = 1 then for i:= 10 step 1 until 13 do 
t[i]:= read(2C);
if error then for i:= 14 step 1 until 23 do 
t[i]:= read(2C);

comment The subscripted variables t[1] 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;

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(2C);
    em[i]:= read(2C);
    if q = 1 then h[i]:= read(2C);
    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[14]+(t[13]-(t[12]-h[i]))/t[11];
        cl[i]:= vm/u[i]
end;
if error then
begin
    pvv := v[1]x[t[19]];
    svo := t[14]xvo;
    svc := t[3]x2x(t[17]x2 + t[18]x2);
    sM[i] := (pm[i]xexM[i])x2x((t[23]x2 +
                      t[22]x2)/(em[i] - t[9] - t[8])x2
                      + (t[21]/t[7])x2);
    sv := (svox2 + (if v[1]=c.c then c.c
              else t[19]x2))/u[1]x2;
    sta[i] := ta[i]x2x(t[15]x2 + t[16]x2 + sv);
    stm[i] := tm[i]x2x((svc + vmx2x(t[2]x2 +
                      (if v[1]=c.c then c.c else (t[19] /
                      v[1])x2)))/(t[3] + vm)x2 + sv);
end;
end;

gap(1c,25c);
write text (1c, [c] 1 ;£cival)
write(1c, format(Tnddd;c), s);
print: for i := b+1-s step 1 until b do
begin newline(1c,1);
    write(1c,F1,ta[i]);
    write(1c,F1,tm[i]);
    write(1c,F1, M[i]);
    if q = 1 then begin write(1c,F3*h[i])
                          write(1c,F1,cl[i])
    end;
end;

if error then
begin
    gap(1c,5c);
    newline(1c,1c);
    for i := b+1-s step 1 until b do
begin
    newline(1c,1);
    write(1c,F1,sta[i]);
    write(1c,F1,stm[i]);
    write(1c,F1, sM[i])
end;
end;

if pr then goto skip;
if b /= n then goto plus;

main: KMA := SSK := c.c;
for i := 1 step 1 until n do
begin
    MA[i] := tm[i] - M[i];
    if q = 1 then h[i] := exp(-exh[i]);
    A[i] := if q = c then ta[i] - MA[i]
            else (h[i] + tm[i] - axA[i] - cl[i] -
                 kw/h[i])/(a + (a - 1)/kA2xh[i]);
    K[i] := MA[i]/(M[i]xA[i]);
A.2e

if error then
else
    SK[1] := 1.0;
    SSK := SSK + 1.0/SK[1];
    KMA := KMA + K[1]/SK[1];

end;

writetext(7C, [[cc6s]KMA*=-]);
write(7C, F4, KMA/SSK);

if error then
begin
    writetext(7C, [[cc6s]error*in*KMA*=-]);
    write(7C, F4, sqrt(1.0/SSK))
end else
    writetext(7C, [[cc6s]unit*weights*applied]);
    if error then writetext(7C, [[cc6s]SIGK]);
    newline(7C, 2);

for i := 1 step 1 until n do
begin
    write(7C, F2, M[i]);
    write(7C, F2, MA[i]);
    write(7C, F2, A[i]);
    write(7C, F2, K[i]);
    if error then write(7C, F2, sqrt(SK[i]));
    newline(7C, 1);
end;

if in basic symbol(2C) = 185 then
begin
    pr := true;
    F1 := format([ssss-d.ddddf-nd]);
    gap(1C, 15C);
    goto print
end;

skip : if in basic symbol(2C) = 142 then goto again;

close(2C);  close(7C);
if dev = 1C then close(1C);

end
begin comment This program calculates \( K_{MA} = MA/(MxA) \) and 
\( KM_{2A} = M_{2A}/(M_{AXM}) \) from \( pM \) measurements by a least 
squares procedure and if \( pH \) data are available
also calculates \( K_{MA} \) and \( KM_{2A} \) 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 \( INDIV1, INDIV2; \)

\[
\begin{align*}
F1 &:= \text{format}([ssss-d.ddddjo-ndrJJ]) \\
F2 &:= \text{format}([ssss-ndd.dddd]) \\
F3 &:= \text{format}([ss-d.ddddjo-ndyfi]) \\
F4 &:= \text{format}([ssss-d.dddd10-ndJ]) \\
e &:= \ln(A) \\
\end{align*}
\]

