STUDIES ON
THE THERMODYNAMICS OF ION ASSOCIATION IN AQUEOUS SOLUTIONS

A Thesis
Submitted to the University of Glasgow
for the degree of

DOCTOR OF PHILOSOPHY

by

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September, 1961.

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, F.R.S.

The material of Part I has been published in the Transactions of the Faraday Society. A paper dealing with the metal oxalates of Part II appeared in the Journal of the Chemical Society and another on the metal succinates will be published shortly in the same journal. Reprints are 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.Bruges of the Mechanical Engineering Department of the University of Glasgow for the loan of a precision potentiometer. I acknowledge the assistance of Mr. C.A.Vincent for photographs of the apparatus and thank Mr. J. Rae for construction of the calorimeters.

I am also indebted to the Department of Scientific and Industrial Research for the award of a Maintenance Grant from October 1958 to October 1961 which made the research possible.

PART II - SOME TRANSITION METAL OXALATES AND SUCCINATES..........

CONTENTS

CONTENTS (contd.)

SUMMARY

The association in aqueous solutions between divalent transition metal cations and the anions of dicarboxylic acids has been studied.

The thesis is divided into four parts.

Part I describes studies of association in copper oxalate solutions at 25°C. Potentiometric measurements, using a glass electrode system with a saturated calomel reference electrode, at an ionic strength of 0.1M were used to identify the species present in these solutions. These were found to be $CuHC_2O_4^+$, CuC_2O_4 and $Cu(C_2O_4)_2^{2-}$ and stability constants at this ionic strength were derived. Subsequent work at low concentrations yielded the thermodynamic association constants. Using a polarographic technique at ionic strengths varying from 0.2 to 0.6M, a value for the stability constant of the doubly charged anionic complex was obtained and this is compared with the potentiometric result.

Part II is devoted to a study of 2:2 electrolytes. The thermodynamic equilibrium constants for the association of divalent nickel, cobalt and manganese

ions with oxalate and succinate anions have been determined over the temperature range 0° to 45°C using the cell,

$$H_2, Pt \ / \ H_2A, NaOH, MCl_2 \ / \ AgCl, Ag,$$

in which e.m.f.s were measured to ± 0.01m.v. Thermodynamic properties for each association have been derived. The first dissociation constant of oxalic acid was also measured over this temperature range using the cell,

$$H_2, Pt \ / \ H_2Ox, HCl \ / \ AgCl, Ag.$$

Results are compared with those in the literature. It was thought that in metal succinate solutions, due to the high concentrations of $HSucc^-$ present, there might exist in solution, along with the 2:2 electrolyte, a complex of the form $MHSucc^+$. E.m.f. measurements on manganese succinate solutions at 0.2M using the glass electrode system of Part I confirmed this and stability constants were obtained.

Part III consists of a general discussion of the results. The entropies of the ion-pairs have been calculated and correlations between ΔG, ΔH and ΔS with ionic parameters are investigated.

Part IV deals with a calorimetric study of the heat of formation of manganese malonate at 25°C. The heat of solution of potassium chloride was also measured. Results are compared with existing data.

GENERAL INTRODUCTION

GENERAL INTRODUCTION

In electrolyte solutions, there are ions of opposite sign and in any comprehensive treatment of thermodynamic properties, it is necessary to take into account the various forces involved, e.g., the long range (Coulombic) interionic attractive forces and the shorter interactions between ions and solvent molecules. Debye and Hückel,[1] introduced the concept of an "ionic atmosphere" of ions of one type around a central ion of opposite charge, and showed that for strong electrolytes, deviations from ideality could be interpreted in terms of a potential arising from the arrangement of the surrounding ions. In ion association, the ions are caught up in one another's field. They are close together so that the energy of their mutual attraction is greater than the thermal energy which permits their random motion. In this case the approximations on which the Debye-Hückel theory depends are no longer valid and a new entity is formed in solution which is stable enough to withstand collisions with solvent molecules and which is called an ion-pair.

The ion association reaction may be described by the equilibrium

$$M^{a+}_{aq} + X^{b-}_{aq} \rightleftharpoons MX^{(a-b)+}_{aq} \quad \text{------------}(1)$$

where M_{aq}^{a+} .. etc., are the hydrated ionic species present in the solution. If a = b then a symmetrical uncharged ion-pair is formed.

Bjerrum[2] developed a theory to account for ion association by considering the formation of ion-pairs in terms of purely electrostatic and Coulombic forces between ions. Ions are regarded as unpolarisable spheres contained in a medium of fixed macroscopic dielectric constant. Non-polar quantum mechanical bonds as well as ion-solvent interactions are excluded. He suggested that ions within a certain minimum distance 'q' of one another are "associated" into ion-pairs, though in reality a fast moving ion might come within this distance of another and no pair be formed. If we consider a solution of a symmetrical electrolyte then the average distribution of negative (i) ions will be greater in the vicinity of a positive (j) ion than in the bulk solution. The number of i ions round a selected j ion is given by the Boltzmann expression, and the number in a shell of thickness dr at a distance r is $n_i.\exp\left(-z_i e\psi_j/kT\right).\ 4\pi r^2.dr$, where $z_i e\psi_j$ is the potential energy of an i ion of valency z and n_i the bulk concentration of i ions. If r is small then the potential of the central ion will be dominant and interionic forces can be neglected, so that $\psi_j = z_j e\ /\varepsilon\ r$ where ε is the dielectric constant) and substitution in the above expression gives the number of i ions in the shell to be

$$4\pi n_i . \exp\left(\frac{-z_i . z_j e^2}{\varepsilon kTr}\right) . \; r^2 \; dr.$$

If a series of such shells is considered, the number of ions in each shell can be estimated on a time-average basis. It can be seen that with increasing r, the probability of finding an i ion in any unit of volume decreases, but since the volume of the shell also increases, the two opposing effects combine to give a critical distance in which there is a minimum probability of finding an i ion anywhere in the sphere surrounding a j ion. This distance 'q' is the ionic separation at which the mutual potential energy of the ions is equal to 2kT.

$$q = \frac{|z_i z_j| . \; e^2}{2\varepsilon kT} = z^2 | \; 3.57 | \; \text{Å}$$

in water at 25°C. Bjerrum showed how the mass action constant of the equilibrium (1) depends on the dielectric constant of the solvent as well as on the temperature and ionic size.

If the two ions are at a distance greater than q then the Deby-Hückel theory may be applied. The expression for the activity coefficient is given by

$$\log f_{\pm} = \frac{-A\,|z_1 z_2|\,I^{\frac{1}{2}}}{1 + B\mathring{a}I^{\frac{1}{2}}}$$

where A and B are constants depending on the temperature and dielectric constant of the medium and å is the distance of closest approach of the ions. The equation represents observed values with good accuracy by choosing a suitable value for å the only factor not directly determinable in the expression. In the derivation of the equation, ions are treated as rigid spheres and the numerator and denominator of the right hand side represent the effect of long range Coulombic forces and short range interactions respectively. In any actual solution, there will be ion-solvent interactions to consider as well as other forces resulting from the deformation of the spherical model. These are thought bo be of a type causing linear variation with log f and Guggenheim[3] and Davies[4] have put forward extended equations of the type

$$\log f_{\pm} = \frac{-A\,|z_1 z_2|\,I^{\frac{1}{2}}}{1 + B\mathring{a}I^{\frac{1}{2}}} + \beta I$$

The Davies equation, used throughout the present work is

$$\log f_{\pm} = -A|z_1 z_2|\left[\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.2I\right] \text{---------(2)}$$

and agreement with experiment for 1:1 and 2:1 electrolytes in water at 25°C up to an ionic strength of 0.1M is within 2%.[5]

The thermodynamic association constant, K, resulting from equilibrium (1) may be written

$$K = \frac{\{MX^{(a-b)+}\}}{\{M^{a+}\}.\{X^{b-}\}} = \frac{[MX^{(a-b)+}]}{[M^{a+}].[X^{b-}]} . \frac{f_{MX^{(a-b)+}}}{f_{M^{a+}} . f_{X^{b-}}} \text{-------(3)}$$

where the braces enclose activities, the square brackets concentrations and f's are the corresponding activity coefficients. In experiments at constant ionic strength, it is convenient to neglect the f's and the corresponding equilibrium quotient or stability (or formation) constant is obtained.

A number of methods are available for the study of ion association in solution. These include (a) conductivity, (b) solubility, (c) potentiometry, (d) spectrophotometry, (e) polarography.

(a). Davies[6] has attributed deviations from the Onsager limiting equation to ion association and he and his co-workers have used the conductimetric method to study association in 1:1, 2:2 and 3:3 electrolytes. These symmetrical ion-pairs lend themselves to investigation by this method since, having no residual charge they do not contribute to the observed conductivity.

(b). Measurement of the solubility of sparingly soluble salts in the presence of added electrolytes was first used by Davies[7] to study association in calcium salts of organic acids. The method has been employed by Bell and George[8] and Nair and Nancollas[9] to study calcium and thallous salts.

(c). Many e.m.f. methods have been introduced. Covington and Prue[10] have made very accurate measurements using the glass electrode and among many examples of the use of Harned cells may be cited the work of Nair and Nancollas[11] on transition metal sulphates and Monk et al.[12] on metal dicarboxylates.

(d). The spectrophotometric method takes advantage of the fact that the metal ion and the ion-pair have different extinction coefficients and although it is the concentration of complex which is measured it does have the disadvantage in that an extra extinction coefficient has to be measured. Using this method, however, Monk[13] and his collaborators have studied ion-pair formation between the uranyl ion and thiocyanate and chloride anions. In his investigation of the copper sulphate system, Prue[13a] has discussed the errors involved in this method.

(e). The polarographic half wave potential of a metal ion is shifted to a more negative value when an association with an anion takes place. The extent of the shift may be expressed in terms of the number of electrons involved and the number of anions associated with each cation.[29] The method has been used by Gelles and Nancollas[14] in their study of the copper malonate system. Other workers employing this method include Meites[14a] who studied metal ion association with citrate ions.

These and other methods of investigation have recently been reviewed by Nancollas.[15]

Much of the data on ion association refer to work done at a single temperature or overaa small temperature range. If, however, a range of 45 or 60 degrees is used, it is possible to calculate the thermodynamic properties of the association. The heat of formation of the ion-pair may be derived from the variation in log K with temperature. Entropy changes may be obtained, and these can arise in two ways. Firstly, in the formation of the ion pair there is a net reduction in the number of ions in solution leading to an entropy decrease, but there is also an opposing effect in that the neutralisation of charge leads to a greater freedom of solvent (water) molecules around the ions, giving an entropy increase. Depending on which of the factors predominates, an entropy increase or decrease is given. Many temperature data yielding these properties are available for weak acids where association has been extensively studied.[16, 5] Also while there are many data for formation constants in the literature,[18] the conditions under which these have been measured very widely and direct comparison between systems is sometimes difficult. The published work on heats and entropies of formation is still scanty. Recently the results of calorimetric ΔH measurements [17] on the reactions of ethylenediamine with transition metals have been combined with free energy data[18] in order to provide the thermodynamic properties. Although calorimetric heats are the most reliable, the isochore method does have the advantage in that if ΔH varies with temperature, the change in specific heat, ΔC_p may also be obtained.

In the present work, Part I deals with the association between copper and oxalate ions in solutions of varying ionic strengths at 25°C. This has been studied using an e.m.f. method and various equilibria have been found depending on the pH of the solution and the metal and acid concentrations. Polarographic techniques were also used and the results are in good agreement.

Part II is devoted to a study of 2:2 electrolytes. The oxalates and succinates of nickel, cobalt and manganese have been studied by a precise e.m.f. method over a temperature range from 0° to 45°C. Thermodynamic properties have been derived for each association and the first dissociation constant of oxalic acid has also been measured over this temperature range.

In Part III thermodynamic properties are discussed and correlations between ΔH, ΔS and ΔG with ionic parameters are investigated.

Part IV consists of the description of a calorimetric study of the heat of formation of manganese malonate. The heat of solution of potassium chloride has been used to test the apparatus and values obtained are compared with existing data.

PART I

ASSOCIATION IN COPPER OXALATE SOLUTIONS

The reactions in solution between transition metal cations and the anions of weak acids or neutral molecules have been extensively studied and the corresponding association constants measured.[18, 19, 41] Irving and Williams[41] found that these stability constants, K, were in the order

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

along the first transition row, and suggested that the reason for increments in K from metal to metal was due to some stabilising factor which increased in extent along the series, indicating the tendency towards the formation of a covalent bond between the metal atom and the ligand. They also showed that the stability increment from metal to metal was greatest for nitrogen-type ligands (e.g., ethylenediamine) and least for oxygen-type (e.g., salicylates and oxalates). There is a large spread in log K values for dicarboxylate complexes, but the values for the sulphates are very similar and the latter are thought to be electrostatic ion-pairs. The association between copper and oxalate ions has not been studied, however, and it would be desirable to have this value in order to test the Irving-Williams order.

It is well known that if the size of the chelate ring is increased there is an accompanying decrease in stability. This has been confirmed recently[21] in a study which has shown that the relative stability of dicarboxylates decreases uniformally as the ring size increases.

Irving, R.J.P.Williams, Ferrett and A.E.Williams[21a] showed that complexes formed by aliphatic diamines, amino acids and carboxylic acids were most stable when the rings had five atoms and interpreted the decrease in stability on increasing size in terms of entropy and heat changes.

The main reason that copper oxalate solutions have not been studied is probably due to the fact that the CuC_2O_4 complex has a very low solubility ($1.6x10^{-4}$ at 18°C). It is, however, more soluble in the presence of excess oxalate anion due to the formation of increasing amounts of the species $Cu(C_2O_4)_2^{2-}$. This was noted by Britton and Jarrett,[22] who studied the system:- sodium oxalate, copper oxalate and water and obtained a value of $2x10^8$ for the association constant of the doubly charged anionic complex at 18°C. Riley[23] prepared the double salt $Na_2C_2O_4.CuC_2O_4.2H_2O$ and, using an e.m.f. method at 20°C,found a value of $3x10^8$ for the complex association constant. Both these workers studied solutions at an ionic strength of about 0.1M. Meites,[24] using a polarographic method, made measurements at widely differing ionic strengths and gave a K value for the soluble species of 2×10^{10}, considerably higher than those previously reported.

In the present work a technique was evolved by which, with careful control of concentrations and experimental technique, it was possible to prepare solutions containing equivalent ionic concentrations of copper and oxalate which were stable long enough for e.m.f.s to measured and depending on the pH of the solutions various complex species were present. The data from these experiments were interpreted in terms of the formation of three species $CuHC_2O_4^+$, CuC_2O_4 and $Cu(C_2O_4)_2^{2-}$. Measurements were made at a constant ionic strength of 0.1M and at low concentrations and equilibrium quotients and thermodynamic association constants for each of these species have been determined.

In the course of these experiments, values for the dissociation constants of oxalic acid at an ionic strength of 0.1M were also obtained. Polarographic measurements were made at varying ionic strengths from 0.2 to 0.6M in solutions containing a large excess of oxalate anion. The presence of the soluble doubly charged complex species was noted and a value for its stability constant obtained, lower than that of Meites but in good agreement with that derived from e.m.f. measurements.

