STUDIES ON
THE THERMODYNAMICS OF ION ASSOCIATION
IN AQUEOUS SOLUTIONS

A Thesis

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for the degree of

DOCTOR OF PHILOSOPY

by

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Dr. G.H. NANCOLLAS. July, 1962.

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PREFACE

The work described in this thesis was carried out at the University of Glasgow, in the Chemistry Department which is under the direction of Professor J. Monteath Robertson, C.B.E., F.R.S.

The material of Part I has been published in the Transactions of the Faraday Society and a reprint is appended at the end of the thesis.

I wish to express my sincere gratitude for the encouragement and guidance given by Dr. G.H. Nancollas under whose supervision this work was performed. Thanks are due to Dr. H.S. Dunsmore for her help with the Deuce computer and to Mr. J. Leslie for the construction of glass apparatus.

I also thank the Department of Scientific and Industrial Research for the award of a maintenance grant which made this research possible.

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SUMMARY

Studies have been made on the association in aqueous solution between divalent transition metal ions and the anions of mono-and di-carboxylic acids.

The thesis is divided into four parts. In Part I the association between the nickel ion and the malonate and n-butylmalonate anions has been studied using a cell incorporating a pair of glass electrodes and a pair of silver, silver chloride electrodes. In order to determine the best activity coefficient expression to be used, both systems were studied at low concentration, activity coefficients being calculated from the Davies equation, and at constant ionic strengths of 0.03, 0.05, 0.10, 0.15 and 0.20 M. The stability constants have been extrapolated to zero ionic strength and the thermodynamic constants are compared with those determined at low concentration.

Part II deals with the study of the association of the divalent nickel, cobalt and manganese ions with the glycinate and β-alaninate anions over the temperature range of 0^o to 45^oC using the cell

$H_2/Pt/HA,\ NaOH,\ MCl_2/AgCl/Ag.$

Activity coefficients were calculated from the equation

$$-\log \gamma_{\pm} = Az^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - \beta I\right)$$

for various values of β. A comparison of the results shows that for low ionic strengths consistent association constants are obtained with $0 \leqslant \beta \leqslant 1$. The constants determined with $\beta = 0.2$ have been used in the calculation of the thermodynamic properties. The dissociations of β-alanine have been measured over the same temperature range and the results are compared with those in the literature.

Part III describes a calorimetric determination of the heats of formation of the complexes studied in Part II. The heat of solution of potassium chloride has also been determined in order to calibrate the calorimeter.

Part IV consists of a general discussion of the results. The heat and entropy data are discussed in relation to ionic sizes and electronic structure and the entropies of ion-pairs have been calculated.

GENERAL INTRODUCTION

In electrolyte solutions the forces of attraction between ions lead to an "ionic atmosphere" of ions of one type around an oppositely charged central ion. The average distribution of negatively charged ions in the vicinity of a positive ion will therefore be greater than in the bulk of the solution.

Bjerrum[1] considered that if two oppositely charged ions approached so close together that their mutual potential energy was greater than the thermal energy, they should be considered as a separate entity in the solution. He used the Maxwell-Boltzmann distribution to calculate the distance, "q" at which there was a minimum probability of there being an ion of one type on a sphere surrounding an ion of the opposite charge, and suggested that all ions within this distance should be considered associated in ion-pairs. He suggested that the Debye-Huckel[2] activity expression should be applied only to unassociated ions.

The value of "q" obtained by Bjerrum was,

$$q = \frac{z_1 . z_2 . e^2}{2 \varepsilon kT} \qquad \ldots\ldots\ldots\ldots(1)$$

where z_1 and z_2 were the charges on the ions, ε was the dielectric constant of the solution and k was the Boltzmann constant. At 25°C this critical distance, "q", for ions in water becomes, for 1:1 electrolytes 3.6 Å, 2:2 14 Å, and for 3:3 30 Å.

Representing this entity, the ion-pair, by

$MN^{(m-n)+}_{aq}$ we can write

$$M^{m+}_{aq} + N^{n-}_{aq} \rightleftharpoons MN^{(m-n)+}_{aq} \qquad \ldots\ldots(2)$$

for which the thermodynamic association constant

$$K = \frac{\{MN^{(m-n)+}\}}{\{M^{m+}\}\{N^{n-}\}} = \frac{[MN^{(m-n)+}]}{[M^{m+}][N^{n-}]} . \frac{f_{MN}{}^{(m-n)+}}{f_M{}^{m+} \quad f_N{}^{n-}} \qquad \ldots\ldots(3)$$

where the braces enclose activities, the square brackets concentrations and the f's are the corresponding activity coefficients.

It is often impossible, where a number of new species are involved, to calculate the activity coefficients and much work has been done at constant ionic strength[3,4], in which it is assumed that the activity coefficients are also constant. These coefficients are then included in the equilibrium constant and the derived "stability quotient" is valid only at the ionic strength at which the experiments are made. Equation (3) may be written

$$K = K_c \times \frac{f_{MN}{}^{(m-n)+}}{f_M{}^{m+} \quad f_N{}^{n-}} \qquad \text{......(4)}$$

where K_c is the stability quotient or "concentration constant".

The association constant, K, can be calculated either by measuring K_c at various ionic strengths followed by extrapolation to zero ionic strength, or by direct evaluation of the activity coefficients. Although the former method is preferable, a great deal, of work is required for its application, and the calculation of activity coefficients is the method normally adopted.

The first accurate equation for the evaluation of activity coefficients of ions in solution was developed by Debye and Huckel[2]. To obtain a relationship between the potential, ψ , at any point in the solution, and the charge density, ρ , at that point, they used a combination of the Poisson equation and the Maxwell - Boltzmann distribution, obtaining

$$\rho = -\sum_i n_i . z_i . e \quad \exp. \left(\frac{z_i . e . \psi}{kT} \right) \qquad \text{.......(5)}$$

where n_i is the number of ions of charge z_i in the solution and k is the Boltzmann constant. Expansion of the exponential gives

$$\rho = \sum_i n_i \cdot z_i \cdot e - \sum_i n_i \cdot z_i \cdot e \left(\frac{z_i \cdot e \cdot \psi}{kT} \right) + \sum_i \frac{n_i \cdot z_i \cdot e}{2!} \left(\frac{z_i \cdot e \cdot \psi}{kT} \right)^2 - \ldots \qquad \ldots\ldots(6)$$

Since the solution must be electrically neutral the first term, which is a summation over all the ions in solution, is zero. Ignoring all terms higher than the second, which is the equivalent to assuming that $z_i \cdot e \ll kT$, they found

$$\rho = - \sum_i n_i \cdot z_i \cdot e \left(\frac{z_i \cdot e \cdot \psi}{kT} \right) \qquad \ldots\ldots(7)$$

The final expression for the activity coefficients is

$$- \log f_{\pm} = \frac{A z_1 \cdot z_2 \cdot \sqrt{I}}{1 + B\mathring{a} \sqrt{I}} \qquad \ldots\ldots(8)$$

where $f_{\pm}$ is the mean activity coefficient, z_1 and z_2 are the charges on the ions, A and B are constants and $\mathring{a}$ is the distance of closest approach of the ions. Although Debye and Huckel considered $\mathring{a}$ to be the mean ionic diameter of two ions, it is really a parameter correcting for a whole variety of theoretical imperfections, such as ion-solvent interactions and polarisability of ions. Values for å could be chosen such that the mean activity coefficients calculated from equation (8) agreed with experimentally obtained values at low ionic strengths. Huckel[5] attributed deviations at higher ionic strengths to changes in the dielectric constant with varying concentration, and suggested the addition of a term linear in I.

$$- \log f_{\pm} = \frac{A.z_1.z_2.\sqrt{I}}{1 + B\mathring{a}\sqrt{I}} - b\,I \qquad ......(9)$$

Equation (9) now contains two parameters and can be used for the calculation of activity coefficients over a wide concentration range.

Some workers considered that the assumption made in the derivation of equation (7) was incorrect for small ions, and attributed deviations between activity coefficients obtained from equation (8) and experimental values to this assumption. Muller[6] and Gronwall, La Mer and Sandved[7] used some of the higher terms in the expansion of the exponential in the Boltzmann distribution, but Bjerrum[1] considered that allowances should be made for ion-association, and that equations (8) and (9) should be applied only to unassociated or charged species in solution.

Guntelberg[8] put forward an equation containing no parameters,

$$- \log f_{\pm} = \frac{Az^2 \sqrt{I}}{I + \sqrt{I}} \qquad \ldots\ldots.(10)$$

which, while not as accurate as those containing parameters, had the advantage that it could be applied to systems of mixed electrolytes[9]. It could not, however, account for the differences found in activity coefficients for ions of the same charge. This difference was attributed by Guggenheim[9] to specific, short-range interactions, and to allow for these he introduced a term linear in I into equation (10). Values for the parameter were obtained from freezing-point data.

Davies[10] inserted a value for the parameter linear in ionic strength and found that activity coefficients calculated from

$$- \log f_{\pm} = Az_{\pm}^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2\ I \right) \qquad \ldots\ldots.(11)$$

agreed very well with experimental values for 1:1, 1:2 and 2:1 electrolytes. The mean deviation was ± 2% at I = 0.1. Recently[11] he has suggested that a better value for the parameter might be 0.3.

Mayer[12] developed an activity coefficient expression in the form of an infinite series of integrals, by considering a solution as an imperfect gas. The only arbitrary parameter, $\mathring{a}$, could be calculated from experimental values at any ionic strength. However, there is little to choose between this approach and that of Debye and Huckel in that there is little difference in the activity coefficients obtained by the two methods.

Any method which may be used to measure an activity or a concentration in solution is potentially suitable for the study of ion-association. Davies [13,14] and co-workers have made extensive use of conductivity measurements, deviations from the Onsager equation being attributed to ion-association. This method is particularly suited to the study of symmetrical charge-type electrolytes, since the ion-pairs formed may be assumed to have no charge and do not contribute to the observed conductivity.

The solubilities of sparingly soluble salts, in the presence of added electrolytes, have also been used by Davies [15], Monk[16] and other workers[17,18]. The enhanced solubility of the salt in the presence of complexing ions could be used to determine the extent of ion-association. Calcium, barium and copper iodates have been used to study association with carboxylate[15,16a] and amino-acid[16b] anions.

Potentiometry[19,20] has also been used extensively for ion association studies since very precise e.m.f's are obtainable with well-characterised electrodes, such as the hydrogen and silver, silver chloride electrodes. The dissociation of many weak acids has been studied in this way.

In cases where the ion-pair formation is accompanied by a shift in the absorption spectrum of one of the complexing ions, the concentration of the ion-pair can be measured directly by the change in optical density, with and without the addition of the complexing ion[21,22]. Wavelengths are normally chosen at which one of the ions involved does not absorb, thus facilitating the calculation of both the extinction coefficient of the ion-pair and K. Although at first sight an almost ideal method for determining association constants, it does suffer from a number of disadvantages.

Polarographic studies[23,24] yield information about the stability and composition of complexes in solution. The disadvantage here however, is that work must be done in the presence of a relatively large concentration of neutral electrolyte in order to limit the current to one of diffusion. The derived constants are therefore stability constants which are valid only at the ionic strength at which they are measured.

The free energy change for reactions of the type (2) can be calculated from the thermodynamic association constants. Little information can be gained from a direct correlation of these free energies with properties of the ions involved, however, and it is much more useful to regard changes in the free energy as being due to changes in the heats and entropies of ion association. For instance, endothermic reactions are known which take place because the entropy change is sufficiently large, and conversely exothermic reactions which do not because of an unfavourable entropy change. It is therefore desirable to obtain the heats and entropies of formation of the ion-pairs. Heat changes may be calculated from K values, obtained over a range of temperature, using the van't Hoff isochore, or may be obtained by direct calorimetric measurements. The latter, direct method is obviously preferable for the determination of accurate heat values, but we consider that the use of temperature coefficient data is reliable provided that a large range of temperature, such as between 0° and 45°C, is studied. In the work described in the present thesis it is found that ΔC_p is not zero, and the advantage of the temperature coefficient method is that an estimate of ΔC_p can be obtained.

The entropy change accompanying association can be attributed to two factors. The disappearance of a solute species leads to an entropy decrease, but the greater freedom of water molecules around the ions, due to charge neutralisation, gives an entropy increase. The overall entropy change will depend on the extent of hydration of the ions, and charge neutralisation. The relatively small ΔS values obtained for the formation of some lanthanum complexes suggests that the lanthanum ion retains its hydration sheath, and this conclusion is also supported by the Bjerrum distance calculated from the association constant[14].

In Part I of the present work, a cell incorporating a pair of glass electrodes and silver, silver chloride electrodes has been used to study the association of nickel ions with malonate and n-butylmalonate ions. In an attempt to determine the best activity coefficient expression to use, the system was studied, at 25°C, both at low concentration and at a series of constant ionic strengths.

In Part II a precision e.m.f. technique has been used to study the association of nickel, cobalt and manganese ions with the anions of the amino-acids glycine and β - alanine. It has also been necessary to determine the dissociation constants of β-alanine at the temperatures studied. Measurements at 0°, 15°, 25°, 35° and 45°C have yielded the thermodynamic properties of the association reactions and these are discussed.

In Part III the heats of formation have been determined by a direct calorimetric method, and Part IV consists of a general discussion.

PART I

ASSOCIATION IN NICKEL MALONATE AND n-BUTYLMALONATE SOLUTIONS

Introduction.

One of the best methods of obtaining thermodynamic association constants is by extrapolating stability quotients, K_c, obtained at various ionic strengths to zero ionic strength. Accurate extrapolations can only be obtained, however, if K_c is measured at sufficiently low ionic strengths.

Assuming that the activity coefficients in equation (4) can be represented by equations (8) or (9),

$$\log K = \log K_c - A\Delta(z^2)\frac{\sqrt{I}}{1+B\mathring{a}\sqrt{I}} \quad \ldots\ldots(12)$$

or

$$\log K = \log K_c - A\Delta(z^2)\frac{\sqrt{I}}{1+B\mathring{a}\sqrt{I}} + bI, \quad \ldots\ldots(13)$$

where $\Delta(z^2) = \left(Z^{2}_{MN}(m-n)+ \; - Z^{2}_{M}m+\right)^{2} - Z^{2}_{N}n-$.

Nasanen[25] has used a least squares treatment to calculate log K, $\mathring{a}$ and b from equation (13), but other workers have obtained log K as the intercept of a linear plot. Kraus and Nelson[26] chose a value for $\mathring{a}$ such that a plot of $\log K_c$ against $\frac{\sqrt{I}}{1+B\mathring{a}\sqrt{I}}$ was linear, and the slope gave $A\Delta(z^2)$. Monk[27] has plotted

$\log K_c - A\Delta(Z^2)\frac{\sqrt{I}}{1+B\mathring{a}\sqrt{I}}$ against I for various values of $\mathring{a}$, and has obtained values for log K and b.

Although the extrapolation method yields accurate association constants, experiments are normally done at low concentrations and equation (8), or a similar expression, used to calculate the activity coefficients. There is some uncertainty, however, about the equation to be used for this calculation, and it has been suggested that the use of the simple Debye-Huckel expression, equation (8), is unjustified[28]. The values of the parameters are also uncertain. For instance, if $\mathring{a}$ has its original meaning its value will depend on whether or not the ions retain their hydration sheaths when in the associated form. Many workers prefer to consider $\mathring{a}$ as an arbitrary parameter, and Fernelius[29] has used an $\mathring{a}$ value of 10Å for the association of the acetylacetonate ion with various metal ions.

Guggenheim[30] has suggested that for 2:2 electrolytes a value of $\mathring{a}$ similar to q, the Bjerrum distance, should be used. He considered that $\mathring{a}$ should be about 10Å - and, instead of the Davies equation, gave

$$- \log f_{\pm} = Az^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 2.0I \right) \qquad \ldots\ldots(14)$$

which corresponds to a value of 9Å in equation (8). When used for calculations with bivalent metal sulphates, however, Nair and Nancollas[31] found that the K values were no longer constant, but varied by as much as 20%.

Brown and Prue[32] used freezing point measurements to study association in solutions of bivalent metal sulphates. Using equation (8) with å ranging from 4 to 14 Å, they found that all values fitted the experimental results reasonably well, although the best fit was obtained with the lower values. Prue, however, suggested that the association constant, K, was in fact an arbitrary parameter dependent upon the value of å used.

In some cases X-ray data can be used to justify particular å values. Beevers and Lipson[33] for instance, in the study of $Cu\ SO_4.5H_2O$, found Cu-S distances of 3.5 and 3.6 Å. This appears to support the adoption of small å values for bivalent metal sulphates, as does some work by Nasanen[25], who studied spectrophotometrically the association in copper sulphate solutions at various ionic strengths, and using equation (13), obtained an å of 4.7 Å.

Some recent sound-absorption measurements by Eigen[34] have shown kinetically the existance of distinct species e.g. $M\ OH_2\ N^{(m-n)+}$ and $MN^{(m-n)+}$, in solutions. Measured K values contain contributions from both species and, if a sufficiently large å value is chosen, a definite K rather than the arbitrary parameter suggested by Prue should be obtained.

The work presented in this part of the thesis was done in order to determine the best expression to be used for calculating activity coefficients in a solution of a 2:2 electrolyte. Nickel malonate solutions have been studied both at low concentration, the activity coefficients being evaluated by means of Davies' equation, and at a series of constant ionic strengths. In order to study the effect of a variation in the size of the anion, nickel-butylmalonate has also been studied. Accurate values for the dissociation constants of n-butylmalonic acid have been obtained and both acids have been studied at constant ionic strengths of 0.03, 0.05, 0.10, 0.15 and 0.20.

EXPERIMENTAL

Preparation of Reagents

Malonic Acid: Hopkins and Williams material was recrystallised three times from a mixture of ether and benzene containing 5% petroleum ether (60 - 80)[35], and dried in vacuo at 45° to 50°C. Analysis gave H, 4%; C, 34.84%; (calculated: H, 3.87%; C, 34.62%).

n-Butylmalonic Acid: This was prepared by hydrolysis of the diethyl ester followed by ether extraction, and recrystallised as for malonic acid. Analysis gave H, - 7.70%; C, 52.55%; (calculated: H, 7.55%; C, 52.49%).

Sodium Hydroxide: Samples of a saturated solution of sodium hydroxide, which had been prepared by shaking AnalaR pellets with distilled water for 24 hours and then allowed to stand for 3 to 4 weeks, were diluted with carbon dioxide free distilled water in a nitrogen atmosphere. Solutions were stored in a container connected to an automatic burette and suitably protected with soda-lime tubes. They were standardised by titrating against weighed samples of potassium hydrogen phthalate and duplicate experiments agreed to 0.1%.

Nickel Chloride: Solutions were prepared from the AnalaR salt and were standardised either by gravimetric analysis of the chloride, as silver chloride[36], or by using an ion-exchange column. In the latter method

10 ml. portions were passed through a column of Amberlite I.R. 120 resin, in the hydrogen form, and the column washed with distilled water until free from acid. The eluted hydrochloric acid was estimated by titration with standard sodium hydroxide.

Sodium Perchlorate: Solutions were either prepared by neutralising AnalaR perchloric acid with carbonate-free sodium hydroxide, or were made up from solid sodium perchlorate. The B.D.H. material, low in chloride, was found to contain appreciable quantities of chlorate. This was removed by recrystallising three times from absolute alcohol. The concentrations of solutions were estimated on an ion-exchange column as described above.

Potassium chloride and potassium hydrogen phthalate were of AnalaR grade and were used without further purification.

All volumetric apparatus was of Grade A quality. Flasks and cells were cleaned with chromic acid and, where possible, were steamed for thirty minutes. Samples of reagents were weighed out from small pyrex weighing bottles using an Oertling single-pan balance.

APPARATUS

E.m.f. measurements were made using the cell $Ag/AgCl$, HCl (0.2M) /glass/ solution under study /$AgCl/Ag$.

In the early work a pair of silver, silver chloride electrodes and a single glass electrode were used, but in later work a pair of glass electrodes were substituted. These were of a screened type (E.I.L. type G.G.33.) to prevent leakage of current, and when two were used any irregularity in the behaviour of one of them was immediately detectable. The silver, silver chloride electrodes were of the thermal-electrolytic type, described by Harned[37], set in a standard, Quickfit B.19 cone. Platinum spirals, sealed into glass tubes which were curved to fit the cell, were given two coatings of spectroscopically pure silver oxide (Johnston-Matthey and Co., Hatton Garden, London), made into a paste with conductivity water. The silver oxide was converted to silver by heating at 450°C in a muffle furnace. The electrodes, approximately 100 mgms. in weight, were chloridised, in the absence of light, by electrolysis in normal hydrochloric acid at a current density of 2 m.amps per sq.cm. They were then conditioned by warming in distilled water at 50°C for two hours[38], and stored in the dark, in distilled water containing a little potassium chloride.

E.m.f.'s were measured using a Pye potentiometer. A Vibron electrometer (E.I.L. model 33B) was used as a null detector, and readings were reproducible to ± 0.1m.v.

Experimental Technique.

The cell used is shown in Fig. 1. A known volume of solution was introduced and the electrodes placed in the ground glass sockets. Nitrogen was bubbled through the capillary tube A to remove carbon dioxide and to stir the solution, and an outlet bubbler, B, prevented diffusion of air back into the cell. A capillary attachment from the automatic burette entered the cell by the socket C. When solution was initially put into the cell one hour was allowed for equilibration, but during a titration 10 to 15 minutes after each addition was all that was necessary.

For the determination of the dissociation constants of the acids, sodium hydroxide was added to a solution containing known weights of acid and potassium chloride. When necessary a constant ionic strength was maintained by the addition of the calculated amount of sodium perchlorate. In the calculations, any readings were discarded in which the ionic strength was not within 1%

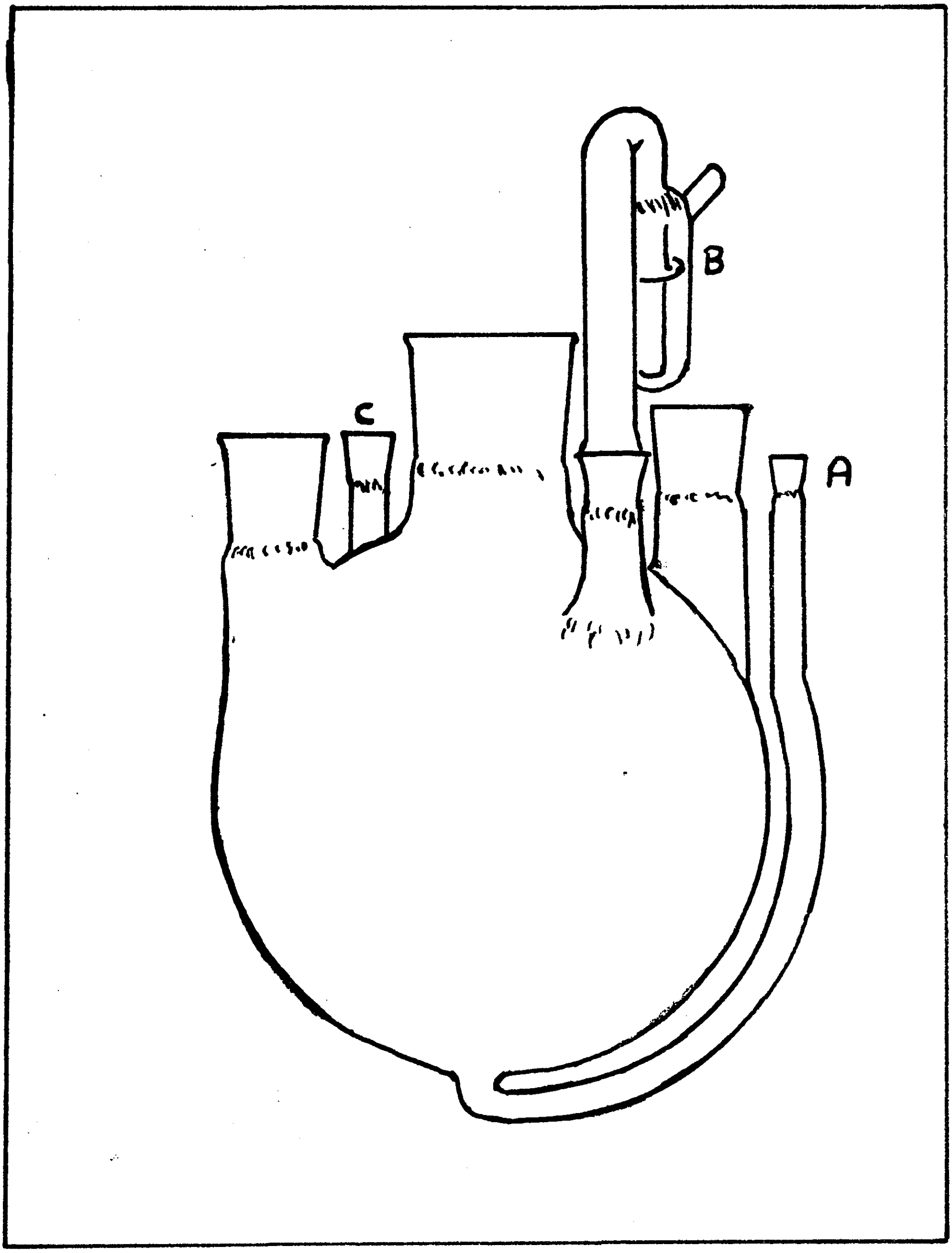


Fig. 1

of the required value.

In the association studies, nickel chloride replaced potassium chloride in the cell, and sodium hydroxide was added slowly to prevent precipitation of the hydroxide. Occasionally, however, additions of nickel chloride were made during an experiment, or solutions containing all of the necessary electrolytes were introduced into the cell.

Standardisation of Electrodes.

The electrodes were standardised before each titration and two methods were employed.

1) Standardisation with Hydrochloric Acid Solutions.

For low concentration studies, standard hydrochloric acid was added, from a burette, to distilled water in the cell, and linear plots of $- \log [H^+] [Cl^-] f_1^2$ against E, the e.m.f., were obtained. E^o was given by the intercept and, since $[H^+] = [Cl^-]$, the slope of the line was $(k+k')/2$, where $k = 2.303RT/F$ and k' is the modified value of k for the glass electrode.

At constant ionic strength, the calculated amount of sodium perchlorate was added to the hydrochloric acid, and additions of this were made to a sodium perchlorate solution in the cell. Plots of $- \log [H^+] [Cl^-]$ against E were again linear, as shown in Fig. 2.

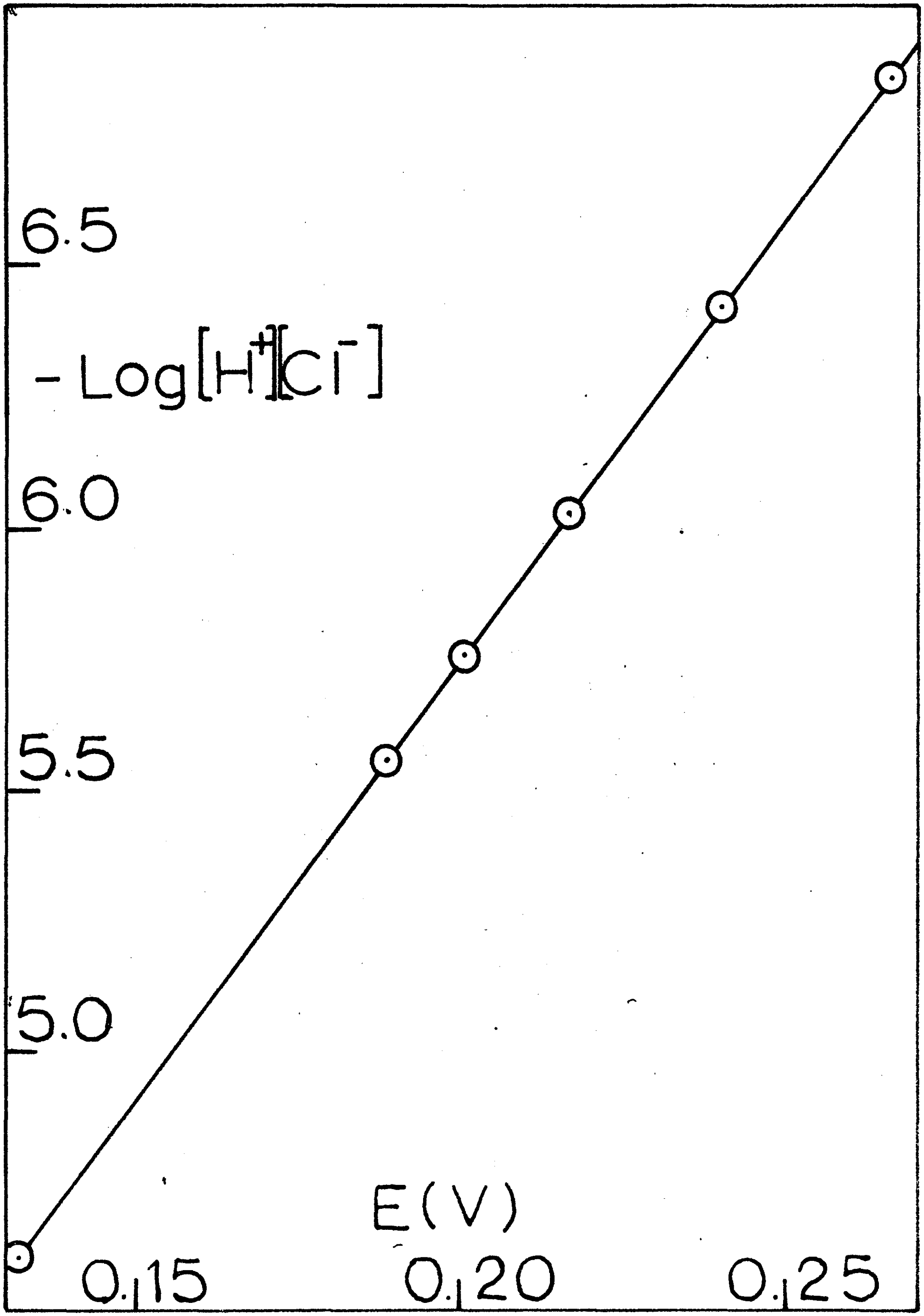


FIG. 2

2) Standardisation in Situ.

Additions of sodium hydroxide were made to a solution containing potassium chloride and malonic acid. The dissociation constants of malonic acid[39] were then used to calculate the hydrogen ion activities from

$$\left[H^+\right]^3 + \frac{k_1}{f_1^2}\left\{1 + \frac{\left[Na^+\right]^2 f_1^2}{k_1}\right\}\left[H^+\right]^2$$

$$+ \frac{k_1}{f_1^2 f_2}\left\{k_2 + \left[Na^+\right] f_2 - Ta\, f_2\right\}\left[H^+\right]$$

$$+ \frac{k_1 k_2}{f_1^2 f_2}\left\{\left[Na^+\right] - 2Ta\right\} = 0 \qquad ......(15)$$

Equation (15) was solved, using a high-speed, electronic Deuce computer, by successive approximations for I, the ionic strength, where

$$I = \left[H^+\right] + \left[Na^+\right] + \left[Cl^-\right] + \left[A^=\right]. \qquad ......(16)$$

A linear plot of $-\log\left[H^+\right] f_1$ against $E + k \log\left[Cl^-\right] f_1$ yielded k' and E^o, and unknown $\log\left\{H^+\right\}$ values could be derived from the observed e.m.f.'s to within ± 0.003.

RESULTS

It was necessary to study the dissociation of n-butylmalonic acid at low concentration and of both acids at the ionic strengths to be used.