\[\text{open}(2C); \quad \text{open}(7C); \]

again: \text{copytext}(2C,7C,[]);

comment \( n= \text{total no of points}, p=1 \text{ for } pM \text{ only and }
2 \text{ for } pM \text{ and } pH(\text{proc data}) \text{ p=3 for } pM \text{ only and 4 }
\text{ for } pM \text{ and } pH(\text{original data}).\text{s= no of points in }
\text{section, } \text{kw = ion product of solvent, } \text{KA2 = 2nd }
dissociation constant of acid,} \text{a is charge on acid }
anion;
\[\begin{align*}
a &:= \text{read}(2C) \\
n &:= \text{read}(2C) \\
b &:= C \\
\text{INDIV1} &:= \text{false}; \quad \text{INDIV2} := \text{false}; \\
\end{align*}\]

\[
\begin{align*}
\text{begin array } h,c1,tm,ta,v,em,x,y,u,M,MA,M2A,A,HA,K,KK[1:n], \\
t[1:13]; \\
\text{plus: } p := \text{read}(2C); \\
& \text{goto if } p<3 \text{ then proc else emf;}
\end{align*}
\]

\[
\begin{align*}
\text{proc: } s := \text{read}(2C); \\
& \text{if } p=2 \text{ then begin } \text{kw} := \text{read}(2C); \text{KA2} := \text{read}(2C) \text{end}; \\
b &:= b+s; \\
& \text{for } i := b-s+1 \text{ step 1 until } b \text{ do}
& \text{begin comment Data columns are total acid, total metal,} \\
& \text{free metal, } pH, \text{ total salt added;}
& \text{ta}[i] := \text{read}(2C); \\
& \text{tm}[i] := \text{read}(2C); \\
& \text{M}[i] := \text{read}(2C); \\
& \text{if } p=2 \text{ then begin } \text{h}[i] := \text{read}(2C); \\
& \text{cl}[i] := \text{read}(2C) \text{ end end; }
& \text{goto if } b=n \text{ then main else plus;}
\end{align*}
\]
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[1C-13] are reference pH, slope of pH response, buffer emf, reference emf on calibration graph;

emf:

\[ s := \text{read}(2C); \]
\[ b := b + s; \]
\[ \text{if} \ p = 4 \ \text{then begin} \ w := \text{read}(20); K_{A2} := \text{read}(20) \ \text{end}; \]
\[ \text{for} \ i := 1 \ \text{step} \ 1 \ \text{until} \ 9 \ \text{do} \ t[i] := \text{read}(2C); \]
\[ \text{if} \ p = 4 \ \text{then for} \ i := 1C \ \text{step} \ 1 \ \text{until} \ 13 \ \text{do} \ t[i] := \text{read}(2C); \]
\[ \text{for} \ i := b - s + 1 \ \text{step} \ 1 \ \text{until} \ b \ \text{do} \]
\[ \begin{align*}
&v[i] := \text{read}(2C); \\
&em[i] := \text{read}(2C); \\
&\text{if} \ p = 4 \ \text{then begin} \ h[i] := \text{read}(2C); \\
&cl[1] := v[i]xt[6]/u[1] \end{align*} \]
\[ \text{open}(1C); \]
\[ \text{gap}(1C, 25C); \]
\[ \text{write}(1C, \text{format}([\text{d}; \text{c}]), p - 2); \]
\[ \text{write}(1C, \text{format}([\text{n}; \text{d}; \text{c}]), s); \]
\[ \text{for} \ i := b - s + 1 \ \text{step} \ 1 \ \text{until} \ b \ \text{do} \]
\[ \begin{align*}
&\text{writetext}(1C, [\text{c}]); \\
&\text{write}(1C, F1, ta[1]); \\
&\text{write}(1C, F1, tm[1]); \\
&\text{write}(1C, F1, M[1]); \\
&\text{if} \ p = 4 \ \text{then begin} \text{write}(1C, F2, h[i]); \\
&\text{write}(1C, F1, cl[1]) \end{align*} \]
\[ p := p - 2; \]
\[ \text{close}(1C); \]
\[ \text{goto} \ \text{if} \ b = n \ \text{then} \ \text{main} \ \text{else} \ \text{plus}; \]

main: \ sx := syy := sx2 := C.C; \]
\[ K2 := C.C; \]
\[ b := C; \]
\[ \text{for} \ i := 1 \ \text{step} \ 1 \ \text{until} \ n \ \text{do} \begin{align*}
&h[1] := \exp(-\exp h[i]); \\
&\text{else} \ C.C; \\
- 2xta[1] + HA[1]x2\right) \end{align*} \]
if $x[1] > C.C$ then begin
    $b := b + 1$;
    $sx := sx + x[1]$;
    $sy := sy + y[1]$;
    $sx2 := sx2 + x[1]^2$
end

if $b < 2$ then begin
    $sx := sy := sxy := sx2 := C.C$;
    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