Preparation of Reagents

Copper perchlorate: An excess of copper oxide was added to a 1N solution of perchloric acid in the cold and the mixture was then heated and stirred at 80°C for a period of four to five hours. The solution, after cooling, was decanted and centrifugation and filtration removed any traces of copper oxide. The solution was analysed for copper both iodometrically[47] and by using an ion-exchange method. A column of Amberlite I.R.120 resin about 18 cm long and 1 cm in diameter was converted to the hydrogen form by passing through it about 100 ml. of 3 - 4 N hydrochloric acid and washing with about five litres of distilled water until the eluate had a pH similar to that of water. 10 ml. portions of copper solution (0.1N) were then slowly passed through the column which was again washed with distilled water until acid free, the eluates being collected in conical flasks. Titration of the perchloric acid obtained in this manner against standard sodium hydroxide yielded the copper concentration. A check that all the acid had been washed free from the column was made by further titration of the eluate.

Sodium perchlorate: B.D.H. material was recrystallised from distilled water and solutions were analysed using an ion exchange column in a manner similar to that described for copper perchlorate.

Sodium hydroxide: Saturated solutions of sodium hydroxide were prepared from "AnalaR" sodium hydroxide pellets which were mechanically shaken in distilled water for 24 hours. The solution was allowed to stand for three to four weeks, after which samples were diluted with carbon dioxide - free distilled water in an atmosphere of nitrogen. The hydroxide solution was stored in a flask with an automatic burette attachment having soda-lime tubes on all air outlets. Samples of the solution were titrated (a) by volume against B.D.H. volumetric hydrochloric acid stock solutions, and (b) against weighed samples of potassium hydrogen phthalate. Agreement was always better than 0.1%.

Oxalic Acid: This was of "AnalaR" grade and solutions were prepared by volume. Titration against the standard sodium hydroxide solution acted as a check on the concentration.

Copper chloride: The hydrated cupric salt was of "AnalaR" quality and solutions which were prepared by volume were estimated both iodometrically for copper and by Mohr's method for chloride.

"AnalaR" quality potassium chloride, potassium hydrogen phthalate and sodium oxalate were used and the gelatin was 'Polaritan' material.

Stock solutions were kept in stoppered pyrex stock flasks with ground glass joints. All volumetric apparatus was of grade A quality. The flasks were cleaned by standing in chromic acid and, where possible, steaming for one hour. When not in use they were filled with distilled water. Samples of the reagents were weighed out from small pyrex weighing bottles using a Stanton semi-micro balance and weights which had been calibrated by the method of Kohlrausch[76].

APPARATUS

I. Potentiometric Measurements

E.m.f. measurements were made using the cell

Calomel / Satd.KCl / Solution / Glass / HCl (0.2M), AgCl/Ag.

The design of the cell has been previously described[25] by Dunsmore and Speakman. The glass electrode was made of Corning 015 glass and had a resistance of about 10^7 ohms. E.m.f.s reproducible to within 0.1 mv. were obtained using duplicate solutions. The cell was kept in an oil bath which was maintained at 25 0.1°C even when not in use, to prevent fluctuating calomel electrode potentials.

The calomel electrode was of conventional design. A small quantity (0.5 - 1 ml.) of doubly distilled mercury was placed at the bottom of vessel H in Fig.1 and this was covered with a layer of calomel paste prepared by rubbing together in a mortar, calomel, mercury and a few drops of saturated potassium chloride solution. The whole was then covered with potassium chloride crystals. A tube, having a platinum wire sealed in it, was placed in position as shown by means of a rubber bung, the joints being coated with paraffin wax to prevent stray potentials. The vessel was filled with saturated potassium chloride solution from reservoir G. The glass electrode bulb contained a solution of 0.2M

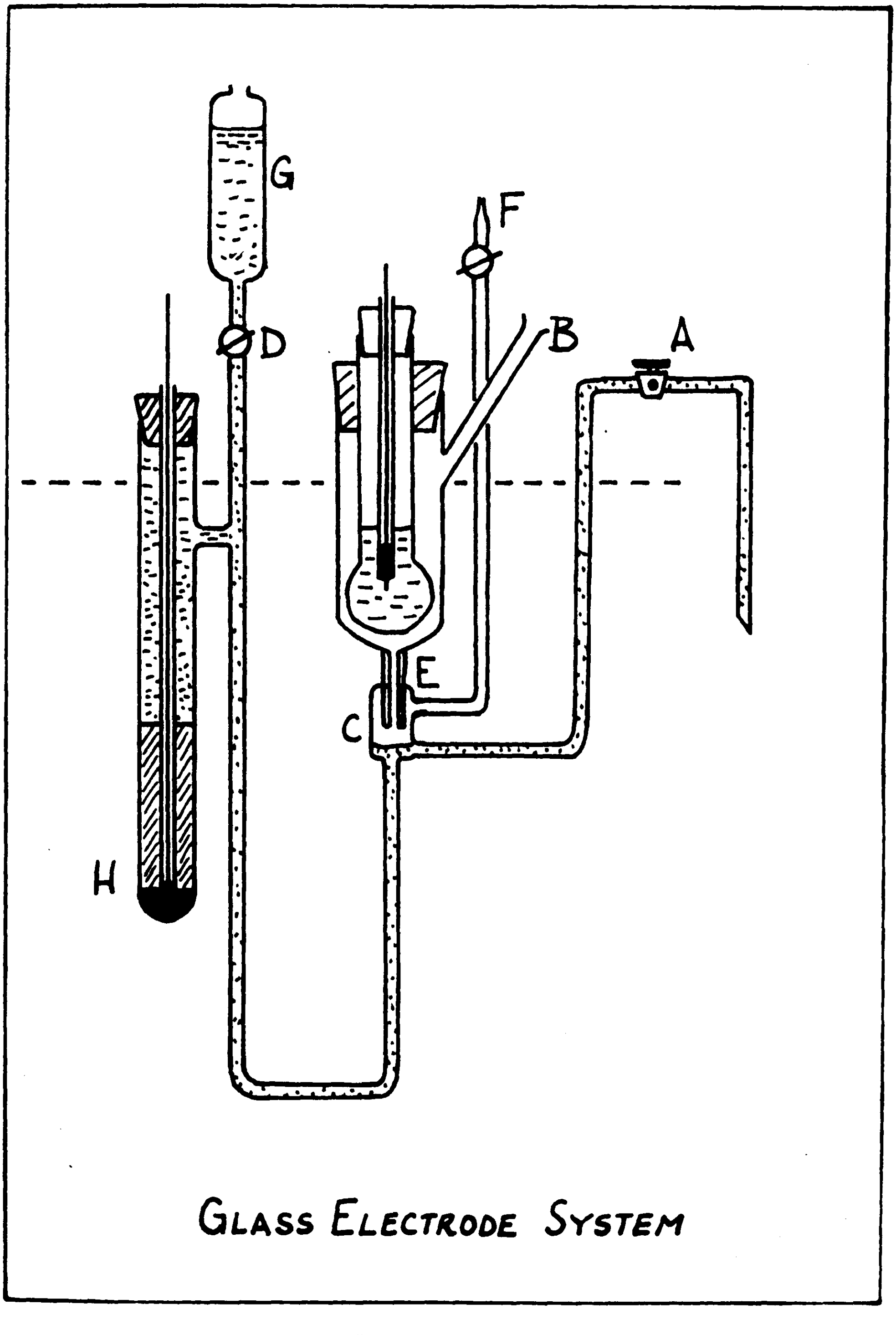


Fig. 1.

hydrochloric acid prepared from volumetric reagent. The silver - silver chloride electrode was made by the method of Brown[77], the platinum-pyrex seal being perfected by the use of Araldite resin cast in the bottom of the tube.

E.m.f. measurements were made using a Tinsley potentiometer with a Vibron electrometer (E.I.L. model 33B) as a null indicator.

Experimental Procedure.

The apparatus used in measuring pH values with the glass electrode is shown in Fig.1. The solution was removed from the cell by means of the syphon controlled by tap A. When in use, the electrode vessel was flushed three or four times with the solution to be studied by filling it through B and emptying it through A. Saturated potassium chloride was then admitted to the junction C from the reservoir via tap D. After rinsing with several charges of this liquid, its level was adjusted in the junction vessel so that it almost touched the tip of the capillary tube E. The test solution was then added through B and due to the airlock in C the solution did not descend to the foot of capillary tube E. The air was released from C using the tap F which controlled an air bleed such that the solution flowed slowly down E and gently made a junction with the potassium chloride solution in C. It was possible to see the junction formed and the solution was left for ten to twenty minutes during which time constant readings were given.

Due to the very low solubility of the copper oxalate, solutions were made up immediately before use. Any drifts in the e.m.f. readings were accounted for by salt precipitation and the solution in the electrode vessel was immediately removed and discarded. The glass electrode was then washed with very dilute ammonia, water and allowed to stand for some days in dilute hydrochloric acid before further use.

Standardisation of Electrodes.

(a). At Constant Ionic Strength, I = 0.1M.

Before, during and after each run, the electrode system was calibrated using hydrochloric acid solutions of known concentration containing sufficient sodium perchlorate to give an ionic strength of 0.1M. The e.m.f. values corresponding to these solutions were plotted against log $[H^+]$ and using these plots unknown log $[H^+]$ values could be derived from the observed e.m.f.s to within ± 0.005. A typical calibration curve is shown in Fig.2 for which the data are given in Table I.

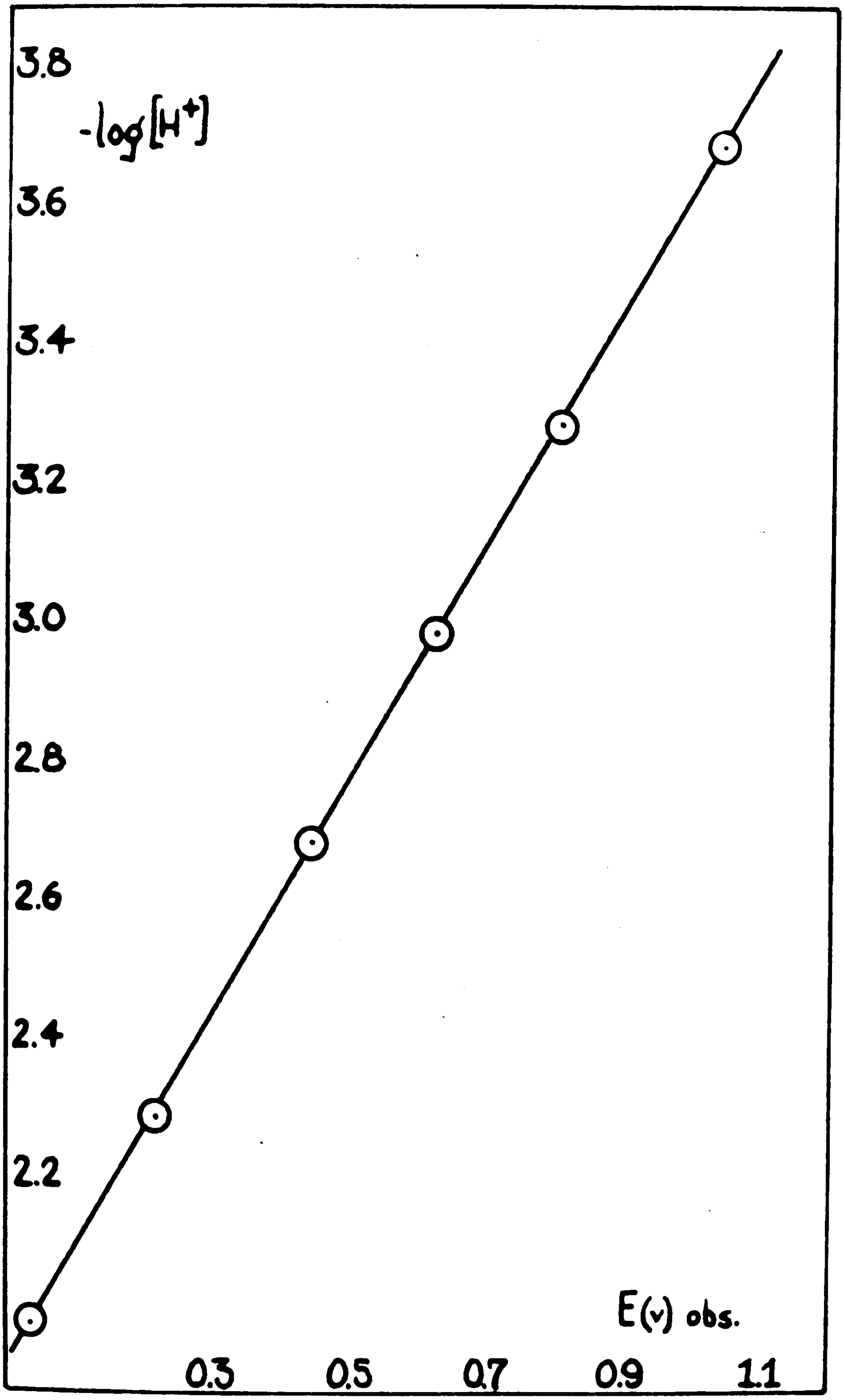


Fig. 2.

Table I

Standardisation of Electrode system, I = 0.1M

$[H^+]$	E(v),obs.	log $[H^+]$
2×10^{-4}	0.1038	-3.699
5×10^{-4}	0.0805	-3.301
10^{-3}	0.0627	-3.000
2×10^{-3}	0.0443	-2.699
5×10^{-3}	0.0217	-2.301
10^{-2}	0.0033	-2.000

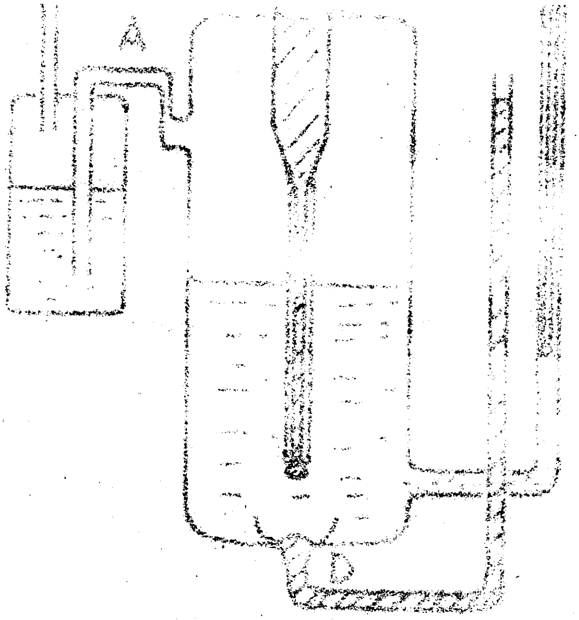
The slope of the line is 0.059 and in all calibrations gradients fell within the range 0.058 to 0.060.

(b) At Low Ionic Strengths I→0.

When the concentrations were low, the electrodes were standardised with hydrochloric acid solutions, using the activity data of Robinson and Stokes,[5] and with buffer solutions of known pH : 0.01M hydrochloric acid + 0.09M potassium chloride, pH = 2.078,[27] and 0.05M potassium hydrogen phthalate, pH = 4.005.[26]

Preparation of Copper Oxalate Solutions.

Mixtures containing known amounts of oxalic acid and sodium hydroxide were made in a 250 ml. graduated flask and diluted using distilled water to about 230 ml. The cupric perchlorate (or chloride) stock solution was slowly added from a 10 ml. pipette and the whole made up to the mark. Solutions prepared in this way were stable for 3 to 4 hours. Some solutions where the buffer was diluted to only 150 to 180 ml. before the copper was introduced showed precipitation after half an hour. In experiments at constant ionic strength, the calculated volume of sodium perchlorate stock solution was also added.