In solutions containing the acid, potassium chloride and sodium hydroxide, the concentrations of the ionic species were obtained from the equations for total acid,

$$Ta = [H_2A] + [HA^-] + [A^=] \qquad \ldots\ldots(17)$$

electroneutrality,

$$[H^+] + [K^+] + [Na^+] = [Cl^-] + [HA^-] + 2[A^=] \ldots\ldots(18)$$

and the ionic strength

$$I = [H^+] + [Na^+] + [Cl^-] + [A^=] . \qquad \ldots\ldots(16)$$

A graphical method, suggested by Speakman[40] for the dissociation of dibasic acids, was used in the determination of

$$k_1 = \frac{[H^+][HA^-] f_1^2}{[H_2A]}$$

and

$$k_2 = \frac{[H^+][A^=] f_2}{[HA^-]} .$$

$$Y = Xk_1 + k_1k_2 \qquad \ldots\ldots(19)$$

$$\text{where } X = \frac{[H^+]\left\{Ta - [Na^+] - [H^+]\right\} f_2}{2Ta - [Na^+] - [H^+]}$$

and

$$Y = \frac{[H^+]^2 \left\{[Na^+] + [H^+]\right\} f_1^2 f_2}{2Ta - [Na^+] - [H^+]} .$$

X and Y were calculated by successive approximations using the Deuce computer, and $[A^=]$ was obtained from the equation

$$[A^=] = \frac{k_2\, Ta}{[H^+]\, f_2 + \frac{[H^+]^2 f_1^2 f_2}{k_1} + k_2} \quad \text{......(20)}$$

An approximate value of k_2 was used in the initial calculations.

k_1 was determined, by the method of least squares, from solutions in which $Ta > [Na^+]$ and the plots of X against Y are shown in Fig. 3. When $Ta < [Na^+]$ k_2 was obtained by substituting the average k_1 in equation (19). The new value of k_2 was then used in the calculation of $[A^=]$ and the process repeated until k_1 and k_2 were constant. These values are given in Table 1 which shows the good agreement between the results of two titrations, and also between the pairs of electrodes. In subsequent experiments, however, where a pair of glass electrodes were employed the mean $[H^+]$ value has been used in the calculations.

k_1', at constant ionic strength, was calculated in

Expt.	1	2	3	4	5
$10^3 Ta$	5.479	5.458	5.436	5.416	5.520
$10^3 b$	2.543	2.923	3.300	3.674	1.968

Expt.	$10^4[H^+]$	$10^2 I$	$10^5[A^=]$	$10^5 X$	$10^8 Y$
	RUN 53		Electrode 1		
1	7.809	1.278	0.751	13.853	13.234
2	6.480	1.299	0.969	10.425	10.124
3	5.170	1.321	1.306	7.407	7.134
4	3.966	1.343	1.827	4.908	4.649
			$k_1 = 9.60 \times 10^{-4}$		
	RUN 54		Electrode 1		
5	10.265	1.267	0.512	20.286	19.595
6	8.643	1.286	0.655	15.911	15.364
7	7.136	1.305	0.854	12.074	11.579
8	5.799	1.326	1.129	8.837	8.476
9	4.513	1.348	1.561	6.055	5.677
10	3.486	1.372	2.152	3.930	3.768
			$k_1 = 9.61 \times 10^{-4}$		

b = Total Base = $\{Na^+]$

TABLE 1a

k_1 Determination

6	7	8	9	10
5.498	5.477	5.455	5.434	5.413
2.352	2.734	3.112	3.488	3.860
$10^4[H^+]$	$10^2 I$	$10^5[A^=]$	$10^5 X$	$10^8 Y$
		Electrode 2		
7.864	1.279	0.745	13.924	13.450
6.485	1.300	0.970	10.431	10.141
5.143	1.321	1.316	7.379	7.054
3.986	1.343	1.818	4.926	4.699

$k_1 = 9.64 \times 10^{-4}$

Electrode 2

10.227	1.267	0.514	20.234	19.420
8.651	1.286	0.654	15.922	15.396
7.147	1.305	0.852	12.088	11.620
5.813	1.326	1.125	8.852	8.519
4.528	1.348	1.555	6.070	5.716
3.486	1.372	2.151	3.930	3.768

$k_1 = 9.60 \times 10^{-4}$

Mean $k_1 = 9.61\ (\pm 0.01) \times 10^{-4}$

Expt.	1	2	3	4	5
$10^3 T_a$	5.244	5.224	5.205	5.186	5.167
$10^3 b$	6.741	7.089	7.435	7.778	8.118

Expt.	$10^6[H^+]$	$10^2 I$	$10^3[A^-]$	$-10^6 X$	$10^{12} Y$	$10^6 k_2$
			Electrode 1			
1	4.608	1.730	1.508	1.090	17.315	1.11
2	3.368	1.797	1.871	1.095	10.703	1.11
3	2.500	1.866	2.245	1.087	6.893	1.10
4	1.892	1.933	2.607	1.088	4.680	1.09
5	1.443	1.999	2.955	1.097	3.288	1.10
6	3.884	1.778	1.678	1.170	13.120	1.08
7	2.879	1.846	2.040	1.074	8.375	1.08
8	2.167	1.913	2.404	1.073	5.585	1.08
9	1.670	1.978	2.743	1.092	3.959	1.10
10	1.219	2.048	3.143	1.056	2.576	1.06
11	0.889	2.115	3.511	1.042	1.714	1.04

TABLE 1b

k_2 Determination

6	7	8	9	10	11
5.242	5.223	5.203	5.184	5.165	5.146
6.916	7.262	7.607	7.948	8.287	8.624
$10^6[H^+]$	$10^2 I$	$10^3[A^=]$	$-10^6 X$	$10^{12} Y$	$10^6 k_2$
		Electrode 2			
4.828	1.731	1.516	1.142	19.006	1.16
3.551	1.798	1.871	1.155	11.902	1.17
2.643	1.866	2.242	1.150	7.706	1.16
2.005	1.933	2.601	1.153	5.255	1.16
1.521	1.999	2.957	1.157	3.652	1.16
3.960	1.778	1.678	1.091	13.642	1.11
2.961	1.845	2.029	1.105	8.864	1.11
2.206	1.913	2.407	1.092	5.783	1.10
1.682	1.979	2.760	1.099	4.011	1.10
1.238	2.049	3.147	1.073	2.651	1.08
0.914	2.114	3.501	1.073	1.823	1.08

Mean k_2 = 1.11 (±0.03) x 10^{-6}

Y ordinates displaced for clarity

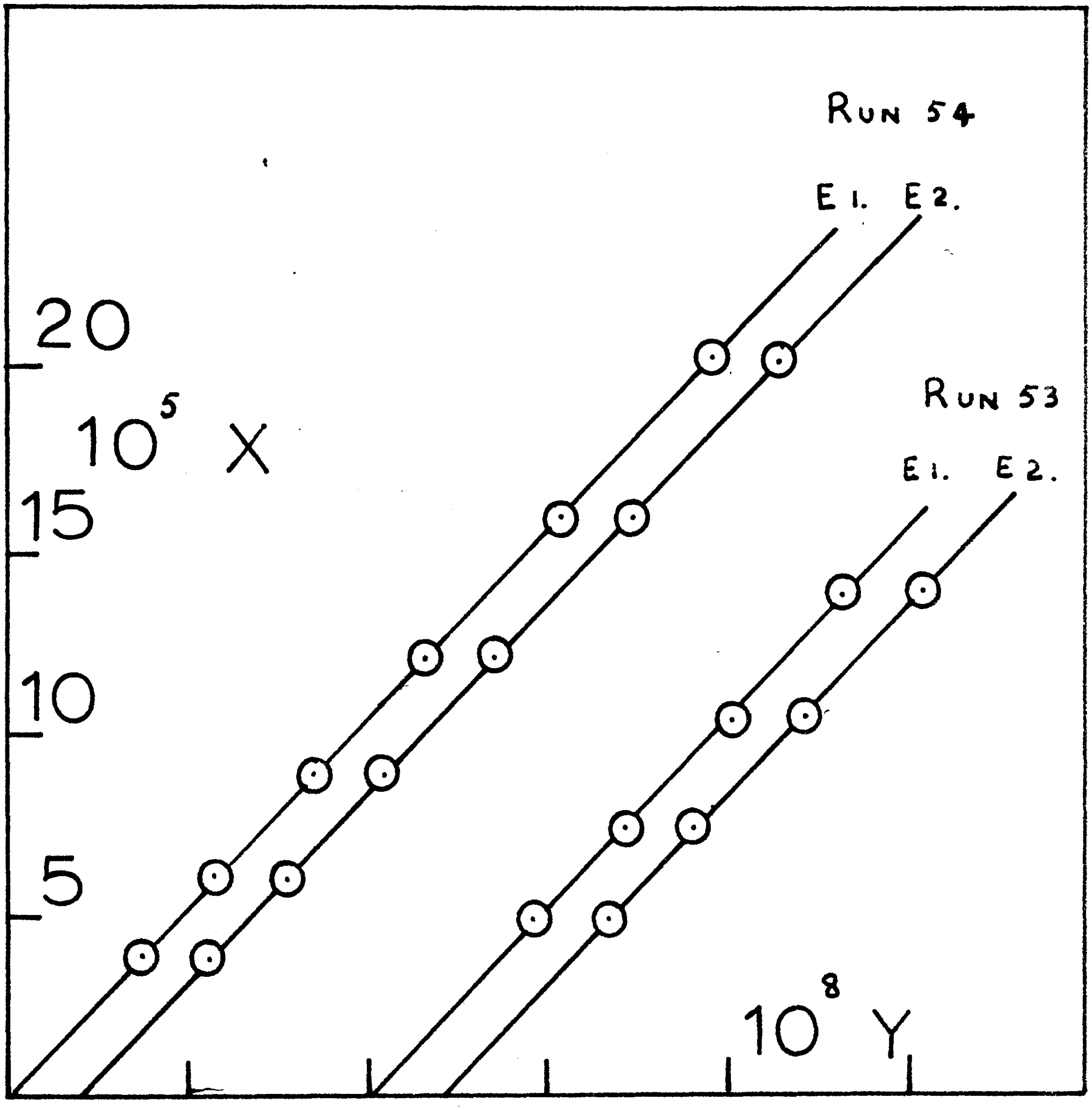


Fig. 3

TABLE 2

RUN 25 $I = 0.03$

10^3Ta	10^3b	$10^3[H^+]$	10^4 X	10^7Y
5.267	1.616	1.429	4.240	8.309
5.246	1.968	1.242	3.472	6.793
5.236	2.143	1.155	3.120	6.126
5.216	2.490	0.984	2.463	4.829
5.205	2.663	0.900	2.160	4.217

Mean $k_1' = 1.96 \times 10^{-3}$

RUN 26

5.590	2.038	1.320	3.767	7.478
5.557	2.559	1.058	2.738	5.399
5.547	2.731	0.973	2.425	4.741
5.525	3.074	0.815	1.862	3.610
5.515	3.245	0.741	1.608	3.103

Mean $k_1' = 2.01 \times 10^{-3}$

Mean $k_1' = 1.99\ (\pm\ 0.03) \times 10^{-3}$

TABLE 3

RUN 19 I = 0.05

10^3Ta	10^3b	$10^3[H^+]$	10^4X	10^7Y
5.066	1.968	1.263	3.358	7.461
5.046	2.317	1.076	2.656	5.866
5.026	2.663	0.893	2.021	4.361
5.007	3.006	0.735	1.484	3.224
4.988	3.347	0.586	1.024	2.238

Mean $k_1' = 2.16 \times 10^{-3}$

RUN 20

10^3Ta	10^3b	$10^3[H^+]$	10^4X	10^7Y
5.245	1.792	1.324	3.823	7.411
5.221	2.212	1.109	2.959	5.742
5.200	2.559	0.947	2.327	4.559
5.160	3.245	0.644	1.273	2.503
5.140	3.583	0.507	0.859	1.695

Mean $k_1' = 1.92 \times 10^{-3}$

Mean $k_1' = 2.04\ (\pm\ 0.12) \times 10^{-3}$

TABLE 4

RUN 90 — I = 0.10

$10^3 Ta$	$10^3 b$	$10^3 [H^+]$	$10^4 X$	$10^7 Y$
5.586	1.970	1.430	4.021	8.944
5.564	2.486	1.165	2.981	6.629
5.542	2.997	0.917	2.082	4.592
5.520	3.505	0.700	1.347	3.012
5.499	4.008	0.494	0.758	1.694

Mean $k_1' = 2.22 \times 10^{-3}$

RUN 91

5.567	1.970	1.425	3.999	8.911
5.550	2.357	1.223	3.203	7.113
5.534	2.742	1.037	2.497	5.579
5.518	3.124	0.857	1.866	4.139
5.486	3.883	0.540	0.877	1.971

Mean $k_1' = 2.22 \times 10^{-3}$

Mean $k_1' = 2.22 \times 10^{-3}$

TABLE 5

RUN 31 I = 0.15

$10^3 T_a$	$10^3 b$	$10^3 [H^+]$	$10^4 X$	$10^7 Y$
5.413	2.320	1.199	3.108	6.937
5.392	2.667	1.038	2.473	5.623
5.371	3.011	0.873	1.894	4.319
5.351	3.352	0.722	1.390	3.199
5.330	3.691	0.578	0.960	2.230

Mean $k_1' = 2.22 \times 10^{-3}$

RUN 32

5.371	2.494	1.101	2.736	6.100
5.350	2.839	0.933	2.125	4.735
5.329	3.182	0.772	1.584	3.511
5.309	3.522	0.631	1.129	2.560
5.289	3.859	0.487	0.737	1.657

Mean $k_1' = 2.22 \times 10^{-3}$

Mean $k_1' = 2.22 \times 10^{-3}$

TABLE 6

RUN 41 I = 0.20

$10^3 Ta$	$10^3 b$	$10^3[H^+]$	$10^4 X$	$10^7 Y$
5.355	1.968	1.424	3.819	9.396
5.323	2.544	1.115	2.655	6.502
5.303	2.924	0.923	1.988	4.849
5.282	3.301	0.747	1.415	3.465
5.262	3.675	0.577	0.929	2.257

Mean $k_1' = 2.42 \times 10^{-3}$

RUN 42

5.206	1.968	1.358	3.602	8.658
5.185	2.353	1.152	2.820	6.779
5.165	2.734	0.955	2.123	5.071
5.145	3.113	0.774	1.521	3.637
5.106	3.861	0.450	0.606	1.478

Mean $k_1' = 2.39 \times 10^{-3}$

Mean $k_1' = 2.41\ (\pm 0.02) \times 10^{-3}$

TABLE 7

RUN 80

I = 0.03

10^3Ta	10^3b	$10^3[H^+]$	10^4X	10^7Y
5.461	2.076	0.992	3.023	3.845
5.439	2.527	0.802	2.241	2.836
5.429	2.751	0.712	1.893	2.378
5.407	3.197	0.554	1.298	1.627
5.397	3.419	0.480	1.043	1.305

Mean $k_1' = 1.27 \times 10^{-3}$

RUN 81

5.495	2.415	0.873	2.502	3.256
5.484	2.639	0.787	2.147	2.313
5.473	2.863	0.699	1.810	2.360
5.463	3.086	0.619	1.507	1.968
5.452	3.308	0.543	1.232	1.609

Mean $k_1' = 1.30 \times 10^{-3}$

Mean $k_1' = 1.29\ (\pm 0.02) \times 10^{-3}$

TABLE 8

RUN 73 $I = 0.05$

$10^3 T_a$	$10^3 b$	$10^3 [H^+]$	$10^4 X$	$10^7 Y$
5.521	1.849	1.173	3.655	5.183
5.488	2.527	0.873	2.406	3.417
5.456	3.197	0.617	1.428	2.049
5.435	3.640	0.468	0.919	1.333
5.414	4.079	0.334	0.521	0.767

Mean $k_1' = 1.41 \times 10^{-3}$

RUN 74

$10^3 T_a$	$10^3 b$	$10^3 [H^+]$	$10^4 X$	$10^7 Y$
5.533	1.621	1.295	4.158	5.999
5.495	2.415	0.931	2.617	3.789
5.468	2.975	0.701	1.730	2.486
5.447	3.419	0.552	1.176	1.747
5.426	3.860	0.396	0.702	1.011

Mean $k_1' = 1.42 \times 10^{-3}$

Mean $k_1' = 1.42\ (\pm\ 0.01) \times 10^{-3}$

TABLE 9

RUN 58 $I = 0.10$

10^3Ta	10^3b	$10^3[H^+]$	10^4X	10^7Y
5.467	2.161	1.075	3.116	4.854
5.446	2.544	0.900	2.420	3.747
5.425	2.923	0.748	1.827	2.862
5.404	3.300	0.600	1.306	2.035
5.373	3.860	0.410	0.698	1.108

Mean $k_1' = 1.55 \times 10^{-3}$

RUN 59

5.491	1.775	1.263	3.901	6.103
5.459	2.352	0.985	2.756	4.266
5.438	2.734	0.823	2.115	3.292
5.396	3.488	0.538	1.090	1.724
5.375	3.860	0.410	0.699	1.107

Mean $k_1' = 1.55 \times 10^{-3}$

Mean $k_1' = 1.55 \times 10^{-3}$

TABLE 10

RUN 63 I = 0.15

$10^3 Ta$	$10^3 b$	$10^3 [H^+]$	$10^4 X$	$10^7 Y$
5.438	2.123	1.115	3.211	5.265
5.416	2.537	0.922	2.447	3.987
5.395	2.948	0.754	1.800	2.965
5.374	3.357	0.595	1.245	2.057
5.354	3.762	0.452	0.793	1.324

Mean $k_1' = 1.61 \times 10^{-3}$

RUN 64

$10^3 Ta$	$10^3 b$	$10^3 [H^+]$	$10^4 X$	$10^7 Y$
5.474	1.914	1.219	3.652	5.962
5.453	2.330	1.012	2.823	4.523
5.431	2.743	0.833	2.121	3.405
5.410	3.153	0.675	1.528	2.495
5.389	3.560	0.518	1.182	1.634

Mean $k_1' = 1.62 \times 10^{-3}$

Mean $k_1' = 1.62\ (\pm 0.01) \times 10^{-3}$

TABLE 11

RUN 55 I = 0.20

10^3Ta	10^3b	$10^3[H^+]$	10^4X	10^7Y
5.390	2.161	1.106	3.126	5.317
5.348	2.923	0.767	1.815	3.101
5.328	3.300	0.612	1.248	2.172
5.307	3.674	0.479	0.855	1.472
5.287	4.046	0.355	0.509	0.896

Mean $k_1' = 1.68 \times 10^{-3}$

RUN 56

10^3Ta	10^3b	$10^3[H^+]$	10^4X	10^7Y
5.194	1.968	1.120	3.232	5.310
5.174	2.352	0.941	2.509	4.137
5.153	2.774	0.772	1.871	3.075
5.133	3.112	0.614	1.321	2.149
5.114	3.488	0.479	0.877	1.453

Mean $k_1' = 1.64 \times 10^{-3}$

Mean $k_1' = 1.66\ (\pm\ 0.02) \times 10^{-3}$

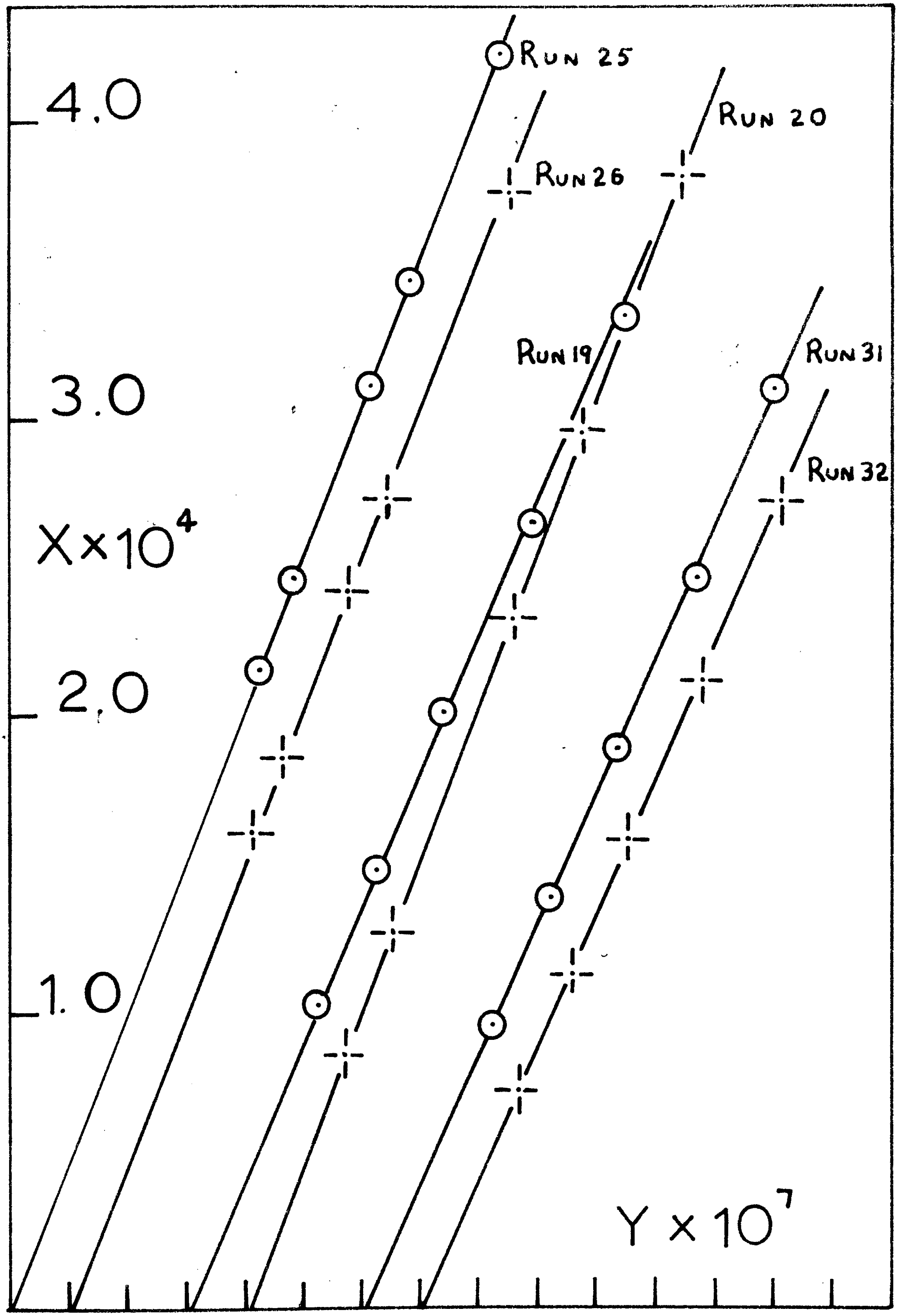


Fig. 4

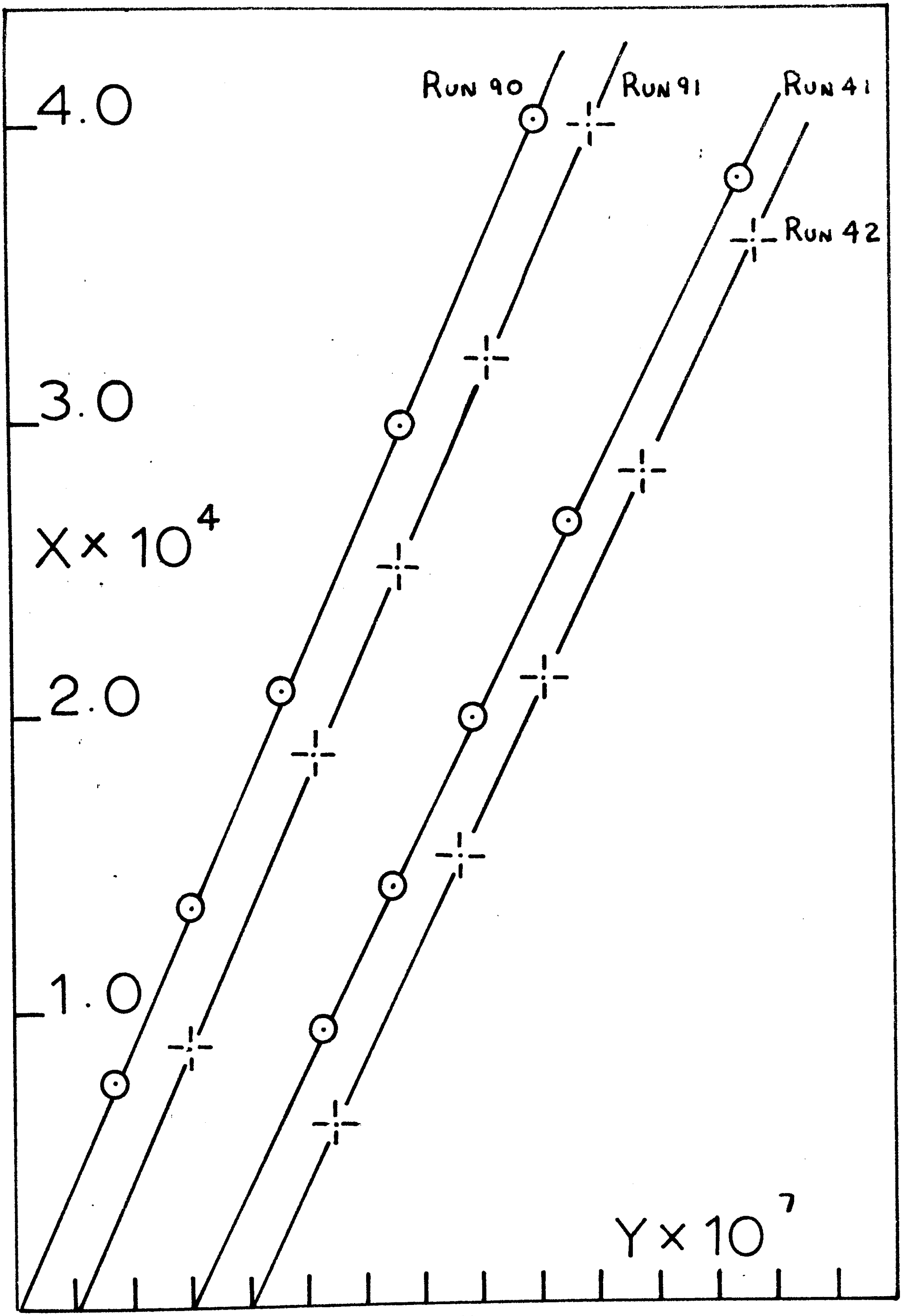


Fig. 5

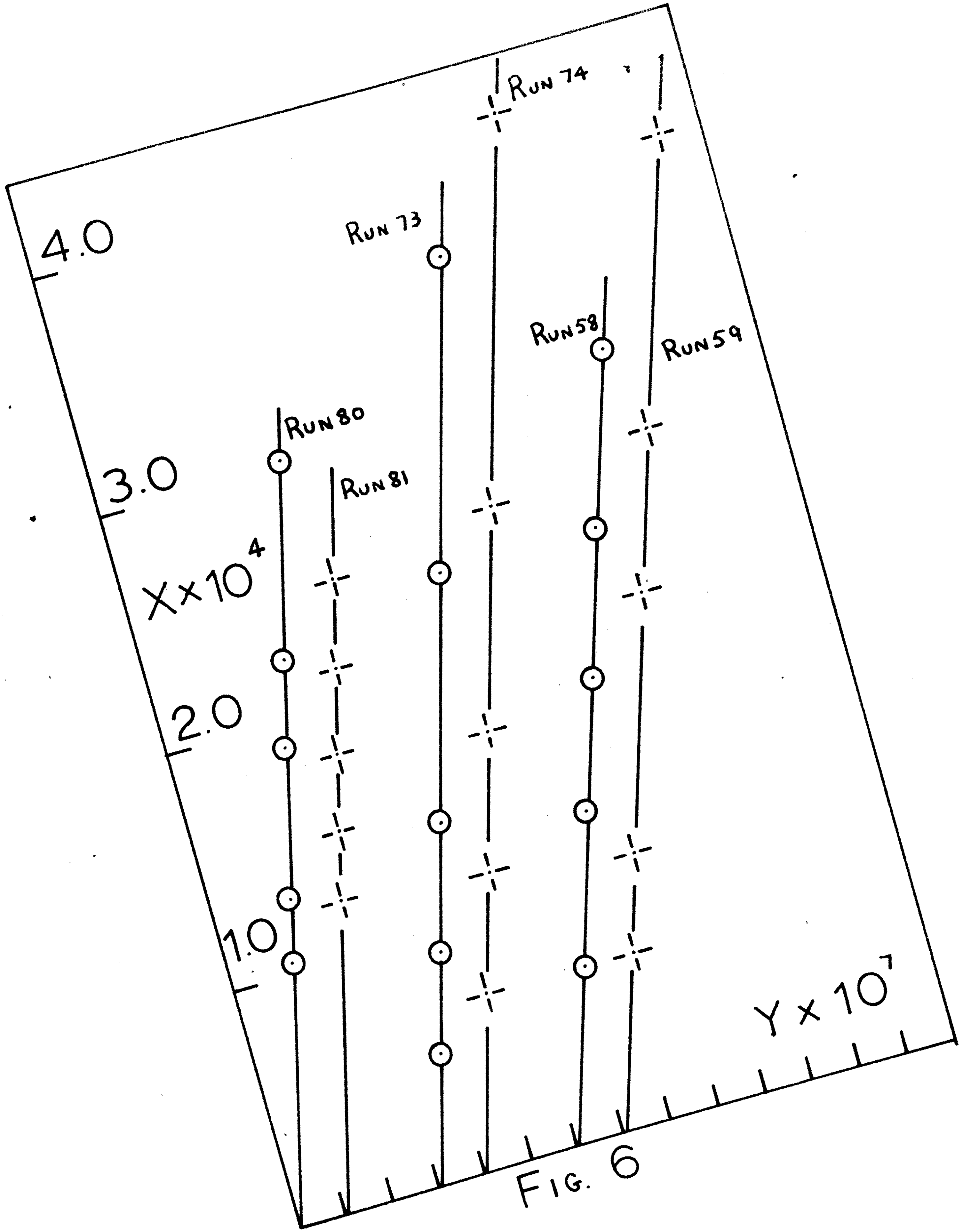


Fig. 6

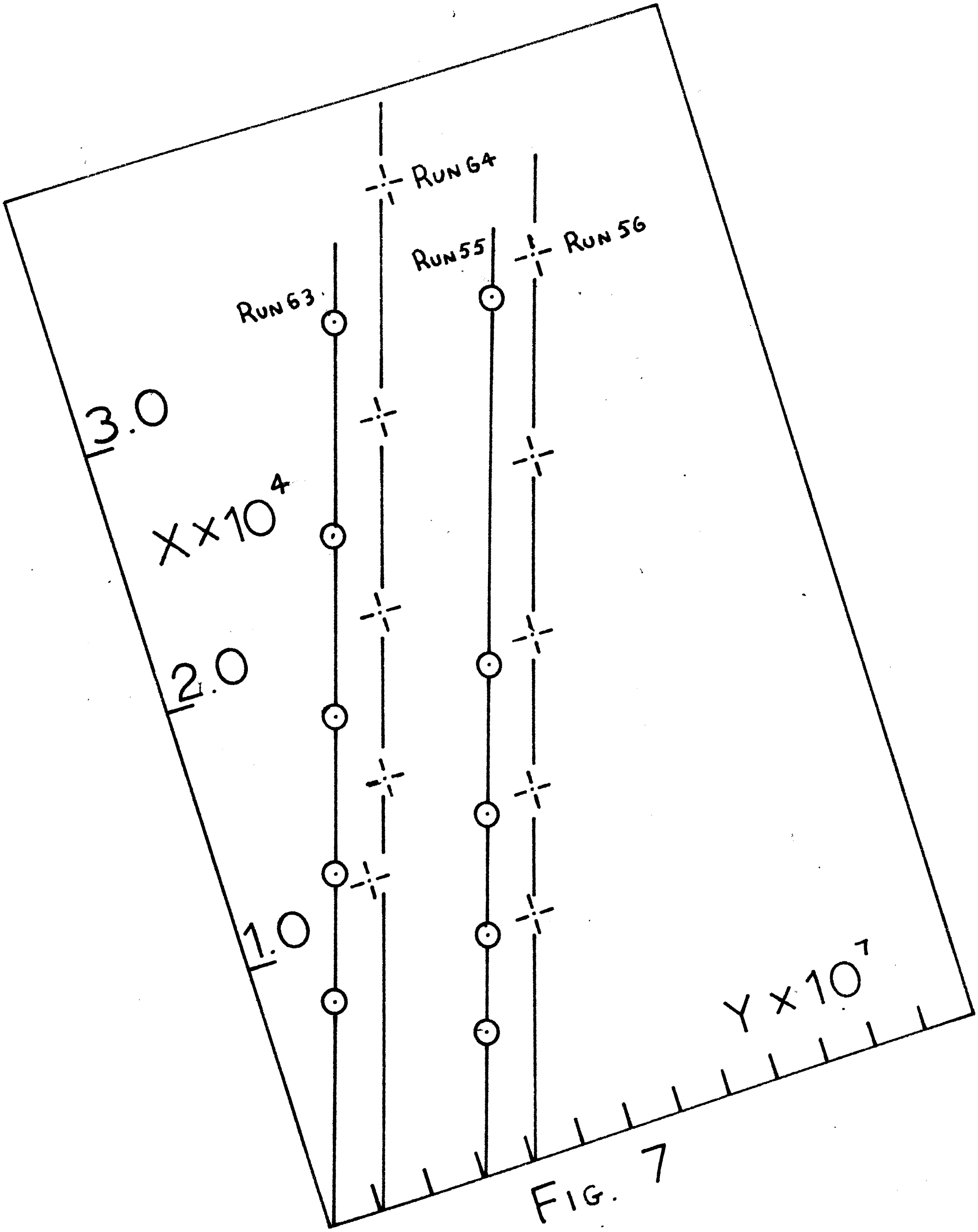


Fig. 7

TABLE 12 I = 0.03

$10^3 Ta$	$10^3 b$	$10^5[H^+]$	$10^3[HA^-]$	$10^3[A^=]$	$10^6 k_2'$
5.427	8.007	0.3969	2.832	2.590	3.63
5.417	8.159	0.3546	2.663	2.750	3.66
5.408	8.310	0.3168	2.494	2.910	3.70
5.114	8.442	0.1948	1.780	3.332	3.65
5.844	7.553	0.3674	4.091	1.736	3.68
5.370	8.886	0.1950	1.847	3.520	3.72
5.589	7.998	0.5053	3.159	2.422	3.87

Mean $k_2 = 3.70 \pm 0.05$

TABLE 13 I = 0.05

$10^3 Ta$	$10^3 b$	$10^5[H^+]$	$10^3[HA^-]$	$10^3[A^=]$	$10^6 k_2'$
5.012	6.928	0.6652	3.070	1.932	4.19
5.003	7.084	0.5776	2.900	2.095	4.17
4.994	7.239	0.5076	2.730	2.257	4.20
4.975	7.548	0.3887	2.390	2.581	4.20
4.966	7.702	0.3416	2.220	2.742	4.22
4.771	6.614	0.6521	2.904	1.859	4.17
4.754	6.928	0.4909	2.563	2.185	4.19
4.736	7.239	0.3624	2.222	2.501	4.08
4.719	7.548	0.2683	1.882	2.834	4.04