$K1 := \begin{cases} 
    \frac{(sxxsy - nxsxysy)}{(sx^2 - nxsx^2)} & \text{if } b < 2 \\
    \frac{(sxxsy - bxsxysy)}{(sx^2 - bxsx^2)} & \text{else}
\end{cases}$

for $i := 1$ step 1 until $n$ do begin
    if $x[i] < C.C$ then begin
        $K[i] := (y[i] - K1x[i])/K1$;
        $K2 := K2 + K[i]$;
    end
end

if $b = n$ then ($sy - K1xsx)/K1/n$ else \(K2/(n - b)\);

if $b/n$ then INDIV2 := true;

out: writetext(7C,[[3c6s]ABSCISSA[6s]ORDINATE]);
    for $i := 1$ step 1 until $n$ do
        newline(7C,1);
        write(7C,F4,x[i]);
        write(7C,F4,y[i]) end;

for $i := 1$ step 1 until $n$ do
    begin
    end;

print: writetext(7C,[[3c4s]K1*];
    write(7C,F3,K1);
    writetext(7C,[[6s]K2*];
    write(7C,F3,K2);

if $p = 2$ then writetext(7C,[[1Ts]HA]);
if INDIV1 then writetext(7C,[[1Ts]K1]);
if INDIV2 then writetext(7C,[[1Ts]K2]);
for i:= 1 step 1 until n do
begin newline(7C,1);
    write(7C,F3,M[1]);
    write(7C,F3,MA[1]);
    write(7C,F3,M2A[1]);
    write(7C,F3,A[1]);
if p=2 then write(7C,F3,HA[1]);
if INDIV1 then write(7C,F3,KK[i]);
if INDIV1 or x[i]<C.C then write(7C,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:=C.C;
for i:=1 step 1 until n do
begin
    A[i]:= KA2×HA[1]/h[1];
    MA[i]:=tm[i] - M[i] - 2×M2A[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;
write text(7C,[[6c3s]INDIVIDUAL*CALCULATIONS]);
goto print end;

emerg: p:= read(2C);
if p=2 then goto again;
close(2C);  close(7C);
Appendix 2g

\[ \begin{align*}
&\text{begin real } e, k, es, vo, v, t, kw, pm, ts, K1, \\
&\quad K2, T, dha, dhb, D, s, u, ao, be; \\
&\quad \text{integer } p, q, r, i, n, F1, F2, a, b, pp, g, l; \\
&\quad \text{real procedure ACTCO (z, I);} \\
&\quad \text{value } I, z; \\
&\quad \text{real } I; \\
&\quad \text{integer } z; \\
&\quad \text{begin} \\
&\quad \text{ACTCO:}=\exp(-exdhaxzt^2x(\sqrt(I)/(1+dhbXaoXsqrt(I)) \\
&\quad \quad \quad \quad \quad \quad \quad \quad - bexI)) \\
&\quad \text{end activity coefficients from Davies equation;}
\end{align*} \]

\[ e:= \ln(1C.C); \]
\[ F1:=\text{format([-d.dddd]-ndj\[) }2; \]
\[ F2:=\text{format([3s-d.dddd]-ndj^)}; \]
\[ \text{open(2C); open(7C); } \]
\[ \text{again: copytext(2C, 70, [; I]); } \]