POLAROGRAPHY CELL

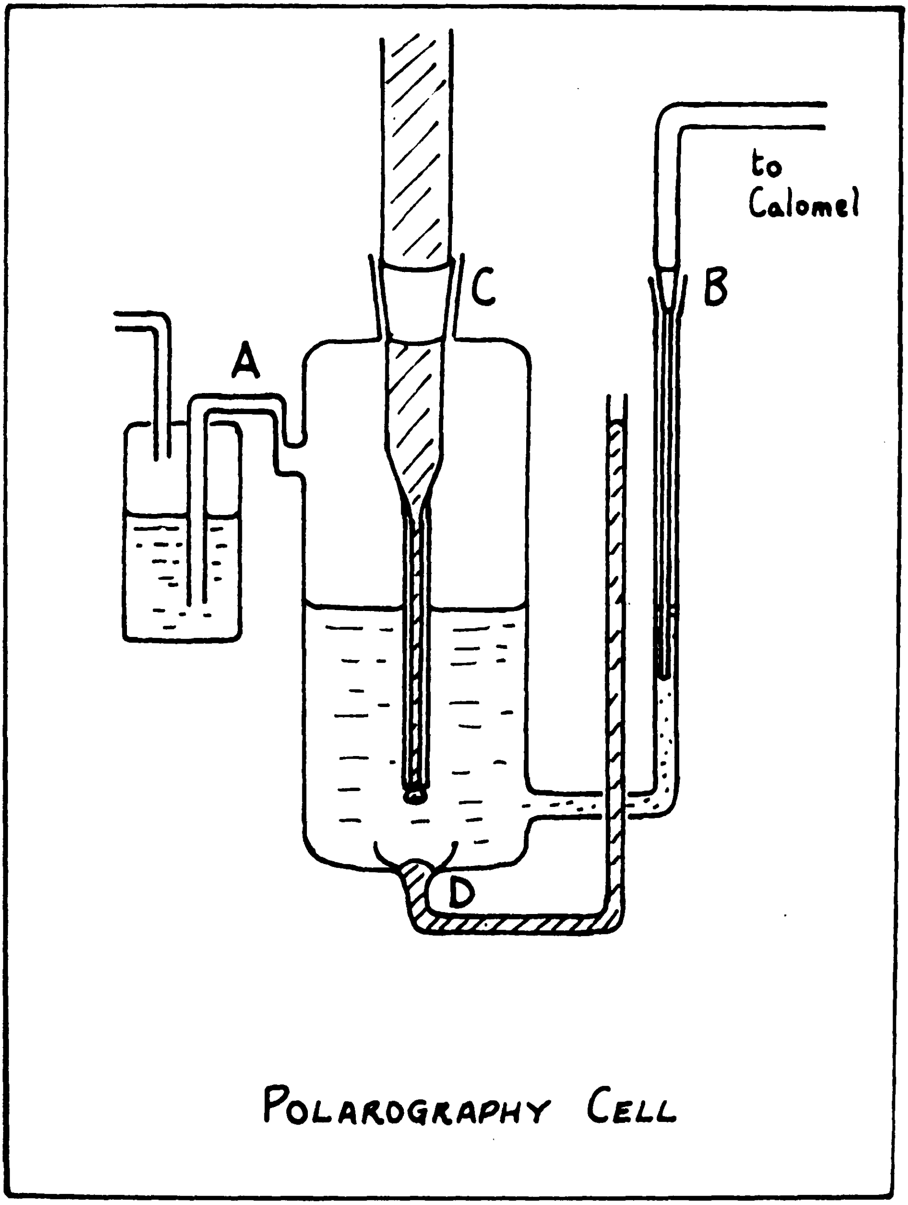


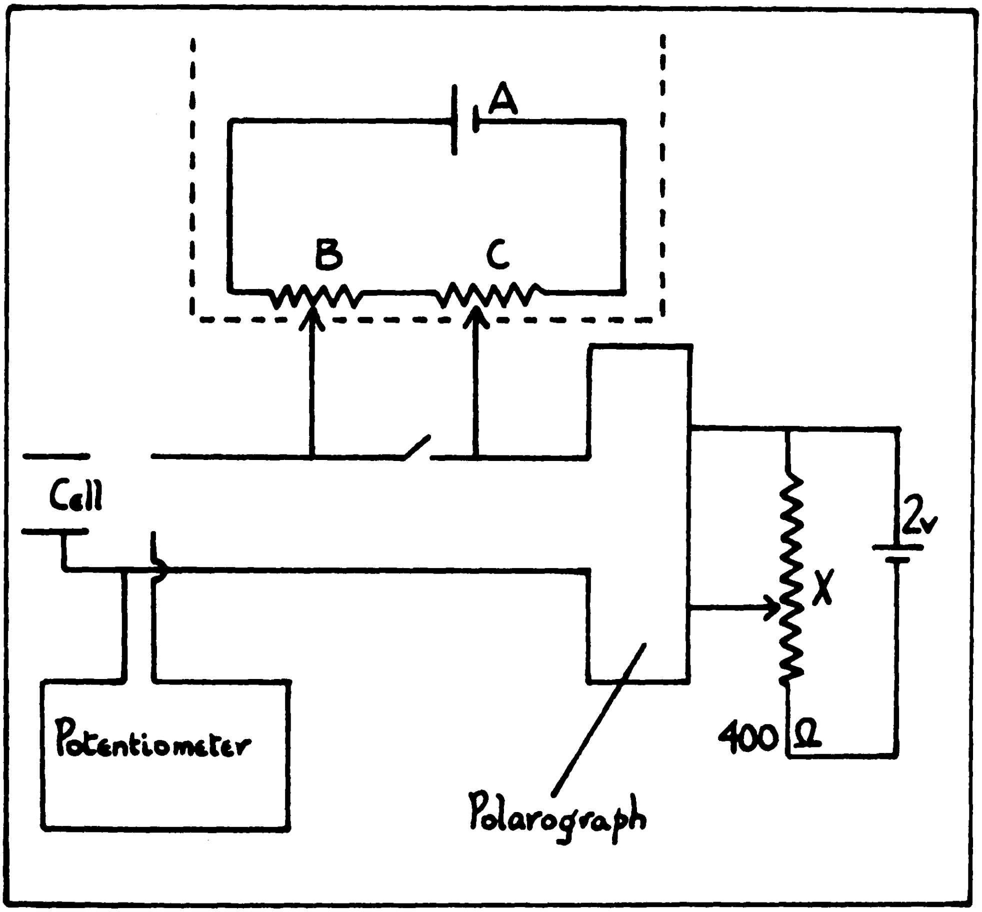
Fig. 3.

II. Polarographic Measurements.

The apparatus used has been described by Gelles and Nancollas.[14] The solution was electrolysed in a cell between a dropping mercury cathode and a saturated calomel electrode, the current corresponding to the applied potential being recorded on a Tinsley pen recording polarograph. It was possible to determine potentials to ± 1 mv. by decreasing the voltage span of the instrument from 3 to 0.3 volts.

The Cell

A diagram of the cell is given in Fig.3. The bubbler attached to sidearm A prevented the diffusion of oxygen back into the solution after it had been flushed out with nitrogen. The cell was filled with solution through C, into which was then fitted a dropping mercury capillary which could be adjusted so that the mercury drops (drop time 3.3 - 0.3 secs) fell into the cup D. Sidearm B served as a nitrogen inlet. Nitrogen was obtained from an oxygen free cylinder and was passed through two vessels containing vanadium sulphate solution standing over amalgamated zinc to remove any final traces of oxygen. It was then bubbled through water and passed through the cell solution for about fifteen minutes before each experiment. The nitrogen supply was then disconnected and the calomel electrode salt bridge, consisting of



POLAROGRAPHY CIRCUIT

Fig. 4.

saturated sodium chloride solution boiled with 3% agar, was introduced in tube B. 0.005% gelatin was used as a maximum suppressor. Cell resistances amounted to 4000 to 7000 ohms and corrections for the iR drop were of the order of 2-3 mv.

The Circuit.

A diagram of the circuit is shown in Fig.4. The batteries in the polarograph were replaced by the potentiometric adjustment shown which reduced its voltage span from 3.0 volts to 0.3 volts. More accurate potential measurements could thus be made. If a half wave potential greater than -0.3 volts was to be measured, another accumulator (A in Fig.4) was put into the circuit together with potentiometers B and C so that a constant known potential could be superimposed on the gradually increasing potential from the polarograph.

Experimental

Half wave potentials $E_{\frac{1}{2}}^{s}$ for the copper ion were measured in solutions of cupric nitrate, potassium nitrate, and sodium perchlorate. Solutions containing varying amounts of cupric nitrate and sodium oxalate with gelatin as suppressor and sufficient potassium nitrate or sodium perchlorate to give varying ionic strengths from I = 0.2 to 0.6M, were prepared and the shifts in the half wave potentials noted for each oxalate concentration.

RESULTS AND DISCUSSION

Interpretation of e.m.f. data at low concentrations in terms of only one complex (CuC_2O_4) led to values of K which were not constant, indicating that more than one complex was present. It was therefore decided to use the data at constant ionic strength to identify the species since calculations were simplified by the fact that activity coefficients were incorporated in the stability constants and could be neglected. It was found that the species present in solution depended on the pH and the concentrations of metal and acid. The three equilibria required for the interpretation of the data corresponding to the formation of the complexes identified were:-

$$Cu^{2+} + HC_2O_4^- \rightleftharpoons CuHC_2O_4^+ \qquad \text{------(4)}$$

$$Cu^{2+} + C_2O_4^{2-} \rightleftharpoons CuC_2O_4 \qquad \text{------(5)}$$

$$CuC_2O_4 + C_2O_4^{2-} \rightleftharpoons Cu(C_2O_4)_2^{2-} \qquad \text{------(6)}$$

Formation constants and thermodynamic association constants for each species have been measured.

It was necessary to obtain the values for the dissociation constants of oxalic acid at an ionic strength of 0.1M

$$k_1' = [H^+].[HC_2O_4^-] / [H_2C_2O_4]$$

and

$$k_2' = [H^+].[C_2O_4^{2-}] / [HC_2O_4^-] .$$

The first dissociation of oxalic acid is rather extensive and it was necessary to limit this by the addition of hydrochloric acid. Solutions, containing these ingredients and sufficient sodium perchlorate to raise the ionic strength to 0.1M were examined and measured e.m.f.s were used to yield log $[H^+]$ values. At sufficiently low log $[H^+]$ values, the contribution made by $[C_2O_4^{2-}]$ from the second dissociation may be neglected and the expression for total acid concentration becomes

$$Ta = [H_2C_2O_4] + [HC_2O_4^-] \quad \text{-------}(7).$$

Since the solution is electrically neutral, we can write

$$[H^+] = [HC_2O_4^-] + [Cl^-] \quad \text{-------}(8).$$

The chloride concentration is known and the hydrogen ion concentration is interpolated from Fig.2, so that $[HC_2O_4^-]$ can be obtained from (8) and using this in (7), $[H_2C_2O_4]$ is found. The results of these experiments are given in Table II.

The second dissociation constant of oxalic acid was measured using solutions containing sodium hydroxide, oxalic acid and sodium perchlorate. Here the log $[H^+]$

TABLE II

First dissociation constant of oxalic acid, at I= 0.1M.

$Ta.10^3$	$[H^+].10^3$	$[Cl^-].10^3$	$[H_2C_2O_4]10^3$	$k_1'.10^2$
4.058	8.035	4.657	0.680	4.1
7.596	10.47	4.371	1.497	4.2
10.926	12.59	4.102	2.438	4.3
12.902	13.80	3.943	3.045	4.5
14.106	14.45	3.845	3.501	4.4

Mean $k_1' = 4.3 \times 10^{-2}$.

TABLE III

Second dissociation constant of oxalic acid, at I= 0.1M.

$Ta.10^3$	$[Na^+].10^3$	$[H^+].10^4$	$[C_2O_4^{2-}].10^3$	$[HC_2O_4^-].10^3$	$k_2'.10^4$
1.978	1.852	5.56	0.430	1.548	1.54
1.974	2.040	4.52	0.518	1.456	1.61
1.968	2.305	3.24	0.661	1.307	1.64
1.962	2.575	2.16	0.829	1.133	1.58
1.956	2.897	0.135	1.058	0.898	1.59
0.381	0.351	1.95	0.165	0.216	1.49
0.374	0.461	1.19	0.206	0.168	1.46

Mean $k_2' - 1.56 \times 10^{-4}$.

values were high enough to neglect the concentration of any undissociated acid, and in this case,

$$Ta = [HC_2O_4^-] + [C_2O_4^{2-}] \text{ ---------------(9)}$$

and electroneutrality yielded

$$[Na^+] + [H^+] = [HC_2O_4^-] + 2[C_2O_4^{2-}] \text{---------(10).}$$

Knowing $[Na^+]$, $[H^+]$ and Ta, $[HC_2O_4^-]$ and $[C_2O_4^{2-}]$ were obtained. The results of these experiments are given in Table III.

Interpretation of the data from copper solutions was now undertaken. Calculations were made on the basis that only equilibrium (4) (i.e. the formation of CuC_2O_4) was operative. The stability constant (K_2') values showed a considerable drift suggesting the presence of other species. It was then thought that inclusion of terms for the $Cu(C_2O_4)_2^{2-}$ complex might eliminate this drift. A graphical method was used and three sets of points were recognised as being independent. Investigation showed that each group of points was given under certain experimental conditions. The complex species found to be present were CuC_2O_4, $CuHC_2O_4^+$ and $Cu(C_2O_4)_2^{2-}$, ($CuOH^+$ was not expected at such low pH's), and it was possible to adjust the concentrations so that any two of these complexes could be made to predominate. The conditions yielding the different species were found to be :

(a) Ta much smaller than Tm with low $[Na^+]$, where the species present were $CuHC_2O_4^+$ and CuC_2O_4.

(b) Ta smaller than Tm with high $[Na^+]$, the complexes here being CuC_2O_4 and $Cu(C_2O_4)_2^{2-}$ and

(c) Ta greater than Tm with varying $[Na^+]$, where all three complexes were present.

For solutions of copper perchlorate, sodium hydroxide and oxalic acid where all three complex species, $CuHC_2O_4^+$, CuC_2O_4 and $Cu(C_2O_4)_2^{2-}$ are present, a comprehensive treatment at low concentrations would involve the following.

Total metal ion concentration is

$$Tm = [Cu^{2+}] + [CuC_2O_4] + [CuHC_2O_4^+] + [Cu(C_2O_4)_2^{2-}] \text{----}(11)$$

and that of the total acid,

$$Ta = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}] + [CuC_2O_4] + [CuHC_2O_4^+] + 2[Cu(C_2O_4)_2^{2-}] \text{-----}(12)$$

and the electroneutrality condition is

$$[Na^+] + [H^+] + 2[Cu^{2+}] + [CuHC_2O_4^+] = [HC_2O_4^-] + 2[C_2O_4^{2-}] + 2[Cu(C_2O_4)_2^{2-}] + 2\ Tm \text{------------}(13)$$

where $Cu(ClO_4)_2$ is assumed to be completely dissociated. The thermodynamic dissociation constants of oxalic acid are

$$k_1 = [H^+].[HC_2O_4^-].f_1^2/[H_2C_2O_4] \text{------------------}(14)$$

$$k_2 = [H^+].[C_2O_4^{2-}].f_2/[HC_2O_4^-] \text{------------------}(15).$$

From the equilibria represented by equations (4), (5) and (6), the corresponding thermodynamic association constants may be written:-

$$K_1 = [CuHC_2O_4^{\,+}] / [Cu^{2+}].[HC_2O_4^{\,-}].f_2 \quad \text{------------------}(16)$$

$$K_2 = [CuC_2O_4] / [Cu^{2+}].[C_2O_4^{\,2-}].f_2^2 \quad \text{------------------}(17)$$

and

$$K_3 = [Cu(C_2O_4)_2^{\,2-}] / [CuC_2O_4].[C_2O_4^{\,2-}] \text{------------------}(18)$$

The ionic strength of the solution may be calculated from the expression $I = \frac{1}{2}\Sigma c_i z_i^2$, where c_i is the concentration of species i and z its valency. The expression for the ionic strength of a solution containing all three species is found to be

$$I = 3Ta - Tm - 3[H_2C_2O_4] - 2[HC_2O_4^{\,-}] + \frac{4(2Ta - [Na^+] - [H^+] - 2[H_2C_2O_4] - [HC_2O_4^{\,-}])}{K_1.[HC_2O_4^{\,-}].f_2} \text{--}(19)$$

The method of calculation is to use an approximate value for the ionic strength (e.g., 3Ta - Tm) in order to calculate activity coefficients by means of the Davies equation

$$-\log f_z = A.z^2\left[\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.2I\right], \text{-------------}(2)$$

A being the Debye-Hückel constant which at 25°C has the value 0.5092 on the molar scale. Using these approximate activity coefficients, the concentrations of the ionic species are calculated using equations (11) to (18) and are used to derive a more accurate value of I from equation (19). This prowess of approximations is continued until identical I values are obtained in successive cycles.