Mean $k_2 = 4.15 \pm 0.05$

TABLE 14

$I = 0.10$

10^3Ta	10^3b	$10^5[H^+]$	$10^3[HA^-]$	$10^3[A^=]$	$10^6k'_2$
5.384	6.709	1.5349	3.988	1.368	5.27
5.364	7.188	1.0158	3.496	1.851	5.38
5.343	7.664	0.6822	2.998	2.336	5.32
5.323	8.136	0.4708	2.496	2.822	5.32
5.303	8.604	0.3186	1.994	3.307	5.28
5.361	6.829	1.3108	3.834	1.505	5.15
5.345	7.188	0.9556	3.463	1.868	5.15
5.330	7.545	0.7186	3.088	2.232	5.19
5.300	8.253	0.4080	2.335	2.961	5.17
5.285	8.604	0.3021	1.959	3.324	5.13

Mean $k'_2 = 5.24 \pm 0.08$

TABLE 15

$I = 0.15$

10^3Ta	10^3b	$10^5[H^+]$	$10^3[HA^-]$	$10^3[A^=]$	$10^6k'_2$
5.139	6.782	1.2902	3.443	1.676	6.28
5.120	7.095	0.9818	3.108	1.999	6.31
5.111	7.251	0.8516	2.940	2.160	6.26
5.064	8.020	0.4528	2.095	2.965	6.41
5.046	8.324	0.3366	1.759	3.284	6.28
5.012	6.309	1.6683	3.644	1.341	6.14
4.993	6.625	1.2428	3.312	1.663	6.24
4.957	7.251	0.7070	2.638	2.310	6.19
4.938	7.560	0.5427	2.300	2.633	6.21
4.920	7.867	0.4087	1.962	2.955	6.16

Mean $k'_2 = 6.25 \pm 0.06$

TABLE 16 I = 0.20

$10^3 T_a$	$10^3 b$	$10^5 [H^+]$	$10^3 [HA^-]$	$10^3 [A^=]$	$10^6 k_2'$
5.136	6.916	1.2255	3.309	1.810	6.70
5.116	7.263	0.9082	2.938	2.167	6.70
5.098	7.607	0.6860	2.566	2.524	6.75
5.079	7.949	0.5144	2.194	2.880	6.75
5.060	8.288	0.3742	1.823	3.235	6.64
5.281	7.090	1.2576	3.424	1.839	6.75
5.262	7.436	0.9360	3.055	2.195	6.73
5.242	7.779	0.7128	2.683	2.551	6.78
5.223	8.119	0.5387	2.312	2.906	6.77
5.204	8.457	0.3996	1.941	3.260	6.71

Mean $k_2' = 6.73 \pm 0.03$

TABLE 17 I = 0.03

$10^3 T_a$	$10^3 b$	$10^5 [H^+]$	$10^3 [HA^-]$	$10^3 [A^=]$	$10^6 k_2'$
5.291	7.268	0.3741	3.291	1.990	2.26
5.286	7.371	0.3433	3.180	2.097	2.26
5.281	7.474	0.3238	3.069	2.204	2.33
5.276	7.577	0.2868	2.959	2.311	2.24
5.242	7.268	0.3623	3.194	2.039	2.31
5.237	7.371	0.3200	3.084	2.146	2.23
5.232	7.474	0.3077	2.972	2.253	2.33
5.227	7.577	0.2693	2.862	2.359	2.22

Mean $k_2' = 2.27 \pm 0.04$

TABLE 18 I = 0.05

10^3Ta	10^3b	$10^5[H^+]$	$10^3[HA^-]$	$10^3[A^=]$	$10^6k'_2$
5.208	7.474	0.3308	2.926	2.276	2.57
5.189	7.884	0.2342	2.483	2.702	2.55
5.170	8.292	0.1665	2.041	3.126	2.55
5.190	6.829	0.5441	3.518	1.658	2.56
5.180	7.069	0.4396	3.266	1.904	2.56
5.170	7.308	0.3602	3.014	2.149	2.57

Mean k'_2 = 2.56 ± 0.01

TABLE 19 I = 0.10

10^3Ta	$10^3[Na^+]$	$10^5[H^*]$	$10^3[HA^-]$	$10^3[A^=]$	$10^6k'_2$
5.193	7.089	0.5645	3.267	1.914	3.31
5.174	7.435	0.4143	2.893	2.273	3.26
5.155	7.778	0.3113	2.518	2.631	3.25
5.215	6.741	0.7213	3.647	1.551	3.07
5.195	7.089	0.5285	3.274	1.911	3.08
5.176	7.435	0.3903	2.899	2.270	3.06
5.157	7.778	0.2929	2.524	2.629	3.05

Mean k'_2 = 3.15 ± 0.1

TABLE 20

$I = 0.15$

$10^3\mathrm{Ta}$	$10^3\mathrm{b}$	$10^5[\mathrm{H}^+]$	$10^3[\mathrm{HA}^-]$	$10^3[\mathrm{A}^=]$	$10^6 k'_2$
5.164	7.459	0.4558	2.849	2.307	3.69
5.145	7.833	0.3352	2.444	2.696	3.70
5.107	8.572	0.1724	1.637	3.469	3.65
5.237	6.511	1.0890	3.900	1.311	3.66
5.198	7.271	0.5430	3.100	2.088	3.66
5.179	7.646	0.3978	2.695	2.473	3.66
5.160	8.019	0.2948	2.290	2.866	3.69

Mean $k'_2 = 3.67 \pm 0.02$

TABLE 21

$I = 0.20$

$10^3\mathrm{Ta}$	$10^3\mathrm{b}$	$10^5[\mathrm{H}^+]$	$10^3[\mathrm{HA}^-]$	$10^3[\mathrm{A}^=]$	$10^6 k'_2$
5.148	6.566	1.0198	3.675	1.451	4.03
5.110	7.262	0.5429	2.933	2.167	4.01
5.091	7.607	0.4130	2.559	2.526	4.08
5.077	6.566	0.9467	3.538	1.579	4.06
5.058	6.916	0.6764	3.168	1.877	4.01
5.040	7.262	0.5026	2.795	2.236	4.02
5.021	7.607	0.3808	2.420	2.595	4.08

Mean $k'_2 = 4.04 \pm 0.03$

the same manner, the activity coefficients being omitted from equation (19). The results are given in Tables 2 to 6 for malonic acid and 7 to 11 for n-butylmalonic acid, and the plots of X against Y are shown in Figs. 4 to 7. The concentrations of the ionic species required for the calculation of the corresponding k'_2 values were obtained from equations (17) and (18). The results of these calculations are given in Tables 12 to 21.

Solutions were prepared containing nickel chloride, the required acid and sodium hydroxide in such proportions that only the complex NiA would be expected.

$$Ni^{2+} + A^{=} \rightleftharpoons NiA \qquad \text{......(21)}$$

The concentrations of the ionic species in such solutions were obtained from the equations for total acid,

$$Ta = [H_2A] + [HA^-] + [A^=] + [NiA], \qquad \text{......(22)}$$

total metal,

$$Tm = [Ni^{2+}] + [NiA], \qquad \text{......(25)}$$

electroneutrality,

$$[H^+] + [Na^+] + 2[Ni^{2+}] = [Cl^-] + [HA^-] + 2[A^=] \text{......(24)}$$

and ionic strength

$$I = \tfrac{1}{2}\left\{6Tm - 4Ta + [Na^+] + [H^+] + 4[H_2A] + 5[HA^-] + 8[A^=]\right\} \text{....(25)}$$

The association constant

$$K = \frac{[NiA]}{[Ni^{2+}][A^=]\,f_2^2} \qquad \text{.......(26)}$$

was obtained by successive approximations of I, using the Deuce cumputer. Results are given in Table 22 for malonate and in Table 23 for n-butylmalonate. The stability constants, K_c, at constant ionic strength, were calculated in a similar manner, and the results are given in Tables 24 to 33. Data for all the experiments are summarised in Tables 34 and 35.

Writing equation (26) as

$$K = K_c \times \frac{1}{f_2^2}$$

and, representing the activity coefficients by the extended Debye-Huckel equation,

$$\log K = \log K_c + \frac{4.072\sqrt{I}}{1+B\mathring{a}\sqrt{I}} - 2bI \qquad \ldots\ldots(13)$$

or

$$\log K = \alpha - 2bI.$$

α was calculated for various values of å, between 0 and 20Å, and plotted against I. The choice of the correct activity expression was governed by the fact that the plot was necessarily to be linear and that the curves for values of å close to the correct value should intersect of the α-axis. Figs. 8 and 9 show such curves for malonates and n-butylmalonates for å from 0 to 20Å.

Figs. 10 and 11 show a more detailed analysis for å between 0 and 5Å. It is seen that the required straight lines are only obtained for å values between 2 and 3Å.

10^3Ta	10^3Tm	10^3b
4.269	4.428	6.026
4.254	4.590	6.005
4.247	4.670	5.995
4.240	4.750	5.985
3.784	4.474	5.218
3.777	4.555	5.209
3.771	4.637	5.200
3.765	4.451	5.191

10^3Ta	10^3Tm	10^3b
5.214	5.177	6.916
5.195	5.158	7.262
5.176	5.139	7.607
5.157	5.120	7.948
5.060	4.165	6.391
5.041	4.149	6.741
5.022	4.134	7.089
4.985	4.104	7.778

b = total base= $[Na^+]$.

TABLE 22

Nickel Malonate   Low Concentration

$10^5[H^+]$	10^2I	$10^4[A^{2-}]$	$10^3[MA]$	$10^{-4}K$
5.647	1.694	1.431	1.742	1.29
5.904	1.737	1.367	1.748	1.30
6.047	1.759	1.333	1.751	1.31
6.181	1.780	1.303	1.754	1.31
6.634	1.710	1.124	1.465	1.24
6.762	1.733	1.102	1.467	1.24
6.867	1.755	1.085	1.469	1.24
7.002	1.778	1.063	1.471	1.24

Mean K = 1.27 ± 0.03

TABLE 23

Nickel n-Butyl Malonate   Low Concentration

$10^5[H^+]$	10^2I	$10^4[A^{2-}]$	$10^3[MA]$	$10^{-3}K$
1.626	1.879	4.024	1.359	2.65
1.163	1.844	5.027	1.605	2.66
0.838	1.811	6.130	1.844	2.69
0.593	1.788	7.479	2.061	2.63
1.875	1.612	3.563	1.048	2.63
1.280	1.584	4.704	1.276	2.62
0.902	1.558	5.928	1.505	2.65
0.446	1.525	8.933	1.912	2.66

Mean K = 2.65 ± 0.02

10^3Ta	10^3Tm	10^3b
5.042	4.898	7.251
5.032	4.889	7.406
5.014	4.871	7.714
5.215	3.918	7.251
5.206	3.911	7.406
5.196	3.904	7.560

10^3Ta	10^3Tm	10^3b
4.810	4.925	6.771
4.801	4.916	6.928
4.793	4.907	7.084
4.775	4.889	7.394
4.766	4.880	7.548
5.294	3.925	7.084
5.274	3.911	7.394
5.265	3.904	7.548
5.246	3.889	7.855
5.236	3.882	8.007

TABLE 24 I = 0.03

$10^5[H^+]$	$10^3[HA^-]$	$10^4[A^=]$	$10^3[NiA]$	$10^{-3}K$
4.447	2.668	2.219	2.092	3.36
3.800	2.524	2.458	2.214	3.37
2.710	2.226	3.039	2.454	3.34
3.981	3.018	2.799	1.856	3.22
3.364	2.875	3.165	1.966	3.19
2.842	2.725	3.538	2.078	3.22

Mean K_c = 3.28 ± 0.07

TABLE 25 I = 0.05

$10^5[H^+]$	$10^3[HA^-]$	$10^4[A^=]$	$10^3[NiA]$	$10^{-3}K$
4.610	2.682	2.416	1.826	2.44
3.922	2.538	2.689	1.945	2.44
3.324	2.390	2.989	2.064	2.43
2.384	2.084	3.635	2.303	2.45
1.985	1.927	4.041	2.416	2.43
4.781	3.302	2.868	1.628	2.47
3.461	3.018	3.622	1.843	2.46
2.979	2.868	3.996	1.955	2.51
2.148	2.561	4.949	2.163	2.53
1.821	2.404	5.484	2.262	2.55

Mean K_c = 2.47 ± 0.04

10^3Ta	10^3Tm	$10^3[Na^+]$
5.217	5.193	7.251
5.169	5.660	7.185
5.123	6.119	7.120
5.032	7.011	6.993
5.014	6.987	7.292
5.202	4.162	7.095
5.183	4.147	7.406
5.164	4.131	7.714
5.117	4.606	7.644
5.071	5.071	7.575

TABLE 26 I = 0.10

$10^5[H^+]$	$10^3[HA^-]$	$10^4[A^=]$	$10^3[NiA]$	$10^{-3}K$
4.714	3.009	3.345	1.810	1.60
5.135	2.965	3.026	1.833	1.58
5.575	2.923	2.747	1.851	1.58
6.443	2.841	2.311	1.877	1.58
4.998	2.570	2.694	2.117	1.61
4.140	3.149	3.986	1.595	1.56
3.027	2.851	4.935	1.799	1.55
2.204	2.541	6.041	1.993	1.54
2.510	2.508	5.235	2.057	1.54
2.827	2.475	4.588	2.105	1.55

Mean $K_c = 1.57 \pm 0.02$

$10^3 T_a$	$10^3 T_m$	$10^3 b$
4.967	5.231	6.625
4.948	5.212	6.939
4.939	5.202	7.095
4.912	5.174	7.560
4.894	5.155	7.867
5.303	4.131	7.714
5.274	4.109	8.172
5.264	4.101	8.324
5.217	4.572	8.249
5.170	5.035	8.175

$10^3 T_a$	$10^3 T_m$	$10^3 b$
5.104	5.456	6.535
5.085	5.435	6.868
5.048	5.396	7.525
5.029	5.376	7.851
5.237	5.461	6.452
5.217	5.441	6.785
5.179	5.401	7.444
5.160	5.381	7.770

TABLE 27 I = 0.15

$10^5[H^+]$	$10^3[HA^-]$	$10^4[A^=]$	$10^3[NiA]$	$10^{-3}K$
5.971	3.083	3.227	1.478	1.22
4.447	2.801	3.934	1.698	1.23
3.838	2.653	4.318	1.809	1.23
2.420	2.192	5.660	2.130	1.24
1.742	1.874	6.731	2.332	1.23
2.703	2.797	6.474	1.825	1.22
1.723	2.322	8.438	2.090	1.23
1.473	2.161	9.189	2.170	1.22
1.660	2.136	8.043	2.260	1.22
1.871	2.111	7.055	2.336	1.23

Mean $K_c = 1.23 \pm 0.01$

TABLE 28 I = 0.20

$10^5[H^+]$	$10^3[HA^-]$	$10^4[A^=]$	$10^3[NiA]$	$10^{-3}K$
7.352	3.394	3.107	1.297	1.00
5.420	3.109	3.860	1.521	1.01
2.946	2.481	5.668	1.970	1.01
2.138	2.149	6.765	2.187	1.01
9.339	3.645	2.627	1.187	1.06
6.963	3.384	3.271	1.408	1.07
3.827	2.787	4.901	1.858	1.07
2.798	2.464	5.927	2.074	1.06

Mean $K_c = 1.04 \pm 0.03$

10^3Ta	10^3Tm	10^3b
5.264	5.235	6.957
5.259	5.230	7.061
5.254	5.225	7.165
4.967	4.196	6.749
4.963	4.192	6.853
4.958	4.188	6.957
4.953	4.184	7.061

10^3Ta	10^3Tm	10^3b
5.122	4.184	7.061
5.113	4.176	7.268
5.103	4.168	7.474
5.094	4.160	7.680
5.314	5.279	6.829
5.304	5.269	7.069
5.284	5.249	7.545
5.274	5.240	7.782

TABLE 29 $I = 0.03$

$10^5[H^+]$	$10^3[HA^-]$	$10^4[A^=]$	$10^3[NiA]$	$10^{-2}K$
1.650	3.465	4.766	1.278	6.78
1.497	3.363	5.089	1.348	6.82
1.359	3.260	5.442	1.415	6.82
1.166	3.117	6.048	1.217	6.76
1.040	3.013	6.576	1.268	6.60
0.952	2.906	6.944	1.336	6.75
0.852	2.800	7.477	1.387	6.63

Mean $K_c = 6.74 \pm 0.07$

TABLE 30 $I = 0.05$

$10^5[H^+]$	$10^3[HA^-]$	$10^4[A^=]$	$10^3[NiA]$	$10^{-2}K$
1.012	3.129	7.931	1.178	4.94
0.852	2.914	8.776	1.304	5.17
0.686	2.699	10.013	1.390	5.00
0.581	2.481	10.952	1.507	5.19
1.865	3.684	5.043	1.078	5.09
1.500	3.452	5.891	1.227	5.15
0.973	2.973	7.845	1.507	5.13
0.788	2.728	8.841	1.647	5.19

Mean $K_c = 5.11 \pm 0.07$

10^3Ta	10^3Tm	10^3b
5.207	5.313	6.511
5.187	5.293	6.892
5.168	5.274	7.271
5.149	5.254	7.646
5.090	4.259	6.320
5.071	4.243	6.702
5.052	4.227	7.082

10^3Ta	10^3Tm	10^3b
5.132	5.313	6.511
5.113	5.293	6.892
5.093	5.274	7.271
5.245	5.308	6.607
5.226	5.289	6.987
5.206	5.269	7.365
5.187	5.249	7.739

TABLE 31 I = 0.10

$10^5[H^+]$	$10^3[HA^-]$	$10^4[A^=]$	$10^3[NiA]$	$10^{-2}K$
2.046	3.782	5.811	0.794	3.02
1.419	3.406	7.555	0.995	3.06
0.996	3.017	9.502	1.182	3.04
0.713	2.621	11.627	1.354	2.98
1.937	3.746	6.083	0.688	3.17
1.317	3.368	8.038	0.870	3.21
0.932	2.976	10.081	1.049	3.28

Mean K_c = 3.11 ± 0.08

TABLE 32 I = 0.15

$10^5[H^+]$	$10^3[HA^-]$	$10^4[A^=]$	$10^3[NiA]$	$10^{-2}K$
1.990	3.642	6.717	0.773	2.53
1.392	3.263	8.614	0.960	2.57
0.990	2.871	10.643	1.140	2.59
2.101	3.766	6.581	0.773	2.59
1.470	3.388	8.459	0.961	2.63
1.048	2.998	10.480	1.140	2.64
0.748	2.603	12.736	1.298	2.58

Mean K_c = 2.59 ± 0.03

10^3Ta	10^3Tm	10^3b
5.181	5.303	6.702
5.161	5.284	7.082
5.142	5.264	7.459
5.123	5.244	7.833
5.245	5.308	6.607
5.231	5.293	6.892
5.211	5.274	7.271
5.192	5.254	7.646

TABLE 33 $I = 0.20$

$10^5[H^+]$	$10^3[HA^-]$	$10^4[A^=]$	$10^3[NiA]$	$10^{-2}K$
1.829	3.562	7.865	0.792	2.23
1.303	3.178	9.876	0.971	2.28
0.925	2.785	12.099	1.132	2.26
0.667	2.387	14.396	1.286	2.26
2.123	3.767	7.178	0.713	2.16
1.623	3.485	8.690	0.843	2.18
1.151	3.097	10.881	1.004	2.16
0.836	2.702	12.994	1.177	2.22

Mean K_c= 2.22 ± 0.04

TABLE 34

Nickel Malonate Equilibrium Constants

I	$10^3 k_1$	$10^6 k_2$	$10^{-3} K$
0	1.40	2.07	12.7±0.3
0.03	1.99±0.03	3.70±0.05	3.28±0.07
0.05	2.04±0.12	4.15±0.05	2.47±0.04
0.10	2.22±0.01	5.24±0.08	1.57±0.02
0.15	2.22±0.01	6.25±0.06	1.23±0.01
0.20	2.41±0.02	6.73±0.03	1.04±0.03

TABLE 35

Nickel n-Butyl Malonate Equilibrium Constants

I	$10^3 k_1$	$10^6 k_2$	$10^{-2} K$
0	0.96±0.01	1.11±0.03	26.5±0.2
0.03	1.29±0.02	2.27±0.04	6.74±0.07
0.05	1.42±0.01	2.56±0.01	5.11±0.07
0.10	1.55±0.01	3.15±0.10	3.11±0.08
0.15	1.62±0.01	3.67±0.02	2.59±0.03
0.20	1.66±0.03	4.04±0.03	2.22±0.04

All the available data have not been given in Tables 1 to 33. While the constants are the average values of all results the mean deviations differ in some cases from those reported in Trans. Faraday Soc., 1962, 58, 354.

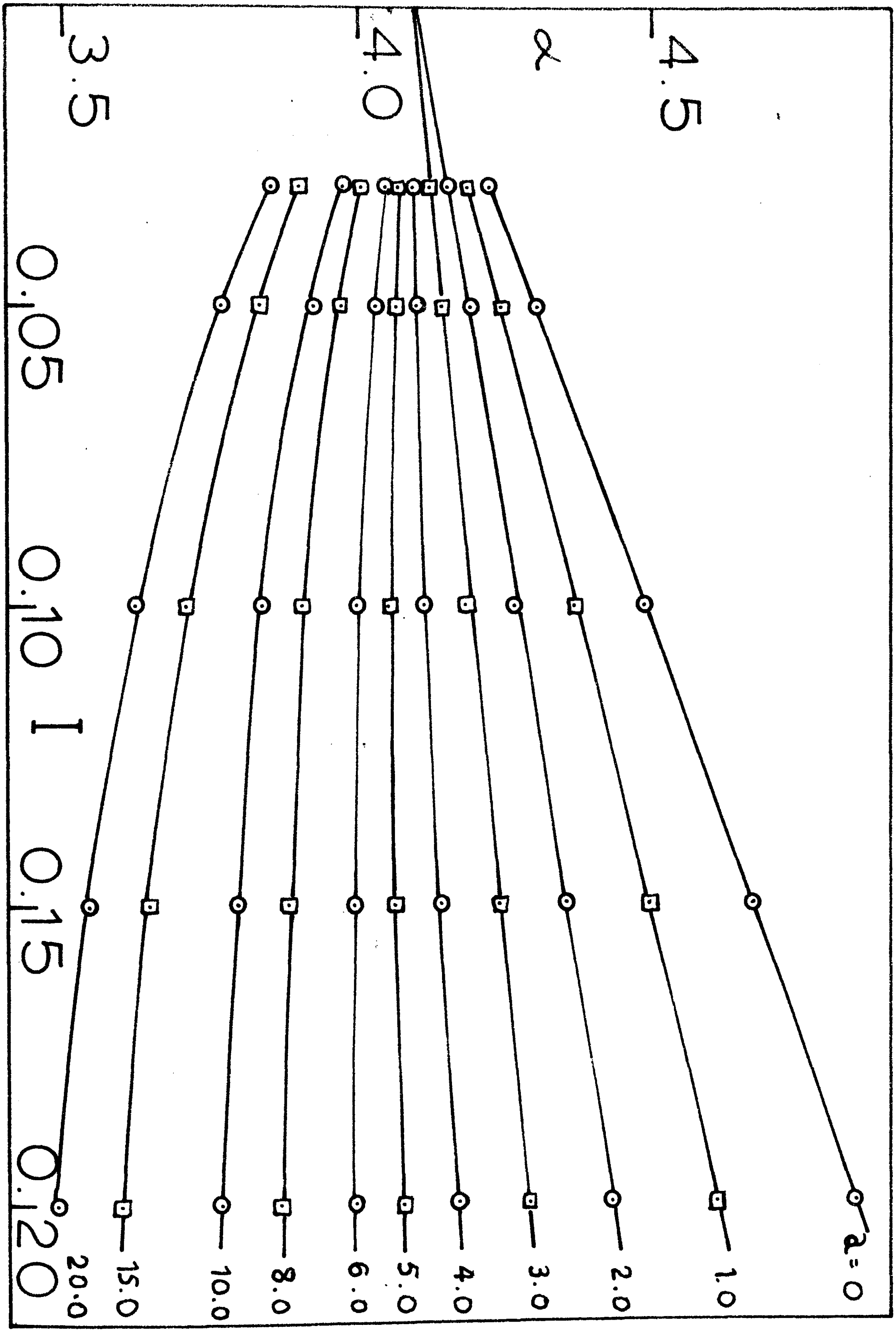


FIG. 8

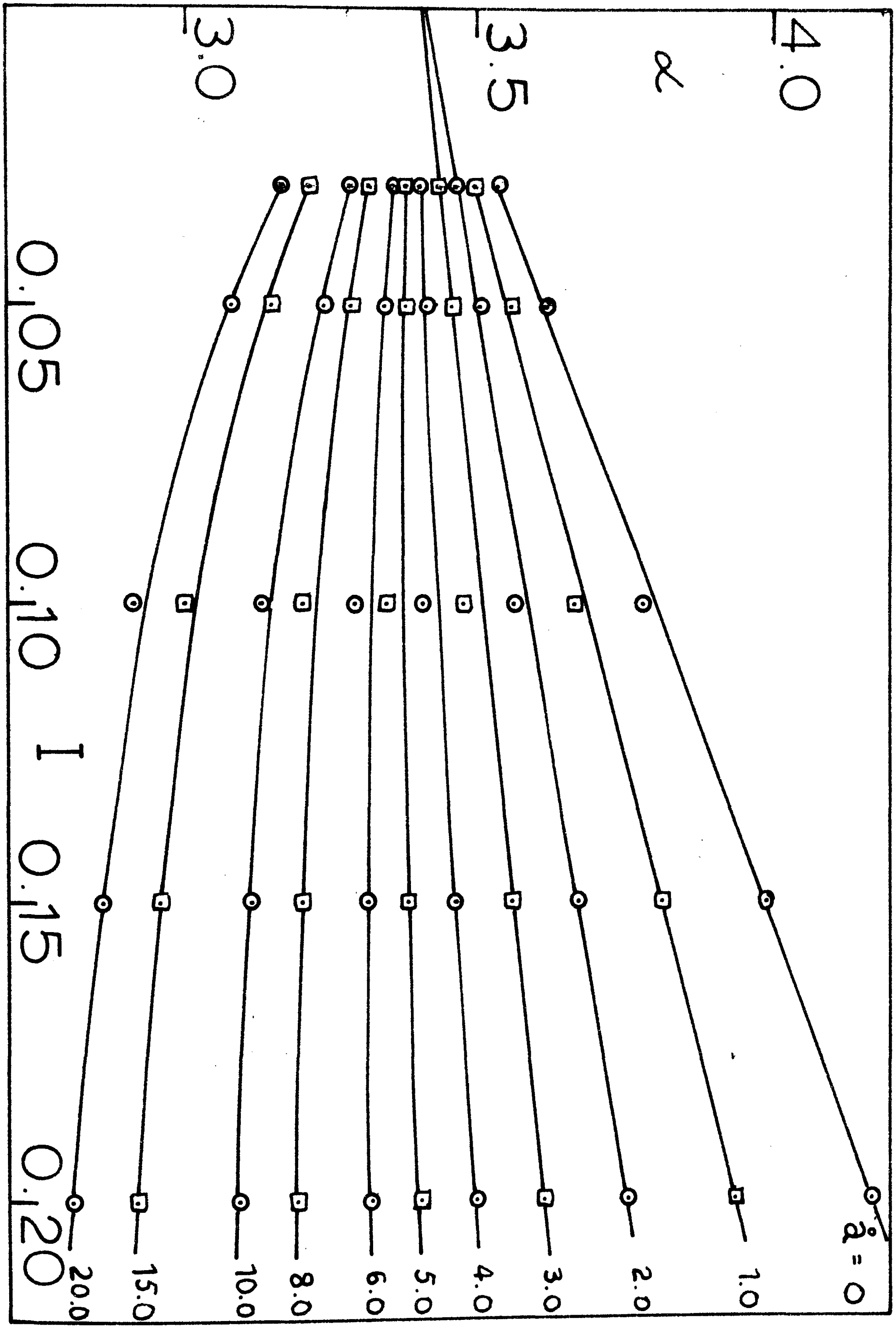


FIG. 9

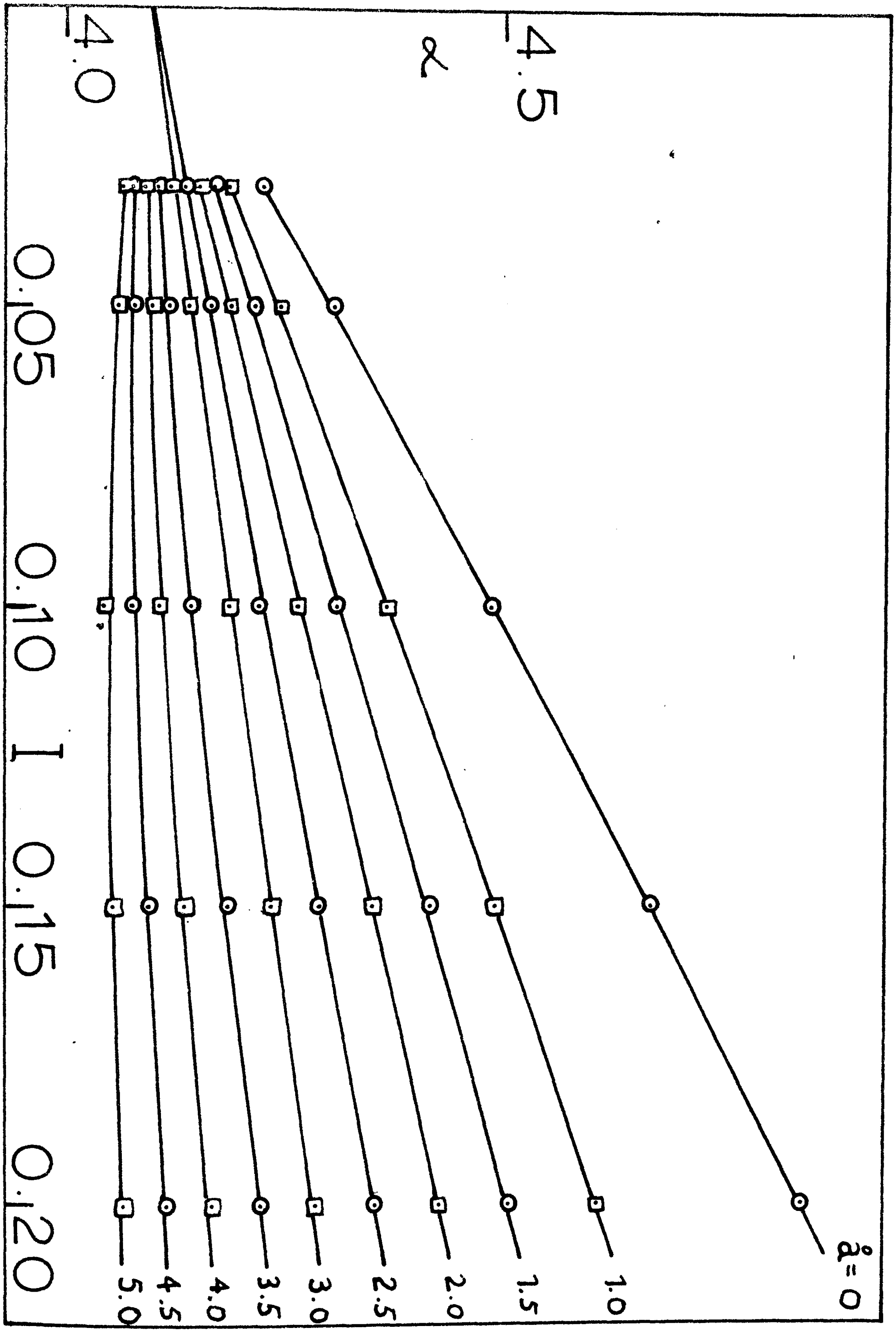


FIG. 10

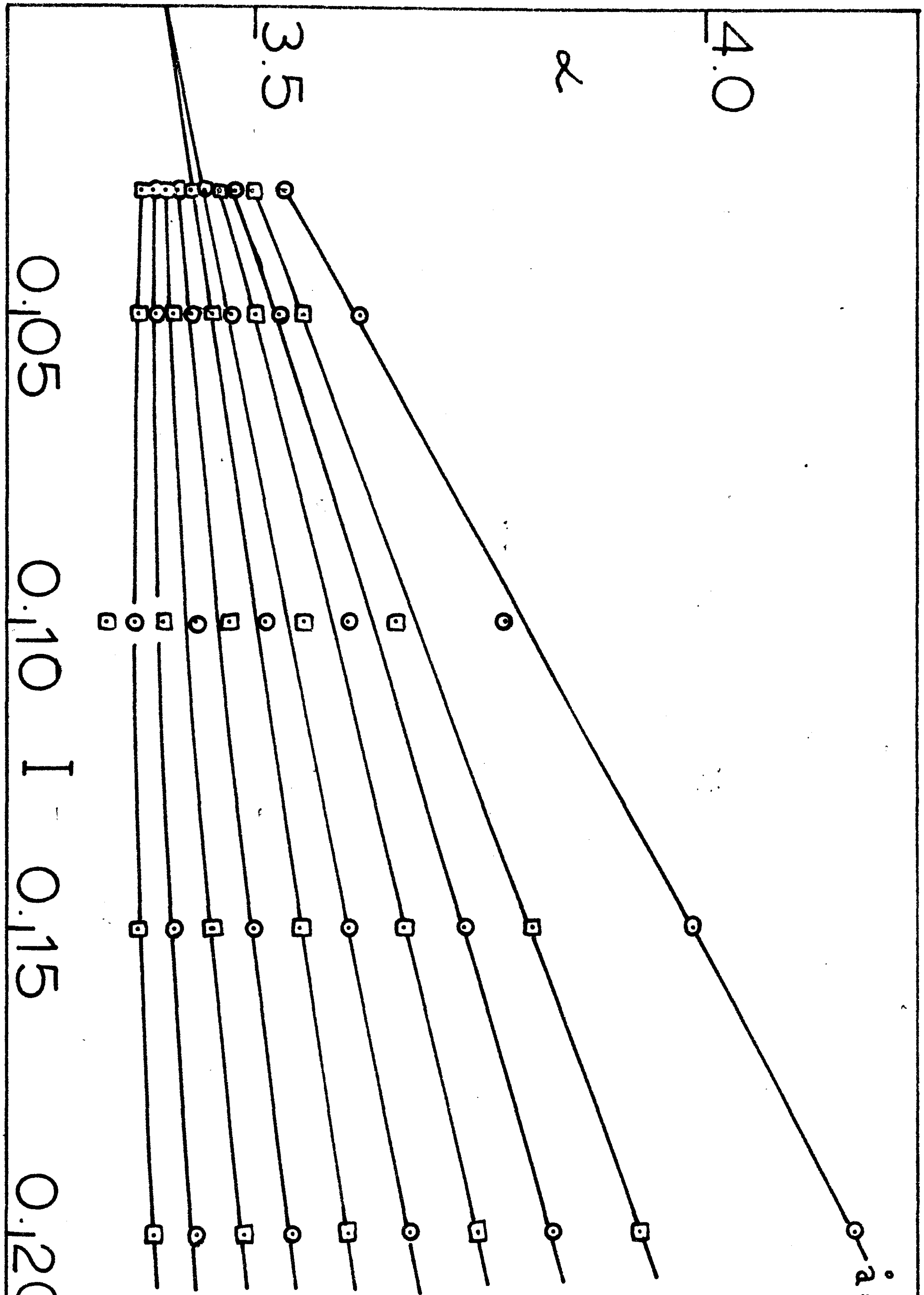


FIG. 11

DISCUSSION

The values of K obtained for the two systems by extrapolation are 1.25×10^{4} for nickel malonate, and 2.58×10^{3} for n-butylmalonate. These are in excellent agreement with 1.27×10^{4} and 2.65×10^{3} respectively, obtained by direct evaluation of the activity coefficients using equation (11). The nickel malonate value may be compared with 1.26×10^{4} given by Davies[41], and also by Nair and Nancollas[42] using the cell.