\begin{align*}
\text{comment} & \quad \text{pp = C for emfs, 1 for direct pH readings.} \\
& \quad \text{q = C if activity coefficients are to be calculated else 1.} \\
& \quad \text{Gran plots: } r=1,2 \text{ or } 3 \\
& \quad \text{1 for strong acid - strong base with indicator ion in excess,} \\
& \quad \text{2 for strong acid - strong base with counter-ion in excess,} \\
& \quad \text{3 for weak acid - strong base.} \\
& \quad \text{Explicit plots: } r=4,5,6 \text{ or } 7 \\
& \quad \text{4 for strong acid - strong base and precipitation titrations,} \\
& \quad \text{5 for weak(dibasic) acid - strong base,} \\
& \quad \text{6 for weak monobasic acid - strong base in presence} \\
& \quad \quad \text{of a salt of a weak base,} \\
& \quad \text{7 for weak acid - weak base;}
\end{align*}

\[ pp:=\text{read(2C)}; \]
\[ q:=\text{read(2C)}; \]

\begin{align*}
\text{if } q=C & \text{ then begin } T:=\text{read(2C)}; \\
& \quad D:=\text{read(2C)}; \\
& \quad ao:=\text{read(2C)}; \\
& \quad be:=\text{read(2C)}; \\
& \quad s:=\text{read(2C)}; \\
& \quad u:=\text{read(2C)}; \\
& \quad \text{dha:=1.8249b6/sqrt((DXT)\uparrow3);} \\
& \quad \text{dhb:=5.029341/sqrt(DXT)}
\end{align*}

\[ \text{end } T \text{ is abs temp D dielectric const} \]
\[ \text{ao distance of closest approach be empirical} \]
\[ \text{coefficient } s \text{ conc of salt present} \]
\[ \text{u estimated conc of sample;} \]

\[ r:=\text{read(2C)}; \]
\[ n:=\text{read(2C)}; \]
vo:=read(2C);
v:=read(2C);
t:=read(2C);
k:=if pp=1 then 1.0 else read(2C);

if r<4 then begin a:= b:= 1;
es:= pm:= C.C end;
if r>3 then begin es:= if pp=1 then C.C else read(2C);
         pm:= if pp=1 then C.C else read(2C);
kw:= read(2C);
b:= read(2C);
a:= read(2C) end;
if r>4 then begin K1:= read(2C);
         K2:= read(2C) end;
if r=6 then ts:= read(2C);

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 = -log(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:

<table>
<thead>
<tr>
<th>r</th>
<th>K1</th>
<th>K2</th>
<th>b</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>H2A/(HA)</td>
<td>HA/(HA)</td>
<td>no of titrable protons</td>
<td></td>
</tr>
<tr>
<td>6 or 7</td>
<td>HA/(HA)</td>
<td>BH/(HB)</td>
<td>charge on B charge on A</td>
<td></td>
</tr>
</tbody>
</table>

For a monobasic weak acid r=5 and K1 = C.C;

\[
g := 0;\]
\[
vo := vo+v;\]
if q=C then u := s+u;

readings: begin real sx, sy, sxy, sx2, sy2, m, c, d,
dy, dm, c1, c2;
array f, x, y, h, 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>C, if abs(p)=1 then soln of indicator ion is standard else abs(p)=2;
A.2g