The Davies equation has been used in the evaluation of association constants of 2;2 electrolytes e.g., dicarboxylates,[37] as well as other symmetrical complexes. Guggenheim,[74] however, has recently critised its use for other than 1 : 1 electrolytes. He suggests a coefficient of 2 rather than 0.2 for 2 : 2 electrolytes, which defines the distance of approach of the ions in association as about 9Å. There is still some uncertainty as to which equation to use in the case of mixed electrolytes. It has been found, however, that use of the Guggenheim formula leads to negative concentrations of complex in transition metal sulphate data and to a reduction of about 15 to 20% in the K value obtained for copper oxalate in this work. Studies on the association of malonate and substituted malonate ions with the nickel cation have shown that at low concentrations the Davies equation represents the results satisfactorily.

In work at constant ionic strength, the activity coefficients may be omitted and the corresponding stability (or formation) constants are written K_1', K_2', K_3'.

TABLES IV and V

Stability constant K_1' (using

$Tm.10^3$	$Ta.10^4$	$[Na^+].10^4$
1.683	5.745	1.576
1.683	5.745	2.495
1.683	5.745	3.086
1.683	5.745	3.782

Graphical plot

$Tm.10^3$	$Ta.10^4$	$[Na^+].10^4$	$[H^+].10^4$
1.683	5.745	9.263	2.138
1.683	5.745	8.475	2.904
1.683	5.745	7.911	3.451
1.683	5.745	7.176	4.154
1.346	5.745	8.206	3.119
2.356	5.745	8.206	3.204

TABLE IV

$K_2' = 7 \times 10^4$) at $I = 0.1M$.

$[H^+].10^4$	$[C_2O_4^{2-}].10^6$	$[HC_2O_4^-].10^5$	$[H_2C_2O_4].10^7$	$K_1'.10^{-2}$
9.33	6.37	3.78	7.87	3.4
8.51	6.46	3.48	6.57	3.1
7.94	6.50	3.27	5.76	3.4
7.295	6.59	3.04	4.93	2.9

Mean $K_1' = 3.2 \times 10^2$

TABLE V

yielding K_2' and K_3'.

$[HC_2O_4^-].10^5$	$[C_2O_4^{2-}].10^6$	$[H_2C_2O_4].10^7$	$X.10^{-4}$	$Y.10^{-9}$
0.88	6.51	0.42	6.15	4.70
1.10	5.96	0.71	6.72	5.58
1.26	5.77	0.97	6.95	5.94
1.57	5.98	1.45	6.72	5.50
1.63	8.24	1.13	4.51	3.78
0.79	3.89	0.56	11.11	8.97

When Ta was much smaller than Tm and the $[Na^+]$ was low, the data were analysed in terms of the two species $CuHC_2O_4^+$ and CuC_2O_4. In the calculations for the ionic strength an estimated value of K_2' of 7×10^4 was used and the good constancy in the values of K_1' obtained indicated that the value of K_2' inserted was probably a correct one. The results on solutions seen to contain these species are given in Table IV.

When the pH of the solution was increased by adding more sodium hydroxide, $[C_2O_4^{2-}]$ increased, and it was expected that the species CuC_2O_4 and $Cu(C_2O_4)_2^{2-}$ would predominate. The calculation procedure now involved the total metal ion concentration,

$$Tm = [Cu^{2+}] + [CuC_2O_4] + [Cu(C_2O_4)_2^{2-}]$$

the total acid,

$$Ta = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}] + [CuC_2O_4] + 2[Cu(C_2O_4)_2^{2-}]$$

the electroneutrality condition,

$$[Na^+] + [H^+] + 2[Cu^{2+}] = [HC_2O_4^-] + 2[C_2O_4^{2-}] + 2[Cu(C_2O_4)_2^{2-}] + 2\ Tm$$

and the dissociation constants k_1 and k_2 of oxalic acid.

From these equations, a graphical solution, similar to that of Gelles and Nancollas,[28] was applied leading to a curve based on the equation

$$Y = XK_2' + K_2'.K_3',$$

in which

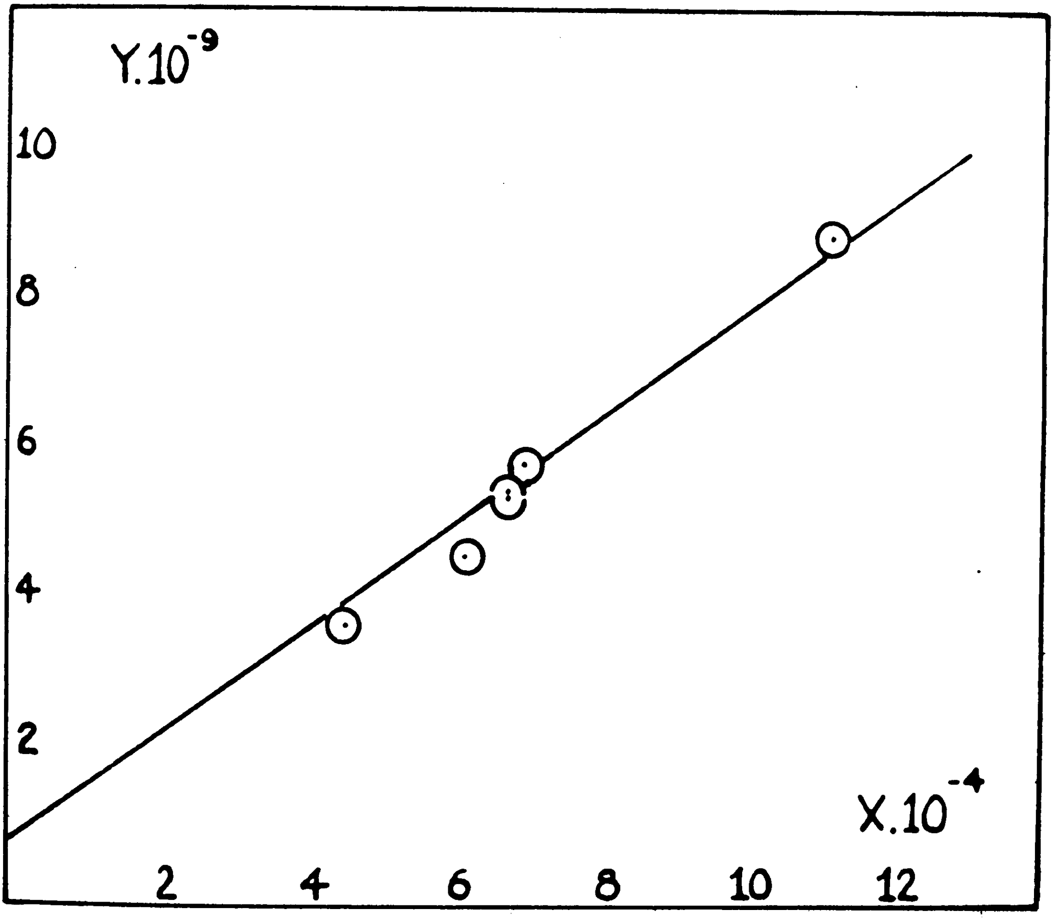


Fig. 5.

$$X = \frac{Tm - Ta + [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]}{[C_2O_4^{2-}]\{2Tm - Ta + [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]\}}$$

and

$$Y = \frac{Ta - [H_2C_2O_4] - [HC_2O_4^-] - [C_2O_4^{2-}]}{[C_2O_4^{2-}]^2\{2Tm - Ta + [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]\}}$$

Data are given in Table V and the good linearity of the plots of X against Y is shown in Fig.5. The slope of the line, K_2', has the value 6.9×10^4, the value which was used to calculate K_1', and the intercept gives a K_3' value of 1.5×10^4.

Since K_3' is obtained by extrapolation which is somewhat inaccurate, it was necessary to obtain a confirmatory value. When the metal ion concentration was less than that of the total acid, it was expected that all three complexes would be present and, using the calculation scheme described earlier, concentrations of the various species present in the solution were evaluated. Values of $K_1' = 3.2 \times 10^2$ and $K_2' = 7 \times 10^4$ were introduced and calculated K_3' values are given in Table VI.

The mean K_3' of 2.3×10^4 is in reasonable agreement with the approximate extrapolated value of 1.5×10^4.

Having identified the species present in the solutions, measurements at low concentrations were made in order to determine the thermodynamic association constants. At an ionic strength of 0.1M the K_2' and K_3' values are comparable in magnitude but on introducing the activity coefficient values (f_2 into K_1' and f_2^2 into K_2') there is a greater difference between K_1, K_2 and K_3. For this reason, it is possible to choose conditions where CuC_2O_4 only need be considered. In this case the treatment of the results is simpler, the equations (11), (12), (13) and (19) respectively reducing to

$$Tm = [Cu^{2+}] + [CuC_2O_4]$$

$$Ta = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}] + [CuC_2O_4]$$

$$[Na^+] + [H^+] + 2[Cu^{2+}] = 2\,Tm + [HC_2O_4^-] + 2[C_2O_4^{2-}]$$

and

$$I = \frac{1}{2}\Big[6Tm - 4\,Ta + 4[H_2C_2O_4] + 8[C_2O_4^{2-}] + 5[HC_2O_4^-] + [Na^+] + [H^+]\Big]$$

Successive approximations for I yielded the ionic concentrations. These results are given in Table VII and good constancy is seen.

TABLE VI

Measurements with Tm<Ta giving K_3' at I = 0.1M

$Ta.10^3$	$Tm.10^3$	$[H^+].10^3$	$[Na^+].10^3$	$K_1'.10^{-2}$	$K_2'.10^{-4}$	$K_3'.10^{-4}$
2.828	4.378	2.075	5.886	3.0	7.0	1.8
2.828	4.378	2.399	5.481	3.0	6.9	2.1
2.828	4.378	2.483	5.405	3.0	7.0	2.1
2.828	4.378	2.754	5.128	3.0	7.7	2.3
2.828	4.378	2.944	2.889	2.9	6.6	2.7
2.828	4.378	3.177	4.469	3.0	7.1	1.8
2.828	4.378	3.342	4.342	3.0	7.0	2.0
		Mean values		3.0	7.0	2.3

TABLE VII

Association constant K_2 at I→0

$Tm.10^3$	$Ta.10^3$	$[Na^+].10^3$	$[H^+].10^3$	$I.10^3$	$K_2.10^{-6}$
4.328	3.829	5.170	2.257	9.63	1.43
4.328	3.829	4.722	2.689	9.65	1.58
4.328	3.829	4.701	2.720	9.63	1.69
4.328	3.829	4.211	3.152	9.74	1.47
4.328	3.829	4.130	3.234	9.73	1.51
4.328	3.829	3.437	3.890	9.80	1.57

Mean $K_2 = 1.54 \times 10^6$.

To obtain values of K_1 and K_3, experiments were done using conditions similar to those in the constant ionic strength work where all three complexes were seen to exist in solution. The data are summarised in Table VIII.

TABLE VIII

Association constants at $I \to 0$ (where $T_a = 3.829 \times 10^{-3}$)

$T_m 10^3$	$[Na^+].10^3$	$[H^+].10^3$	$I.10^3$	$K_1.10^{-3}$	$K_2.10^{-6}$	$K_3.10^{-4}$
2.165	3.807	2.541	7.16	1.50	1.45	1.0
2.165	4.715	1.773	7.39	1.50	(1.05)	0.9
2.165	5.710	1.048	7.71	1.50	1.49	0.9
4.328	5.941	1.520	10.28	1.52	1.50	1.4
4.328	6.446	1.069	10.32	1.50	1.50	1.3
		Mean values		1.50	1.49	1.1

A summary of all the association and formation constants is given at the end of this discussion.

In polarographic measurements, if the reaction occurring at a mercury dropping electrode is the reduction of a complex ion to an amalgam i.e.

$$MX_p^{n+} + ne + Hg \rightleftharpoons M/Hg + pX$$

where M/Hg represents the amalgam, then the potential at the mercury electrode is given by

$$E_{d.e.} = E_a^o - \frac{RT}{nF} \ln \frac{C_a^o . f_a}{\{a_{Hg.}\} [Cu^{2+}]_s . f_m} \quad \text{----} (20)$$

where C_a^o and $[Cu^{2+}]_s$ represent concentrations of amalgam and metal ion at the drop surface, fa and fm are activity coefficients and $\{a_{Hg}\}$ is the activity of the mercury at the surface of the drop. Since C_a^o is small, $\{a_{Hg}\}$ will not vary much and may be regarded as constant, so that the equation reduces to

$$E_{d.e.} = E - \frac{RT}{nF} \ln \frac{C_a^o \cdot f_a}{[Cu^{2+}]_{s} . f_m} \text{ ---------------(21)}$$

if it is assumed that the electrode reaction is governed by diffusion and that the diffusion rate is dependent on the concentrations of metal ions in solution, and at the drop surface, then i, the current at any point on the wave is given by

$$i = k_s \left([Cu^{2+}] - [Cu^{2+}]_s \right).$$

The maximum (diffusion) current, i_d, flows when $[Cu^{2+}]_s = 0$ so that $\frac{[Cu^{2+}]_s}{[Cu^{2+}]} = \frac{(i_d - i)}{i_d}$

The current is also proportional to C_a^o, i.e., $i = k_m C_a^o$ where k_m depends on the diffusion of M atoms in the amalgam. Substitution for C_a^o and $[Cu^{2+}]_s$ gives

$$E_{d.e.} = E - \frac{RT}{nF} \ln \frac{(fa.k_s)}{(fm.km)} - \frac{RT}{nF} \ln \frac{i}{(i_d - i)} \text{ ----(22)}$$

and using the voltage $E_{\frac{1}{2}}$ at $i = i_d/2$ the expression becomes

$$E_{d.e.} = E_{\frac{1}{2}} - 2.303 \frac{RT}{nF} \log \frac{i}{(i_d - i)} \quad \text{------(23)}$$

Polarograms of solutions of copper perchlorate in 0.1M potassium nitrate showed a reversible two electron wave potential $E^s_{\frac{1}{2}} = 0.014$v relative to a saturated calomel electrode. In sodium perchlorate, (0.4M), $E^s_{\frac{1}{2}}$ was 0.017v.