$H_2/Pt/H_2Mal$, NaOH, $NiCl_2/AgCl/Ag$.

The suggestion made by Guggenheim that å should, in fact, have a value similar to q is not supported by these results. In both cases å = 2.5 to 3Å and the b value 0.6 to 0.4, corresponds closely to that required by the Davies equation (0.4). For 2:2 electrolytes this is equivalent to an å of approximately 4.2Å. Monk[27] studied cobalt dicarboxylates at a series of ionic strengths and, using equation (13), obtained association constants å, and b values. The best å was constant, 4.5Å, for most of the systems studied, while the b values varied from 0.05 to 0.22. The results are in general agreement with the work of Brown and Prue[32] who found that small values of å gave a better fit to the data for bivalent metal sulphates.

When suggesting the use of equation (14) for bivalent electrolytes, Guggenheim assumed that the ions which approached within a distance of q of one another were not influenced by the other ions in solution. A consideration of the interactions between the ion-pair and other ions leads to the introduction of an activity coefficient for the ion-pair. Rossiensky[43] has attributed the sucess of activity coefficient expressions containing low å or b values to the neglect of this term.

The very close similarity in the å values to be used for the two acids suggests that it is dependent not on the actual sizes of the ions, but on the sizes of the bonding centres. This is supported by the almost constant values obtained by Monk for the cobalt dicarboxylates. While å may thus appear to have a definite physical meaning, it is better to consider it as an arbitrary parameter.

It would also appear, from the good agreement between the K values obtained from direct evaluation of the activity coefficients and extrapolation, that the Davies equation may be used in the study of divalent metal dicarboxylates. For these systems at least, there appears to be less uncertainty about the value of å to be used than was supposed by Prue.

PART II

SOME TRANSITION METAL GLYCINATES AND β-ALANINATES

INTRODUCTION

In their study of the association between various diamines and the divalent ions of the first transition row metals, Irving and Williams[44] found that the stability constants were in the order,

$Mn < Fe < Co < Ni < Cu > Zn$.

They showed that this order held for a large number of ligands and suggested that it was due to two factors; (i) the decrease in ionic radius along the series, leading to an increase in the electrostatic attraction, and (ii) an increase in the second ionisation potential of the metal, which they assumed to be a measure of the ability of the metal to form covelent bonds.

The decrease in the stability of chelates with increasing ring size has also been studied[45]. The five-membered ring chelates, oxalates, glycinates and ethylenediamines, were found to be more stable than the corresponding six-membered malonates, β-alaninates and 1:3 diaminopropanes, and this has been interpretted in terms of heat and entropy effects.

Heat and entropy data have been obtained for the association of diamines with metal ions, both by direct calorimetric measurements[46] and by association studies over a large temperature range[47], and metal dicarboxylates have also been studied from 0° to 45°C[43,42].

However, association data for amino acids are only available over a small temperature range[49], and it was therefore considered desirable to measure the stability of the chelates formed between transition metal ions and the glycinate and β-alaninate anions over a large range of temperature.

The association of the glycinate ion with metal ions has been extensively studied[50]. Albert[51] and Maley amd Mellor[52] have used potentiometric measurements at constant ionic strength, and thermodynamic constants have been obtained by Monk[53]. Davies[34], Monk[55] and Keefer[56] also calculated thermodynamic constants by measuring the solubilities of sparingly soluble metal iodates.

Few studies have been made with the β-alaninate anion[50]. Potentiometry has been used by Albert[51] and Irving et al[45], and polarographic methods by Li and Doody[57]: other techniques have been employed in the study of the association with copper ions[58,59].

The work described in this part of the thesis consists of the study of the association between nickel, cobalt and manganese ions and the glycinate and β-alaninate anions at 0°, 15°, 25°, 35° and 45°C. For nickel and cobalt glycinates two complexes, MA^+

and MA_2, have been found to be present, but for the other systems the results are best interpretted in terms of only one complex, MA^+. In the manganese β-alaninate studies, however, accurate results have not been obtained due to the preferential formation of the hydroxide complex.

EXPERIMENTAL

APPARATUS

Potentiometer

A precision Vernier potentiometer (Type P.10, Croydon Precision Co. Croydon, Surrey.) was used. This had an overall range of 1.9 volts to 1 microvolt in two ranges, and the accuracy was 1 part in 100,000 of the 1 volt setting. The coil was of well aged bare Manganin Telcuman wire, of the same guage throughout, thus reducing the temperature coefficient to a minimum. All terminals were of copper, tipped with a precious metal alloy to ensure good contact. A five decade system in the battery circuit was used when standardising the potentiometer, and the standard cell voltage was preset with an auxiliary divider, calibrated from 1.01800 to 1.01900 volts in steps of 50 microvolts. The potentiometer rested on a large, earthed metal sheet. A multiple switch box was incorporated in the circuit between the cells and the potentiometer terminals in order to select for measurement any pair of electrodes.

Two Weston Standard cells (Cambridge Instrument Co. Ltd., London.), mounted in metal cases, were kept in a small oil thermostat, maintained at $25^{\circ} \pm 0.2^{\circ}C$ by means of a bimetallic "Sunvic" relay. The standard cells were compared regularly and the difference between them was 60 ± 10 microvolts.

A sensitive, spot-reflecting, moving coil galvanometer (Cambridge Instrument Co. Ltd., London) was used in conjunction with a scale at a distance of one meter.

Thermostat

The thermostat was a large metal tank insulated with cork and containing water and ethyleneglycol. The temperature was kept constant to within ± 0.005°C by means of a mercury-toluene regulator, of large capacity, situated near the heating unit. This operated a system of any combination of three bulbs, painted red to reduce the effect on the light-sensitive silver, silver chloride electrodes. The relay coil was of high resistance so that no sparking occured in the regulator during make and break. Temperatures below that of the room were obtained with a refrigerating unit (Frigidaire Division of General Motors Ltd., London, W.9.), and for large rises in temperature a booster heater, which gave an increase of 1° per two minutes, was used. Since the e.m.f. measurements were made to ± 0.01m.v. temperature control of the order of ± 0.005°C was necessary. The temperatures 15°, 25°, 35° and 45°C were measured using Beckmann thermometers which had been calibrated against platinum resistance thermometers. The $0^{o}C$ thermometer was standardised using a triple-point cell.

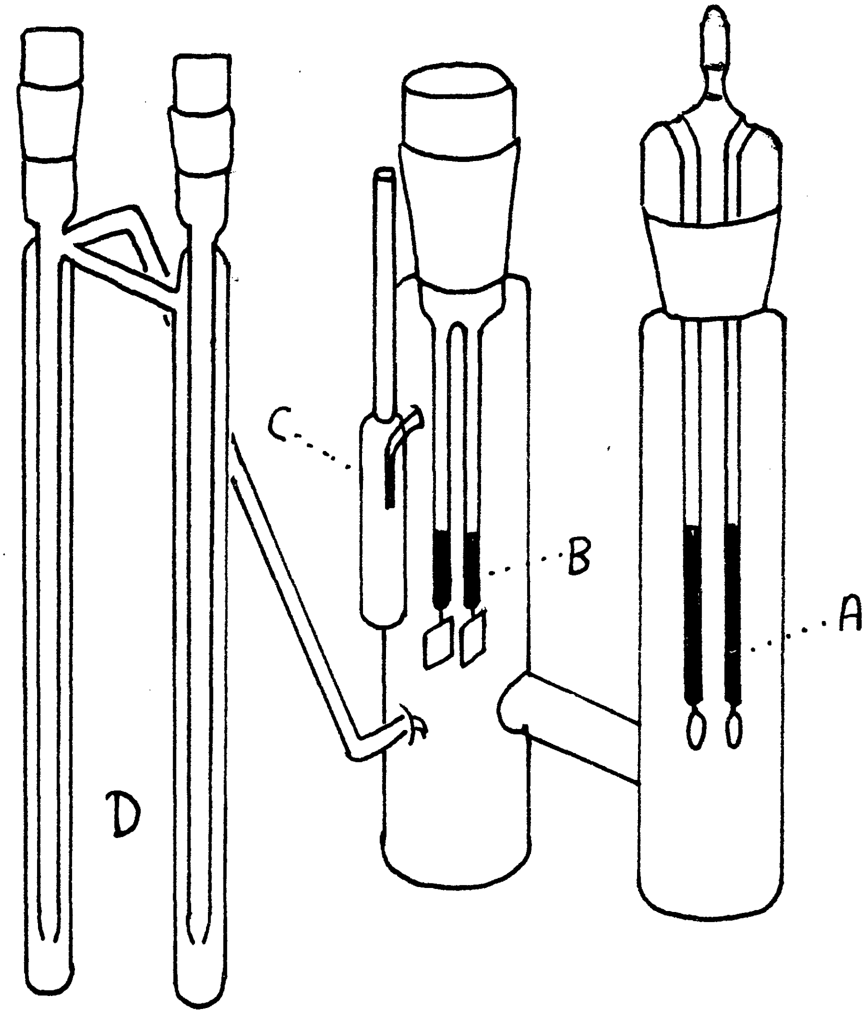
Cell and Electrodes

The cell employed was similar to that used by Noyes and Ellis[60]. Two hydrogen presaturators were incorporated as suggested by Harned and Morrison[61], and the modifications of Ashby, Crook and Datta[38] were also included. The cell was fitted with standard, B29, ground glass sockets, and the electrodes were supported in standard cones. Each cell contained a pair of silver, silver chloride electrodes and a pair of hydrogen electrodes, so that four estimates of the e.m.f. were possible. A guard tube was fitted to the hydrogen electrode compartment, and any liquid collecting in it was immediately removed. A diagram of the cell and electrodes is shown in Fig. 12.

Hydrogen Electrodes

Pieces of platinum foil were welded to platinum wires which were then sealed into pyrex-glass tubes attached to B29 cones. The electrodes were cleaned with nitric acid, washed, and a little araldite resin cast, at $120^{o}C$, in the bottom of the tubes, thus ensuring good platinum-pyrex seals. They were then platinised for

THE E.M.F. CELL



A - Silver - Silver Chloride Electrodes.
B - Hydrogen Electrodes.
C - Guard Tube.
D - Presaturators.

FIG. 12

three minutes, at a current density of 0.2 amps per sq.cm., in a solution containing 2.5% chloroplatinic acid in normal hydrochloric acid, the current being reversed every 15 seconds. The coating, which was not sufficiently thick to obscure the brightness of the underlying metal, was removed with aqua regia after each alternate run, and a fresh deposit made. The electrodes were stored in conductivity water saturated with hydrogen.

Silver, Silver Chloride Electrodes.

Taniguchi and Janz[62] used small electrodes and found that they took from a few hours to one week to come to constant potential. Bates[63] suggested that electrodes should be about 150 to 200 m.gms. in weight. The electrodes used in the present work were of the thermal-electrolytic type, described in PartI, set in B29 ground glass cones. They weighed from 200 to 300 m.gms., and were given from 3 to 4 weeks to settle.

Preparation of Reagents

AnalaR glycine was used without further purification. The β-alanine, which was B.D.H. Laboratory Reagent grade was recrystallised three times from conductivity water and dried, in vacuo, at 50° to 70°C (Analysis. Found:

C, 40.55%; H, 7.71%; N, 15.50%: Theoretical: C, 40.44%; H, 7.36%; N, 15.72%). AnalaR metal chlorides were recrystallised once from conductivity water to remove insoluble material. Solutions were analysed by gravimetric analysis for chloride as silver chloride, the agreement being ± 0.02%. Sodium hydroxide solutions were prepared with conductivity water, and standarised as in Part I.

Conductivity water, which was used for all solutions, was prepared by mixed-bed deionisation[64]. Distilled water was passed down a column consisting of an intimate mixture of one part of the strong acid resin, Amberlite I.R. 120, and two parts of the strong base resin, Amberlite I.R.A. 400.

Constant boiling hydrochloric acid was prepared by the method of Foulk and Hollingworth[65] and Shaw[66], using the modifications of Titus and Smith[67]. Determinations of chloride as silver chloride agreed to ± 0.02% and were in very good agreement with the theoretical values[36].

Cylinder hydrogen was freed from oxygen by passage through a "Deoxo" purifier (Baker Platinum Division, Engelhard Industries Ltd., London) and saturated with water vapour by passing through a series of bubblers.

Calibration of Silver, Silver Chloride Electrodes

Harned and Ehlers[68] determined the standard potential of the silver, silver chloride electrode over a temperature range of 0° to 60°C at 5° intervals using an extrapolation technique, and most subsequent workers have used their values. More recently it has been shown, however, that there is a difficulty in establishing the E^0 value better than 0.2 m.v.[69], and it has been recommended that each worker standardise his own electrodes in 0.01 molal hydrochloric acid. It was also suggested that the mean activity coefficient, $\gamma_{\pm}$, of hydrochloric acid at 0.01 molal be taken as 0.904 at 25°C, and 0.908 at 0°C. These values were used in the present work, and the activity coefficients of Harned and Owen[126] were used for the other temperatures.

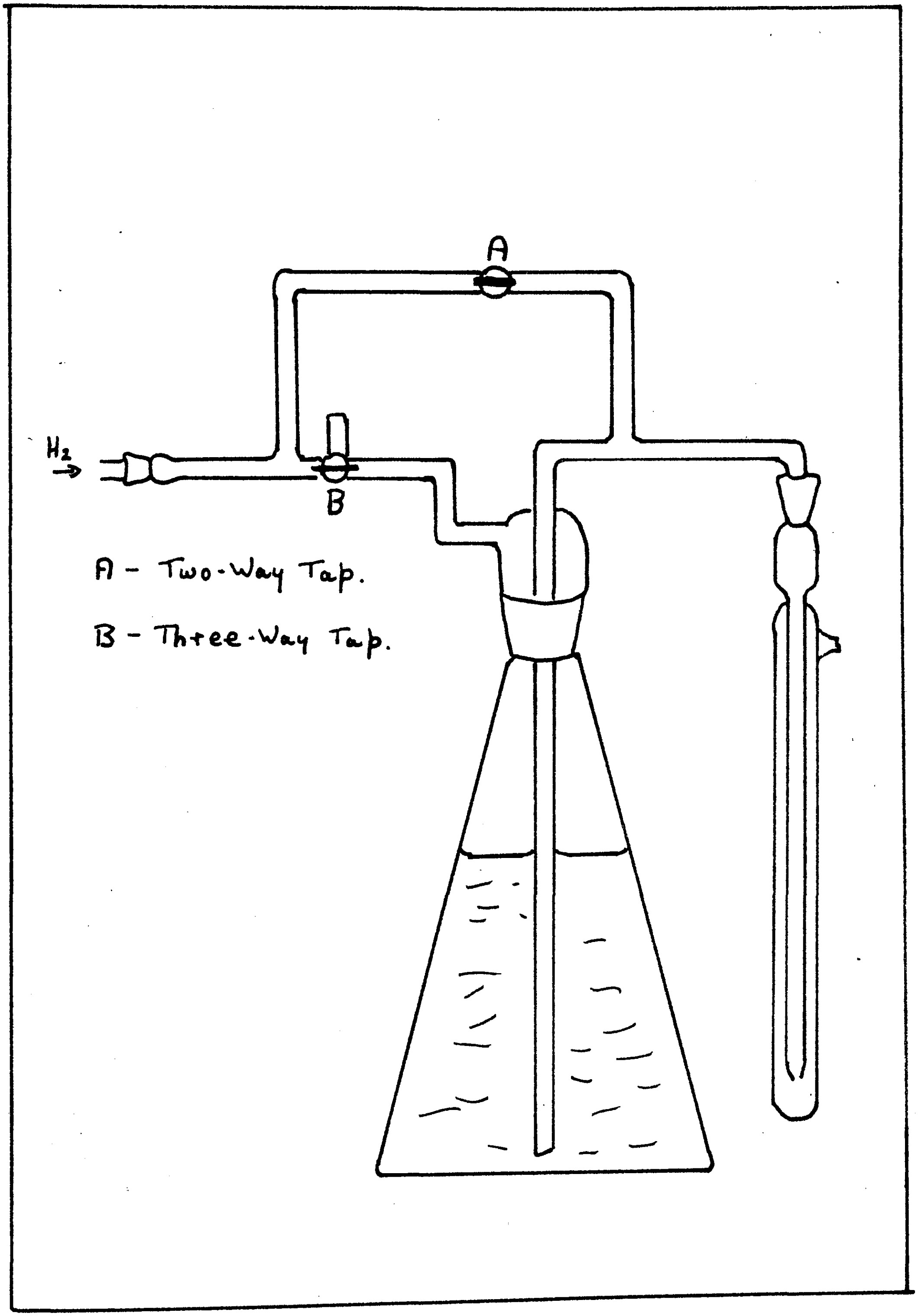
E.m.f. Measurements

Stock solutions of glycine and the metal chlorides were prepared by weight in stoppered pyrex flasks. The experimental solutions were prepared by weight dilution of stock solutions in 500 ml. Quickfit flasks. In order to prevent the formation of metal hydroxides, however, it was necessary to use relatively large concentrations of β-alanine. This acid was therefore weighed directly into the Quickfit flasks, vacuum corrections being applied to all weights.

Each flask was fitted with a bubbler head, shown in Fig. 13. Hydrogen was bubbled through the solution for over half an hour and the electrodes were washed three times with the solution in the V - shaped vessel shown in Fig.14.

A cell, previously oven dried at 120°, was attached to the bubbler head through a standard B10 joint (Fig.13), and hydrogen blown through to remove air. The electrodes were then placed in the cell and hydrogen passed for a few more minutes. The taps were adjusted so that the solution was transferred from the flask to the cell by hydrogen pressure. The filled cell was then placed in the thermostat and hydrogen bubbling continued at a slow rate.

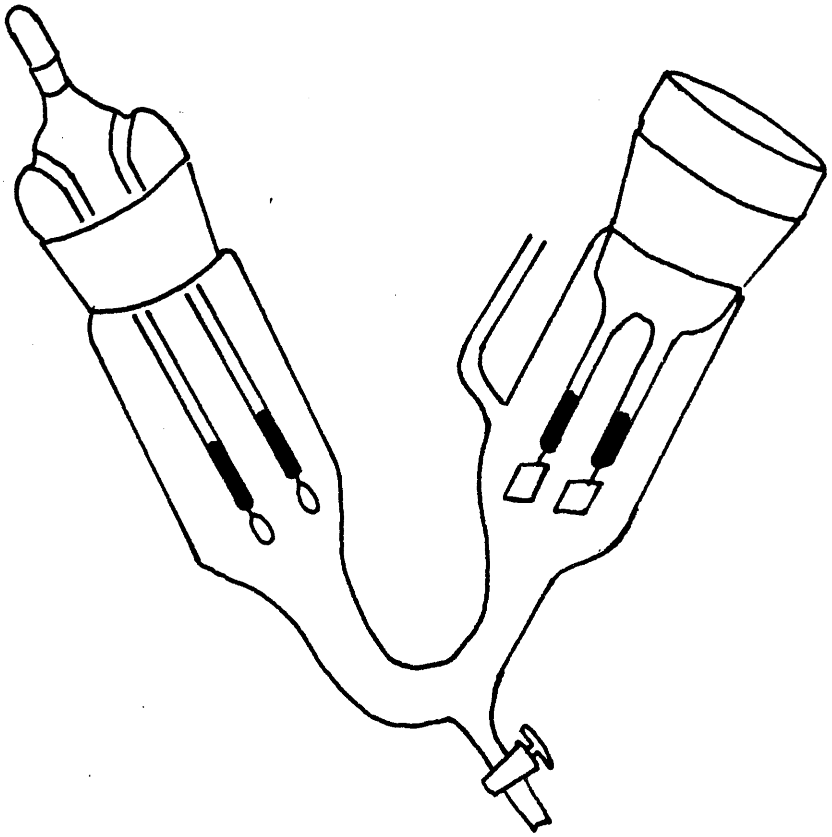
It was possible to make measurements with four cells at a time. They were allowed to settle for 2 to 3 hours, after which the e.m.f.'s were measured, four readings being obtained for each cell. When these had been constant for half an hour, barometric pressure and room temperature were recorded and the e.m.f.'s corrected for pressure. In making the pressure correction, the effect of bubbler depth observed by Hills and Ives[70] was ignored, since this amounted to only 5 microvolts at 25°C. When measurements had



A - Two-Way Tap.

B - Three-Way Tap.

FIG. 13



ELECTRODE-WASHING VESSEL

FIG. 14

been taken at one temperature, the thermostat was raised to the next and the cells allowed to settle for half an hour.

RESULTS

METAL GLYCINATES

Owen[71] and King[72] have determined k_1 for glycine using the cell

$$H_2/Pt/HA\ (m_1),\ H_2ACl\ (m_2)/AgCl/Ag.$$

The only ionic species in solution were H_2A^+, H^+ and Cl^-, and the ionic strength $I = m_2$. Dissociation constants were obtained at a series of m_2 values from the equation

$$k_1' = \frac{(m_1 + m_{H^+})\ m_{H^+}}{(m_2 - m_{H^+})}$$

where m_{H^+}, the hydrogen ion concentration, was given by

$$-\log m_{H^+} = \frac{E - E^o}{k} + \log m_2 + 2\log\gamma_{HCl};$$

γ_{HCl} was the mean activity coefficient of hydrochloric acid in water at the concentration m_2. The thermodynamic constant k_1, was then obtained by plotting $\log k_1'$ against m_2 and extrapolating to $m_2 = 0$. A similar method was used for the calculation of k_2.

Datta and Grzybowski[73] also determined k_2 and in order to obtain linear plots of $-\log k_2'$ against I, they represented the activity coefficients by an expression containing terms in I and $I^{3/2}$, obtaining log k_2 by a least squares extrapolation.

The best k_2 values appear to be those of King and Datta and Grzybowski. Accurate data were therefore available at 15°, 25°, 35° and 45°C and since the temperature coefficients were small it was considered sufficiently reliable to obtain the values at 0°C by extrapolation of a plot of log k against 1/T. The values are summarised in Table 36 which includes King's k_2 values.

TABLE 36

Acid Dissociation Constants

Temp. °C	10^3k_1	$10^{10}k_2$	
		D and G	K
0	3.67	0.327	-
15	4.17	0.896	0.893
25	4.46	1.67	1.66
35	4.66	2.97	2.95
45	4.77	5.06	5.02

In the association of the glycinate anion with nickel, cobalt and manganese ions, Monk[53] found it necessary to assume that two complexes, MA^+ and MA_2, were present in solutions of the first two. In manganese solutions, however, it appeared that only one complex,

MA^+, was present. Maley and Mellor[52] and Albert[51], however, found that in all systems it was necessary to assume the presence of both complexes. In the present work two complexes were sufficient in solutions of nickel and cobalt ions, but under the experimental conditions used, only one complex appeared to be formed with manganese ions.

In measurements using the cell

$H_2/Pt/HA\ (m_1),\ NaOH\ (m_2),\ MCl_2\ (m_3)/AgCl/Ag$

where m_1, m_2 and m_3 are the molal concentrations of glycine, sodium hydroxide and metal chloride respectively, the concentration of hydrogen ion is given by

$$-\log\left[H^+\right] = \frac{E - E^o}{k} + 2\log m_3 + 2\log\gamma, \quad .....(27)$$

where E is the corrected e.m.f., E^o the standard potential of the silver, silver chloride electrode, $k = 2.303\ RT/F$ and γ, the activity coefficient of the univalent ions.

In the general case the concentrations of the ionic species were obtained from the equations,

$$m_1 = \left[H_2A^+\right] + \left[HA\right] + \left[A^-\right] + \left[MA^+\right] + 2\left[MA_2\right], \quad ....(28)$$

$$m_3 = \left[M^{2+}\right] + \left[MA^+\right] + \left[MA_2\right], \quad ....(29)$$

electroneutrality

$$[H^+] + 2[M^{2+}] + [MA^+] + m_2 + [H_2A^+] = [A^-] + 2m_3, \quad \ldots(30)$$

the ionic strength

$$I = \tfrac{1}{2}\left\{[H^+] + [MA^+] + [H_2A^+] + [A^-] + m_2 + 2m_3 + 4[M^{2+}]\right\}, \quad \ldots(31)$$

and the dissociation constants of the acid,

$$k_1 = \frac{[H^+][HA]}{[H_2A^+]} \quad \ldots(32)$$

and

$$k_2 = \frac{[H^+][A^-]\gamma_1^2,}{[HA]} \quad \ldots(33)$$

Where only one complex, MA^+, was formed

$$m_1 = [H_2A^+] + [HA] + [A^-] + [MA^+] \quad \ldots(34)$$

and

$$m_3 = [M^{2+}] + [MA^+]. \quad \ldots(35)$$

In all solutions studied $[OH^-]$ was negligibly small.

The association constants

$$K_1 = \frac{[MA^+]}{[M^{2+}][A^-]\gamma_2} \quad \ldots(36)$$

and

$$K_2 = \frac{[MA_2]}{[MA^+][A^-]\gamma_1^2} \quad \ldots(37)$$

were obtained by succesive approximations for I, using the Deuce computer. For nickel and cobalt an approximate value of K_2 was used in the initial calculation of K_1. A more accurate value of K_2 was then obtained, and the process repeated until K_1 and K_2 were constant.

The activity coefficients were calculated from the expression.

$$-\log \gamma_{\pm} = AZ^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - \beta I\right), \qquad \ldots\ldots(38)$$

and in order to determine the best value of β to be used, calculations were made with $\beta =$ 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0.

The values of the constants used in the calculations are given in Table 37.

TABLE 37

Values of Constants used in Calculations

Temp. °C	A	k
0	0.4883	0.054197
15	0.5000	0.057173
25	0.5085	0.059158
35	0.5175	0.061141
45	0.5270	0.063126

The results of K_1 and K_2 determinations with $\beta =$ 0.2 in equation (38) are given in Tables 38, 39, 40, 41 and 42. Calculations with other β values are summarised in Tables 43, 44, 45, 46 and 47.

TABLE 32

TABLE 38

Molal Concentrations in Nickel Glycinate Experiments

2	3	4	5	6	7
6.2971	6.9927	5.8195	5.5262	6.3292	5.9371
1.8722	2.2291	1.0678	0.9834	1.0590	3.8055
6.1272	0.8316	0.9847	0.7859	0.6374	2.9797

9	10	11	12	13	14
5.5410	6.0667	5.1350	5.4071	5.6186	6.3358
2.7295	4.9962	2.6031	3.0628	3.1015	3.4016
3.1635	5.3758	6.7398	5.4922	5.7036	5.9861

Results on Nickel Glycinate

$10^3[HA]$	$10^7[A^-]$	$10^4[MA^+]$	$10^6[MA_2]$	$10^{-6}K_1$
	Temp = 0°C.			
6.058	0.211	2.180	0.69	2.93
6.762	1.449	2.166	5.48	3.00
5.416	0.646	1.034	1.16	2.87
6.212	0.854	1.095	1.65	2.92
5.545	0.725	3.792	4.41	2.93
5.725	0.575	3.966	3.56	2.89
5.551	0.572	5.010	4.34	2.92
4.845	0.251	2.774	1.01	2.93
5.078	0.346	3.175	1.66	2.90
5.283	0.342	3.226	1.66	2.89
5.966	0.359	3.547	1.91	2.92

Mean $K_1 = 2.92 \pm 0.02$

Expt.	$E - E^{o}$	$10^{3}I$	$10^{6}[H^{+}]$
2	0.38435	18.146	20.147
5	0.46454	2.249	5.286
6	0.47368	1.797	4.465
7	0.43338	8.551	5.340
8	0.41914	11.789	7.151
10	0.41285	15.615	7.168
11	0.39089	19.930	14.231
12	0.40247	16.148	10.698
13	0.40033	16.777	11.275
14	0.39710	17.591	12.151

2	0.38978	18.131	27.530
3	0.48555	2.268	4.140
5	0.47259	2.245	7.231
6	0.48155	1.793	6.244
7	0.43920	8.546	7.672
8	0.42451	11.782	10.260
10	0.41807	15.609	10.265
11	0.39588	19.919	19.961
12	0.40757	16.140	15.173
13	0.40540	16.768	15.962
14	0.40251	17.580	17.113

$10^3[MA]$	$10^7[A^-]$	$10^4[MA^+]$	$10^6[MA_2]$	$10^{-6}. K_1$
	Temp. = 15°C			
6.032	0.349	2.350	0.75	1.94
5.409	1.016	1.080	1.18	1.93
6.206	1.366	1.135	1.69	1.92
5.537	1.125	3.843	4.26	1.93
5.715	0.892	4.034	3.45	1.92
5.541	0.888	5.078	4.20	1.93
4.828	0.401	2.889	1.50	1.94
5.064	0.546	3.266	1.66	1.92
5.269	0.541	3.323	1.66	1.91
5.949	0.570	3.657	1.92	1.93
		Mean K_1 = 1.93 ± 0.01		
	Temp. = 25°C.			
6.008	0.477	2.502	0.816	1.53
6.753	3.023	2.222	5.416	1.50
5.403	1.375	1.118	1.240	1.49
6.200	1.820	1.172	1.738	1.50
5.530	1.460	3.892	4.192	1.52
5.705	1.160	4.100	3.406	1.51
5.531	1.157	5.142	4.140	1.52
4.812	0.532	2.996	1.079	1.53
5.051	0.718	3.352	1.668	1.51
5.255	0.713	3.415	1.680	1.51
5.933	0.744	3.761	1.948	1.51
		Mean K_1 = 1.51 ± 0.01		

Expt.	$E - E^0$	$10^3 I$	$10^6 [H^+]$
1	0.50666	1.693	4.332
2	0.39559	18.113	36,360
3	0.49317	2.264	5.748
4	0.46977	2.823	11.854
5	0.48035	2.240	9.851
6	0.48964	1.789	8.469
7	0.44509	8.540	10.737
8	0.43005	11.774	14,288
9	0.43549	9.190	14.612

1	0.51587	1.691	5.648
2	0.40168	18.091	46,732
3	0.50078	2.260	7.822
4	0.47750	2.815	15.0629
5	0.48831	2.234	13,035
6	0.49798	1.783	11.173
7	0.45108	8.532	14.669
8	0.43571	11.763	19.420
9	0.44150	9.179	19.723

$10^3[HA]$	$10^7[A^-]$	$10^4[MA^+]$	$10^6[MA_2]$	$10^{-6}.K_1$
	Temp. = 35°C.			
8.945	6.727	2.615	10.94	1.23
5.980	0.641	2.684	0.90	1.24
6.747	3.878	2.259	5.37	1.20
5.672	1.599	1.304	1.26	1.21
5.395	1.808	1.168	1.30	1.20
6.192	2.388	1.218	1.80	1.20
5.521	1.859	3.956	4.12	1.22
5.692	1.484	4.183	3.38	1.22
5.221	1.300	2.995	2.17	1.21
		Mean $K_1 = 1.21 \pm 0.01$		
	Temp. = 45°C			
8.940	8.812	2.631	11.83	0.95
5.947	0.852	2.900	1.05	1.02
6.740	4.865	2.300	5.63	0.99
5.660	2.070	1.379	1.42	1.00
5.385	2.331	1.230	1.44	0.99
6.183	3.089	1.272	2.00	0.99
5.508	2.325	4.033	4.30	1.01
5.676	1.866	4.287	3.56	1.01
5.205	1.645	3.094	2.32	1.00
		Mean $K_1 = 1.00 \pm 0.02$		