\[
\text{switch sr:= R1,R2,R3,R4,R5,R6,R7;}
\]
\[
\text{switch si:= I1,I2,I3,I4,I5,I6,I7;}
\]
\[
\text{boolean array bo[1:n];}
\]
\[
\text{for i:=1 step 1 until n do begin x[1]:=read(2C);}
\]
\[
\text{y[1]:=read(2C);}
\]
\[
\text{vx[1]:= vo+x[1];}
\]
\[
\text{bo[1]:=true}
\]
\[
\text{end;}
\]
\[
p:=read(2C);
\]
\[
c2:=C.0;
\]
\[
\text{for i:= 1 step 1 until n do begin if q=1 then}
\]
\[
\text{fh[1]:=fha[1]:=fa[1]:=fha[1]:=fb[1]:=fhh[1]:=1.C}
\]
\[
\text{else I[1]:=u×v/vx[1]}
\]
\[
\text{end;}
\]
\[
\text{if r>3 then for i:= 1 step 1 until n do}
\]
\[
\text{h[1]:= exp(ex((es-y[1])/k - pm));}
\]
\[
\text{recalc: c1:= c2;}
\]
\[
\text{if q=C and r<5 then for i:= 1 step 1 until n do}
\]
\[
\text{begin fh[1]:= ACTCO(b,I[1]);}
\]
\[
\text{fha[1]:= ACTCO(b-a,I[1]);}
\]
\[
\text{fa[1]:= ACTCO(a,I[1]);}
\]
\[
\text{end;}
\]
\[
\text{if q=C and r>4 then for i:= 1 step 1 until n do}
\]
\[
\text{begin fh[1]:= ACTCO(1,I[1]);}
\]
\[
\text{fa[1]:= ACTCO(a,I[1]);}
\]
\[
\text{fha[1]:= ACTCO(a-I,I[1]);}
\]
\[
\text{end;}
\]
\[
\text{goto sr[r];}
\]
\[
\text{R1: for i:= 1 step 1 until n do}
\]
\[
f[I]:= vx[I]×exp(-exy[I]/k)/fh[I];
\]
\[
\text{goto fit;}
\]
\[
\text{R2: for i:= 1 step 1 until n do}
\]
\[
f[I]:= vx[I]×exp(exy[I]/k)/fh[I];
\]
\[
\text{goto fit;}
\]
\[
\text{R3: for i:= 1 step 1 until n do}
\]
\[
f[I]:= x[I]×exp(-exy[I]/k)×fha[I]/fh[I]/fa[I];
\]
\[
\text{goto fit;}
\]
\[
\text{R4: for i:= 1 step 1 until n do}
\]
\[
f[I]:= vx[I]×(b×h[I]/fh[I]-ax(kw/h[I]a)×(1/b)/fa[I]);
\]
\[
\text{goto fit;}
\]
R5: for i:= 1 step 1 until n do begin
  if q=G then fhha[i]:= ACTCO(a-2,I[1]);
  fb[i]:= h[i]xK1/fhha[i];
  fbh[i]:= h[i]xK2xfa[i];
  if p=1 then f[i]:= vx[i]x((h[i] - kw/h[i])/fh[i])
    x(1 + fbh[i]x(1/fhha[i]+fb[i])) + txx[i]/
    vx[i]x(fb[i]x(1/fhha[i]+2xfb[i]))/
    (b + fbh[i]x((b-1)/fhha[i] + (b-2)xfb[i]));
  if p=2 then f[i]:= vx[i]x((h[i]-kw/h[i])/fh[i] +
    txxv/vx[i]x(fb[i]x(1/fhha[i] + 2xfb[i]))
    /(1 + fbh[i]x(1/fhha[i] + fb[i])))
end; goto fit;

R6: for i:= 1 step 1 until n do begin
  if q=C then begin
    fb[i]:= ACTCO(b ,I[1]);
    fbh[i]:= ACTCO(b-1,I[1])
  end;
  fhha[i]:= h[i]xK1xfa[i];
  f[i]:= ((h[i]-kw/h[i])/fh[i]xvx[i]) - tsx
  v/(1 + K2xh[i]/fbh[i])
  x (1 + fhha[i]) + txx[i]xfhha[i]
end; goto fit;

R7: for i:= 1 step 1 until n do begin
  if q=C then begin
    fb[i]:= ACTCO(b ,I[1]);
    fbh[i]:= ACTCO(b-1,I[1])
  end;
  fhha[i]:= h[i]xK1xfa[i];
  I[i]:= h[i]xK2xfb[i];
  if p = 1 then f[i]:= (vx[i]x(h[i]-kw/h[i])/fh[i])
    - txx[i]x(a- fhha[i]/(fh[i] +
    +fhha[i])) - I[i]/(fbh[i] + I[i]))/(a - fhha[i]/(fh[i] +
    + fhha[i]));
  if p = 2 then f[i]:= (vx[i]x(h[i]-kw/h[i])/fh[i])
    - txxv(a - fhha[i]/(fh[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:=C.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]xf[i];
sy2 := sy2 + f[i]f[i];
sx2 := sx2 + x[i]f[i];
end
end;
d := (n-1)xsx2-sx2;
m := ((n-1)x(sxy-sx2sy))/d;
c := (sx2xsy-sxxsy)/d;
if r<5 then c2 := if p>0 then -c/mxt/vx(if p=1 then b/a else a/b)
else -txvxm/cx(if p=-1 then b/a else a/b);
if r=5 then c2 := if p=1 then -c/mxt/v/b else -vxtxbxmxm/c;
if r>5 then c2 := if p=1 then -c/mxt/v else -vxtxm/c;
if r=4 then begin
for i := 1 step 1 until n do
begin if (kw/h[i]a)/(if p>0 then c2
else t)x(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>G then goto fit
end;
goto if q=1 or abs(c2-c1) < c2x-4 then OUT
else si[r];
I1: I2:
for i := 1 step 1 until n do
I[i] := (sxv+tx((if p=1 then -c/m else v))/vx[i];
goto recap;
I3 :
if pp = 1 then for i := 1 step 1 until n do
I[i] := (sxv+x[i]x((if p=1 then t else c2)/)
vx[i]x+exp(-exy[i]);
goto recap;
I4 :
for i := 1 step 1 until n do
I[i] := sxv/vx[i] + C.5x(bx2xh[i]/fh[i] + a/fh[i]
x(i/kw/h[i]a)/(1/b)/fa[i] + (if p>C then (tx
x[i]x((if p=1 then b else a) + c2xvX((if p=1
then a else b)))/vx[i] else (txvX((if p=-1
then b else a) + c2xx[i]x(if p=-1 then a
else b))/vx[i]));
goto recap;
A.2g