If the dissociation of the complex ion is rapid, equation (20) may be described in terms of the association constant of the complex, $K = a^o_c \,/\, a^o_s \,.\, (a^o_x)^p$ where a^o_c and a^o_s are activities of the complex and metal ions respectively on the mercury surface and p is the number of ligands, X, bound to one metal ion in the complex. The equation for the half wave potential of the complex, $E^c_{\frac{1}{2}}$, may be derived in a manner similar to that for the simple metal ion described above and is

$$E^c_{\frac{1}{2}} = E - \frac{RT}{nF} \ln K. \frac{fa.ks}{fm.km.} - \frac{p\ RT}{nF} \ln[C_2O_4{}^{2-}].fx \quad \text{--(24)}$$

where $[C_2O_4{}^{2-}]$ is the concentration of ligand in the solution and f_x its activity coefficient. Subtraction of $E^s_{\frac{1}{2}}$ in (22) from $E^c_{\frac{1}{2}}$ in (24) gives at 25°C

$$\Delta E_{\frac{1}{2}} = \frac{0.0592}{n} \,.\, \log K_c - p.\frac{0.0592}{n} \log[C_2O_4{}^{2-}] \quad \text{[29] --(25)}$$

in which K_c is a formation constant.

Half wave potentials were obtained from the intercept of the plot of log $i/(i_d - i)$ against the applied voltage E

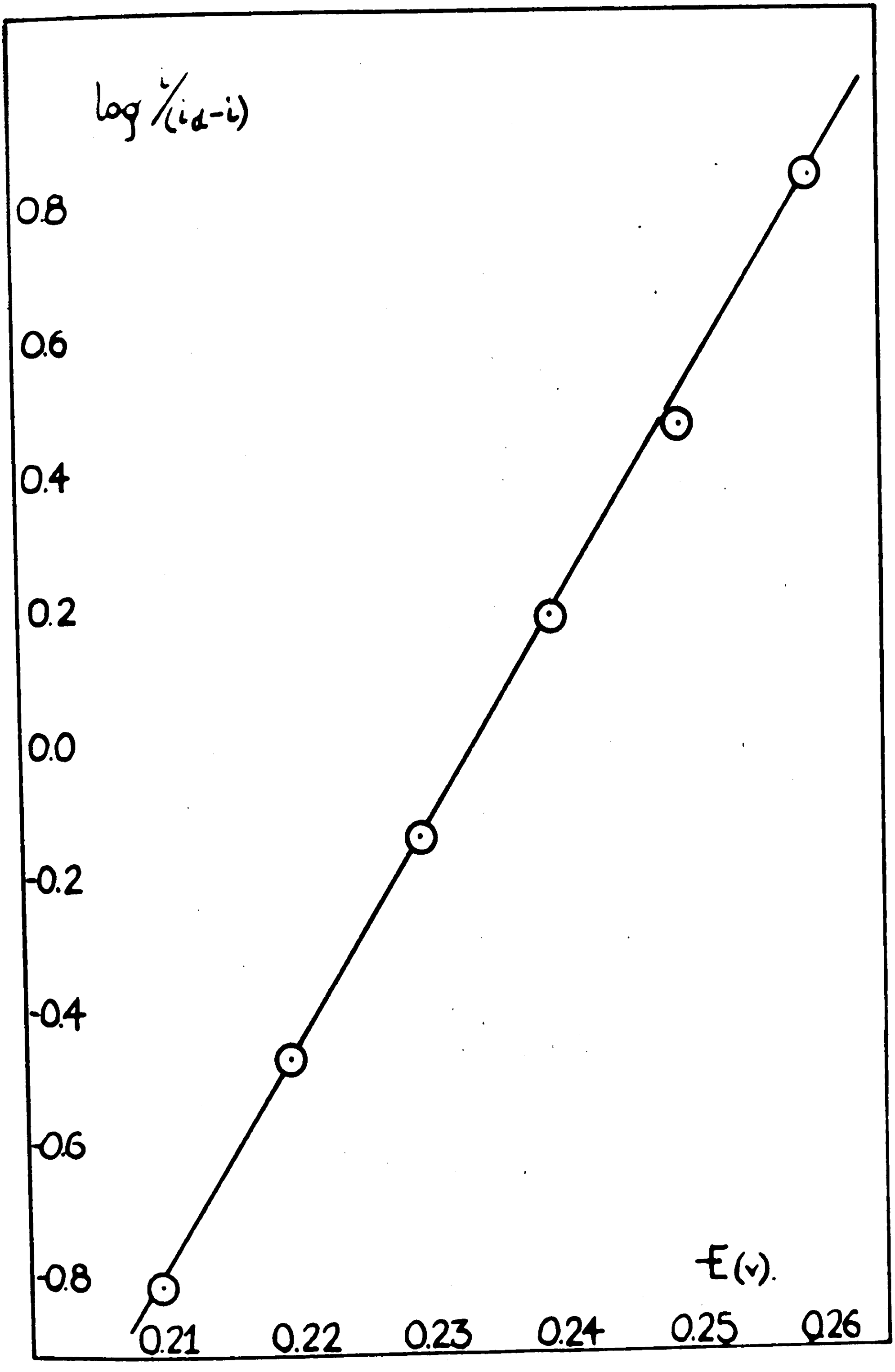


Fig. 6.

and if the reaction is essentially reversible, for a two electron reduction, a straight line should be obtained of slope 0.0296 at 25°C. Data for a reversibility check are given in Table IX

TABLE IX

Reversibility curve in a typical experiment. $i_d = 6.5\ \mu a$.

$-E(v)$	$i(\mu a)$	$\log i/(i_d - i)$
0.21	0.9	-0.795
0.22	1.7	-0.451
0.23	2.8	-0.122
0.24	4.0	$+0.204$
0.25	4.9	$+0.486$
0.26	5.7	$+0.854$

the plot of which is shown in Fig.6 in which the slope is 0.030 and the half wave potential -0.234v. Measurements were made in solutions containing a large excess of sodium oxalate and these are summarised in Table X. All the waves were reversible as is seen from the values of the slopes.

With the oxalate ion in large excess, the concentrations of free oxalate anion in the solution and on the mercury surface may be assumed equal. $\Delta E_{\frac{1}{2}}$ is plotted against $\log [C_2O_4^{2-}]$ in Fig.7, and it is seen

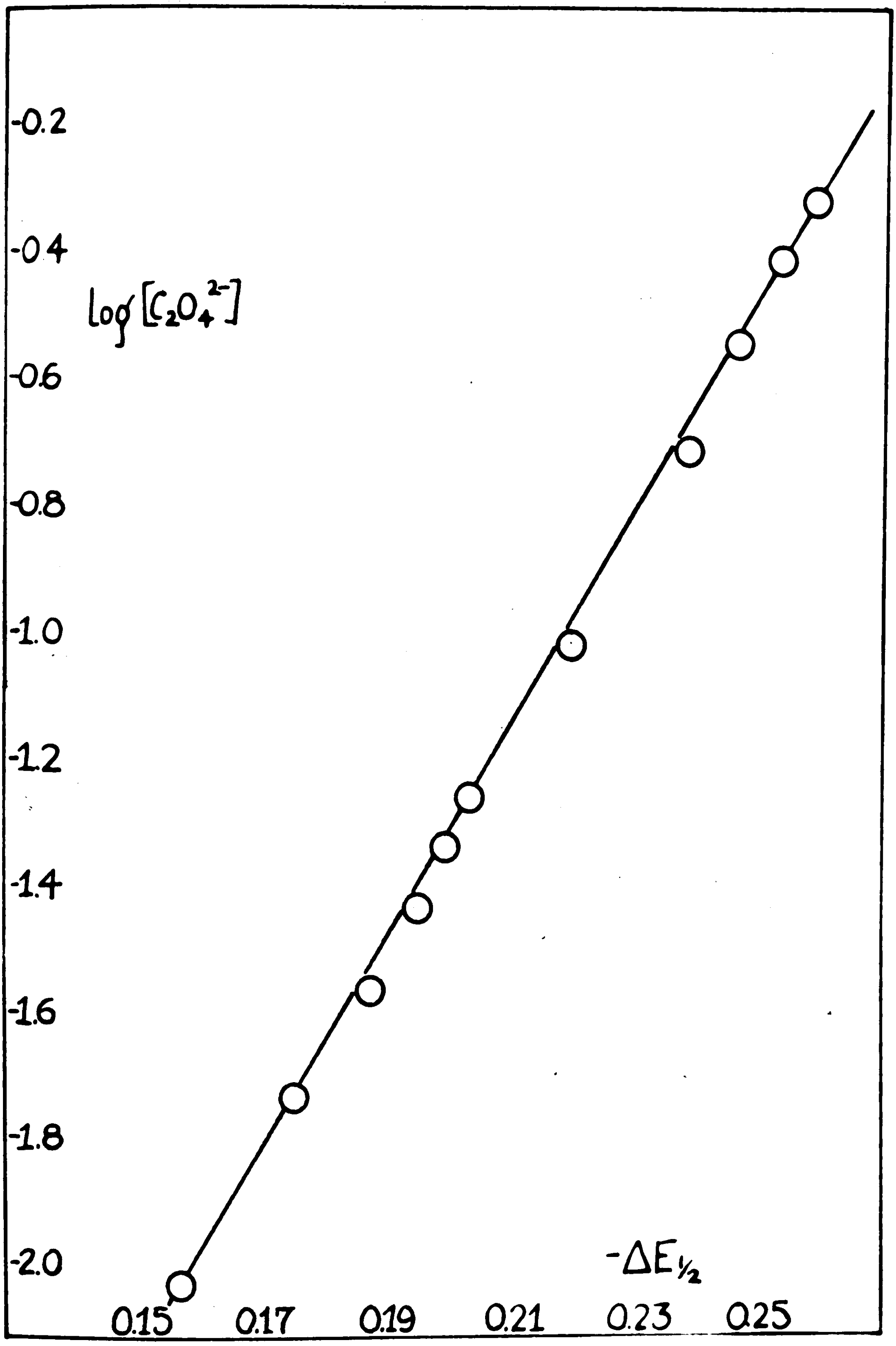

-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
$\log[C_2O_4^{2-}]$
$-\Delta E_{1/2}$
0.15
0.17
0.19
0.21
0.23
0.25

Fig. 7.

TABLE X

Experiments in copper oxalate solutions

$Tm.10^4$	$[C_2O_4^{2-}].10$	$-E^c_{\frac{1}{2}}$	Slope	$\Delta E_{\frac{1}{2}}$
		in 0.1M KNO_3		
4.95	5.00	0.245	0.030	0.259
4.95	4.00	0.240	0.029	0.254
4.95	3.00	0.233	0.030	0.247
4.95	2.00	0.225	0.029	0.239
4.95	1.00	0.206	0.029	0.220
		in 0.4M $NaClO_4$		
5.90	0.576	0.187	0.031	0.204
5.90	0.480	0.183	0.031	0.200
5.90	0.384	0.178	0.030	0.195
5.90	0.288	0.171	0.030	0.188
5.90	0.192	0.159	0.031	0.176
5.90	0.0961	0.141	0.030	0.158

that there is good linearity, despite the change in ionic strength from 0.3 to 0.6. The slope of the line is 0.060 corresponding to a p value of 2. The complex species predominating is thus $Cu(C_2O_4)_2^{2-}$. The intercept given is -0.278 and from equation (25) the stability constant

$$K_c = [Cu(C_2O_4)_2^{2-}] / [Cu^{2+}].[C_2O_4^{\ 2-}]^2 = 2.5 \times 10^9$$

The linear relationship implies an insensitivity of K to changes in ionic strength at these high values and this has often been observed in polarographic measurements. It is seen that in the range I = 0.3 to 0.6 M, f_2 values, calculated using mean activity coefficient data for divalent metal chlorides and hydrochloric acid,[5] change by only 15 to 20%. Also working on the corresponding malonate complex, Gelles and Nancollas (loc cit) obtained a value for K of 2.7×10^7 at I = 1 which is comparable with Riley's[30] potentiometric value of 3×10^7 at an ionic strength of about 0.3.

The constants derived in the present work are summarised below

$I \rightarrow 0$	K_1	K_2	K_3	$K_2.K_3$
	1.5×10^3	1.54×10^6	1.1×10^4	1.7×10^{10}
I = 0.1	K_1'	K_2'	K_3'	$K_2'.K_3'$
	3.1×10^2	7.0×10^4	2.3×10^4	1.6×10^9
I = 0.2 - 0.6				2.5×10^9

Assuming an f_2 value of 0.2 at I = 0.1 the K' values reduced to zero ionic strength, become

$K_1 = 1.6 \times 10^4$, $K_2 = 1.7 \times 10^6$, $K_3 = 2.3 \times 10^4$.

The agreement with measured values is good.

The log K_3 value of 4.3 may be compared with 3.6 obtained by Schafer and Abegg[31] at an ionic strength of 0.4M. The log $K_2' K_3'$ value of 9.2 is higher than those of Riley[23] (8.5) and Britton and Jarrett[22] (8.3) but their values were obtained at temperatures lower than that in the present work. Meites[24] obtained an overall K of 2.08×10^{10} for $Cu(C_2O_4)_2^{2-}$ from polarographic measurements but this value was based on only two solutions of ionic strength 0.09 and 0.95 respectively. This is rather a large range of I in which to expect constancy of K.

The log K_2 value of 6.19 for the formation of the CuC_2O_4 complex may be compared with 5.75 and 3.40 for the corresponding malonate and succinate complexes. This confirms the expected gradual decrease in stability as the ring size increases from five to seven members. The Irving-Williams order of transition metal oxalate stabilities using log K values[19] is

Mn	< Co	< Ni	< Cu
3.91	4.7	5.3	6.19

and the value for copper obtained in this work is seen to fit in with this.

Although much reference is made in the literature to the formation of 2 : 2 dicarboxylate complexes with metals, there has been some doubt as to the species existing in solution. Scholder and [illegible][illegible] measured the conductivities of the sparingly soluble oxalates of bivalent Mn, Fe, Co, Ni and Cd ions at 18°C and attributed their results to the existence of the doub [illegible]

[illegible]

PART II

SOME TRANSITION METAL OXALATES AND SUCCINATES

[illegible]

been made indicating the presence in cobalt succinate solutions of the 1 : 1 complex[35]. Cannon and [illegible] studied at an ionic strength of 0.1M the succinate [illegible]

INTRODUCTION

Although much reference is made in the literature to the formation of 2 : 2 dicarboxylate complexes with metals, there has been some doubt as to the species existing in solution. Scholder and Lindstrom[32] studied the conductivities of the sparingly soluble oxalates of bivalent Mn, Fe, Co, Ni and Cd ions at 18°C and attributed their results to the existence of the doubly charged anion $M(C_2O_4)_2^{2-}$. Money and Davies[6] recalculated their data on the basis of incomplete dissociation and showed that it was satisfactorily represented when the uncharged complex was assumed to be present. They also gave some dissociation constants for other oxalate and malonate complexes at 18°C and indicated that the complex described by Scholder could exist in solution. This was subsequently confirmed, using a solubility method, both by Money and Davies[33] and by Clayton and Vosburgh[34]. The corresponding metal succinates have been much less studied, although a spectrophotometric investigation has been made indicating the presence in cobalt succinate solutions of the 1 : 1 complex[35]. Cannan and Kibrick,[36] studied at an ionic strength of 0.1M the succinate complexes of Ba, Mg, and Zn and showed that two complexes $MHSucc^+$ and MSucc were present and gave stability constants for these ion pairs.

Irving and Williams[20, 41] found that the order of stability constants of transition metal cations with neutral ligands or the anions of weak acids followed the order Mn < Fe < Co < Ni < Cu > Zn. It is also well known that chelated complexes are more stable than non chelated (the chelate effect) and that in the chelates the stability decreases as the ring size increases. In the present study this effect has been investigated since the complexes formed have five and seven membered rings.