TABLE 39

Expt.	$E - E^{\circ}$	$10^3.I$
1	0.47819	5.756
2	0.47478	6.812
3	0.47293	6.400
4	0.46676	7.502
5	0.51680	2.207
6	0.53051	1.626
7	0.52851	1.737
8	0.55118	1.519
9	0.46937	6.239
10	0.46691	6.983

TABLE 39

Molal Concentrations in Cobalt Glycinate Experiments

Expt.	1	2	3	4	5
$10^3 m_1$	7.4284	7.3796	8.2576	8.2049	7.5728
$10^4 m_2$	1.5516	1.8040	1.6441	1.7241	1.3634
$10^3 m_3$	1.9699	2.3304	2.1385	2.5581	0.7795
	6	7	8	9	10
$10^3 m_1$	6.4364	7.0639	6.6283	7.1659	5.8391
$10^4 m_2$	1.1744	1.3466	2.2921	1.2526	1.1185
$10^3 m_3$	0.5796	0.6220	0.5767	2.1214	2.3652

Results on Cobalt Glycinate

$10^7[H^+]$	$10^3[HA]$	$10^6[A^-]$	$10^4[MA^+]$	$10^{-5}.K_1$
	Temp. = 0°C.			
4.458	7.271	6.227	1.531	1.85
4.409	7.197	6.310	1.779	1.84
5.054	8.038	6.156	1.645	1.83
5.691	8.029	5.494	1.710	1.85
2.065	7.435	1.299	1.305	1.90
1.530	6.318	1.470	1.113	1.93
1.557	6.929	1.589	1.273	1.95
0.637	6.399	3.565	2.034	1.86
6.054	7.038	0.446	1.250	1.94
6.081	5.725	0.365	1.119	1.92

Mean $K_1 = 1.89 \pm 0.04$

Expt.	$E - E^{o}$	$10^{3}.I$
1	0.48695	5.755
2	0.48325	6.812
3	0.48149	6.399
4	0.47515	7.501
5	0.52772	2.207
6	0.54230	1.627
7	0.54037	1.738
8	0.56383	1.521
9	0.47942	6.238
10	0.47611	6.982

1	0.49238	5.754
2	0.48854	6.811
3	0.48678	6.398
4	0.48036	7.500
5	0.53448	2.207
6	0.54955	1.627
7	0.54777	1.738
8	0.57173	1.522
9	0.48489	6.237
10	0.48156	6.981

$10^6[H^+]$	$10^3[HA]$	$10^6[A^-]$	$10^4[MA^+]$	$10^{-5}.K_1$
	Temp. = 15°C.			
0.905	7.269	8.440	1.542	1.39
0.899	7.195	8.517	1.790	1.38
1.023	8.086	8.373	1.658	1.37
1.144	8.027	7.526	1.724	1.38
0.417	7.435	1.765	1.308	1.40
0.308	6.318	2.006	1.114	1.42
0.311	6.928	2.184	1.273	1.42
0.130	6.399	4.810	2.034	1.38
1.145	7.036	0.650	1.260	1.35
1.184	5.723	0.516	1.130	1.38
		Mean K_1 = 1.39 ± 0.02		
	Temp.=25°C			
1.419	7.267	10.050	1.554	1.18
1.410	7.193	10.137	1.802	1.17
1.601	8.084	9.988	1.672	1.17
1.781	8.024	9.027	1.740	1.17
0.657	7.434	2.095	1.313	1.20
0.485	6.317	2.380	1.116	1.21
0.485	6.927	2.612	1.275	1.20
0.205	6.398	5.685	2.039	1.18
1.774	7.033	0.783	1.275	1.14
1.328	5.721	0.623	1.143	1.16
		Mean K_1 = 1.18 ± 0.02		

Expt.	$E - E^o$	$10^3.I$
1	0.49787	5.753
2	0.49391	6.809
3	0.49226	6.396
4	0.48564	7.498
5	0.54119	2.207
6	0.55676	1.627
7	0.55500	1.738
8	0.57952	1.523
9	0.49029	6.235
10	0.48687	6.980

1	0.50341	5.751
2	0.49926	6.807
3	0.49764	6.394
4	0.49098	7.495
5	0.54789	2.206
6	0.56387	1.627
7	0.56221	1.738
8	0.58718	1.524
9	0.49575	6.232
10	0.49220	6.977

$10^6[H^+]$	$10^3[HA]$	$10^6[A^-]$	$10^4[HA^+]$	$10^{-5}.K_1$
	Temp. = 35°C			
2.154	7.264	1.130	1.570	1.02
2.141	7.190	1.191	1.818	1.02
2.415	8.080	1.181	1.692	1.00
2.685	8.021	1.068	1.762	1.01
1.004	7.432	2.443	1.319	1.03
0.740	6.316	2.774	1.119	1.04
0.739	6.926	3.055	1.278	1.03
0.315	6.398	6.589	2.040	1.02
2.678	7.030	0.925	1.295	0.99
2.757	5.718	0.737	1.161	1.01
		Mean K_1 = 1.02 ± 0.01		
	Temp. = 45°C			
3.184	7.260	1.366	1.594	0.903
3.173	7.186	1.375	1.842	0.898
3.566	8.076	1.368	1.720	0.888
3.941	8.015	1.245	1.793	0.885
1.495	7.430	2.803	1.329	0.913
1.106	6.315	3.173	1.125	0.919
1.099	6.925	3.514	1.284	0.902
0.474	6.397	7.433	2.043	0.901
3.933	7.025	1.077	1.323	0.876
4.052	5.714	0.858	1.188	0.890
		Mean K_1 = 0.893 ± 0.010		

TABLE 40

Expt.	1	2
$10^2 m_1$	9.7058	8.6262
$10^4 m_2$	5.6134	5.7306
$10^2 m_3$	3.7319	3.3796

Expt.	$E - E^0$	$10^2.I$
1	0.43695	11.142
2	0.44316	10.087
3	0.44799	8.245
4	0.45492	5.382
5	0.45101	6.631
6	0.44670	8.701
7	0.45122	10.237

1	0.43794	11.142
2	0.44435	10.087
3	0.44942	8.245
4	0.45630	5.382
5	0.45263	6.631
6	0.44807	8.701
7	0.45261	10.237

TABLE 40

Molal Concentrations in Manganese Glycinate Experiments

3	4	5	6	7
7.9700	7.3594	7.9639	7.1301	4.0712
4.6713	2.9607	3.6167	4.3108	4.0549
2.7622	1.8025	2.2210	2.9134	3.4246

Results on Manganese Glycinate

$10^7[H^+]$	$10^2[HA]$	$10^5[A^-]$	$10^4[MA^+]$	$10^{-3}.K_1$
	Temp. = 0°C.			
1.938	9.647	2.715	5.600	1.56
1.618	8.568	2.843	5.486	1.57
1.561	7.923	2.637	4.443	1.57
1.670	7.329	2.137	2.782	1.63
1.651	7.927	2.412	3.413	1.54
1.577	7.086	2.356	4.107	1.56
1.136	4.030	1.908	3.878	1.63
		Mean K_1 = 1.58 ± 0.03		
	Temp. = 15°C			
4.956	9.645	2.947	5.643	1.49
4.159	8.567	3.069	5.513	1.49
4.013	7.922	2.845	4.467	1.50
4.361	7.328	2.265	2.815	1.59
4.237	7.926	2.604	3.441	1.46
4.053	7.036	2.542	4.129	1.49
2.926	4.030	2.057	3.880	1.55
		Mean K_1 = 1.51 ± 0.03		

Expt.	E - E^o	10^2.I
1	0.43852	11.142
2	0.44500	10.086
3	0.45020	8.245
5	0.45367	6.631
6	0.44888	8.701
7	0.45360	10.237
1	0.43916	11.141
2	0.44573	10.086
3	0.45120	8.244
5	0.45475	6.630
6	0.44971	8.701
7	0.45449	10.237
1	0.44020	11.139
2	0.44686	10.085
3	0.45254	8.243
5	0.45627	6.629
6	0.45093	8.700
7	0.45553	10.236

$10^6[H^+]$	$10^2[MA]$	$10^5[A^-]$	$10^4[MA^+]$	$10^{-3}.K_1$
	Temp. = 25°C			
0.883	9.644	3.105	5.708	1.45
0.746	8.566	3.215	5.560	1.46
0.721	7.921	2.974	4.509	1.47
0.756	7.925	2.739	3.485	1.43
0.726	7.085	2.665	4.167	1.46
0.528	4.030	2.142	3.894	1.52.
		Mean K_1 = 1.47 ± 0.02		
	Temp. = 35°C			
1.514	9.641	3.253	5.822	1.44
1.284	8.564	3.351	5.644	1.45
1.235	7.919	3.112	4.582	1.45
1.297	7.923	2.861	3.564	1.42
1.250	7.083	2.775	4.236	1.45
0.913	4.029	2.222	3.921	1.50
		Mean K_1 = 1.45 ± 0.02		
	Temp.=45°C			
2.477	9.637	3.426	6.001	1.44
2.109	8.561	3.518	5.779	1.45
2.026	7.916	3.266	4.701	1.44
2.120	7.920	3.011	3.689	1.42
2.055	7.081	2.906	4.346	1.45
1.521	4.028	2.298	3.969	1.50
		Mean K_1 = 1.45 ± 0.02		

TABLE 41

Expt.	1	2
$10^2\ m_1$	3.7992	3.2694
$10^3\ m_2$	0.9139	1.0490
$10^3\ m_3$	0.7927	0.9694

Expt.	$E - E^o$	$10^3.I$
1	0.49267	1.673
2	0.48782	2.071
3	0.46943	2.298
4	0.48047	1.896
5	0.47343	2.343
6	0.47172	2.424
7	0.46117	3.059
8	0.47532	2.278
1	0.50671	1.671
2	0.50075	2.069
3	0.49252	2.292
4	0.49361	1.891
5	0.48640	2.336
6	0.48426	2.420
7	0.47301	3.051
8	0.48809	2.273

TABLE 41

Molal Concentrations in Nickel Glycinate Experiments

3	4	5	6	7	8
3.6302	3.8354	4.5382	6.2537	5.4038	4.4874
1.0942	0.8727	1.1191	1.2847	1.3672	1.1028
1.0637	0.8726	1.0845	1.1448	1.4018	1.0580

Results on Nickel Glycinate

$10^6[H^+]$	$10^6[A^-]$	$10^4[MA^+]$	$10^4[MA_2]$	$10^{-5}\ K_2$
	Temp. = 0°C			
0.559	2.363	4.962	2.108	1.96
0.567	2.007	6.267	2.129	1.87
0.742	1.716	6.896	2.054	1.92
0.857	1.566	5.662	1.573	1.95
0.940	1.704	6.959	2.169	2.03
0.959	2.315	7.256	2.869	1.90
1.241	1.556	9.122	2.362	1.87
0.888	1.782	6.823	2.151	1.96
		Mean $K_2 = 1.93 \pm 0.04$		
	Temp. = 15°C			
0.946	3.838	5.031	2.081	1.18
0.993	3.150	6.309	2.117	1.18
1.267	2.761	7.000	2.017	1.16
1.465	2.519	5.743	1.552	1.18
1.592	2.765	7.069	2.139	1.22
1.647	3.705	7.297	2.886	1.19
2.141	2.480	9.208	2.365	1.17
1.522	2.855	6.900	2.137	1.20
		Mean $K_2 = 1.19 \pm 0.02$		

Expt.	$E - E^{o}$	$10^{3}.I$
1	0.51547	1.670
2	0.50905	2.067
3	0.50065	2.290
4	0.50172	1.889
5	0.49476	2.331
6	0.49248	2.416
7	0.48081	3.044
8	0.49628	2.270

1	0.52437	1.669
2	0.51770	2.065
3	0.50910	2.286
4	0.51078	1.883
5	0.50290	2.327
6	0.50082	2.413
7	0.48864	3.037
8	0.50446	2.266

$10^6[H^+]$	$10^6[A^-]$	$10^4[MA^+]$	$10^4[MA_2]$	$10^{-4}.K_2$
	Temp. = 25°C			
1.336	5.067	5.057	2.078	8.89
1.417	4.119	6.335	2.115	8.97
1.800	3.625	7.036	2.015	8.78
2.085	3.300	5.760	1.565	9.07
2.222	3.694	7.132	2.132	9.01
2.304	4.938	7.322	2.908	8.96
3.000	3.300	9.277	2.373	8.75
2.143	3.781	6.941	2.140	9.06
		Mean K_2 = 8.94 ± 0.10		
	Temp. = 35°C			
1.835	6.571	5.082	2.078	6.83
1.948	5.335	6.380	2.104	6.85
2.467	4.711	7.092	2.007	6.69
2.796	4.382	5.843	1.546	6.66
3.058	4.780	7.160	2.152	7.01
3.139	6.456	7.335	2.946	6.95
4.107	4.295	9.327	2.403	6.78
2.952	4.891	6.967	2.159	7.06
		Mean K_2 = 6.85 ± 0.11		

Expt.	$E - E^0$	$10^3, I$
1	0.53323	1.668
2	0.52619	2.064
3	0.51742	2.283
5	0.51063	2.325
6	0.50872	2.411
7	0.49601	3.032
8	0.51216	2.265

Temp. = 45°C

$10^6[H^+]$	$10^6[A^-]$	$10^4[MA^+]$	$10^4[MA_2]$	$10^{-4}K_2$
2.476	8.324	5.094	2.090	5.42
2.644	6.719	6.401	2.112	5.45
3.334	5.956	7.119	2.021	5.32
4.193	5.958	7.127	2.217	5.83
4.267	8.117	7.281	3.037	5.75
5.611	5.373	9.281	2.505	5.69
4.059	6.078	6.928	2.226	5.89

Mean $K_2 = 5.62 \pm 0.20$

TABLE 42

Expt.	1	2
$10^2\ m_1$	3.4170	6.4753
$10^3\ m_2$	1.3904	1.1048
$10^3\ m_3$	1.3658	0.9961

Expt.	$E - E^{\circ}$	$10^3.I$
1	0.51238	3.017
2	0.53026	2.172
3	0.52006	2.556
4	0.53005	2.152
5	0.51185	2.800
6	0.50915	3.002
7	0.51279	2.484

1	0.52369	3.022
2	0.54201	2.182
3	0.53141	2.566
4	0.54196	2.161
5	0.52321	2.808
6	0.52001	3.011
7	0.52409	2.494

TABLE 42

Molal Concentrations in Cobalt Glycinate Experiments

3	4	5	6	7
9.2361	6.5973	12.1177	12.6328	14.1085
1.3370	1.1019	1.4619	1.5389	1.3279
1.1797	0.9372	1.2936	1.3856	1.1513

Results on Cobalt Glycinate

$10^7[H^+]$	$10^5[A^-]$	$10^4[MA^+]$	$10^4[MA_2]$	$10^{-4}K_2$
	Temp. = 0°C.			
1.445	2.101	8.295	2.716	1.75
0.911	2.518	6.013	2.400	1.75
1.197	2.765	7.091	3.016	1.71
0.928	2.521	5.919	2.433	1.80
1.554	2.814	7.797	3.296	1.68
1.633	2.801	8.487	3.339	1.58
1.667	3.043	6.975	3.032	1.59
		Mean K_2 = 1.69, ± 0.07		
	Temp. = 15°C			
2.853	2.926	8.420	2.625	1.20
1.839	3.432	6.078	2.329	1.24
2.399	3.792	7.173	2.936	1.20
1.858	3.460	5.999	2.352	1.25
3.059	3.931	7.924	3.197	1.15
3.261	3.858	8.574	3.265	1.11
3.297	4.232	7.080	2.945	1.10
		Mean K_2 = 1.18 ± 0.05		

[illegible]	3	[illegible]	[illegible]	[illegible]
[illegible]	4	4.170	[illegible]	[illegible]
[illegible]	5	[illegible]	[illegible]	[illegible]
[illegible]	6	4.470	[illegible]	[illegible]
[illegible]	7	[illegible]	[illegible]	[illegible]

Mean K_y = [illegible]

Temp. = 35°C

[illegible]	1	[illegible]	[illegible]	[illegible]
[illegible]	2	[illegible]	[illegible]	[illegible]
[illegible]	3	[illegible]	[illegible]	[illegible]
[illegible]	4	[illegible]	[illegible]	[illegible]
[illegible]	5	[illegible]	[illegible]	[illegible]
[illegible]	6	[illegible]	[illegible]	[illegible]
[illegible]	7	[illegible]	[illegible]	[illegible]

Mean K_y = [illegible]

Expt.	$E - E^{o}$	$10^{3}.I$
1	0.53113	3.024
2	0.54951	2.189
3	0.53882	2.573
4	0.54960	2.168
5	0.53055	2.814
6	0.52705	3.017
7	0.53112	2.501

1	0.53789	3.030
2	0.55666	2.196
3	0.54581	2.580
4	0.55684	2.175
5	0.53737	2.821
6	0.53373	3.024
7	0.53808	2.509

$10^7[H^+]$	$10^5[A^-]$	$10^4[MA^+]$	$10^4[MA_2]$	$10^{-3}.K_2$
	Temp. = 25°C			
4.342	3.587	8.551	2.539	9.34
2.862	4.114	6.136	2.272	9.98
3.694	4.596	7.261	2.864	9.60
2.876	4.170	6.071	2.288	10.02
4.671	4.802	8.030	3.119	9.09
5.017	4.679	8.660	3.203	8.92
5.102	5.101	7.139	2.897	8.88
		Mean $K_2 = 9.40 \pm 0.40$		
	Temp. = 35°C			
6.597	4.209	8.592	2.507	7.84
4.384	4.786	6.167	2.233	8.41
5.618	5.387	7.307	2.820	8.03
4.393	4.867	6.109	2.244	8.39
7.073	5.654	8.077	3.083	7.60
7.604	5.504	8.700	3.175	7.50
7.690	6.032	7.187	2.864	7.39
		Mean $K_2 = 7.88 \pm 0.34$		

Expt.	$E - E^{\circ}$	$10^{3}.I$
1	0.54485	3.033
2	0.56392	2.203
3	0.55285	2.587
4	0.56429	2.182
5	0.54438	2.828
6	0.54055	3.030
7	0.54530	2.516

$10^7[H^+]$	$10^5[A^-]$	$10^4[MA^+]$	$10^4[MA_2]$	$10^{-3}.K_2$
	Temp. = 45°C			
9.700	4.315	8.673	2.460	6.57
6.517	5.505	6.221	2.185	7.11
8.311	6.226	7.367	2.773	6.79
6.486	5.636	6.179	2.185	6.99
10.376	6.591	8.146	3.042	6.40
11.186	6.398	8.757	3.148	6.37
11.202	7.081	7.256	2.827	6.17

Mean $K_2 = 6.63 \pm 0.29$

TABLE 43

β	0.0	0.1
Expt.		
2	2.99	2.96
3	3.01	3.01
5	2.88	2.88
6	2.93	2.92
7	2.95	2.94
8	2.92	2.91
10	2.97	2.94
11	2.99	2.96
12	2.95	2.92
13	2.94	2.91
14	2.97	2.95
Mean $K_1 \times 10^6$	2.95 ±0.03	2.94 ±0.03

TABLE 43

Nickel Glycinate Results Varying β

0.2	0.3	0.4	0.5	1.0
Temp. = 0°C				
2.93	2.91	2.88	2.86	2.73
3.00	3.00	3.00	2.99	2.98
2.88	2.87	2.87	2.87	2.85
2.92	2.92	2.92	2.91	2.90
2.93	2.92	2.90	2.89	2.84
2.89	2.88	2.86	2.85	2.77
2.92	2.90	2.88	2.86	2.76
2.93	2.90	2.88	2.85	2.72
2.90	2.88	2.86	2.84	2.73
2.89	2.87	2.85	2.82	2.71
2.92	2.90	2.88	2.85	2.74
2.92 ±0.02	2.90 ±0.02	2.89 ±0.03	2.87 ±0.03	2.79 ±0.07

Expt.	β 0.0	0.1
2	1.97	1.96
5	1.93	1.93
6	1.92	1.92
7	1.95	1.94
8	1.94	1.93
10	1.96	1.95
11	1.98	1.96
12	1.95	1.93
13	1.94	1.93
14	1.96	1.94
Mean $K_1 \times 10^6$	1.95 ±0.01	1.94 ±0.01

0.2	0.3	0.4	0.5	1.0
	Temp. = $15^{o}C$			
1.94	1.92	1.90	1.88	1.80
1.93	1.93	1.93	1.92	1.91
1.92	1.91	1.91	1.91	1.90
1.93	1.92	1.92	1.91	1.87
1.92	1.91	1.90	1.89	1.84
1.93	1.92	1.90	1.89	1.82
1.94	1.92	1.90	1.89	1.80
1.92	1.90	1.89	1.87	1.80
1.91	1.89	1.88	1.86	1.79
1.93	1.91	1.90	1.88	1.80
1.93 ±0.01	1.91 ±0.01	1.90 ±0.01	1.89 ±0.01	1.83 ±0.04

β Expt.	0.0	0.1
2	1.56	1.55
3	1.51	1.50
5	1.49	1.49
6	1.50	1.50
7	1.53	1.53
8	1.53	1.52
10	1.54	1.53
11	1.56	1.55
12	1.54	1.53
13	1.53	1.52
14	1.54	1.53
Mean $K_1 \times 10^6$	1.53 ±0.02	1.52 ±0.02

0.2	0.3	0.4	0.5	1.0
	Temp. = 25°C			
1.53	1.52	1.50	1.49	1.42
1.50	1.50	1.50	1.50	1.49
1.49	1.49	1.49	1.49	1.48
1.50	1.50	1.50	1.50	1.49
1.52	1.51	1.50	1.50	1.47
1.51	1.51	1.50	1.49	1.45
1.52	1.51	1.49	1.48	1.42
1.53	1.51	1.50	1.49	1.41
1.51	1.50	1.49	1.48	1.42
1.51	1.50	1.48	1.47	1.41
1.51	1.50	1.49	1.47	1.41
1.51 ±0.01	1.51 ±0.01	1.50 ±0.01	1.49 ±0.01	1.44 ±0.03

β	0.0	0.1
Expt.		
1	1.23	1.23
2	1.26	1.25
3	1.20	1.20
4	1.22	1.21
5	1.20	1.20
6	1.20	1.20
7	1.24	1.23
8	1.23	1.23
9	1.22	1.21
Mean K_1 x 10^6	1.22 ±0.02	1.22 ±0.02
1	0.95	0.95
2	1.04	1.03
3	0.99	0.99
4	1.01	1.01
5	0.99	0.99
6	0.99	0.99
7	1.02	1.01
8	1.02	1.01
9	1.01	1.00
Mean K_1 x 10^6	1.00 ±0.02	1.00 ±0.02

0.2	0.3	0.4	0.5	1.0
		Temp. = 35°C		
1.23	1.22	1.22	1.22	1.22
1.24	1.22	1.21	1.20	1.14
1.20	1.20	1.20	1.20	1.19
1.21	1.21	1.21	1.21	1.20
1.20	1.20	1.19	1.19	1.19
1.20	1.20	1.20	1.20	1.19
1.22	1.22	1.21	1.21	1.18
1.22	1.21	1.21	1.20	1.16
1.21	1.20	1.20	1.19	1.17
1.21 ±0.01	1.21 ±0.01	1.21 ±0.01	1.20 ±0.01	1.18 ±0.02
		Temp. = 45°C		
0.95	0.95	0.95	0.95	0.94
1.02	1.01	1.00	0.99	0.94
0.99	0.99	0.98	0.98	0.98
1.00	1.00	1.00	1.00	0.99
0.99	0.99	0.99	0.99	0.98
0.99	0.98	0.98	0.98	0.98
1.01	1.00	1.00	1.00	0.97
1.01	1.00	0.99	0.99	0.96
1.00	0.99	0.99	0.98	0.96
1.00 ±0.01	0.99 ±0.01	0.99 ±0.01	0.98 ±0.01	0.97 ±0.01

TABLE 44

β	0.0	0.1
Expt.		
1	1.86	1.86
2	1.85	1.84
3	1.84	1.84
4	1.87	1.86
5	1.90	1.90
6	1.94	1.93
7	1.95	1.95
8	1.87	1.86
9	1.95	1.95
10	1.93	1.92
Mean $K_1 \times 10^5$	1.90 $\pm$0.04	1.89 $\pm$0.04

TABLE 44

Cobalt Glycinate Results Varying β

0.2	0.3	0.4	0.5	1.0
Temp. = 0°C				
1.85	1.85	1.84	1.84	1.81
1.84	1.83	1.82	1.82	1.79
1.83	1.83	1.82	1.82	1.79
1.85	1.85	1.84	1.84	1.80
1.90	1.90	1.89	1.89	1.88
1.93	1.93	1.93	1.93	1.92
1.95	1.95	1.94	1.94	1.94
1.86	1.86	1.86	1.86	1.85
1.94	1.93	1.93	1.92	1.90
1.92	1.91	1.90	1.90	1.87
1.89 ±0.04	1.88 ±0.04	1.88 ±0.04	1.88 ±0.04	1.86 ±0.05

β	0.0	0.1
Expt.		
1	1.39	1.39
2	1.39	1.38
3	1.38	1.37
4	1.39	1.38
5	1.41	1.41
6	1.43	1.42
7	1.43	1.42
8	1.39	1.39
9	1.36	1.36
10	1.39	1.38
Mean $K_1 \times 10^5$	1.40 ±0.02	1.39 ±0.02

0.2	0.3	0.4	0.5	1.0
	Temp. = 15°C			
1.39	1.38	1.38	1.37	1.36
1.38	1.38	1.37	1.37	1.35
1.37	1.37	1.36	1.36	1.34
1.38	1.37	1.37	1.36	1.34
1.40	1.41	1.40	1.41	1.40
1.42	1.42	1.42	1.42	1.41
1.42	1.42	1.42	1.42	1.41
1.38	1.38	1.38	1.38	1.38
1.35	1.35	1.35	1.34	1.32
1.38	1.37	1.37	1.37	1.34
1.39 ±0.02	1.39 ±0.02	1.38 ±0.02	1.38 ±0.02	1.37 ±0.03

β	0.0	0.1
Expt.		
1	1.19	1.18
2	1.18	1.18
3	1.17	1.17
4	1.18	1.17
5	1.20	1.20
6	1.21	1.21
7	1.20	1.20
8	1.18	1.18
9	1.15	1.15
10	1.17	1.17
Mean $K_1 \times 10^5$	1.18 ±0.01	1.18 ±0.01

0.2	0.3	0.4	0.5	1.0
Temp. = 25°C				
1.18	1.18	1.17	1.17	1.15
1.17	1.17	1.18	1.16	1.14
1.17	1.16	1.16	1.16	1.14
1.17	1.16	1.16	1.15	1.13
1.20	1.19	1.19	1.19	1.18
1.21	1.21	1.20	1.20	1.20
1.20	1.20	1.19	1.19	1.19
1.18	1.18	1.18	1.17	1.17
1.14	1.14	1.14	1.14	1.14
1.16	1.16	1.15	1.15	1.13
1.18 ±0.02	1.18 ±0.02	1.17 ±0.02	1.17 ±0.02	1.16 ±0.02

β	0.0	0.1
Expt.		
1	1.03	1.02
2	1.02	1.02
3	1.01	1.01
4	1.01	1.01
5	1.04	1.04
6	1.04	1.04
7	1.03	1.03
8	1.03	1.02
9	1.00	0.99
10	1.01	1.01
Mean K_1 x 10^5	1.02 ±0.01	1.02 ±0.01

0.2	0.3	0.4	0.5	1.0
	Temp. = 35°C			
1.02	1.02	1.02	1.01	1.00
1.02	1.01	1.01	1.01	0.99
1.00	1.00	1.00	0.99	0.98
1.01	1.00	1.00	1.00	0.98
1.03	1.03	1.03	1.03	1.03
1.04	1.04	1.04	1.04	1.03
1.03	1.03	1.03	1.03	1.02
1.02	1.02	1.02	1.02	1.01
0.99	0.99	0.98	0.98	0.97
1.01	1.00	1.00	0.99	0.98
1.02 ±0.01	1.01 ±0.01	1.01 ±0.02	1.01 ±0.02	1.00 ±0.02

β	0.0	0.1
Expt.		
1	9.08	9.05
2	9.04	9.01
3	8.94	8.91
4	8.92	8.89
5	9.15	9.14
6	9.21	9.20
7	9.04	9.03
8	9.02	9.02
9	8.82	8.79
10	8.97	8.93
Mean $K_1 \times 10^4$	9.02 ±0.09	9.00 ±0.09

0.2	0.3	0.4	0.5	1.0
Temp. = 45^oC				
9.03	9.00	8.98	8.95	8.82
8.98	8.95	8.92	8.89	8.74
8.88	8.85	8.83	8.80	8.66
8.85	8.82	8.79	8.75	8.59
9.13	9.12	9.11	9.10	9.04
9.19	9.19	9.18	9.17	9.13
9.02	9.02	9.01	9.00	8.96
9.01	9.00	9.00	8.99	8.95
8.76	8.73	8.71	8.68	8.54
8.90	8.87	8.84	8.81	8.65
8.98 ±0.10	8.96 ±0.11	8.94 ±0.12	8.91 ±0.13	8.81 ±0.17

TABLE 45

β	0.0	0.1
Expt.		
1	1.73	1.65
2	1.72	1.64
3	1.69	1.63
4	1.71	1.67
5	1.63	1.58
6	1.69	1.63
7	1.79	1.71
Mean K_1 x 10^3	1.71 ±0.04	1.64 ±0.03
1	1.65	1.57
2	1.64	1.57
3	1.62	1.55
4	1.67	1.63
5	1.55	1.51
6	1.62	1.55
7	1.70	1.62
Mean K_1 x 10^3	1.64 ±0.04	1.57 ±0.03

TABLE 45

Manganese Glycinate Results Varying β

0.2	0.3	0.4	0.5	1.0
		Temp. = 0°C		
1.56	1.49	1.41	1.35	1.05
1.57	1.50	1.43	1.37	1.09
1.57	1.51	1.46	1.40	1.17
1.63	1.59	1.55	1.52	1.34
1.53	1.49	1.44	1.40	1.20
1.56	1.50	1.45	1.39	1.14
1.63	1.56	1.49	1.42	1.13
1.58 ±0.03	1.52 ±0.03	1.46 ±0.03	1.41 ±0.04	1.16 ±0.07
		Temp. = 15°C		
1.49	1.41	1.34	1.27	0.98
1.49	1.43	1.36	1.30	1.03
1.50	1.44	1.39	1.33	1.10
1.59	1.55	1.51	1.47	1.30
1.46	1.42	1.37	1.33	1.14
1.49	1.43	1.37	1.32	1.08
1.55	1.48	1.41	1.34	1.06
1.51 ±0.03	1.45 ±0.04	1.39 ±0.04	1.34 ±0.04	1.10 ±0.07

β	0.0	0.1
Expt.		
1	1.62	1.53
2	1.61	1.54
3	1.59	1.53
5	1.52	1.47
6	1.58	1.52
7	1.67	1.59
Mean $K_1 \times 10^3$	1.60 ±0.04	1.53 ±0.02
1	1.61	1.53
2	1.60	1.53
3	1.57	1.51
5	1.52	1.47
6	1.58	1.51
7	1.66	1.58
Mean $K_1 \times 10^3$	1.59 ±0.03	1.52 ±0.03

0.2	0.3	0.4	0.5	1.0
Temp. = 25°C				
1.45	1.38	1.31	1.24	0.95
1.46	1.40	1.33	1.27	1.00
1.47	1.41	1.36	1.31	1.07
1.43	1.38	1.34	1.30	1.11
1.46	1.40	1.34	1.29	1.05
1.52	1.45	1.38	1.31	1.03
1.47 ±0.02	1.40 ±0.02	1.34 ±0.02	1.29 ±0.02	1.04 ±0.04
Temp. = 35°C				
1.44	1.37	1.29	1.23	0.93
1.45	1.38	1.32	1.25	0.98
1.45	1.39	1.34	1.29	1.05
1.42	1.37	1.33	1.29	1.09
1.45	1.39	1.33	1.28	1.03
1.50	1.43	1.36	1.29	1.01
1.45 ±0.02	1.39 ±0.02	1.33 ±0.02	1.27 ±0.02	1.02 ±0.04

β	0.0	0.1
Expt.		
1	1.61	1.53
2	1.60	1.52
3	1.57	1.51
5	1.52	1.47
6	1.58	1.51
7	1.66	1.58
Mean K_1 x 10^3	1.59 ±0.03	1.52 ±0.02

0.2	0.3	0.4	0.5	1.0
Temp. = $45^{o}C$				
1.44	1.36	1.29	1.22	0.92
1.45	1.37	1.31	1.24	0.97
1.44	1.39	1.33	1.28	1.04
1.42	1.37	1.33	1.28	1.08
1.45	1.38	1.33	1.27	1.02
1.50	1.42	1.35	1.29	1.00
1.45 ±0.02	1.38 ±0.02	1.32 ±0.02	1.26 ±0.02	1.01 ±0.04

TABLE 46

β	0.0	0.1
Expt.		
1	1.96	1.96
2	1.87	1.87
3	1.93	1.92
4	1.95	1.95
5	2.03	2.03
6	1.90	1.90
7	1.88	1.87
8	1.96	1.96
Mean $K_2 \times 10^5$	1.94 ±0.04	1.93 ±0.04

1	1.18	1.18
2	1.18	1.18
3	1.16	1.16
4	1.18	1.18
5	1.22	1.22
6	1.19	1.19
7	1.17	1.17
8	1.21	1.20
Mean $K_2 \times 10^5$	1.19 ±0.02	1.19 ±0.02