15 : if p = 1 then for i:= 1 step 1 until n do
I[i] := sxv/vx[i] + c.5x((h[i] + kw/h[i])/fh[i] +
(x[i]xt + c2vxv(b - a + a^2 - fbh[i]x(fb[i]
+ 0.5x((h[i] + kw/h[i] +
(1/fha[i] + f[i])))/vx[i]));
if p = 2 then for i:= 1 step 1 until n do
I[i] := sxv/vx[i] + c.5x((h[i] + kw/h[i])/fh[i] +
(c2x[i] + txvx((b-a) + (a^2 - f[i]
- 1)/fha[i] + 4x(a-1)xf[b[i]])/(1 + f[i]x
fa[i]x(1/fha[i] + f[i])))/vx[i]);
go to recalc;

16 : for i:= 1 step 1 until n do
I[i] := h[i]/fh[i] + (txx[i] + tsxv/(1 + fbh[i]/
K2/h[i]))/vx[i];
go to recalc;

17 : if p = 1 then for i:= 1 step 1 until n do
I[i] := (sxv + tx((b-c.5)x[i]/((1 +
((1 + fha[i])/f[i])))/vx[i] +
C.5x((h[i] + kw/h[i])/fh[i] +
+ b)x[i] - (a-1)^2xv2/((1 + fha[i])/f[i]))/vx[i] +
C.5x((h[i] + kw/h[i])/fh[i] +
+ (((b-1)^2 +
(b)x[i]xv2/((1 + fha[i])/f[i])))/vx[i]);
go to recalc;

OUT: dy := sy2 + (n-g)xct2 + m^2xvsx2
      -2x(cxsy + mxsxy - mxcxvsx);
if dy < C.C then dy := C.C;
dm := sqrt((n-g)xxy/(n-g-2)/d);
d := sqrt(dyxvsx2/d/(n-2-g));
write(7C, [[4c] M*=*]);
write(7C, F1, _m);
write(7C, [[3s] STANDARD*ERROR*IN*M*=*]);
write(7C, F1, _dm);
write(7C, [[4c] C*=*]);
write(7C, F1, _c);
write(7C, [[3s] STANDARD*ERROR*IN*C*=*]);
write(7C, F1, _d);
write(7C, [[2c] STANDARD*DEVIATION*IN*Y*=*]);
write(7C, F1, sqrt(dy/(n-2-g)));
write(7C, F1, sqrt(dy/(n-2-g)))+
writetext(7C, [[3c9s] v[8s] f*obs[8s] f*calc[7s] deviation[2c]]);
  for i:= 1 step 1 until n do
    begin newline(7C, 1);
      y[i]:= mxx[i] + c;
      write (7C, F2, x[i]);
      write (7C, F2, f[i]);
      write (7C, F2, y[i]);
      write (7C, F2, f[i]-y[i]);
      if not bo[i] then out basic symbol(7C,2c5)
    end;
  writetext(7C, [[3c3s]VE=*]);
  write(7C, F1, -c/m);
  writetext(7C, [[3s]STANDARD*ERROR*IN*VE=*]);
  write(7C, F1, -sqrt((d/c)+2+(dm/m)+2)*c/m);
  writetext(7C, [[2c]CONCENTRATION*]);
  write(7C, F1, c2);
  if in basic symbol(2c) = 142 then goto again;
    close(2c); close(7c);
  end end→