One of the reasons for the difficulties encountered in the interpretation of the oxalate data is the very low solubility of the neutral MC_2O_4 complex. In the presence of excess oxalate ion, the apparent solubility increases and auto-complex formation becomes significant. In the present work, solutions were prepared in a manner similar to the copper oxalate study in part I. The association between the transition metal ions manganese, cobalt and nickel and the oxalate (Ox) and succinate (Succ) anions was studied at temperatures from 0° to 45°C using the cell

$$H_2, Pt \;/\; MCl_2, NaOH, H_2A \;/\; AgCl, Ag,$$

where M is the metal and A is Ox or Succ. Thermodynamic data have been obtained. The first dissociation constant of oxalic acid has also been measured over the temperature range 0° to 45°C using the mixed acids cell

H_2, Pt / HCl, H_2Ox / AgCl, Ag.

[illegible]

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least 99.9% pure. Sodium hydroxide was prepared as indicated in Part I. Stock solutions of transition metal chlorides were made from "AnalaR" reagents with conductivity water. Gravimetric analysis of chlorid as silver chloride agreed to within 0.02%. The succ acid used was of "AnalaR" quality and concentrations were checked against sodium hydroxide using weight titrations. The conductivity water was prepared by mixed bed deionisation.[43]

<u>Constant boiling hydrochloric acid</u>

This was prepared by the method of Foulk and Hollingsworth,[44] and [illegible][45] using the modifications of Titus and [illegible][46] who used a starting material of spec gravity 1.14 rather than that of 1.06 used by other wo

The material of higher quality [illegible]

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APPARATUS

Preparation of Reagents.

"AnalaR" oxalic acid was recrystallised three times from conductivity water. The solid was filtered in a scintered glass crucible and allowed to stand for one week over anhydrous material. In this way it was converted to the dihydrate, and analysis and titration against standard sodium hydroxide showed that it was at least 99.9% pure. Sodium hydroxide was prepared as indicated in Part I. Stock solutions of transition metal chlorides were made from "AnalaR" reagents with conductivity water. Gravimetric analysis of chloride as silver chloride agreed to within 0.02%. The succinic acid used was of "AnalaR" quality and concentrations were checked against sodium hydroxide using weight titrations. The conductivity water was prepared by mixed bed deionisation.[58]

Constant boiling hydrochloric acid

This was prepared by the method of Foulk and Hollingworth,[44] and Shaw[45] using the modifications of Titus and Smith[46] who used a starting material of specific gravity 1.14 rather than that of 1.06 used by other workers. The material of higher specific gravity equilibrates more quickly. A.R. concentrated hydrochloric acid was diluted to specific gravity 1.14 with conductivity water in a pyrex "Quickfit" distilling flask (3 litres capacity) surmounted with a splash bulb and connected to a pyrex Liebig's condenser having a 75 cm. long water jacket and a 1 cm. inner bore. A few small pieces of platinum cleaned with concentrated nitric acid and washed thoroughly in conductivity water, were added to prevent bumping, and the body and neck of the flask together with the splash bulb were completely covered with asbestos fibre. Uniform heating was ensured using a heating mantle and the distillation was continuous at a steady rate of less than 5ml. per minute. The distillate was collected in a 2 litre pyrex stock flask previously cleaned with chromic acid, ethanolic potassium hydroxide, washed thoroughly with water and steamed for at least one hour. The receiver was cooled in an ice bath. The first 25% of the distillate was rejected and the next 1600ml. collected in the 2 litre flask. This was redistilled, discarding the first 25% and the next 800 ml. were collected as constant boiling hydrochloric acid. The barometric pressure was recorded at the beginning and at the end of each distillation. In other experiments, constant boiling acid was made from material containing equal volumes (ca.1250 ml.each) of concentrated A.R. hydrochloric acid and conductivity water. The resulting acid was found to contain much nearer the theoretical amount of chloride than that described above. Repeated determinations of the chloride as silver chloride over a period of ten months agreed to within 0.02%.

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 containing distilled water.

Potentiometer

A precision Vernier potentiometer (Type P.10, Croydon Precision Instrument Co., Croydon, Surrey) having a five dial decade system in the battery circuit was used to measure e.m.f.s. The overall range of the potentiometer was 1.9 volts to 1 microvolt in two ranges. A divider calibrated from 1.01800 volts to 1.01900 volts in 50 microvolt steps was used when standardising with the Weston Standard cell. The potentiometer had an accuracy of one part in 100,000 of the 1 volt setting. Potentiometer terminals were of copper and these were tipped with precious metal alloy ensuring a good contact and minimising any thermoelectric e.m.f.s generated by the action of the switches. A series sensitivity control was used in the standardisation and a galvanometer key was also included. The potentiometer coil was of well aged bare Manganin Telcuman of the same gauge throughout on the potential divider, thus reducing the temperature coefficient to a minimum.

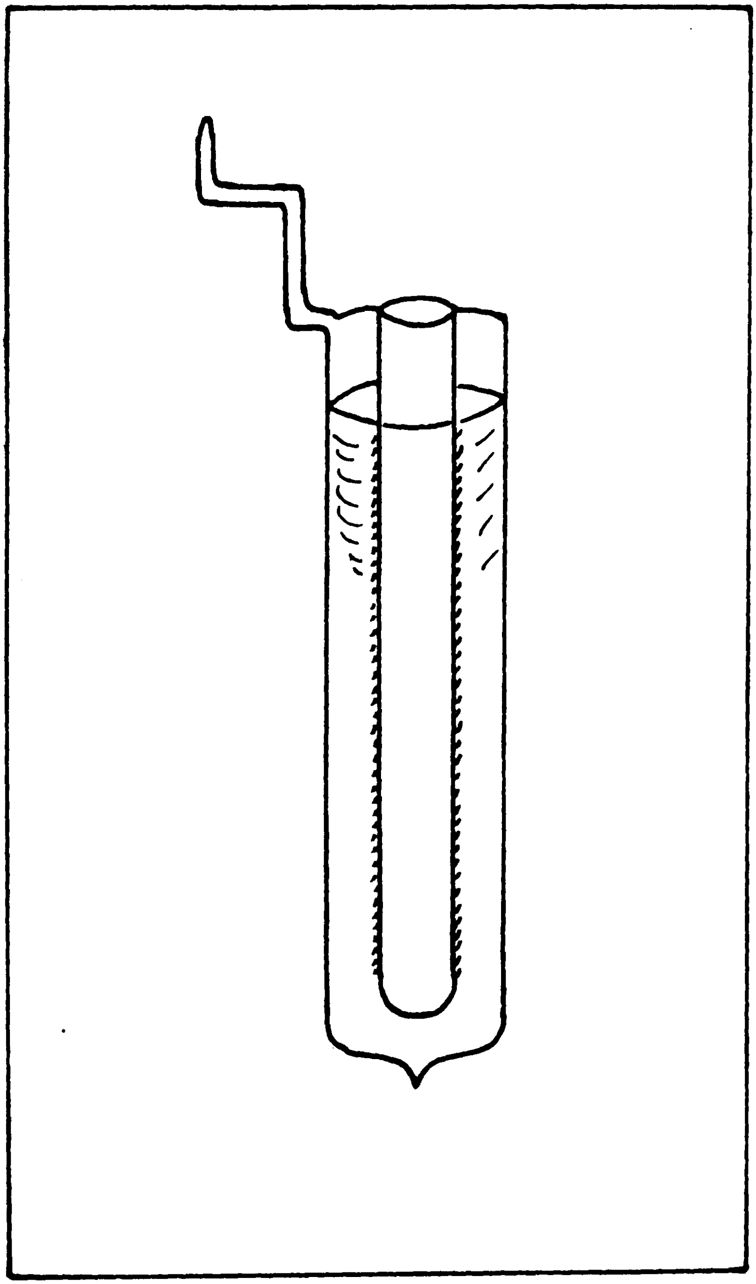
The potentiometer had four selector terminals for four testing positions. Since four cells each with four electrodes were being studied simultaneously and provision had to be made for a standard resistance, a multible switch box was incorporated in the circuit between the cell leads and the potentiometer terminals. The potentiometer rested on a large metal sheet which was earthed.

Two Weston Standard cells, (Cambridge Instrument Co.Ltd., London) mounted in metal cases were used to standardise the potentiometer. They were kept in a small oil thermostat maintained, even when not in use, at 25° ± 0.2°C by means of a Sunvic bimetallic relay operating a 25 watt bulb. The oil was efficiently stirred by an electrically driven stirrer. Comparisons were made regularly between the standard cells and at no time was their difference greater than 20 microvolts.

A sensitive, spot reflecting, moving coil galvanometer of 25 ohm resistance (Cambridge Instrument Co.Ltd., London) was mounted on a shelf away from vibrations and used in conjunction with a lamp and scale at a distance of one metre. The galvanometer was sensitive to changes of less than 5 microvolts in the potentiometer.

Thermostat

This was a large metal tank of about 20 gallons capacity, mounted on a "Dexion" stand and efficiently stirred. The bath contained water, sodium benzoate and the antifreeze, ethylene glycol. Heat transfer was reduced by insulating the tank with cork slabs of about 2" thickness. The temperature control was obtained by means of a mercury toluene regulator of large capacity which was fixed near to the heating unit. The control operated a selected combination of three bulbs of 250, 200 and 100 watts, coated with red paint, to reduce the effect on the light sensitive silversilver chloride electrodes. The relay operated by the regulator was part of an electronic make and break device designed so that no sparking occurred at the platinum-mercury interface in the mercury toluene regulator. The temperature control was ±0.005°C at 25°C. When working at temperatures below that of the room, a refrigeration unit, constructed by the Frigidaire Division of General Motors Ltd., London was incorporated. This unit was provided with two adjustable valves at the two ends of the cooling coil. The rate of cooling could be altered considerably by adjustment of the vapourisation valve on the liquid side of the coil and the constant pressure valve on the vapour side. Gauge readings corresponding to the various rates of cooling were



TRIPLE POINT CELL

Fig. 8.

recorded and used at different temperatures. The cooling coil was of tinned copper tubing about twenty feet long which was coiled around the stirrer near the bottom of the thermostat. Fine control at temperatures below room temperature was obtained by balancing the heating and cooling effects using the mercury toluene regulator. In changing from one temperature to another a booster heater was used which raised the tank temperature by 1°C per minute.

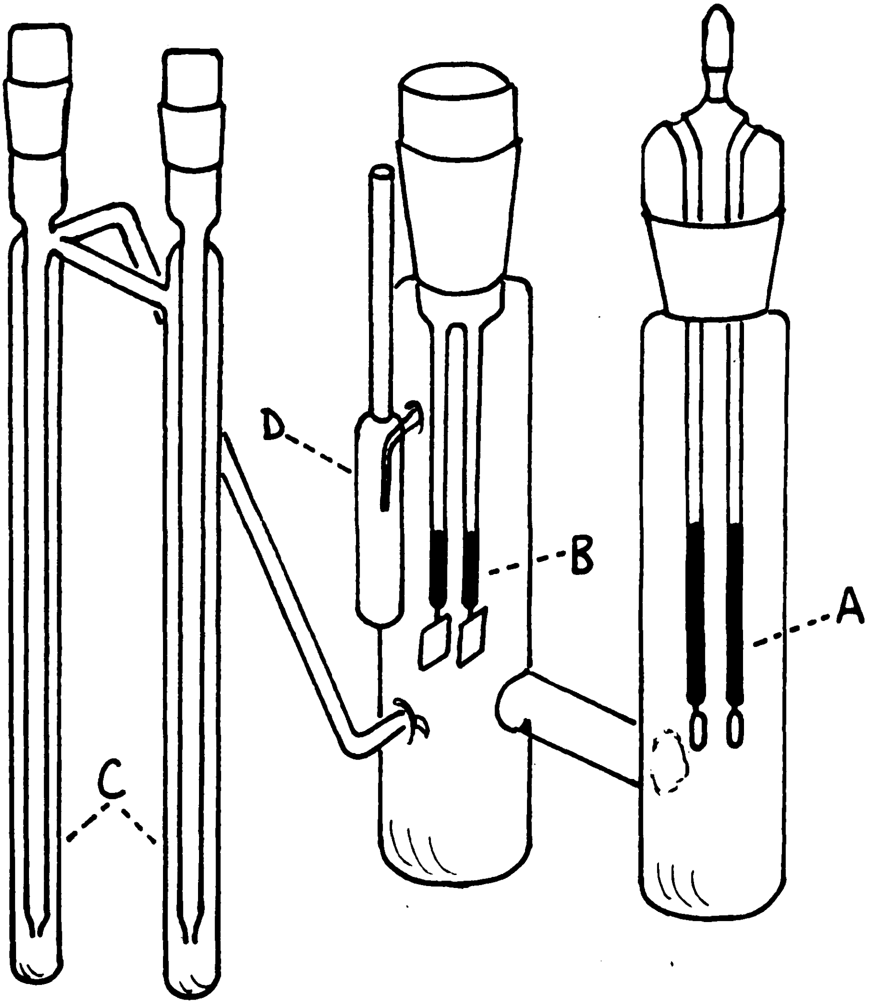
Temperature Measurement

Since very accurate e.m.f. measurements were to be made (to ± 0.01mv.) accurate temperature control of the order of ±0.005°C was necessary. The thermometers used were Beckman thermometers which had been calibrated against platinum resistance thermometers whose accuracy had been checked against one having an N.P.L. standardisation. The temperatures 15°, 25°, 35°, 45° were measured using these thermometers. The 25°C thermometer was checked against another Beckmann independently calibrated at 25°C. The 0°C thermometer was standardised using a triple point cell, (Fig.8) which consisted of two concentric pyrex tubes both of which were sealed and rounded off at the bottom so as to leave a well of about ten inches in depth in the inner tube. Between these tubes was triply distilled water. In use, the cell was immersed in a bath of finely divided ice in a Dewar flask for at least one hour. The ice used was made from distilled water. By rapid cooling from within, a sheath of ice about 1 cm. thick was produced inside the cell over the entire length of the thermometer well. This was achieved by filling the well with a solution of acetone which has been well cooled by the addition of "Drikold". When this was replaced by water, after a few moments, a thin layer of ice adjacent to the wall of the cell was melted. The sheath of ice was released from the glass and a very pure water - ice interface was obtained. The thermometer well was then filled with a solution of ice-cold distilled water and the cell was immersed in a Dewar flask of crushed distilled water ice for 20 hours to equilibrate.

E.m.f. Cell and Electrodes.

The cell employed was similar to that used by Noyes and Ellis.[48] Two hydrogen presaturators were made integral with the hydrogen electrode compartment as was done by Harned and Morrison[49] and modifications of Ashby, Crook and Datta[50] were also incorporated. The cell was fitted with standard (B.29) ground glass sockets the electrodes being supported in standard cones. In each cell there were two silver-silver chloride electrodes and two hydrogen electrodes so that four estimates of the

THE E.M.F. CELL



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

Fig. 9.

cell e.m.f. could be made. Leading from the hydrogen compartment was a guard tube and any liquid blown into this by the stream of hydrogen was immediately removed by suction. A diagram of the cell, presaturators, electrodes and fittings is shown in Fig. (9).