TABLE 46

Nickel Glycinate Results Varying β

0.2	0.3	0.4	0.5	1.0
		Temp. = 0°C		
1.96	1.96	1.96	1.96	1.95
1.86	1.86	1.86	1.86	1.85
1.92	1.92	1.92	1.91	1.90
1.95	1.94	1.94	1.94	1.93
2.03	2.02	2.02	2.02	2.00
1.90	1.89	1.89	1.89	1.88
1.87	1.86	1.86	1,86	1.84
1.96	1.96	1.95	1.95	1.94
1.93 ±0.04	1.93 ±0.04	1.93 ±0.04	1.92 ±0.04	1.91 ±0.04
		Temp. = 15°C		
1.18	1.18	1.18	1.18	1.17
1.18	1.18	1.17	1.17	1.17
1.16	1.16	1.15	1.15	1.14
1.18	1.18	1.18	1.18	1.17
1.22	1.21	1.21	1.21	1.20
1.19	1.19	1.18	1.18	1.18
1.17	1.16	1.16	1.16	1.15
1.20	1.20	1.20	1.20	1.19
1.19 ±0.02	1.18 ±0.01	1.18 ±0.01	1.18 ±0.01	1.17 ±0.01

β	0.0	0.1
Expt.		
1	8.90	8.89
2	8.99	8.98
3	8.81	8.80
4	9.09	9.08
5	9.03	9.02
6	8.99	8.98
7	8.78	8.76
8	9.09	9.07
Mean K_2 x 10^4.	8.96 ±0.10	8.95 ±0.10
1	6.84	6.83
2	6.87	6.86
3	6.71	6.70
4	6.68	6.67
5	7.03	7.02
6	6.96	6.96
7	6.81	6.80
8	7.08	7.07
Mean K_2 x 10^4	6.87 ±0.11	6.86 ±0.11

0.2	0.3	0.4	0.5	1.0
		Temp. = 25°C		
8.89	8.88	8.87	8.86	8.83
8.97	8.95	8.94	8.93	8.88
8.78	8.77	8.76	8.75	8.68
9.07	9.05	9.04	9.03	8.97
9.01	8.99	8.98	8.96	8.90
8.96	8.95	8.94	8.93	8.87
8.75	8.72	8.71	8.69	8.59
9.06	9.05	9.04	9.02	8.96
8.94 ±0.10	8.92 ±0.10	8.91 ±0.10	8.89 ±0.10	8.84 ±0.10
		Temp. = 35°C		
6.83	6.82	6.81	6.81	6.78
6.85	6.84	6.83	6.83	6.78
6.69	6.68	6.67	6.66	6.48
6.66	6.65	6.65	6.64	6.47
7.01	7.00	6.99	6.98	6.92
6.95	6.94	6.93	6.92	6.87
6.78	6.77	6.75	6.74	6.66
7.06	7.04	7.03	7.02	6.97
6.85 ±0.11	6.84 ±0.11	6.83 ±0.11	6.83 ±0.11	6.74 ±0.15

β	0.0	0.1
Expt.		
1	5.43	5.42
2	5.47	5.46
3	5.34	5.33
5	5.85	5.84
6	5.77	5.76
7	5.72	5.71
8	5.91	5.90
Mean $K_2 \times 10^4$	5.64 ±0.20	5.63 ±0.20

0.2	0.3	0.4	0.5	1.0
Temp. = 45°C				
5.42	5.41	5.41	5.40	5.38
5.45	5.44	5.44	5.43	5.40
5.32	5.31	5.30	5.29	5.25
5.83	5.82	5.81	5.80	5.76
5.75	5.74	5.73	5.73	5.69
5.69	5.68	5.67	5.66	5.59
5.89	5.89	5.88	5.87	5.82
5.62 ±0.19	5.61 ±0.18	5.61 ±0.18	5.60 ±0.18	5.56 ±0.18

TABLE 47

β	0.0	0.1
Expt.		
1	1.76	1.75
2	1.75	1.75
3	1.72	1.71
4	1.80	1.80
5	1.69	1.68
6	1.58	1.58
7	1.59	1.59
Mean $K_2 \times 10^4$	1.70 ±0.07	1.69 ±0.07
1	1.20	1.20
2	1.24	1.24
3	1.21	1.21
4	1.26	1.26
5	1.15	1.15
6	1.11	1.11
7	1.10	1.10
Mean $K_2 \times 10^4$	1.18 ±0.05	1.18 ±0.05

TABLE 47

Cobalt Glycinate Results Varying β

0.2	0.3	0.4	0.5	1.0
Temp. = 0°C				
1.75	1.75	1.74	1.74	1.72
1.75	1.75	1.75	1.74	1.73
1.71	1.71	1.71	1.71	1.69
1.80	1.80	1.80	1.79	1.78
1.68	1.68	1.67	1.67	1.66
1.58	1.57	1.57	1.57	1.56
1.59	1.59	1.58	1.58	1.57
1.69 ±0.07	1.70 ±0.07	1.69 ±0.07	1.69 ±0.07	1.67 ±0.07
Temp. = 15°C				
1.20	1.20	1.19	1.19	1.18
1.24	1.23	1.23	1.23	1.22
1.20	1.20	1.20	1.20	1.19
1.25	1.25	1.25	1.25	1.24
1.15	1.15	1.15	1.15	1.14
1.11	1.11	1.11	1.11	1.10
1.10	1.09	1.09	1.09	1.08
1.18 ±0.05	1.18 ±0.05	1.17 ±0.05	1.17 ±0.05	1.16 ±0.05

β	0.0	0.1
Expt.		
1	9.38	9.34
2	10.01	10.00
3	9.63	9.61
4	10.05	10.03
5	9.12	9.10
6	8.95	8.93
7	8.91	8.89
Mean $K_2 x 10^4$	9.44 ±0.40	9.42 ±0.40
1	7.88	7.86
2	8.43	8.42
3	8.05	8.04
4	8.41	8.40
5	7.63	7.62
6	7.53	7.51
7	7.41	7.40
Mean K_2 x 10^4	7.91 ±0.34	7.89 ±0.34

0.2	0.3	0.4	0.5	1.0
Temp. = 25°C				
9.34	9.32	9.30	9.28	9.18
9.98	9.97	9.96	9.94	9.88
9.60	9.58	9.57	9.56	9.49
10.02	10.01	10.00	9.98	9.92
9.09	9.07	9.06	9.05	8.97
8.92	8.90	8.89	8.87	8.79
8.88	8.87	8.86	8.85	8.78
9.40 ±0.40	9.39 ±0.40	9.38 ±0.40	9.36 ±0.40	9.29 ±0.41
Temp. = 35°C				
7.84	7.82	7.81	7.79	7.70
8.41	8.40	8.39	8.37	8.32
8.03	8.02	8.00	7.99	7.93
8.39	8.37	8.36	8.35	8.30
7.60	7.59	7.59	7.57	7.50
7.50	7.48	7.47	7.46	7.39
7.39	7.38	7.37	7.36	7.31
7.88 ±0.34	7.86 ±0.34	7.85 ±0.34	7.84 ±0.34	7.78 ±0.35

β	0.0	0.1
Expt.		
1	6.60	6.58
2	7.13	7.12
3	6.81	6.80
4	7.01	7.00
5	6.42	6.41
6	6.39	6.38
7	6.19	6.18
Mean $K_2 \times 10^4$	6.65 ±0.30	6.64 ±0.29

0.2	0.3	0.4	0.5	1.0
		Temp. = 45°C		
6.57	6.55	6.54	6.52	6.45
7.11	7.10	7.09	7.08	7.03
6.79	6.78	6.77	6.76	6.71
6.99	6.98	6.97	6.96	6.91
6.40	6.38	6.37	6.36	6.31
6.37	6.35	6.34	6.33	6.27
6.17	6.16	6.15	6.14	6.10
6.63 ±0.29	6.61 ±0.29	6.60 ±0.29	6.59 ±0.29	6.54 ±0.29

METAL β-ALANINATES

The dissociation of β-alanine has been studied by May and Felsing[74] who determined k_1 with the cell

$H_2/Pt/HA\ (m_1),\ H_2ACl\ (m_2)/AgCl/Ag.$

The calculation was similar to that of Owen[71] and King[72] for glycine, but k_1 was also obtained from the equation

$$-\log k = \frac{E - E^0}{k} + \log \frac{m_{H_2A^+} m_{Cl^-}}{m_{HA}} + \log \frac{\gamma_{H_2A^+}\gamma_{Cl^-}}{\gamma_{HA}},$$

where $m_{H2A^+} = m_2 - m_{H^+}$, $m_{HA} = m_1 + m_{H^+}$, $m_{Cl^-} = m_2 = I.$

The activity coefficients were represented by the Debye-Huckel limiting law, and a quantity $-\log k_1'$ was defined as

$$-\log k_1 = \frac{E - E^0}{k} + \log \frac{m_{H_2A^+} m_{Cl^-}}{m_{HA}} - 2S\sqrt{I}.$$

An approximate value of m_{H^+} was obtained from

$$-\log m_{H^+} = \frac{E - E^0}{k} + \log m_2 - 2S\sqrt{I},$$

and $-\log k_1'$ calculated. Log k_1 was then determined by extrapolation and used in the calculation of a more accurate m_{H^+}. The process was repeated until k_1 was constant.

May and Felsing determined k_2, for the equilibrium

$HAOH^- \rightleftharpoons HA + OH^-,$

in a similar manner from the equation

$$- \log k_2' = - \log K_W - \frac{E - E^o}{k} - \log \frac{m_{HA}\, m_{Cl^-}}{m_{HAOH^-}} \quad .$$

Experimental solutions were prepared by dilution of four stock solutions, and four separate plots of $- \log k_2'$ against I were obtained. These all showed distinct curvature, and there was therefore considerable doubt about the derived k_2 values.

Since no other data were available for comparison with those of May and Felsing, it was necessary to determine k_1 and k_2.

Using the cell

$$H_2/Pt/HA\ (m_1),\ HCl\ (m_2)/AgCl/Ag,$$

the concentration of the anion, A^-, was negligible, and the concentrations of the ionic species were obtained from

$$- \log [H^+] = \frac{E - E^o}{k} + \log m_2 + \log \gamma_{H^+} \gamma_{Cl^-}, \qquad \text{....(39)}$$

$$m_1 = [H_2A^+]$$

$$m_1 = [H_2A^+] + [HA], \qquad \text{....(40)}$$

$$[H^+] + [H_2A^+] = [Cl^-] , \qquad \text{....(41)}$$

and the ionic strength $I = m_2$.

Activity coefficients were calculated from equation (38) using $\beta = 0.2$, and the results are given in Table 48.

$k_2 = \frac{[H^+][A^-]\gamma_1^2}{[HA]}$ was obtained using the cell

$H_2/Pt/HA(m_1)$, $NaOH(m_2)$, $KCl(m_3)/AgCl/Ag$.

H_2A^+ could be neglected, and the concentrations of ionic species were given by

$$-\log [H^+]\gamma_1^2 = \frac{E - E^o}{k} + \log m_3, \qquad \text{.....(42)}$$

$$m_1 = [HA] + [A^-] \qquad \text{.....(43)}$$

and

$$[H^+] + [Na^+] + [K^+] = [Cl^-] + [OH^-] + [A^-]. \qquad \text{.....(44)}$$

$$K_w = [H^+][OH^-]\gamma_1^2 \qquad \text{.....(45)}$$

was obtained from Robinson and Stokes[75], and the results are given in Table 49, and summarised in Table 50.

The agreement between the k_1 values and those of May and Felsing is seen to be good, but there is considerable deviation in the k_2 values. The k_2 data at 25°C in the present work have therefore been recalculated in the manner of May and Felsing, and Fig.15 shows the plot obtained. This appears to be as reliable as the plot given by the others and the intercept obtained, 3.705, corresponds to $k_2 = 5.11 \times 10^{-11}$.

The association constants for the nickel and cobalt β-alaninate systems were studied using a cell similar to that for the glycinates. To determine the complex species, the nickel β-alaninate results at 25°C were

Table 48

Molal Concentrations in β-Alanine Solutions

Expt.	1	2	3	4
$10^3 m_1$	11.1456	13.5367	10.5218	7.7396
$10^3 m_2$	5.0344	3.9242	3.2742	2.0512
	5	6	7	8
$10^3 m_1$	7.8944	7.5282	9.4399	9.0871
$10^3 m_2$	5.1638	5.0572	4.5933	4.1341

Results on β-Alanine k_1

Expt.	$E - E^0$	$10^4[H^+]$	$10^3[H_2A^+]$	$10^3[HA]$	$10^4.k_1$
	Temp. = 0°C				
1	0.33187	1.732	4.861	6.284	2.24
2	0.35333	0.878	3.836	9.700	2.22
3	0.35518	0.963	3.178	7.344	2.23
4	0.37106	0.765	1.975	5.765	2.23
5	0.31455	3.530	4.811	3.084	2.26
6	0.31389	3.701	4.687	2.841	2.24
7	0.33095	1.961	4.397	5.043	2.25
8	0.33629	1.725	3.962	5.125	2.23

Mean $k_1 = 2.24 \pm 0.01$

Expt.	$E - E^0$	$10^4[H^+]$	$10^3[H_2A^+]$	$10^3[HA]$	$10^4.k_1$
	Temp. = 15°C				
1	0.34666	1.995	4.835	6.311	2.60
2	0.36914	1.018	3.822	9.714	2.59
3	0.37114	1.114	3.163	7.359	2.59
4	0.38792	0.883	1.963	5.777	2.60
5	0.32880	4.001	4.764	3.131	2.63
6	0.32809	4.197	4.637	2.891	2.62
7	0.34584	2.246	4.369	5.071	2.61
8	0.35137	1.984	3.936	5.151	2.60
			Mean k_1 = 2.61 ± 0.01		
	Temp. = 25°C				
1	0.35697	2.139	4.820	6.325	2.81
2	0.38016	1.094	3.815	9.722	2.79
3	0.38222	1.197	3.154	7.367	2.80
4	0.39957	0.949	1.956	5.783	2.81
5	0.33869	4.256	4.738	3.156	2.84
6	0.33804	4.450	4.612	2.916	2.81
7	0.35616	2.406	4.374	5.065	2.79
8	0.36183	2.127	3.921	5.166	2.80
			Mean k_1 = 2.81 ± 0.01		

Expt.	$E - E^0$	$10^4[H^+]$	$10^3[H_2A^+]$	$10^3[HA]$	$10^4.k_1$
	Temp. = 35°C				
1	0.36783	2.236	4.811	6.335	2.94
2	0.39168	1.149	3.809	9.727	2.93
3	0.39384	1.255	3.149	7.373	2.94
4	0.41193	0.989	1.952	5.787	2.93
5	0.34908	4.425	4.721	3.173	2.97
6	0.34837	4.634	4.594	2.934	2.96
7	0.36699	2.513	4.342	5.098	2.95
8	0.37288	2.222	3.912	5.175	2.94
			Mean k_1 = 2.95 ± 0.01		
	Temp. = 45°C				
1	0.37912	2.297	4.805	6.341	3.03
2	0.40365	1.184	3.806	9.731	3.03
3	0.40587	1.294	3.145	7.377	3.03
4	0.42464	1.015	1.950	5.790	3.01
5	0.35982	4.535	4.710	3.184	3.07
6	0.35909	4.748	4.582	2.946	3.05
7	0.37819	2.587	4.335	5.105	3.05
8	0.38435	2.280	3.906	5.181	3.02
			Mean k_1 = 3.04 ± 0.02		

TABLE 49

Molal Concentrations in β-Alanine Solutions

Expt.	1	2	3	4
$10^3\ m_1$	5.1640	5.4704	4.3634	7.3054
$10^3\ m_2$	1.5290	1.3377	0.9654	0.9955
$10^3\ m_3$	2.7297	2.8025	2.7789	3.0129
	5	6	7	8
$10^3\ m_1$	14.0563	13.3120	12.2758	13.4139
$10^3\ m_2$	2.4697	1.0338	1.8575	2.8135
$10^3\ m_3$	6.4307	6.6041	5.7960	6.3115

Results on β-Alanine k_2

Expt.	$E - E^o$	$10^{11}[H^+]\gamma_1^2$	$10^3[A^-]$	$10^3[HA]$	$10^{11}.k_2$
	Temp. = 0^oC.				
1	0.71605	2.248	1.478	3.686	0.902
2	0.70963	2.877	1.298	4.172	0.895
3	0.70677	3.276	0.931	3.433	0.888
4	0.69141	5.803	0.976	6.330	0.895
5	0.68102	4.227	2.443	11.614	0.889
6	0.65876	10.060	1.023	12.289	0.882
7	0.67946	5.012	1.835	10.441	0.881
8	0.68649	3.414	2.780	10.634	0.893

Mean $k_2 = 0.891 \pm 0.06$

Expt.	E - E°	$10^{10}[H^+]\gamma_1^2$	$10^3[A^-]$	$10^3[HA]$	10^{11} k_2
	Temp. = 15°C				
1	0.72815	0.673	1.462	3.702	2.66
2	0.72147	0.858	1.285	4.185	2.63
3	0.71844	0.977	0.919	3.444	2.61
4	0.70251	1.713	0.969	6.336	2.62
5	0.69149	1.250	2.434	11.623	2.62
6	0.66804	3.131	1.019	12.293	2.60
7	0.68971	1.491	1.827	10.448	2.61
8	0.69731	1.008	2.769	10.645	2.62
			Mean k_2 = 2.62 ± 0.01		
	Temp. = 25°C				
1	0.73614	1.319	1.453	3.711	5.16
2	0.72929	1.677	1.278	4.193	5.19
3	0.72612	1.913	0.913	3.451	5.06
4	0.70973	3.340	0.965	6.340	5.09
5	0.69859	2.415	2.428	11.628	5.04
6	0.67429	6.055	1.017	12.295	5.01
7	0.69692	2.859	1.822	10.454	4.98
8	0.70459	1.948	2.762	10.652	5.05
			Mean k_2 = 5.06 ± 0.04		

Expt.	$E - E^0$	$10^{10}[H^+]\gamma_1^2$	$10^3[A^-]$	$10^3[HA]$	$10^{11}\ k_2$
	Temp. = 35°C				
1	0.74426	2.461	1.444	3.720	9.55
2	0.73723	3.123	1.271	4.200	9.45
3	0.73393	3.567	0.907	3.457	9.36
4	0.71708	6.204	0.962	6.344	9.41
5	0.70572	4.459	2.423	11.633	9.29
6	0.68058	11.192	1.015	12.297	9.24
7	0.70395	5.288	1.818	10.453	9.19
8	0.71198	3.589	2.755	10.659	9.28

Mean $k_2 = 9.35 \pm 0.10$

Expt.	$E - E^0$	$10^{10}[H^+]\gamma_1^2$	$10^3[A^-]$	$10^3[HA]$	$10^{11}\ k_2$
	Temp. = 45°C				
1	0.75245	4.406	1.438	3.726	17.0
2	0.74526	5.579	1.266	4.205	16.8
3	0.74181	6.382	0.902	3.461	16.6
4	0.72447	11.079	0.959	6.346	16.8
5	0.71285	7.930	2.419	11.637	16.5
6	0.68710	19.819	1.014	12.298	16.3
7	0.71104	9.399	1.815	10.461	16.3
8	0.71933	6.378	2.751	10.663	16.5

Mean $k_2 = 16.6 \pm 0.2$

TABLE 50

Dissociation Constants of β-Alanine.

Temp. °C	$10^4\ k_1$		$10^{11}\ k_2$	
		M and F		M and F
0	2.24	2.21	0.891	0.999
15	2.61	2.61	2.62	2.98
25	2.81	2.81	5.06	5.83
35	2.95	2.99	9.35	10.88
45	3.04		16.6	

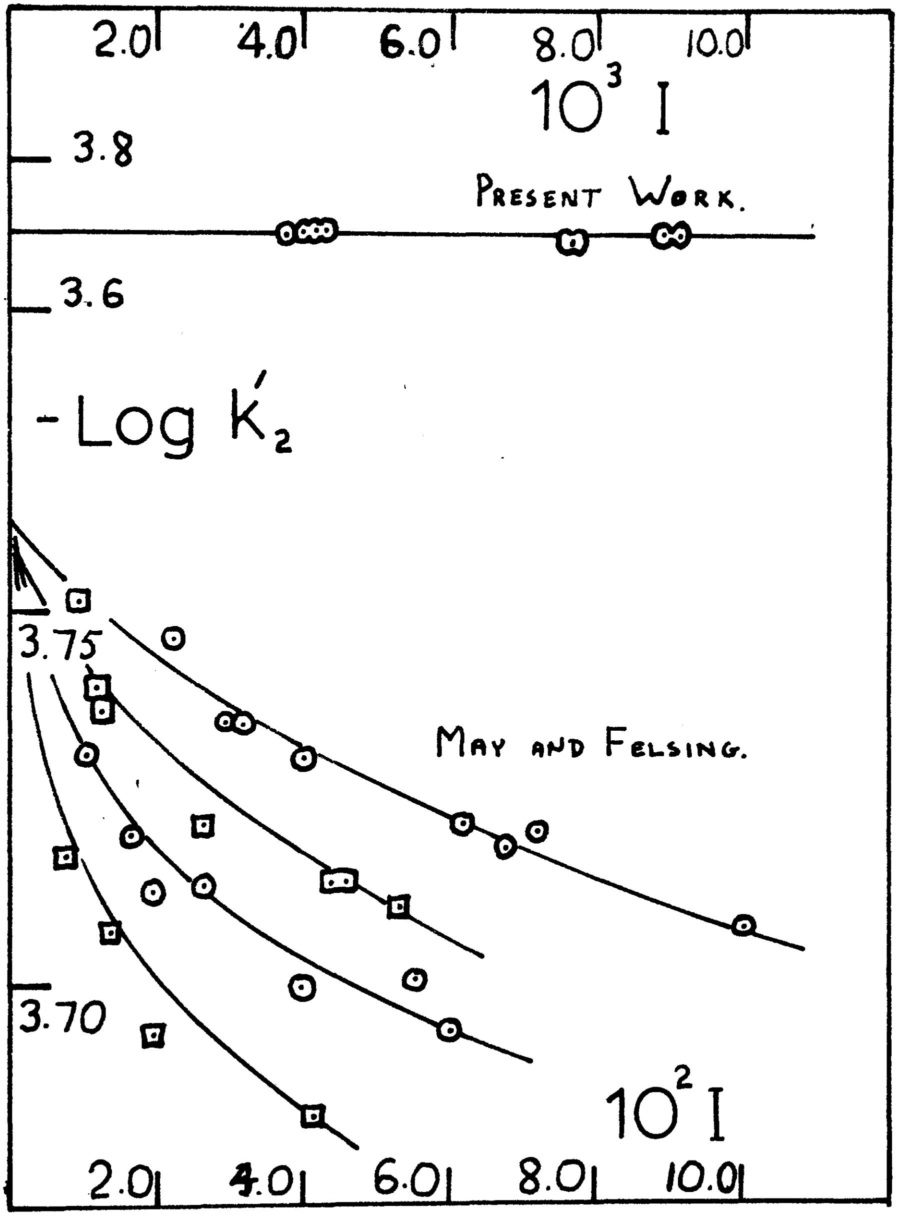

2.0
4.0
6.0
8.0
10.0
10^3 I
3.8
PRESENT WORK.
3.6
-Log K_2'
3.75
MAY AND FELSING.
3.70
10^2 I
2.0
4.0
6.0
8.0
10.0

Fig. 15

calculated using K_2 values of 0 and 1×10^3. It is seen in Table 51 that there is very little difference in the derived K_1 so that it is permissible to assume that only one complex, MA^+, is present. The equations from which the concentrations of the ionic species were determined were therefore similar to those used in the manganese glycinate system. Activity coefficients were again calculated from equation (38), and the results for $\beta = 0.2$ are given in Tables 52 and 53. K_1 values for $\beta = 0$ to 1.0 are given in Tables 54 and 55.

TABLE 51

Nickel β- Alaninate K_1 Values at 25°C

10^3K_2	1.	2.	3.	4.	5.	6.	7.
0	9.39	9.61	9.88	10.37	10.17	9.96	9.83
1	9.32	9.54	9.82	10.30	10.11	9.90	9.77

TABLE 52

Expt.	1	2
$10^2\ m_1$	1.6932	2.0039
$10^4\ m_2$	4.3522	4.0373
$10^3\ m_3$	1.8946	1.7210

Expt.	$E - E^o$	$10^3.I$
1	0.52310	5.249
2	0.52211	4.757
3	0.52163	4.623
4	0.53236	2.661
5	0.52278	3.507
6	0.51936	3.948
7	0.50610	4.917

1	0.53352	5.246
2	0.53280	4.754
3	0.53362	4.621
4	0.54383	2.657
5	0.53374	3.502
6	0.53026	3.941
7	0.51688	4.905

TABLE 52

Molal Concentrations in Nickel β-Alaninate Experiments

3	4	5	6	7
1.7436	2.0336	2.0304	2.4171	2.8592
3.5896	2.3231	2.5388	3.1735	3.1933
1.6613	0.9657	1.2571	1.4238	1.7505

Results on Nickel β-Alaninate

Temp. = 0°C

$10^8[H^+]$	$10^2[HA]$	$10^6[A^-]$	$10^4[MA^+]$	$10^{-5}.K_1$
6.832	1.649	2.496	4.378	1.62
7.791	1.962	2.588	4.081	1.60
8.222	1.706	2.128	3.632	1.74
9.199	2.059	2.354	2.380	1.73
8.686	2.053	2.034	2.663	1.69
10.177	2.383	2.313	3.263	1.67
10.463	2.823	1.918	3.367	1.66

Mean K_1 = 1.67 ± 0.04

Temp. = 15°C

$10^8[H^+]$	$10^2[HA]$	$10^6[A^-]$	$10^4[MA^+]$	$10^{-5}.K_1$
14.329	1.648	3.512	4.409	1.17
16.127	1.961	3.688	4.124	1.15
16.133	1.706	3.200	3.665	1.18
17.807	2.058	3.385	2.432	1.24
20.852	2.051	2.926	2.726	1.22
21.337	2.381	3.344	3.337	1.20
30.174	2.821	2.841	3.495	1.18

Mean K_1 = 1.19 ± 0.02

Expt.	$E - E^{o}$	$10^{3}.I$
1	0.54121	5.245
2	0.53943	4.750
3	0.54033	4.617
4	0.55133	2.653
5	0.54094	3.496
6	0.53740	3.934
7	0.52396	4.893

1	0.54788	5.240
2	0.54621	4.743
3	0.54720	4.611
4	0.55871	2.645
5	0.54825	3.487
6	0.54456	3.924
7	0.53115	4.875

$10^7[H^+]$	$10^2[HA]$	$10^6[A^-]$	$10^4[HA^+]$	$10^{-4}.K_1$
	Temp. = 25°C			
2.190	1.647	4.450	4.439	9.39
2.567	1.960	4.437	4.175	9.61
2.562	1.705	3.901	3.709	9.38
2.778	2.056	4.198	2.488	10.37
3.247	2.050	3.636	2.793	10.17
3.315	2.380	4.165	3.416	9.96
4.615	2.818	3.595	3.626	9.83
		Mean K_1 = 9.89 ± 0.24		
	Temp. = 35°C			
3.383	1.646	5.328	4.491	8.00
3.937	1.958	5.408	4.249	8.20
3.921	1.703	4.713	3.773	8.41
4.227	2.054	5.097	2.571	8.96
4.893	2.048	4.460	2.889	8.70
5.000	2.377	5.105	3.531	8.52
6.839	2.814	4.483	3.808	8.43
		Mean K_1 = 8.46 ± 0.23		

Expt.	$E - E^{o}$	$10^{3}.I$
1	0.55431	5.233
2	0.55296	4.734
3	0.55336	4.602
4	0.56656	2.635
5	0.55584	3.475
6	0.55201	3.909
7	0.53878	4.852

$10^7[H^+]$	$10^2[HA]$	$10^6[A^-]$	$10^4[MA^+]$	$10^{-4}.K_1$
	Temp. = 45°C			
5.133	1.644	6.244	4.573	7.03
5.894	1.956	6.422	4.359	7.19
6.004	1.701	5.471	3.877	7.54
6.165	2.052	6.208	2.684	7.84
7.117	2.045	5.447	3.021	7.58
7.278	2.374	6.230	3.687	7.44
9.735	2.809	5.594	4.048	7.34

Mean K_1 = 7.42 ± 0.20

TABLE 53

Expt.	1
$10^2 m_1$	0.5765
$10^4 m_2$	3.9641
$10^2 m_3$	0.8291

Expt.	$E - E^0$	$10^2.I$
1	0.46023	2.438
2	0.46263	2.051
4	0.44778	3.340
5	0.45665	2.465
6	0.45031	3.072

1	0.47074	2.433
2	0.47440	2.046
4	0.45877	3.334
5	0.46880	2.460
6	0.46058	3.067

TABLE 53

Molal Concentrations in Cobalt β-Alaninate Experiments

2	3	4	5	6
9.1761	8.9598	9.4520	8.1413	7.8930
3.5492	5.1183	4.0928	3.3713	3.2554
0.6990	1.4153	1.1316	0.8364	1.0386

Results on Cobalt β-Alaninate

$10^7[H^+]$	$10^2[HA]$	$10^6[A^-]$	$10^4[MA^+]$	$10^{-4}.K_1$
	Temp. = 0°C			
2.605	8.517	3.903	4.919	2.90
2.734	9.118	3.901	4.627	3.13
3.369	9.383	3.459	5.474	2.86
3.009	8.086	3.211	4.429	3.14
3.261	7.338	2.952	4.371	2.83
		Mean $K_1 = 2.97 \pm 0.13$		
	Temp. = 15°C			
4.752	8.506	6.328	5.458	2.03
4.764	9.107	6.619	5.154	2.10
5.870	9.369	5.876	6.152	1.93
5.224	8.075	5.472	4.942	2.09
5.886	7.825	4.840	4.982	2.01
		Mean $K_1 = 2.03 \pm 0.05$		

Expt.	$E - E^o$	$10^2.I$
1	0.47798	2.429
2	0.48245	2.042
3	0.46130	4.170
4	0.46624	3.328
5	0.47608	2.456
6	0.46821	3.062
1	0.48575	2.423
2	0.49061	2.036
3	0.46816	4.163
4	0.47393	3.321
5	0.48398	2.450
6	0.47594	3.056
1	0.49365	2.416
2	0.49905	2.029
3	0.47488	4.152
4	0.48191	3.312
5	0.49221	2.444
6	0.48402	3.048

$10^7[H^+]$	$10^2[HA]$	$10^6[A^-]$	$10^4[MA^+]$	$10^{-4}.K_1$
	Temp. = 25°C			
6.805	8.496	8.569	5.946	1.66
6.641	9.097	9.207	5.618	1.67
8.210	8.857	7.968	7.639	1.52
8.206	9.356	8.157	6.756	1.55
7.273	8.066	7.623	5.394	1.67
8.186	7.815	6.753	5.477	1.61
		Mean K_1 = 1.61 ± 0.05		
	Temp. = 35°C			
9.332	8.483	11.577	6.544	1.37
9.019	9.085	12.555	6.213	1.38
11.423	8.840	10.619	8.450	1.29
11.127	9.340	11.150	7.519	1.29
9.900	8.053	10.375	5.983	1.38
11.114	7.801	9.218	6.116	1.34
		Mean K_1 = 1.34 ± 0.04		
	Temp. = 45°C			
12.503	8.467	15.391	7.309	1.18
11.914	9.069	16.925	6.950	1.17
15.668	8.817	13.799	9.545	1.14
14.667	9.321	15.075	8.458	1.10
13.079	8.038	13.989	6.706	1.17
14.628	7.785	12.479	6.895	1.14
		Mean K_1 = 1.15 ± 0.02		

TABLE 54

β	0.0	0.1
Expt.		
1	1.63	1.63
2	1.61	1.60
3	1.75	1.75
4	1.73	1.73
5	1.70	1.70
6	1.68	1.67
7	1.67	1.66
Mean $K_1 \times 10^5$	1.68 ±0.04	1.68 ±0.04
1	1.18	1.18
2	1.15	1.15
3	1.19	1.18
4	1.25	1.24
5	1.22	1.22
6	1.20	1.20
7	1.19	1.18
Mean $K_1 \times 10^5$	1.20 ±0.02	1.19 ±0.02

TABLE 54

Nickel β-Alaninate Results Varying β

0.2	0.3	0.4	0.5	1.0
		Temp. = 0°C		
1.62	1.62	1.62	1.61	1.59
1.60	1.60	1.59	1.59	1.57
1.74	1.74	1.74	1.73	1.71
1.73	1.73	1.72	1.72	1.71
1.69	1.69	1.69	1.69	1.67
1.67	1.67	1.66	1.66	1.65
1.66	1.66	1.65	1.65	1.63
1.67 ±0.04	1.67 ±0.04	1.67 ±0.04	1.66 ±0.04	1.65 ±0.04
		Temp. = 15°C		
1.17	1.17	1.17	1.16	1.15
1.15	1.14	1.14	1.14	1.12
1.18	1.18	1.18	1.17	1.16
1.24	1.24	1.24	1.24	1.23
1.22	1.22	1.22	1.21	1.20
1.20	1.20	1.19	1.19	1.18
1.18	1.18	1.18	1.17	1.16
1.19 ±0.02	1.19 ±0.03	1.19 ±0.02	1.18 ±0.03	1.17 ±0.03