Silver - Silver Chloride Electrodes

These were of the thermal-electrolytic type described by Harned[51] and used by Harned and Morrison.[49] A platinum wire, 20mm. in diameter and 5cm. long wound in the form of a helix of about 0.3cm. diameter using a thin glass rod, was sealed into a pyrex glass tube, the other end of which was fixed to a standard B.29 ground glass cone. The helix was filled with a thick paste of spectroscopically pure silver oxide (Johnston - Matthey and Co., Hatton Garden, London.) in conductivity water. The electrodes were heated in a muffle furnace after drying in an oven at 100°C. The furnace temperature was gradually increased to about 400°C and maintained at that value until the decomposition of the metallic oxide was complete (this was seen when the brown oxide had changed to a dull metallic lustre). Another coating of the oxide paste was applied and the electrodes heated as before. This was continued until none of the platinum helix was visible through the silver surface. Two coatings usually sufficed. A little Araldite resin was then cast in the electrode tubes to ensure a complete platinum-pyrex seal. The electrodes were chloridised in the absence of light by electrolysis in a normal hydrochloric acid solution (prepared from constant boiling material) at a current density of 2 amps. per cm.^{2} for two to three hours, using a platinum helix as cathode. The electrodes were conditioned by warming in water at 50°C for two hours. They were preserved in the dark in hydrogen saturated water containing a little potassium chloride. Taniguchi and Janz[52] found that new electrodes showed a higher potential than those which had been allowed to age, due to a concentration polarisation. Depending on the porosity of the silver and the silver chloride, the electrodes took from a few hours to one week to come to constant potential. They used electrodes which were greater than 30 mg. in weight. Bates[53] suggested that for good results electrodes should be 150 to 200 mg. In the present work, all the electrodes were about 400 mg. in weight and were allowed to age between three and four weeks.

Hydrogen Electrodes.

Pieces of platinum foil about 1cm. wide and 2.5cm. long were welded to platinum wires 0.05cm. in diameter which were sealed into pyrex glass tubes attached to B.29 standard glass sockets. The electrodes were cleaned in nitric acid, chromic acid and washed thoroughly. Some Araldite resin was cast at the bottom of the pyrex tubes by heating to 100 - 120°C, ensuring perfect platinum-pyrex seals. The electrodes were platinised in a solution containing 2.5% chloroplatinic acid in normal hydrochloric acid for about 5 minutes at a current density of 0.2 amps per $cm.^2$, the current being reversed every 15 seconds. The platinum black coating was not sufficient to obscure the metallic appearance of the platinum. This surface coating was removed in aqua regia every fourth run and the electrodes replatinised. They were stored in distilled water saturated with hydrogen.

Calibration of Silver-Silver Chloride Electrodes

Harned and Ehlers[54] determined the standard potential (E^o) of the silver - silver chloride electrode over a temperature range 0° to 60°C at 5° intervals. They employed the relationship

$$E + 2k \log m = E^o - 2k \log \gamma_\pm$$

and extrapolated their e.m.f. data to infinite dilution. Substituting the equation $\log \gamma_\pm = -\mathcal{S}\sqrt{I} + B'm$ the relationship $E + 2k \log m - 2k\mathcal{S}\sqrt{I} = E^o - 2kB'm$ is given, where E is the observed potential, I the ionic strength, m the molality and $k = 2.303\ ^{RT}/F$. Many workers have subsequently used the values quoted by

Harned and Ehlers for their own electrodes at the appropriate temperatures.

Recently, however, Bates, Guggenheim, Harned, Ives, Janz, Monk, Robinson, Stokes and Wynne-Jones[55] have indicated that the most extensive and careful measurements of e.m.f.s. confirm the difficulty of establishing the E^o value of the electrode better than 0.2mv. and that the uncertainty is probably due to small differences in the solid phases. However, the activity coefficient of 0.01m hydrochloric acid is uncertain to only about 0.0005, corresponding to an uncertainty of ±0.03 mv. They recommend that each worker standardise his own electrodes at 0.01m in experiments of the highest precision. They also suggest that the value of the mean activity coefficient of hydrochloric acid ($\gamma_\pm$) at 0.01 molality be conventionally standardised as 0.904 at 25°C and 0.908 at 0°C and that these values be used until there is convincing evidence that either value is wrong by as much as 0.001.

In the present work, the electrodes were standardised at all the temperatures using 0.01m hydrochloric acid and the recommended $\gamma_\pm$ values at 0° and 25°C. At other temperatures, the activity coefficients were those of Harned and Owen.[56] The E^o values at 0° and 25°C were checked frequently. The mean standard potentials are shown in Table XI which includes the data of Harned and Ehlers.[54] As is seen from the table, values below 20°C deviate from Harned's by as much as 0.3mv. Agreement above 20°C is very good.

TABLE XI

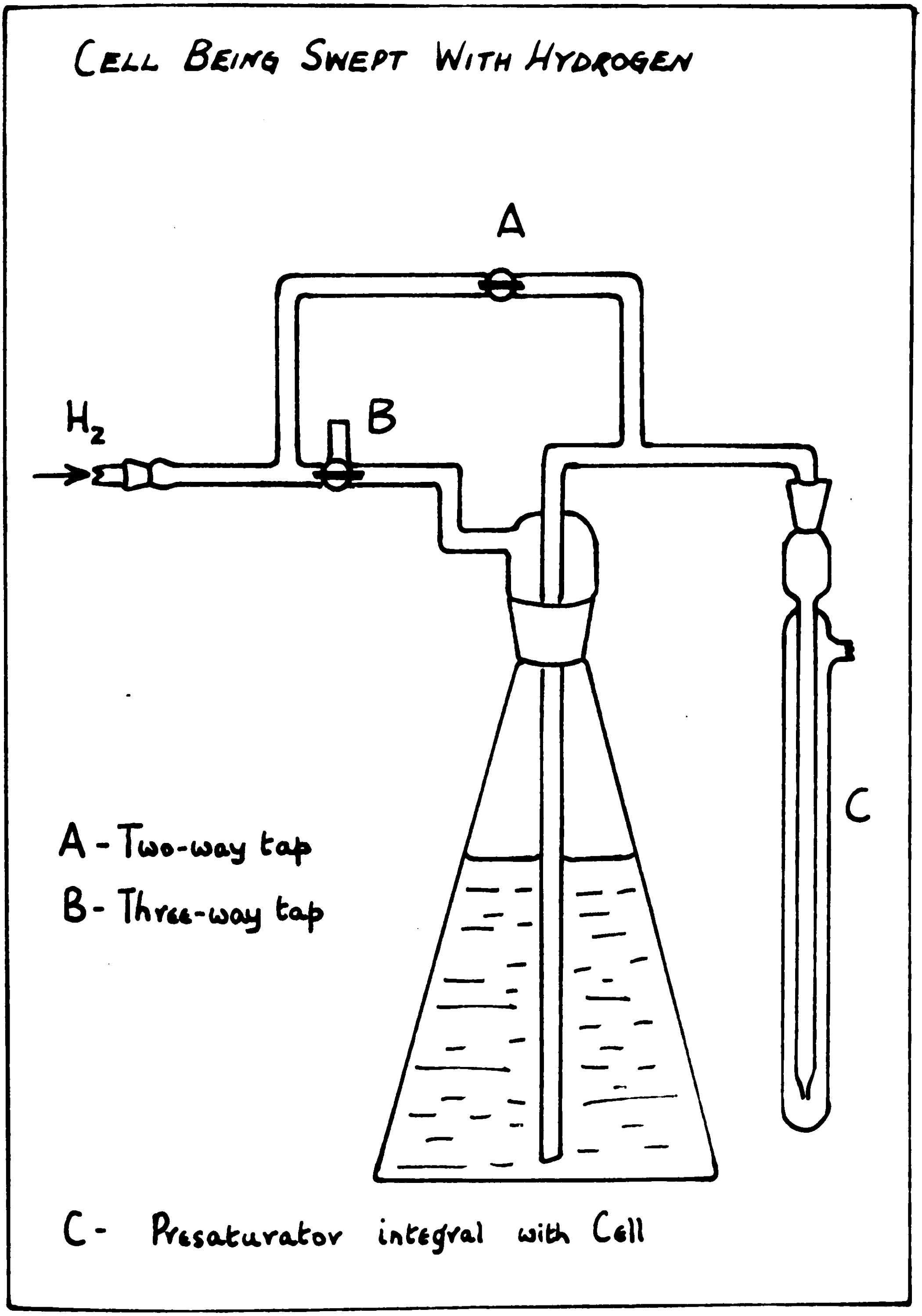
Standard potential of silver-silver chloride electrodes

Temp. °C	$\gamma_{\pm}$0.01mHCl	$E^{o}_{\text{present work}}$	$E^{o}_{\text{Harned \& Ehlers}}$
0	0.9080	0.23665	0.23634
5	0.9056	0.23414	0.23392
15	0.9055	0.22831	0.22847
20	0.9052	0.22560	0.22551
25	0.9040	0.22239	0.22239
35	0.9025	0.21569	0.21563
45	0.9008	0.20838	0.20821

Purlee and Grunwald[57] used electrodes in which the silver was present as a mirror deposit before chloridising. They found, however, that different thermal-electrolytic electrodes and mirror electrodes varied by as much as 0.2 mv. The electrodes used in the present work showed internal consistency using different pairs of electrodes to within 30 microvolts.

Electromotive force measurements.

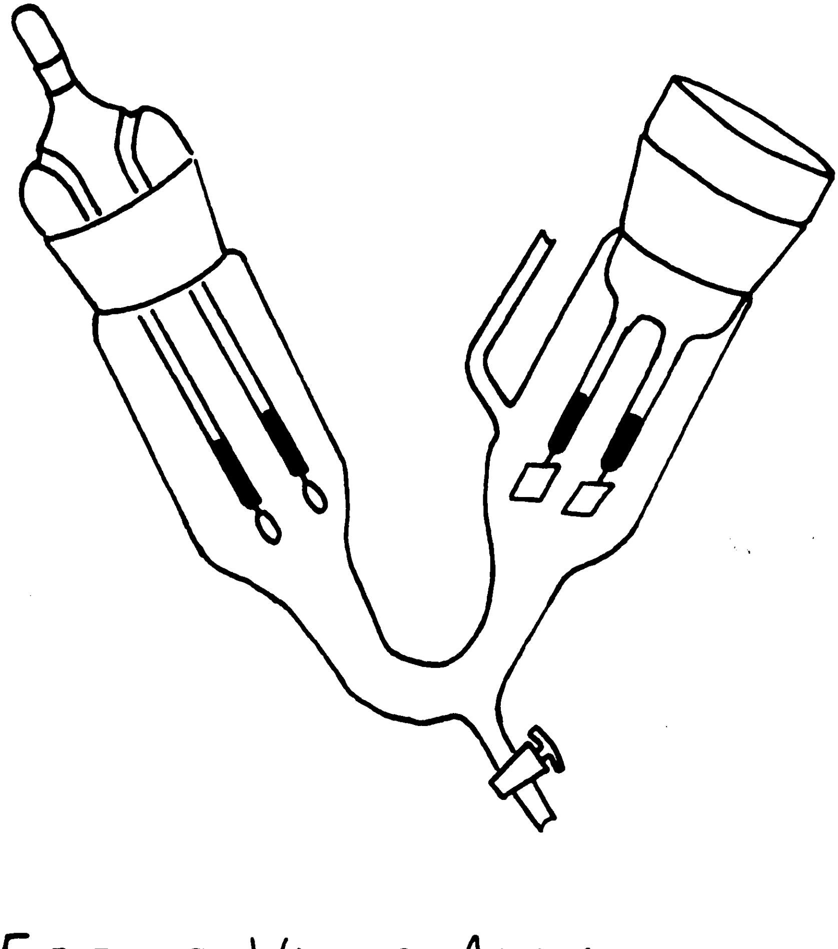
Stock solutions of oxalic acid and the metal chlorides were prepared in stoppered pyrex flasks. Solutions containing oxalic acid, sodium hydroxide and metal chloride



CELL BEING SWEPT WITH HYDROGEN

A - Two-way tap
B - Three-way tap
C - Presaturator integral with Cell

Fig. 10.



ELECTRODE - WASHING APPARATUS

Fig. 11.

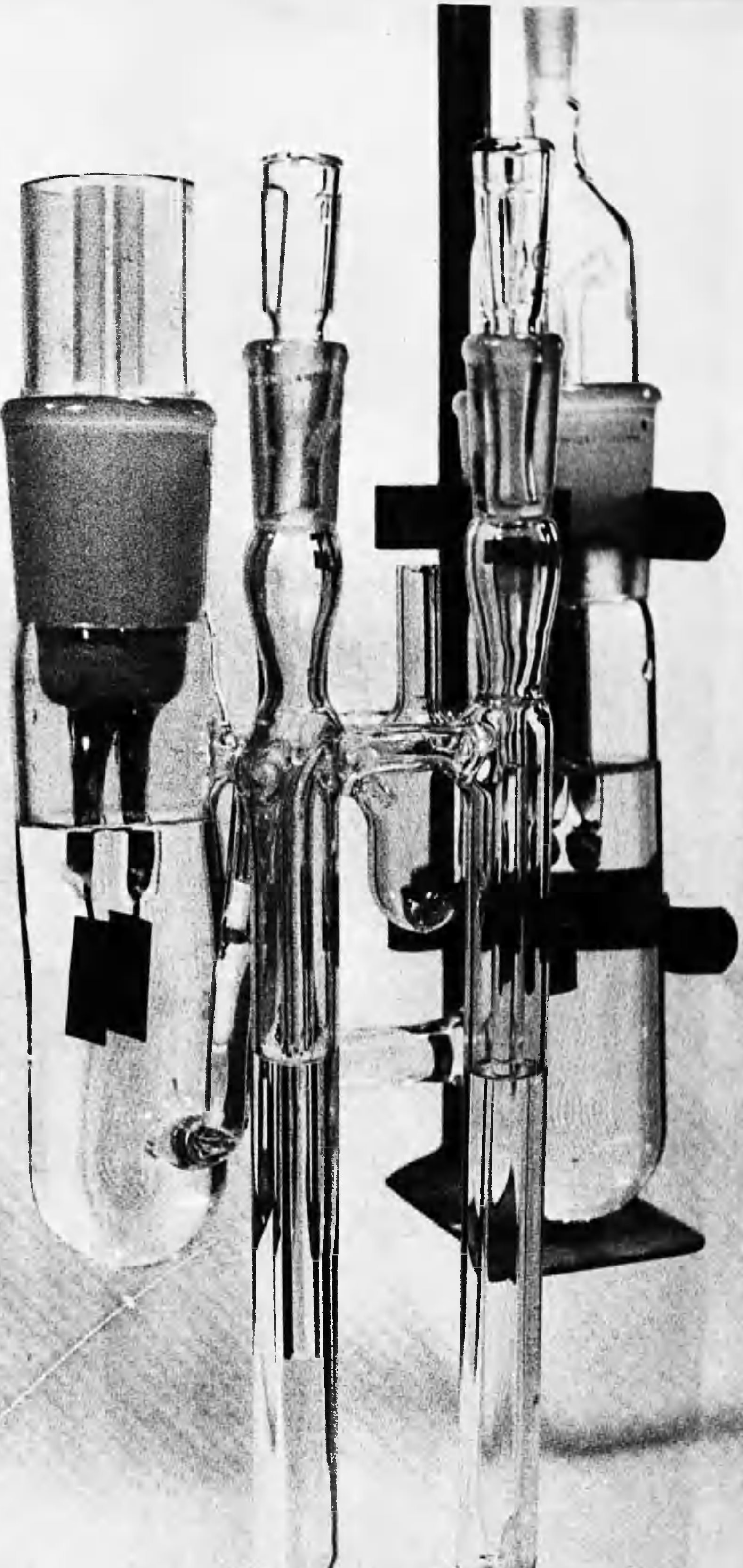
were prepared in a manner similar to that used in the copper oxalate experiments, vacuum corrections being applied to all weights.