β	0.0	0.1
Expt.		
1	9.43	9.41
2	9.66	9.63
3	9.93	9.91
4	10.40	10.38
5	10.21	10.19
6	9.99	9.98
7	9.87	9.85
Mean $K_1 \times 10^4$	9.93 ±0.23	9.91 ±0.24
1	8.05	8.03
2	8.24	8.22
3	8.44	8.43
4	8.99	8.98
5	8.73	8.71
6	8.56	8.54
7	8.47	8.45
Mean $K_1 x 10^4$	8.50 ±0.23	8.48 ±0.23

0.2	0.3	0.4	0.5	1.0
Temp. = 25°C				
9.39	9.36	9.34	9.32	920
9.61	9.59	9.57	9.55	9.44
9.88	9.86	9.84	9.82	9.71
10.37	10.36	10.34	10.33	10.26
10.17	10.15	10.13	10.12	10.03
9.96	9.94	9.92	9.90	9.80
9.83	9.80	9.78	9.75	9.63
9.89 ±0.25	9.87 ±0.24	9.85 ±0.24	9.83 ±0.25	9.72 ±0.25
Temp. = 35°C				
8.00	7.98	7.96	7.94	7.84
8.20	8.18	8.17	8.15	8.05
8.41	8.39	8.37	8.35	8.25
8.96	8.95	8.94	8.93	8.87
8.70	8.68	8.67	8.65	8.57
8.52	8.51	8.49	8.47	8.39
8.43	8.41	8.38	8.36	8.25
8.46 ±0.23	8.44 ±0.23	8.43 ±0.24	8.41 ±0.24	8.32 ±0.26

β	0.0	0.1
Expt.		
1	7.07	7.05
2	7.22	7.20
3	7.58	7.56
4	7.86	7.85
5	7.61	7.60
6	7.47	7.45
7	7.38	7.36
Mean $K_1 \times 10^4$	7.46 ±0.20	7.44 ±0.20

0.2	0.3	0.4	0.5	1.0
	Temp. = 45°C			
7.03	7.02	7.00	6.98	6.89
7.19	7.17	7.15	7.13	7.05
7.54	7.52	7.51	7.49	7.40
7.84	7.83	7.81	7.80	7.75
7.58	7.57	7.55	7.54	7.47
7.44	7.42	7.41	7.39	7.31
7.34	7.32	7.30	7.28	7.18
7.42 ±0.20	7.41 ±0.20	7.39 ±0.21	7.37 ±0.21	7.29 ±0.21

TABLE 57

β	0.0	0.1
Expt.		
1	2.97	2.94
2	3.20	3.17
4	2.96	2.91
5	3.22	3.17
6	2.92	2.88
Mean K_1 x 10^4	3.05 ±0.12	3.01 ±0.12
1	2.08	2.05
2	2.15	2.12
4	2.00	1.97
5	2.15	2.12
6	2.08	2.04
Mean K_1 x 10^4	2.09 ±0.05	2.06 ±0.05

TABLE 55

Cobalt β-Alaninate Results Varying β

0.2	0.3	0.4	0.5	1.0
Temp. = 0°C				
2.90	2.87	2.83	2.80	2.63
3.13	3.10	3.07	3.04	2.88
2.86	2.81	2.76	2.71	2.49
3.14	3.10	3.06	3.02	2.84
2.83	2.79	2.74	2.70	2.50
2.97 ±0.13	2.93 ±0.13	2.89 ±0.14	2.85 ±0.14	2.67 ±0.15
Temp. = 15°C				
2.03	2.00	1.98	1.95	1.83
2.10	2.08	2.05	2.03	1.92
1.93	1.90	1.86	1.83	1.67
2.09	2.07	2.04	2.01	1.88
2.01	1.98	1.94	1.91	1.76
2.03 ±0.05	2.01 ±0.06	1.97 ±0.06	1.95 ±0.06	1.81 ±0.08

β	0.0	0.1
Expt.		
1	1.70	1.68
2	1.71	1.69
3	1.60	1.56
4	1.61	1.58
5	1.71	1.69
6	1.67	1.64
Mean $K_1 \times 10^4$	1.67 ±0.04	1.64 ±0.05
1	1.41	1.39
2	1.42	1.40
3	1.35	1.32
4	1.34	1.32
5	1.42	1.40
6	1.39	1.36
Mean $K_1 \times 10^4$	1.39 ±0.03	1.37 ±0.03

0.2	0.3	0.4	0.5	1.0
		Temp. = 25°C		
1.66	1.64	1.61	1.59	1.49
1.67	1.65	1.63	1.62	1.52
1.52	1.49	1.46	1.42	1.27
1.55	1.53	1.50	1.47	1.34
1.67	1.64	1.62	1.60	1.49
1.61	1.58	1.55	1.53	1.40
1.61 ±0.05	1.59 ±0.06	1.56 ±0.06	1.54 ±0.07	1.42 ±0.08
		Temp. = 35°C		
1.37	1.36	1.34	1.32	1.23
1.38	1.37	1.35	1.33	1.25
1.29	1.26	1.23	1.20	1.06
1.29	1.26	1.24	1.21	1.10
1.38	1.36	1.34	1.32	1.23
1.34	1.32	1.29	1.27	1.16
1.34 ±0.04	1.32 ±0.04	1.30 ±0.05	1.28 ±0.05	1.17 ±0.07

β	0.0	0.1
Expt.		
1	1.21	1.20
2	1.20	1.19
3	1.20	1.17
4	1.14	1.12
5	1.21	1.19
6	1.18	1.16
Mean $K_1 \times 10^4$	1.19 ±0.02	1.17 ±0.02

0.2	0.3	0.4	0.5	1.0
	Temp. = 45°C			
1.18	1.16	1.14	1.13	1.05
1.17	1.16	1.14	1.13	1.06
1.14	1.12	1.09	1.06	0.94
1.10	1.07	1.05	1.03	0.93
1.17	1.16	1.14	1.12	1.04
1.14	1.12	1.10	1.07	0.98
1.15 ±0.02	1.13 ±0.03	1.11 ±0.03	1.09 ±0.04	1.00 ±0.05

DISCUSSION

In his studies on the solubility of cupric iodate in glycine solutions, Keefer[56] showed the existence of a cation-zwitterion complex, $CuHA^{2+}$. Curchod[76] suggested that in solutions of cupric α-alaninate five complexes, $CuHA^{2+}$, CuA^{+}, $Cu(HA)_2^{2+}$, CuA_2 and CuHA A^{+}, were formed, but at $pH > 4.75$ only the anion, A^{-}, appeared to give complexes. The corresponding pH limit for cupric β-alaninates was 6.26[59b]. Curchod and Pelletier[77] have made no mention of zwitterion complexes in solutions containing nickel ion and amino acids, and it was therefore considered that these would be absent in the present work.

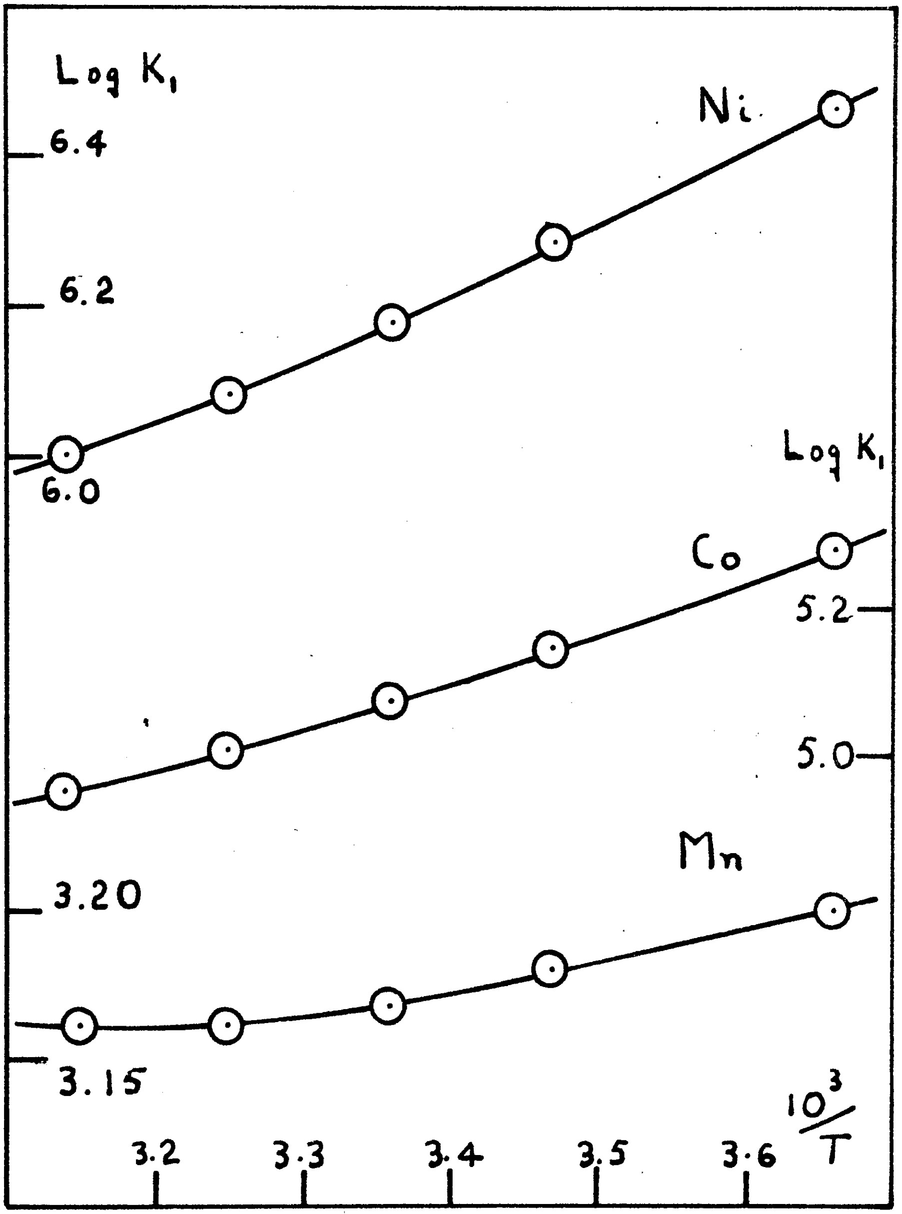
When amino acids are dissolved in water, the dielectric constant is greater than that of pure water. In order to determine what effect this would have on the activity coefficients, the Debye-Huckel constant, A, was recalculated for various values of ε. In the nickel and cobalt glycinate K_1 studies, the increase in ε[78] is approximately 0.2 and the effect on γ_1 and γ_2 is negligible. For K_2, $I \approx 2 \times 10^{-3}$ and the small increase in ε has virtually no effect on the activity coefficients. This is also found with nickel β-alaninate, but for manganese glycinate and cobalt β-alaninate increases in γ_2 from 0.5 to 2.0% are obtained. The variation is, however, within the experimental error and can be ignored.

K_1 and K_2 for the nickel glycinate are in very good agreement with 1.51×10^6 and 9.33×10^4 respectively, calculated by Monk[53] from potentiometric measurements at 25°C. Albert[51], at 20°C with $I \approx 0.01$ obtained a K_1, of 1.26×10^6. After correcting to $I = 0$, $K_1 = 1.9 \times 10^6$, in good agreement with the value at 15°C obtained in the present work. Irving et al[45] measured $K_1(\text{Ni}\beta\text{A})$ at 20°C and $I = 0.1$ which corresponds to 1.20×10^5 at $I = 0$. No data are available with which to compare cobalt β-alaninate but the glycinate results, $K_1 = 1.05 \times 10^5$ and $K_2 = 9.33 \times 10^3$ by Evans and Monk[79] at 25°C are in good agreement with those in Tables 39 and 42. There is a much larger discrepancy in the values of K_1 (MnG). Monk[53] obtained 2.8×10^3 at $I = 0$, Maley and Mellor[52] 4.6×10^3 at 25° with $I \approx 0.01$ and Albert[51] 1.6×10^3 at 20° with $I \approx 0.01$.

Plots of $\log K_1$ and $\log K_2$ against $1/T$ in Figs. 16, 17 and 18 are all curved indicating a non-zero ΔCp. A number of equations are available to describe this variation with temperature[80], and the one used was

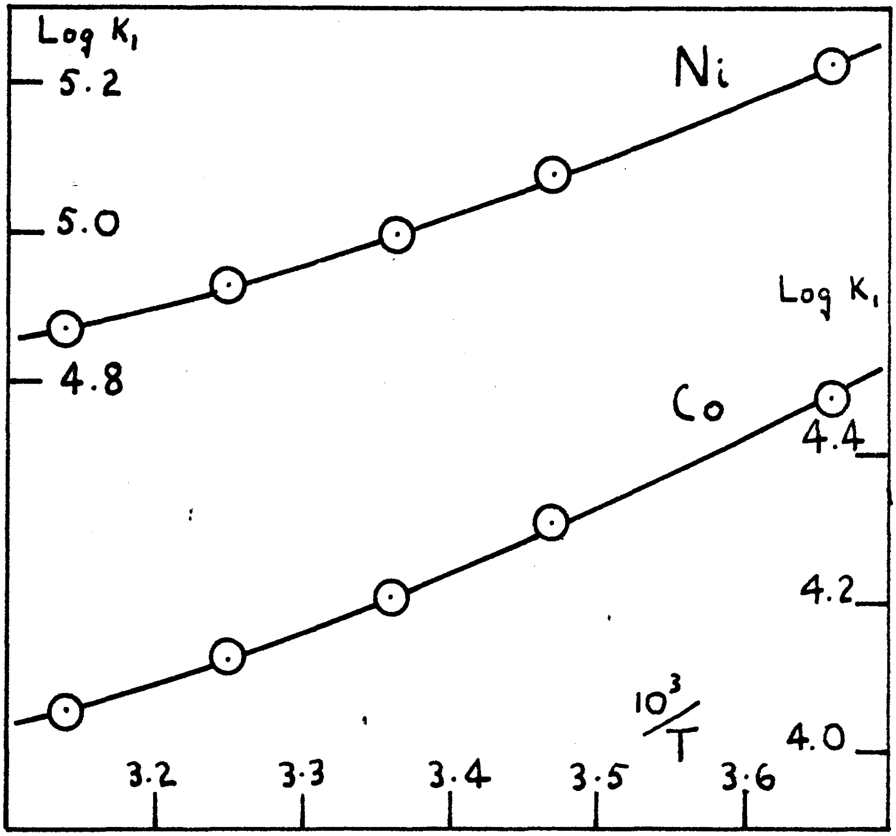
$$\log K = a + bT + CT^2 \qquad \text{......(46)}$$

a, b. and c were calculated by substituting log K values at 0°, 25° and 45° and solving the similtaneous



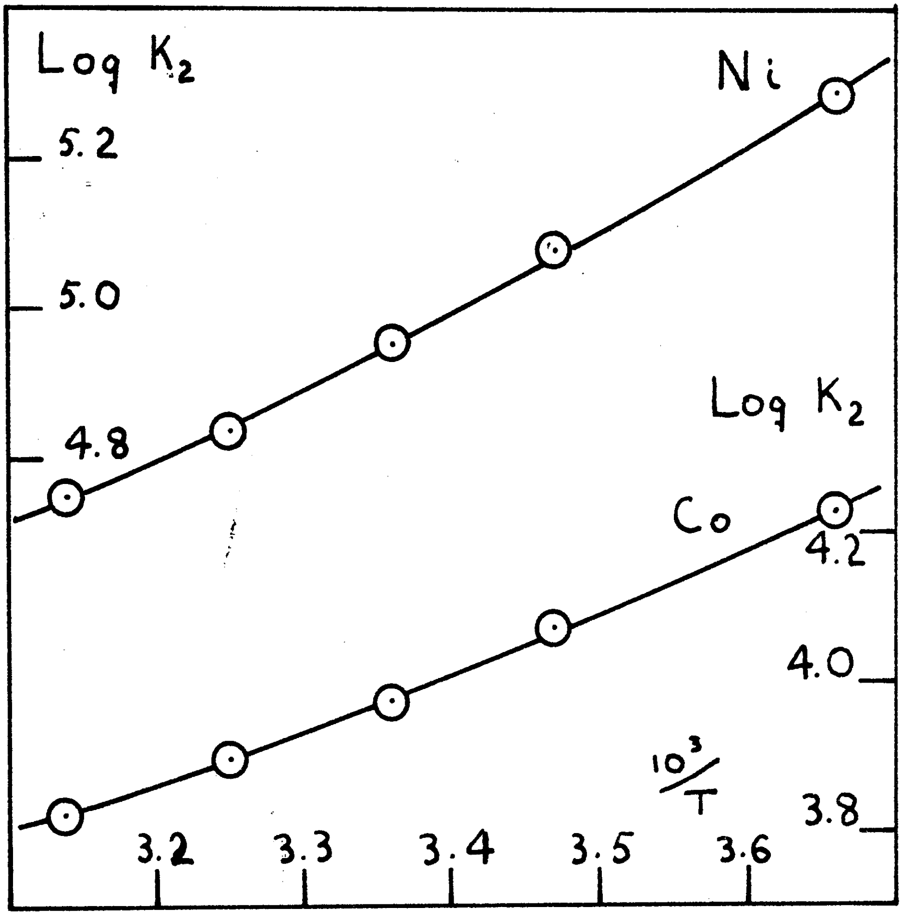
Metal Glycinates

Fig. 16



METAL β-ALANINATES

FIG. 17



Metal Glycinates

Fig. 18

equations. The difference between calculated and observed values at the other temperatures was as much as 2% for K_2, but was never more than 1% for K_1. The values of the parameters are given in Table 56.

Differentiation of equation (46) at constant pressure gives

$$\left(\frac{\partial \log K}{\partial T}\right)_p = \frac{\Delta H}{2.303\ RT^2} = b + 2cT,$$

from which

$$\Delta H = 2.303\ RT^2\ (b + 2cT)\ , \qquad \ldots\ldots(47)$$

The other thermodynamic properties were obtained from

$$-\Delta G = 2.303\ RT \log K, \qquad \ldots\ldots(48)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}, \qquad \ldots\ldots(49)$$

and $\Delta C_p = \frac{d\ \Delta H}{dT} = 4.606\ RT\ (b + 3cT).$ $\qquad \ldots\ldots(50)$

Thermodynamic data have been calculated at 25°C and are given in Table 57. The mean deviations were estimated by using different combinations of experimental values to calculate a, b, and c, and the deviation in ΔG was taken to be the average of the mean deviations of individual log K values at 25°C.

It is seen that the association constants follow the Irving-Williams order, as expected. The five-membered

TABLE 56

Parameters for Temperature Dependence of Log K

Reaction	a	-10^2b	10^5c
$Ni^{2+} + G^-$	14.0904	4.305	5.547
$Co^{2+} + G^-$	11.584	3.675	5.000
$Mn^{2+} + G^-$	5.316	1.370	2.178
$NiG^+ + G^-$	14.889	5.515	7.316
$CoG^+ + G^-$	11.810	4.385	5.889
$Ni^{2+} + A^-$	12.988	4.612	6.475
$Co^{2+} + A^-$	13.242	5.183	7.218

TABLE 57

Thermodynamic Properties

Reaction	$-\Delta G$	$-\Delta H$	ΔS	ΔCp
$Ni^{2+} + G^-$	8.43±0.01	4.09±0.03	14.5±0.1	18 ± 2
$Co^{2+} + G^-$	6.29±0.01	2.82±0.12	13.7±0.5	22 ± 14
$Mn^{2+} + G^-$	4.32±0.01	0.29±0.08	13.5±0.3	16 ± 10
$NiG^+ + G^-$	6.75±0.01	4.69±0.30	6.9±0.8	28 ± 25
$CoG^+ + G^-$	5.42±0.02	3.55±0.20	6.3±0.6	24 ± 20
$Ni^{2+} + A^-$	6.81±0.02	3.06±0.10	12.6±0.2	31 ± 6
$Co^{2+} + A^-$	5.74±0.02	3.60±0.10	7.2±0.5	35 ± 13

$-\Delta G$ and $-\Delta H$ in k.cal./mole.

ΔS in cal./deg.mole.

ΔCp in cal./deg.

ring glycinates are also more stable than the corresponding β-alaninates. Of interest in this connection is some recent work which has shown that for the uranyl ion in its association with glycine and β-alanine, this order of stability is reversed[31]. ΔH_1 is more negative for nickel than for cobalt or manganese glycinates, as has been found for various dicarboxylate complexes and also for the argininates[49]. For the β-alaninates, however, the cobalt association is more exothermic than that of the nickel. $-\Delta H_2$ is slightly larger than $-\Delta H_1$, as has been found for a number of nitrogen-type chelates[49]. The low ΔS_1 values are similar to those found by Pelletier[49] and are probably due to the positively charged complex which is formed. ΔS_2, as expected, is lower than ΔS_1, due to the decrease in the charges of the ions associating.

The unusual feature of the results is the non-zero ΔC_p. Although this has been found for chelates which complex through oxygen atoms it is unknown for nitrogen-type chelates. Pelletier[49] found a linear relationship between log K and 1/T, but the temperature range covered was relatively small and a slight scatter of points was put down to experimental error. The ΔC_p values are smaller than those for the corresponding oxalates[48] and malonates[42], and also for a number of reactions of the hydrogen ion with univalent anions[32].

Tables 43, 44, 45, 46, 47, 54 and 55 show the effect of varying β in equation (38). Only with manganese glycinate was the ionic strength much greater than 10^{-2}, and it was only with this complex that an appreciable variation in K resulted. The range of ionic strength covered was too small to show which value of β gave the best results, but it appears that any value between $\beta = 0.1$ and $\beta = 0.5$ may be used. For $I \leqslant 10^{-2}$ any of the low values can be used without a serious error in K; in nickel glycinate, where $1 \times 10^{-3} \leqslant I \leqslant 2 \times 10^{-2}$, the difference in K values with β's of 0 and 0.5 is only 3%.

PART III

CALORIMETRIC DETERMINATION OF THE HEATS OF FORMATION OF TRANSITION METAL GLYCINATE AND β-ALANINATE COMPLEXES

INTRODUCTION

In order to understand the processes accompanying complex formation in solution, it is necessary to determine the heats and entropies of formation. In most cases where the heats are known they have been calculated from stability constant measurements at more than one temperature. While we consider that this method can yield reliable values if a large temperature range is covered, it is undoubtedly better to measure the heats of formation directly. In some cases where data are available by both methods, good agreement is obtained; for the first stage of the dissociation of sulphuric acid, $\Delta H = -5.2$ k.cal./mole by calorimetry[32] and -5.6 k.cal./mole by temperature cofficients[33]. Both methods have also been used in the study of ethylenediamine complexes[34,35,36].

Lange[37] studied heats of dilution with a system of twin adiabatic calorimeters, one of which was used as a constant temperature reference. Each calorimeter contained a section of a 1,500 junction thermopile, and the calorimeter used in the present work was of a similar design.

Pitzer[32], who measured the ΔH value for the bisulphate ion, used a non-isothermic calorimeter, and modifications of this have been used by Staveley[85,88] and others[89], for studies with amine and ethylenediamine tetraacetate complexes.

Where the amount of material available is extremely small, such as the transuranium elements, microcalorimeters have been used in the study of the heats of solution. Westrum and Eyring[90] studied the dissolution of neptunium in hydrochloric acid, using a resistance thermometer to measure temperature changes of approximately 2 x 10^{-5}°C. Use of thermistors, in place of the resistance thermometer, enabled Cobble[91], with a similar calorimeter, to measure changes of 10^{-5}°C. Tian-Calvet[92] calorimeters have also been used to study small samples[93].

The sensitivity of a calorimeter is normally examined by measuring the heat change in a system which is well characterised. The methods used include the neutralisation of sodium hydroxide by hydrochloric acid[85], the dissolution of magnesium metal in hydrochloric acid[90,91], and the dissolution of potassium nitrate in water[90]. The most common method, however, is to measure the heat of solution of potassium chloride in water, and this is the one which has been employed in the present work.

EXPERIMENTAL

APPARATUS

The calorimeters consisted of two silvered Dewar flasks, of over one litre capacity, set into brass containers (Fig.19). A water-tight seal was obtained by inserting rubber O-rings between the flanges and the lids, which were then screwed down with six thumb screws. Perspex discs, of a half inch thickness, were cemented to the underside of the lids. Four holes in the lid of the first Dewar accomodated the heater, the stirrer diaphragm, a B24 socket for the thermopile and the mixing device. Two holes in the lid of the second Dewar held the stirrer diaphragm and a B24 socket for the constant temperature end of the thermopile. The containers were attached rigidly to a central brass rod and were completely immersed in the thermostat.

In order to reduce to a minimum the effects due to unequal stirring of the two calorimeters, both stirrers were driven by the same motor using a special stirring head. A vibro-rotary motor was used (Vibro-Mischer, Messrs. Shandon and Co. Ltd. England).

The thermopile consisted of sixty junctions of 20 S.W.G. constantan wire and 34 S.W.G. enamelled copper wire. The constantan wires were insulated to within $\frac{1}{4}$ of an inch of their ends with P.V.C. sleaving, and the copper wires were wound on these. The junctions were made by soft soldering the ends of the wires and were arranged to be at $\frac{1}{2}$ cm. intervals when

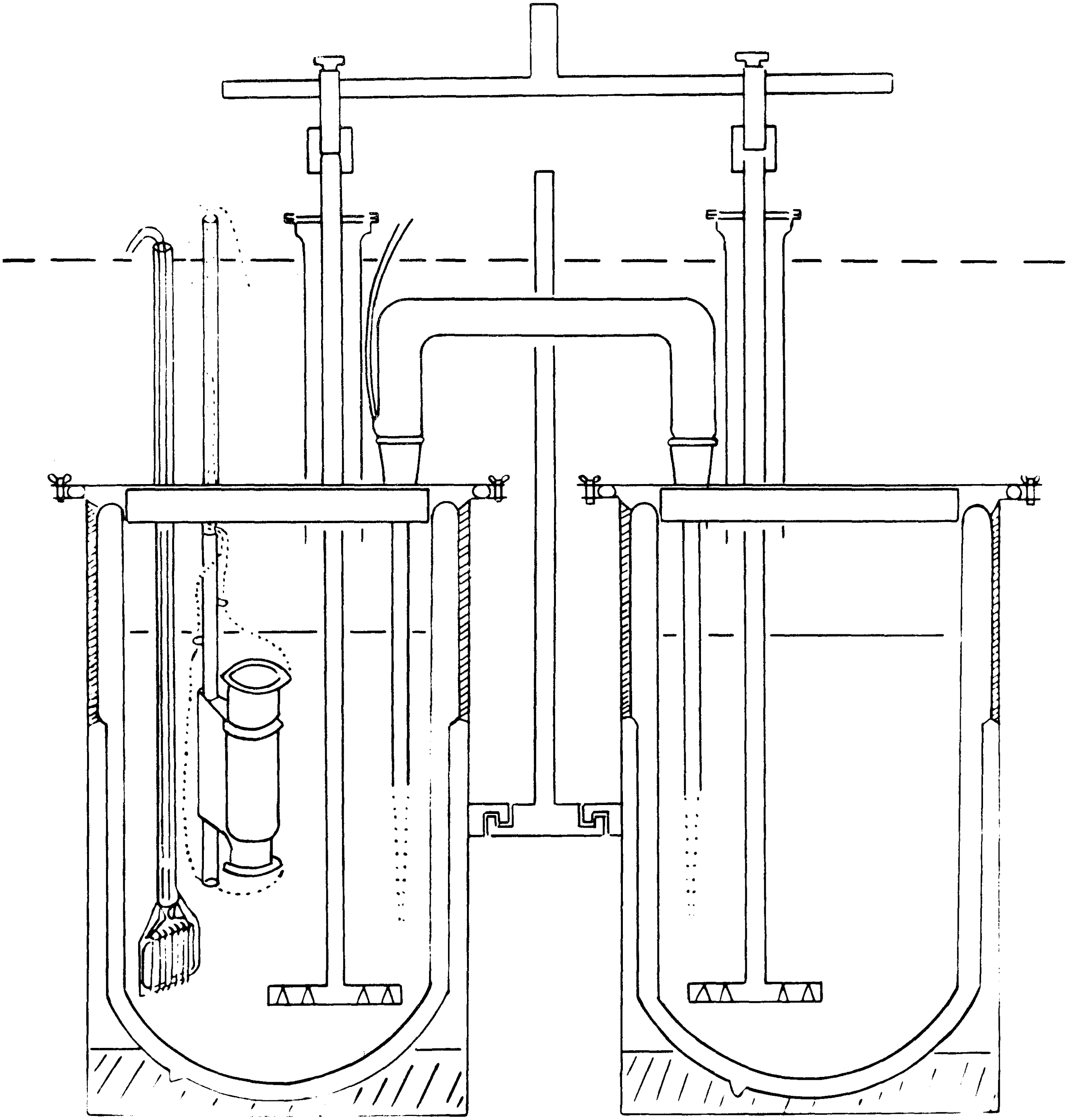


Fig. 19

placed in the Dewar. Araldite cement was used to insulate the junctions and after ensuring that they were on the outer surface of the thermopile it was bound with nylon thread. Two B24 cones completed the thermopile. When the cones were fitted to the lids of the calorimeters the thermopile was at the correct height inside the Dewars.

The mixing device is shown in Fig. 20. It consisted of a B24 cone, of 15 mls. capacity, ground at each end and closed by perspex discs which were sealed on with silicone grease. This was supported in a B24 socket stuck to a glass tube with Araldite cement, and nylon threads, which were attached to the perspex discs, passed up the tube. During an experiment the contents of the mixing device were emptied into the Dewar by pulling on the nylon threads.

The heater was of nichrome wire wound on a glass frame which was attached to a glass tube. The ends of the wire were spot-welded to platinum loops sealed, by means of Araldite cement, into the tube. Inside the tube, the loops were soldered to copper lead wires and the heater was insulated by dipping in a solution of formvar in ethylene dichloride.

The heating circuit was similar to that of Pitzer and is shown in Fig. 21. A variable resistance, A,

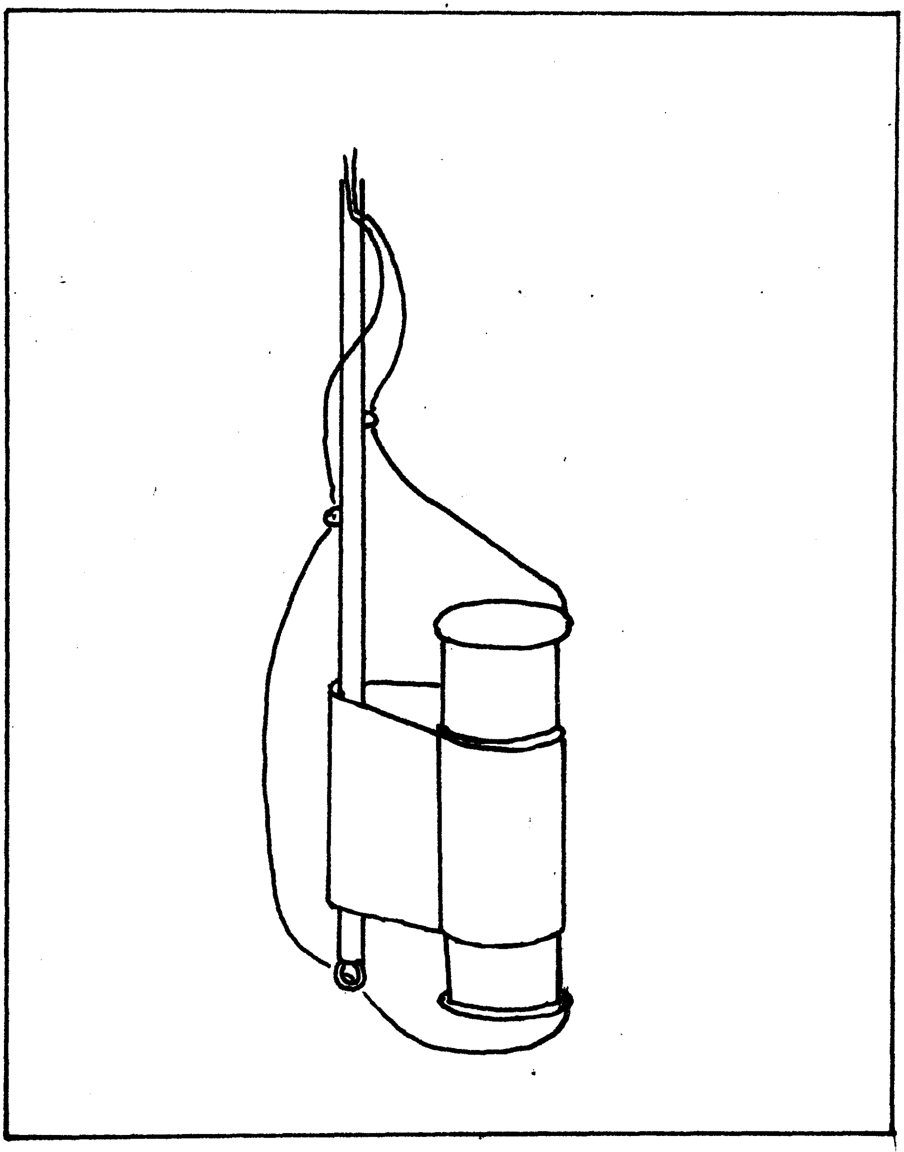


Fig. 20

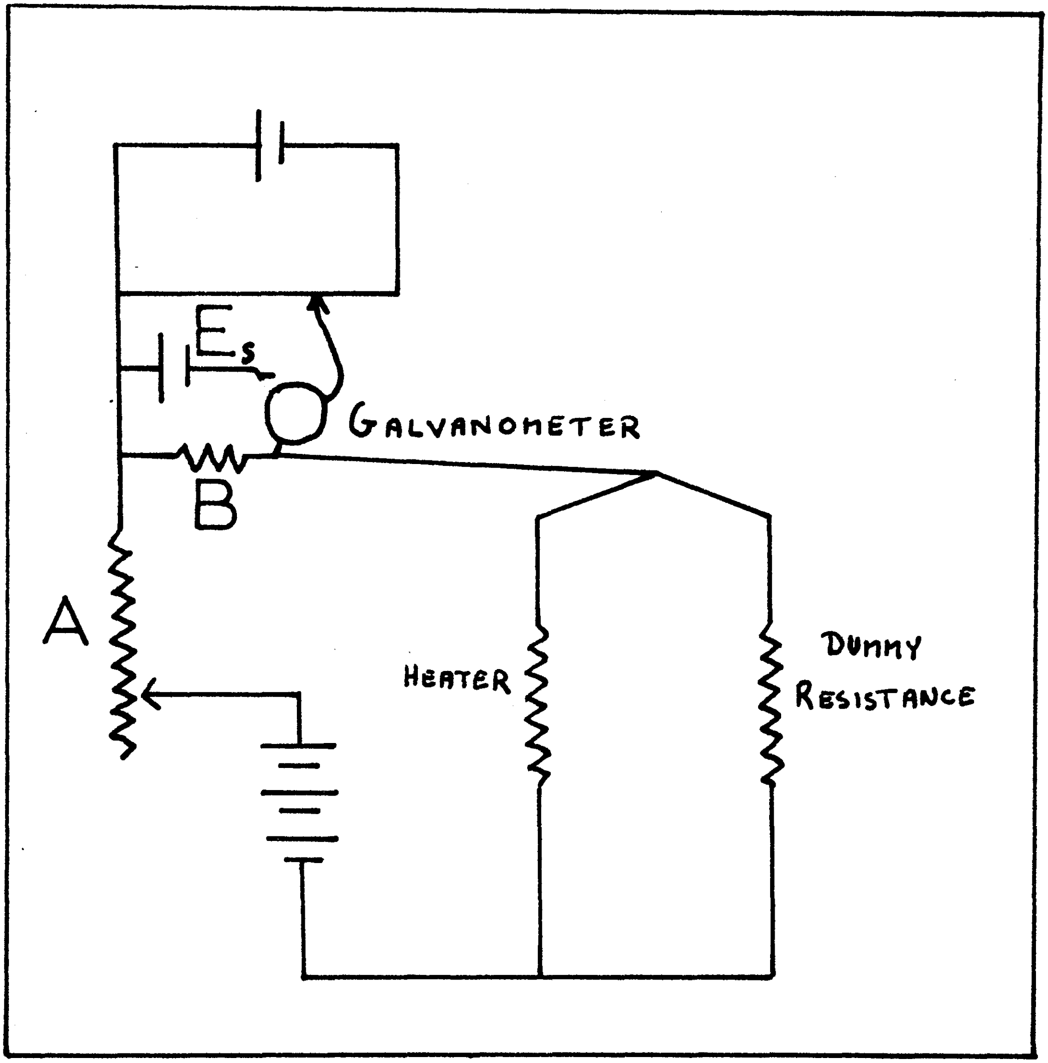


FIG. 21

was used to regulate the current in the circuit, and the voltage drop across the standard 1 ohm resistance, B, was measured using a Cambridge slide-wire potentiometer. By means of a dummy resistance, equal to that of the heater, the 12 volt battery was allowed to settle down before being used in the heating circuit.

The thermopile e.m.f.'s were measured using a Pye Precision Decade potentiometer, which had an overall range of 2.0 volts to 0.1 microvolts in six ranges. It was standardised using a 5 dial decade system in the battery circuit, and the standard cell voltage was preset with a divider calibrated from 1.01800 to 1.01900 volts in steps of 10 microvolts. A switch incorporated in the circuit enabled internal checking of the voltage of the standard cell. Any spurious thermoelectric e.m.f.'s could be detected, and eliminated, by means of a reversing switch. A Scalamp galvanometer was used as a null detector in conjunction with a Pye galvanometer preamplifier, and changes of 0.05 microvolts were easily detected.

The thermostat was maintained at $25^{\circ} \pm 0.01^{\circ}C$ using a mercury-toluene regulator, of large capacity, fitted with a Sunvic proportioning head (Type Tol 3B,) and an A.E.I. electronic relay (Type EA4T).

Experimental Procedure

The sensitivity of the calorimeter was tested by determining the heat of solution of potassium chloride in water. Distilled water, which had been brought to 25°C, was weighed into the calorimeters and two to four grams of potassium chloride were weighed into the mixing device, which was then sealed. The lids were screwed down and the thermopile inserted into the B24 sockets, which had been well greased to ensure a water-tight seal. The calorimeters were then placed in the thermostat.

After stirring for at least an hour, and sometimes overnight, readings were taken every minute. When a steady change of e.m.f. had been obtained, the water equivalent of the calorimeter was determined by switching the heater into the circuit. The voltage-drop across the 1 ohm standard resistance was measured every minute to ensure a steady heating current, and the time of heating was obtained using a stop-watch accurate to 0.1 of a second. After the heater had been turned off and the e.m.f. had settled down to a steady change with time, the mixing device was opened and three to four minutes were usually necessary for the potassium chloride to dissolve completely. When the change in e.m.f. had once more become steady the water equivalent was again determined.

In order to determine the heats of complex formation, 10 to 14 gms. of metal chloride solution were weighed into the mixing device and added to the amino acid, sodium hydroxide buffer in the Dewar. Following Sacconi et al[86] the heat of dilution of the buffer was assumed to be zero, but it was necessary to determine the heat of dilution of the metal chloride solution.

Precautions were taken in these experiments to exclude carbon dioxide from all solutions. Solid amino acid was weighed into the calorimeter and nitrogen blown in to remove the air. Distilled water, from which carbon dioxide had been removed, and sodium hydroxide were then added. The thermopile was then inserted and the calorimeter placed in the thermostat. The dissolution of the amino acid lowered the temperature of the solution and the heater was therefore switched on until the temperature difference between the two calorimeters was less than 0.1°C. The calorimeter was then allowed to equilibrate for at least thirty minutes before mixing.

Method of Calculation

The method used for the evaluation of water equivalents and the heats of solution and formation was that of Eitel[94]. In Fig.22, which is a graphical reproduction of part of one of the experiments, e.m.f. is plotted against time. This is divided into three periods, the Anterior, the Experimental and the Rating periods. The first reading is designated θ_o at time T_0, and at T_1, where the reading is θ_1, the heater is switched on or mixing is effected. The rate of change, v_a is given by $\frac{\theta_o - \theta_1}{T_a}$, and the average reading in this period is $\theta_a = \frac{1}{2}(\theta_o + \theta_1)$.

The experimental period stretches from T_1 to T_e, the corresponding readings being θ_1 and θ_e. The heat effect has been exhausted by T_e and the curve now enters the rating period.

The rating period is treated in the same way as the anterior and the rate of change and average reading are given by $\frac{\theta_e - \theta_1}{T_r}$ and $\frac{1}{2}(\theta_e + \theta_1)$ respectively.

We may now apply the Regnault-Pfaundler formula to correct for the variation in readings. The correction to be applied to $\theta_e - \theta_1$ is

$$\partial\theta = T_x v_a + \frac{(v_r - v_a)}{(\theta_r - \theta_a)} \frac{1}{2}(\theta_e + \theta_1) + \sum_{1}^{T_{x-1}} \theta - T_x \theta_a$$

$$= T_x v_a + \frac{(v_r - v_a)}{(\theta_r - \theta_a)}. \qquad \ldots\ldots(51)$$

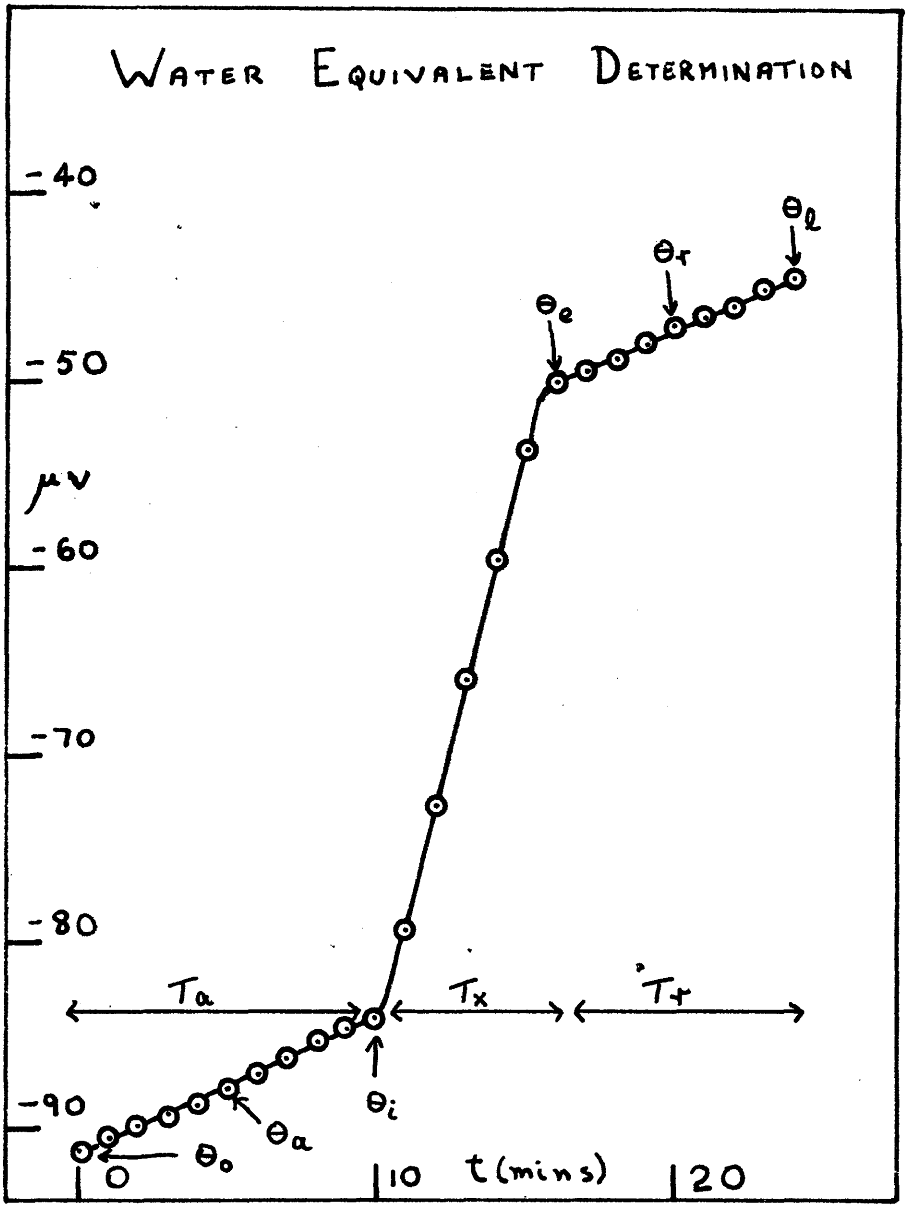

WATER EQUIVALENT DETERMINATION
-40
-50
-60
-70
-80
-90
μv
θl
θr
θe
θi
θa
θo
Ta
Tx
Tr
0
10
t(mins)
20

FIG. 22

and the corrected heat change is given by $\Delta\theta' = \partial\theta + \theta_e - \theta_i$.

Anterior and rating periods were of the order of 10 minutes and the experimental period was from 5 minutes for the dissolution of potassium chloride to 2 minutes for mixing.

RESULTS AND DISCUSSION

Data available for the heat of solution of potassium chloride have been reviewed by Mishchenko and Kaganovich[95] and Rossini[96]. Staveley[35] has corrected the results given by these authors to an arbitrarily fixed dilution of 1 mole of potassium chloride to 167 moles of water and found his values to be comparable.

The heats of solution obtained in the present work have been corrected to the same arbitrary dilution and the results are given in Table 58.

TABLE 58

Heat of Solution of Potassium Chloride

Gms. KCl	Gms. H_2O	W.E.(Ave)	Deflection (cals)	ΔH_{sol} K cals./mole
4.218	1197.8	1.035	242.7	4.29
4.843	1197.7	0.946	266.5	4.10
3.503	1160.7	1.459	198.8	4.21
3.257	1166.6	1.415	176.8	4.05

Mean $\Delta H = 4.16 \pm 0.09$

The calculated ΔH_{sol} is in good agreement with 4.18 given by Staveley.

In the association experiments the concentrations of the ionic species were calculated from the equations

$$m_1 = [H_2A^+] + [HA] + [A^-] + [MA^+], \qquad \ldots\ldots(34)$$

$$m_3 = [M^{2+}] + [MA^+], \qquad \ldots\ldots(35)$$

$$[H^+] + 2[M^{2+}] + [MA^+] + m_2 + [H_2A^+] = [A^-] + 2m_3, \qquad \ldots\ldots(30)$$

the ionic strength,

$$I = \tfrac{1}{2}\left\{[H^+] + [MA^+] + [H_2A^+] + [A^-] + m_2 + 2m_3 + 4[M^{2+}]\right\} \qquad \ldots\ldots(31)$$

and the dissociation constants of the acid. Activity coefficients were obtained from the Davies' equation, (11), and $[H^+]$ was varied, using the Deuce computer, until the calculated K_1 was within 1% of the value given in Part II.

In the calculation of ΔH^o the heats of formation of A^- and H_2A^+ were taken into consideration, and also the heat of dilution of the metal chloride solution, 4.39 k.cal./mole for nickel chloride and 2.77 k.cal./mole for cobalt chloride. Results are given in Table 59 for nickel and cobalt glycinates and nickel β-alaninate.

The values shown are in reasonable agreement with 4.09 ± 0.03, 2.82 ± 0.12 and 3.06 ± 0.1 obtained from e.m.f. measurements. The results, however, are probably only accurate to ± 1 k.cal./mole due to the small concentration of complex and the very high heats of dilution.

Calculation of ΔH° (To be inserted in p.219.)

In solutions containing amino-acid and sodium hydroxide $[A^-]$ was taken as being approximately $[Na^+]$, and additional $[A^-]$ produced by further dissociation of the amino acid on addition of metal ion was therefore $[MA^+] - [Na^+]$. The contribution to the total heat change due to its formation, and also to that of H_2A^+, was calculated from the appropriate heats of dissociation of the amino acids. For glycine $\Delta H_1 = 0{\cdot}95$ k.cal/mole and $\Delta H_2 = 10{\cdot}8$ k.cal/mole were obtained from refs. (73) and (74), and for β-alanine $\Delta H_1 = 1{\cdot}09$ k.cal/mole and $\Delta H_2 = 11.27$ k.cal/mole were calculated from the dissociation constants in Part II. Having obtained the molar heat change for the formation of the complex at the ionic strength studied, the thermodynamic value, ΔH°, was derived using

$$\Delta H^\circ = \Delta H_i + 2{\cdot}303 \times \frac{3RT^2}{2}\left(\frac{1}{D}\cdot\frac{dD}{dT} + \frac{1}{T}\right)\log \gamma_2$$

(Austin, Matheson and Parton, "The Structure of Electrolyte Solutions". Ed. Hamer (Wiley, 1959)). The values of D, the dielectric constant, were those of Akerlof (J.A.C.S., 1932, <u>54</u>, 4130) and

$$2{\cdot}303 \times \frac{3RT^2}{2}\left(\frac{1}{D}\cdot\frac{dD}{dT} + \frac{1}{T}\right) = -7{\cdot}57 \times 10^{-4}$$

γ_2, the activity coefficient of the metal ion, was obtained using Davies' equation.

Expt.	1
$10^1 m_1$	1.0913
$10^3 m_2$	3.0422
$10^2 m_3$	3.4731
Wt. H_2O. (gms.)	1179.1
W.E.	0.960
Exp. Heat Change (cals.)	180.2
Heat of Dil. (cals.)	179.8

Expt.	$10^5[H^+]$
1	8.943
2	9.020
3	1.430
4	1.481
5	0.365
6	0.365

TABLE 59

2	3	4	5	6
1.2700	1.4761	1.3258	1.4176	1.2617
3.1498	1.9629	1.6794	1.6354	1.6044
3.4753	2.1156	2.1179	3.4880	3.4874
1178.4	1175.7	1174.4	1174.1	1174.3
0.958	0.984	0.993	0.949	0.958
174.0	73.8	69.6	166.4	166.4
179.8	68.9	68.9	180.0	179.8

$10^3[H_2A^+]$	$10^6[A^-]$	$10^3[MA^+]$	ΔH^o
Nickel Glycinate			
2.041	0.320	5.071	4.40
2.406	0.368	5.646	3.88
	Mean ΔH^o = 4.14 ± 0.26 k.cal./mole		
Cobalt Glycinate			
0.464	2.612	2.433	4.03
0.432	2.266	2.116	2.65
	Mean ΔH^o = 3.34 ± 0.69 k.cal./mole		
Nickel β-Alaninate			
1.777	3.180	3.413	2.30
1.580	2.830	3.186	1.88
	Mean ΔH^o = 2.09 ± 0.21 k.cal./mole		

PART IV

GENERAL DISCUSSION

Although it is generally accepted that a comparison of association reactions should not be based on free energy data alone, a number of workers have attempted to correlate log K values with properties of the metal ion involved. Duncan and Kepert[97] found two types of relationship between ΔG^o, and $G^o_{(M^{m+})aq}$, the free energy of the metal ion, for a series of bivalent metal oxines. In those cases in which $-\Delta G^o$ increased with increasing $G^o_{(M^{m+})aq}$ they assumed that the ions were in contact. They suggested that such entities should be called complexes, and that where one or two water molecules were interposed between the ions the new entity should be called an ion-pair or ion-associate. The second type of relationship, where $-\Delta G^o$ was almost independent of $G^o_{(M^{m+})aq}$, was assumed to be due to ion-pair formation. Since the hydration radius of similarly charged ions does not vary appreciably, they assumed that the energy between the ions would be fairly constant. A distinction between complexes and ion-pairs was also proposed by Smithson and Williams[98] who suggested that anions would only affect the absorption of transition metals in the visible spectrum if the ions were in contact. Hence where a change in the absorption spectrum was obtained complexing was assumed and if there was no change in the spectrum, an ion-pair was formed.

Williams[99] predicted that for association reactions where the only attractive force was electrostatic, there should be a relationship between log K and the ionic potential of the metal ion. He showed that a linear relationship existed between log K and z/r for a limited number of complexes of the alkaline earth metals. Where reactions involved transition metal ions, in which covalent bonds were possible, Irving and Williams[44] found that log K increased as the ionisation potential of the metal ion increased. These workers assumed that the ionisation potential was a measure of the ability of the ion to form covalent bonds. Others[100, 101, 102] however, have suggested that the order of stability is due to the polarisation of the cation d-electrons by the ligand. This ligand field theory predicts that ions whose d shells contain either 0, 5 or 10 electrons will have no additional stabilisation. The divalent ions of the first transition series corresponding to this condition are Ca^{2+}, Mn^{2+} and Zn^{2+}, and the additional stability of Zn^{2+} complexes compared with Ca^{2+} and Mn^{2+} is considered to be due to the contraction in the radius of the ions. Plots of log K against atomic number for complexes of the divalent ions show an increase from calcium, through manganese, to zinc with, however, maxima at chromium and copper and a minimum at manganese. Williams[103] has argued that, while the ligand field theory predicts this behaviour it is only a qualitative picture. The stability of complexes is really due to the acceptor properties of the ground and excited states, and hence to the ionisation potential of the metal.

It has been shown by Duncan[104] that under certain circumstances a linear relationship will exist between log K and the reciprocal of the radius of the metal ion, and he has attributed the success of other relationships to the dependence of the property concerned on $1/r_{M^{m+}}$. It should be noted, however, that the properties discussed above are related to the heats of complex formation, and correlations with the free energy depend on the entropy change for a series of similar reactions being almost constant.

Gurney[105] has suggested that the work done, W, in forming an ion-pair from the separate ions in solution should be written

$$W = \frac{\Delta G^{o}}{N} - kT \ln 55.5 \qquad \ldots\ldots(52)$$

where N is Avogadro's number and the term $-kT \ln 55.5$ is a characteristic of reactions in aqueous solution in which the number of solute particles decreases by unity, 55.5 being the number of moles in 1000 gms. of water. The forces between two oppositely charged ions in solution can be considered as being made up of long-range, or electrostatic, and short-range, or quantum mechanical, terms. While the electrostatic force will be one of attraction, the quantum mechanical force may be repulsive or attractive depending upon whether or not the ions have the electronic configuration of the inert gases. We may therefore consider W to be composed of two parts, W_{env}, sensitive to environment and temperature, and W_{non}, insensitive to environment and independent of temperature.

$$W = W_{env} + W_{non} = -kT\left(\ln K + \ln 55.5\right) = -kT \ln K_x$$

Since W_{env} is almost entirely electrostatic in origin it will vary with temperature in the same way as the reciprocal of the dielectric constant of the solution and hence will have a minimum value at a certain temperature. Near room temperature this variation can be expressed as

$$\frac{1}{\varepsilon} = \frac{e^{T/\theta}}{\varepsilon_0}$$

where θ is a temperature characteristic of the solvent. We may then write

$$\ln K_x = -C\left(\frac{a + e^{T/\theta}}{T}\right) \qquad \ldots\ldots(53)$$

where $C_a = \frac{W_{non}}{k}$ and $Ce^{T/\theta} = \frac{W_{env}}{k}$

The temperature, T^*, at which the association constant passes through a minimum is obtained by differentiation of equation (53) with respect to T, and equating to zero.

$$T^* = \theta\left(1 + \frac{a}{e^{T/\theta}}\right) = \theta\left(1 + \frac{W_{non}}{W_{env}^*}\right) \qquad \ldots\ldots(54)$$

where W_{env}^* is the value of W_{env} at T^*.

It is seen from equation (54) that T^* is dependent on the ratio W_{non} / W_{env}. At temperatures below T^*, K values will decrease with increasing temperature due to the tendency for thermal agitation to cause dissociation of the ion-pairs. When $T > T^*$, K values will increase with temperature due to the decrease in mutual potential energy.

It has been suggested by Charles[106] that heats of formation of complexes are related to metal-ligand bond strengths, and by Orgel[107] and George[100] that bond strengths are increased by increasing W_{non}. Therefore the higher the value of T^* for a reaction the more exothermic it should be. It is seen from Table 60 that this is the case for various malonates, oxalates, glycinates and β-alaninates. In complex formation the nitrogen atom donates its lone pair of electrons more readily than does the oxygen atom and hence forms more covalent bonds. This leads to a greater W_{non} and higher T_t^* and K values which decrease with increasing temperature. Uusitalo[103] has shown that when the donor atom is oxygen the entropy term is important, but with nitrogen the heat term determines the stability. When both nitrogen and oxygen are present $T\Delta S$ and ΔH are comparable for strong complexes, but $T\Delta S$ increases in importance as the stability of the complex decreases. It is seen in Table 60 that this holds for the glycinates but not for the β-alaninates where $-\Delta H$ (Co) $> -\Delta H$ (Ni). With the introduction of the second glycinate anion $-\Delta H_2 > -\Delta H_1$ and ΔS is very small, as expected for complexes of 1:1 electrolytes.

The entropy change accompanying reactions of type (2) may be considered as being made up of two parts. A decrease in entropy due to the reduction in the number of solute particles in solution, and an increase due to the partial neutralisation of charge which leads to a decrease

TABLE 60

Thermodynamic Properties

Reaction	$-\Delta G$	ΔH	ΔS	T^*
$Ni^{2+} + G^-$	8.43	-4.09	14.5	388
$Co^{2+} + G^-$	6.92	-2.82	13.7	368
$Mn^{2+} + G^-$	4.32	-0.29	13.5	315
$NiG^+ + G^-$	6.75	-4.69	6.9	377
$CoG^+ + G^-$	5.42	-3.55	6.3	372
$Ni^{2+} + A^-$	6.81	-3.06	12.6	356
$Co^{2+} + A^-$	5.74	-3.60	7.2	359
$Ni^{2+} + Ox^{=}$	7.05	0.15	24.2	294
$Co^{2+} + Ox^{=}$	6.54	0.59	23.9	272
$Mn^{2+} + Ox^{=}$	5.41	1.42	22.9	269
$Ni^{2+} + Mal^{=}$	5.60	1.77	24.8	271
$Co^{2+} + Mal^{=}$	5.13	2.57	25.8	264
$Mn^{2+} + Mal^{=}$	4.48	3.53	26.8	254

$-\Delta G$ and $-\Delta H$ in k.cal./mole.

ΔS in cal./deg.mole.

ΔCp in cal./deg.

in the ordering of solvent molecules. Frank and Evans[109] have suggested that ions in solution orientate the water molecules around them so as to form an effective "iceberg", the process being similar to a partial freezing of the liquid. Thus the removal of ions from the solution, as in the process of complex formation, will lead to the breakdown of this structure and a resulting entropy change favouring complex formation. Since the entropy effect will be related to the charge of the ions a large ΔS will be expected in reactions accompanied by considerable charge neutralisation and a low ΔS in reactions for which there is little charge neutralisation. This explains Uusitalo's observation that the entropy change is greater for ligands involving oxygen rather than nitrogen co-ordination and why for oxalates and malonates $\Delta S \simeq 20$ cal/deg.mole. while for glycinates and β-alaninates $\Delta S \simeq 10$ cal/deg. mole.

Gurney[105] has suggested that when comparing the entropies of reactions the equation

$$S^{o\prime} = S^{o} - R \ln 55.5 = S^{o} - 8\Delta n \qquad ......(55)$$

where Δn is the change in the number of solute particles, should be used. This gives an entropy independent of the concentration. Bent[110] considered a number of reactions, for many of which negative entropies had been obtained[111], and, using equation (55), found that only in the case of silver thiosulphate was the entropy change negative. He assumed this to be due to the loss of configurational and librational entropy of the thiosulphate ion on complex formation.

Writing[112],

$$\begin{tikzcd}
M^{m+}_{(g)} & + & N^{n-}_{(g)} \arrow[rr, "\Delta Sg(3)"] & & MN^{(m-n)+}_{(g)} \arrow[d, "\Delta S_{hyd}(4)"] \\
M^{m+}_{aq} \arrow[u, "\Delta S_{hyd}(1)"] & + & N^{n-}_{aq} \arrow[u, "\Delta S_{hyd}(2)"] & & MN^{(m-n)+}_{aq} \arrow[ll, "- S_{assoc}"']
\end{tikzcd}$$

where $-\Delta S_{hyd}(1)$ is the entropy change accompanying the hydration of the gas phase cation, $-\Delta S_{hyd}(2)$ and $+\Delta S_{hyd}(4)$ are the corresponding values for the anion and the ion-pair respectively, and $\Delta Sg(3)$ is the change on association in the gas phase,

$$\Delta S_{assoc.} = \Delta S_{hyd}(1) + \Delta S_{hyd}(2) + \Delta S_g(3) + \Delta S_{hyd}(4).$$

$\Delta S_{hyd}(1)$ and $\Delta S_{hyd}(2)$ may be obtained from the difference in standard entropy of the ions in the gas and aqueous phases. While these are known for a large number of ions[113], they are not known for glycinate or β-alaninate. The aqueous phase entropies of the anions were obtained from the crystal entropies, entropies of hydration and entropies of dissociation of the acids. The crystal entropy of β-alanine has not been determined, but Huffman[114] has shown that no change occurs when a hydrogen atom is replaced by an amino group. β-Alanine was therefore assumed to have the same entropy as α-alanine, for which $S^o = 31.6$ cal/deg.mole. ΔS_{hyd} for glycine was obtained from solubility measurements at a number of temperatures[115], but data was not available for β-alanine. Knowing the value at 25°C only, it was necessary to measure the heat of solution before ΔS could be calculated. $S^o_{A^-}$ was then determined from the dissociation

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

and the values are shown in Table 61.

TABLE 61

Thermodynamic Properties

	$S^o_{cryst.}$	$\Delta S_{hyd.}$	$-\Delta S_{assoc.}$	$S^o_{A^-}$
Glycine	26.1[116]	14.4	-8.8[73]	31.7
β-Alanine	31.6	10.4	-9.3	32.7

All entropies in cal/deg.mole.

Where crystal entropies and solubility data are not available, aqueous phase entropies may be calculated from a number of empirical relationships. Powell and Latimer[117] suggested an equation for the entropy of monatiomic ions, (based on the standard $S^o_{H^+} = 0$)

$$S^o = 3/2\ R\ \ln M + 37 - 270z/r_e^2 \qquad ......(56)$$

where M is the atomic wt. , z the charge and r_e the effective ionic radii of the ions, with corrections for hydration. These corrections were for cations, +2A, and for anions +1A.

Laider[118], using the value of $S^o_{H^+} = -5.5$ cal/deg. mole. suggested by Gurney, proposed for monatomic cations the equation

$$S^o_{(abs)} = 3/2\ R\ \ln M + 10.2 - 116\ Z^2/r+ , \qquad ......(57)$$

which he considered to be theoretically more justified in conforming to the simple Born relationship. Equations have been developed by Cobble[119] for the calculation of the entropies of complex oxyanions and simple complexes, and he has extended the method to aqueous organic solutes, complexes and chelates. Connick and Powell[120] have also given an equation for oxyanions.

For monatomic ions in the gas phase only the translational entropy term will be involved. This may be calculated from the Sackur-Tetrode equation which, at 25°C, has the form

$$S_{trans} = 1.5 \, R \ln M + 26.03$$

where M is the atomic weight of the ion. The entropy of ion-pairs includes both translational and rotational terms and for rigid linear molecules may be obtained from[121]

$$S_{trans} + S_{rot} = 2.2868 \, (7 \log T + 3 \log M + 2 \log I_B - 2 \log \sigma) - 6.661,$$

where I_B is the moment of inertia about the axis and σ is the symmetry number. To deal with rigid, non-linear ion-pairs, however, it is necessary to introduce the moments of inertia about the principal axes,

$$S_{trans} + S_{rot} = 2.2868 \, (8 \log T + 3 \log 7 + \log I_A I_B I_C - 2 \log \sigma) - 7.697 \quad \ldots\ldots(53)$$

The products of the moments of inertia may be obtained quite simply by means of the determinant

$$I_A I_B I_C = \begin{vmatrix} +I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & +I_{yz} & -I_{yz} \\ -I_{xz} & -I_{yz} & +I_{zz} \end{vmatrix}$$

where I_{xx} and I_{xy} are the moments and products of inertia with respect to a co-ordinate system having the centre of mass as origin, i.e.

$$I_{xx} = \sum m_i \quad (y_i^2 + z_i^2) \ldots\ldots$$

$$I_{xy} = \sum m_i \quad x_i \cdot y_i \ldots\ldots$$

where m_i is the mass of the atom i whose co-ordinates are x_i, y_i, z_i and $\sum m_i = M$.

Equation (58) was used in the calculation of the gas entropy of the ion-pair. X-ray determination[122] has shown that nickel glycinate is almost planar and it was assumed to be so in the calculation.

The β-alaninates were also assumed planar, and the entropies are shown in Table 62. The entropies of the metal ions were those of Staveley and Randall[38] and it is seen that $S_g(MN)$ is similar for all of the reactions and could therefore be considered constant for a series of similar reactions. $\Delta S_{assoc.}$ will therefore

TABLE 62

Thermodynamic Properties

	S_g(MN)	$\Delta S_{assoc.}$	S^o(MN)	$-\Delta S_{hyd}$(4)	$S^o_{M^{m+}}$ (aq)
NiG^+	57.0	14.5	23.2	33.8	-23.0
CoG^+	57.0	13.7	23.4	33.6	-22.0
MnG^+	56.8	13.5	27.2	29.6	-18.0
NiG_2	57.0	6.9	61.8	-4.8	
CoG_2	56.9	6.3	61.4	-4.5	
$Ni\beta A^+$	56.9	12.6	22.3	34.6	
$Co\beta A^-$	56.8	7.2	17.9	38.9	

Entropies in cals./deg.mole.

be largely determined by differences in hydration. Staveley and Randall studied the reactions of ethylenediaminetetraacetate with a number of metal ions and assumed ΔS_2 and ΔS_4 to be constant. When, however, $\Delta S_{assoc.}$ was plotted against $1/r_{m^+}$ three separate curves were obtained. Those for divalent ions with inert gas structures and transition metal ions were linear, but in the case of tervalent ions a curve was obtained. Nancollas[123] has shown, however, that if $\Delta S_{assoc.}$ is plotted against ΔS_1 a single straight line is obtained for all ion-pairs.

A number of relationships between entropies and the properties of ions have been demonstrated. Latimer[124] found that $\Delta S_{hyd.}$ values, based on $S^o_{H^+} = -2.1$, were proportional to z/r', where z is the charge on the ion and r' the effective radius (i.e. $r_- + 0.1A$ and $r_+ + 0.85A$). Nair and Nancollas[18] have shown that ΔS_{hyd} (4) varies linearly with $(r_+ + r_-)^{-1}$ for uncharged ion-pairs of 1:1 electrolytes. In the present work neither ΔS_{hyd} (4) nor $\Delta S_{assoc.}$ varies linearly with $1/r_{m^+}$ for the metal glycinates. George[125], however, has found relationships of the type

$$\Delta S_{assoc.} = \Delta S_{hyd} (2) + \text{constant.} \qquad \ldots\ldots(59)$$

Different values for the constant are required for different systems, and Davies[11] has shown that this value is apparently dependent upon the entropy of hydration of the variable ion.

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