Each flask was fitted with a "Quickfit" head shown in Fig.10. Hydrogen was bubbled through the solution at a fairly slow rate. The electrodes were washed three times with solution in the V-shaped vessel in Fig.11.

Each cell was cleaned with chromic acid, washed thoroughly and left to dry overnight in an oven at 110°C. It was then connected to the bubbling head through a standard B.10 joint (Fig.10) and swept out with hydrogen. After five minutes, the electrodes, rinsed with the solution being studied, were placed in position in the cell and hydrogen was again blown through for a few minutes. The taps were now adjusted so that the solution was transferred from the stock flask to the cell by hydrogen pressure, without contact with the atmosphere. The filled cell was placed in a thermostat at the required temperature and hydrogen passed into the hydrogen electrode compartment at a constant rate of 2 - 3 bubbles per second. This hydrogen was passed through a series of distilled water bubblers and then through a short length of capillary tubing (to ensure uniform rate of bubbling) to a small monitoring bubbler before passing

PLATE I

THE E.M.F. CELL



into the cell via the presaturators integral with the hydrogen electrode compartment immersed in the thermostat. (Fig.9).

In each run, four such cells were studied simultaneously. The cells were allowed to equilibrate for 4 to 6 hours (at temperatures about 0°C the longer time was required) after which the e.m.f.s. were measured using the duplicate sets of electrodes to obtain four readings. It was considered that equilibrium was reached when e.m.f. readings remained constant for half an hour and different combinations of electrodes agreed to within 30 microvolts. Barometric pressure and room temperature were recorded. The temperature of the thermostat was then raised to the next required value and the cells again allowed to equilibrate. This usually required only half an hour. It was found convenient to commence at the lowest temperature, gradually increasing in steps of 10°C.

In the experiments on succinates where there was no danger of precipitation, measurements were made with one filling from 0° to 25°C and then another filling of the same solution from 25° to 45°C. The values at 25°C never differed by more than 30 microvolts. In the oxalate experiments where precipitation, if any, occurred after about 24 hours, solutions were studied over the complete temperature range with one filling. After the cells had equilibrated, any serious drift in e.m.f. at a given temperature was regarded as due to oxalate precipitating and the run was stopped. The electrodes were removed and allowed to stand overnight in normal hydrochloric acid and thoroughly washed. A check was made on their E^o values at 25°C before they were again used. All observed e.m.f.s. were corrected for pressure using the barometric readings in making allowances for temperature and latitude. In making the pressure correction, the effect of bubbler depth observed by Hills and Ives[59] was ignored since this would amount to only 5 microvolts at 25°C.

Potentiometric Measurements at High Ionic Strength

The first and second dissociation constants of succinic acid are very close together, rendering the concentration of $HSucc^-$ high, and it might be expected therefore that complexes such as $MHSucc^+$ would be formed as well as the uncharged species. Solutions of manganese succinate were studied at an ionic strength of 0.2M to identify the ion-pairs present in solution. Measurements, using the reproducible liquid junction system of Dunsmore and Speakman, were made on solutions containing succinic acid, sodium hydroxide and manganese chloride with sufficient sodium perchlorate to raise the ionic strength to 0.2M. Commercial screened glass electrodes (E.I.L. Type G.G.33) and those made from Corning 015 glass were used. The experimental procedure has been fully described in part I.

[illegible]

[illegible] 61, 62 have reported values at 25°C but the only measurements at various temperatures were those of [illegible] and Nicholson over the relatively small range of 25° to 35°C. Since measurements of the [illegible] oxalate association were to be made over a [illegible] it was necessary to obtain the [illegible] values. The first dissociation constant is rather large, and a mixed acids cell was used, to limit the amount of HOx^- present in the soln.

$$H_2, Pt / H_2Ox (m_1), HCl (m_2) AgCl / Ag$$

If m_1 and m_2 are the molalities of oxalic acid and hydrochloric acid, E' the corrected e.m.f. of the cell and E^0 the standard potential of the silver-silver chloride electrode, then

METAL OXALATES

RESULTS

Although the second dissociation constant of oxalic acid, $k_2 = a_{H^+} . a_{C_2O_4{}^{2-}} / a_{HC_2O_4{}^-}$, has been studied over a wide temperature range,[60,61,62] the corresponding first dissociation constant, $k_1 = a_{H^+} . a_{HC_2O_4{}^-} / a_{H_2C_2O_4}$ has not been studied extensively. Darken[63], Gene and Ingold[64] and Parton[43, 62] have reported values at 25°C but the only measurements at various temperatures were those of Parton and Nicholson over the relatively small range of 25° to 35°C. Since measurements on the metal oxalate association were to be made over a 45°C temperature range, it was necessary to obtain the corresponding k_1 values. The first dissociation constant is rather large, and a mixed acids cell was used, to limit the amount of HOx^- present in the solutions:

$$H_2 , Pt / H_2Ox (m_1) , HCl (m_4) AgCl / Ag$$

If m_1 and m_4 are the molalities of oxalic acid and hydrochloric acid, E' the corrected e.m.f. of the cell and E^o the standard potential of the silver-silver chloride electrode, then

$$E' = E^o - k \log a_{H^+} . a_{Cl^-}$$

or

$$-\log[H^+] = (E' - E^o)/k + \log m_4 + \log \gamma_{H^+} . \gamma_{Cl^-} \text{ ---(26)}$$

where $k = 2.303RT/F$ and γ is the activity coefficient of the ion on the molality scale.

Activity coefficients were obtained from the Davies equation[4]

$$-\log \gamma_z = A.z^2 \left(I^{\frac{1}{2}} / (1 + I^{\frac{1}{2}}) - 0.2I. \right) \text{ ---------------(2)}$$

which has been found to be satisfactory for similar dicarboxylate systems at 25°C.[37] At the other temperatures the use of the same equation with the correct Debye-Hückel A values has been justified by Nair and Nancollas in their studies on the bisulphate ion, by the absence of any drift in the dissociation constants. Further evidence in support of the equation has been obtained by Brannan and Nancollas[63] in studies on the association between nickel and malonate and substituted malonate ions, at low concentrations and at a series of constant ionic strengths. The values of A and k ($=2.303\ RT/F$) used in all the calculations are given in Table XII.

In the mixed acids cell for k_1 of oxalic acid, expressions for the total oxalate

TABLE XII

Values of constants used in calculations

Temp °C	A	k.
0	0.4883	0.054197
5	0.4921	0.055189
15	0.5000	0.057173
25	0.5085	0.059158
35	0.5175	0.061141
45	0.5270	0.063126

$$m_1 = [H_2Ox] + [HOx^-] + [Ox^{2-}] \text{------------}(27)$$

electroneutrality, $[H^+] = [HOx^-] + 2[Ox^{2-}]$ --(28)

and ionic strength, $I = [H^+] + [Ox^{2-}]$ ------(29)

were used to provide a graphical solution, similar to that of Speakman[65], in which the equation of the line was

$$Y = Xk_1 + k_1k_2$$

where $X = \dfrac{[H^+]\cdot\gamma_2\{m_1 - [H^+] - m_4\}}{\{2m_1 - [H^+] + m_4\}}$

and $Y = \dfrac{\{[H^+] - m_4\}\cdot[H^+]^2\cdot\gamma_1^2\cdot\gamma_2}{\{2m_1 - [H^+] + m_4\}}$

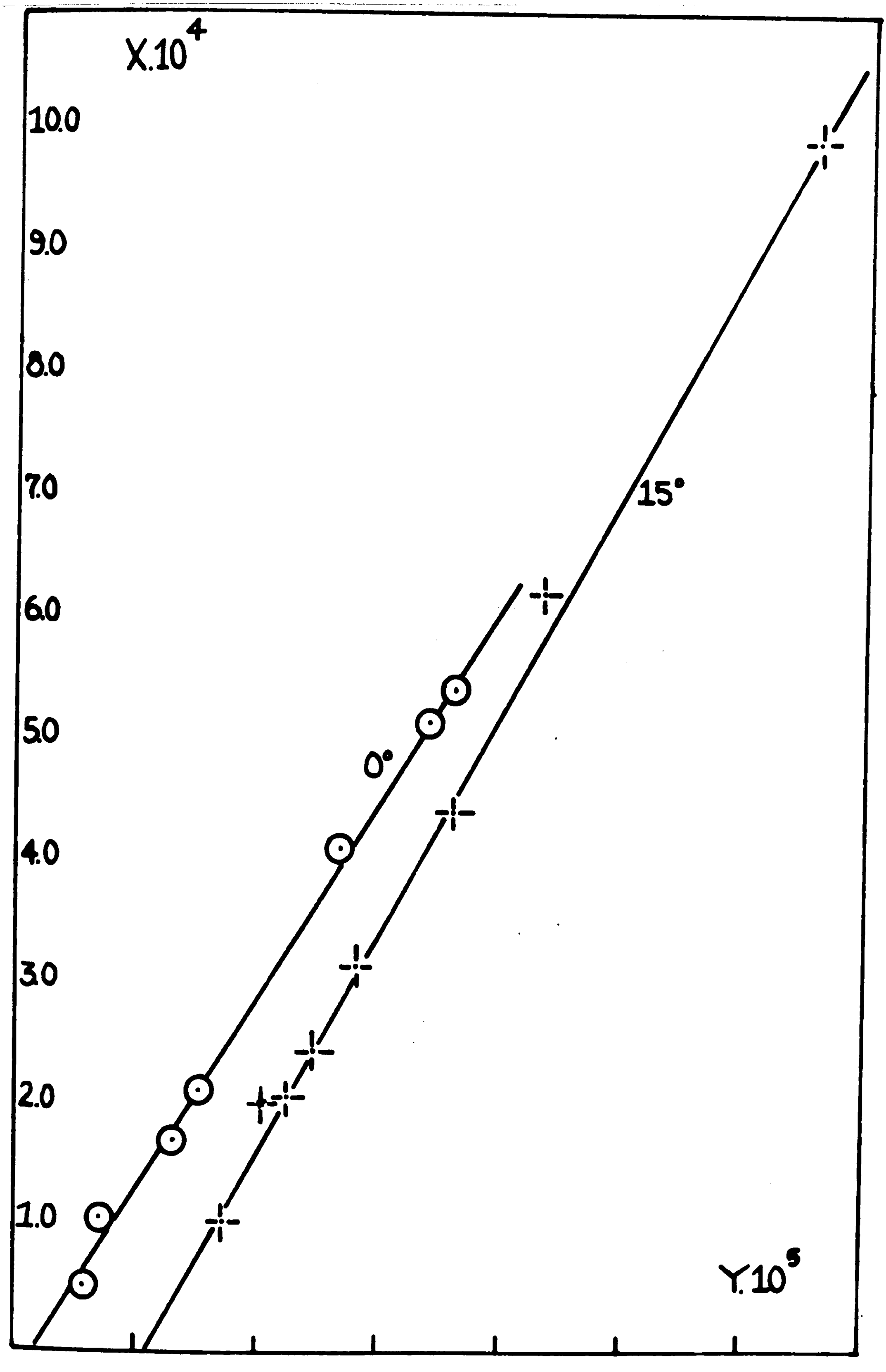


Fig. 12.

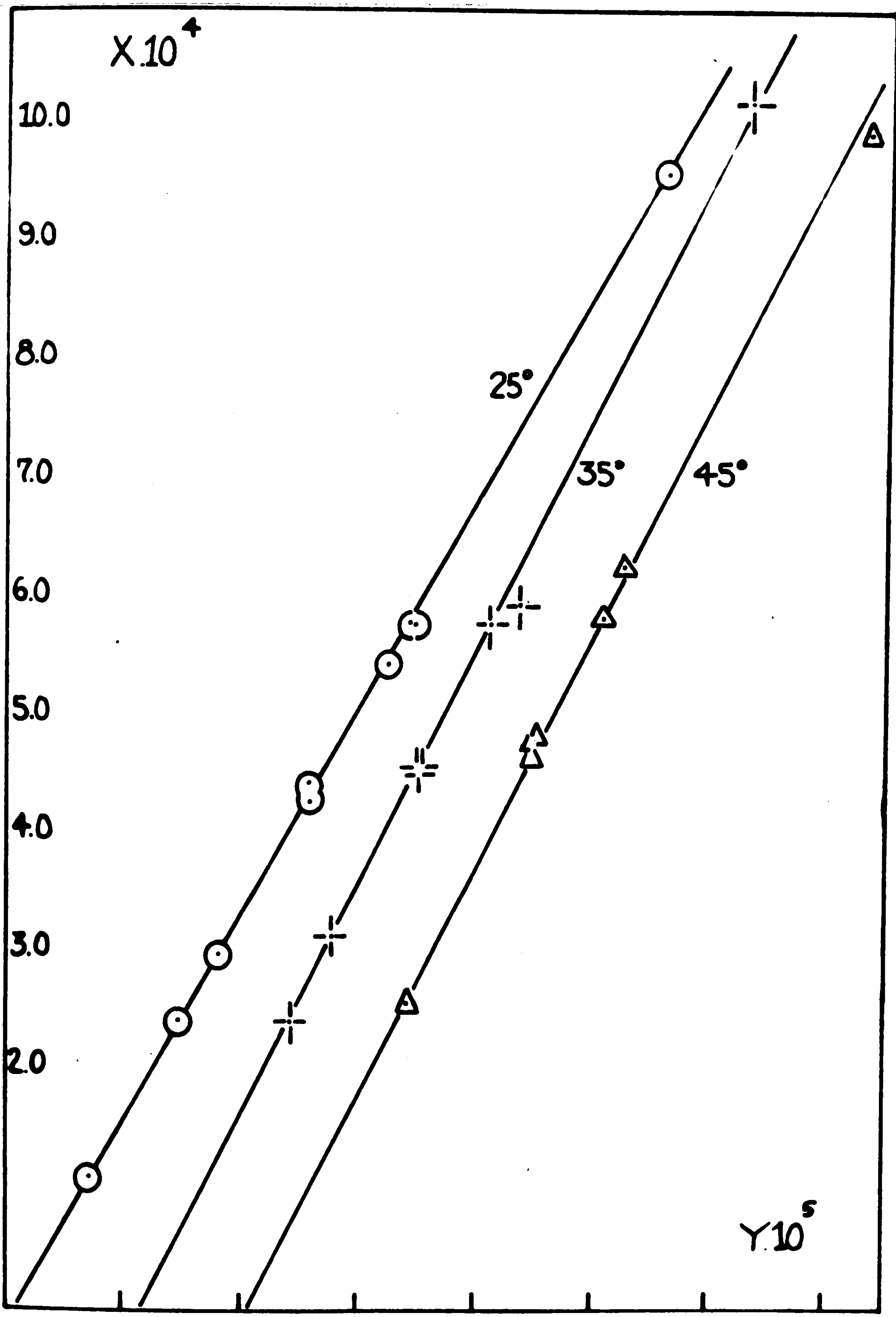


Fig. 13.

An initial approximate I was used to obtain γ values which were in turn used to calculate $[H^+]$ from (26) and consequently the ionic concentrations of the various species from equations (27), (28) and (29). A more accurate value of I was now used to give a new γ value and the cycle repeated until I values differed by less than 0.1%. In a later part of the work calculations were made using a high speed DEUCE electronic computer. A T.I.P. programme was used in which the maximum column length was 30. The results are given in Table XIII and plots of X against Y are shown in Figs. 12 and 13 where for the sake of clarity, the Y ordinates have been displaced. Good linearity is seen at all temperatures. The k_1 values obtained are:-

Temp °C	0	15	25	35	45
$10^2.k_1$	5.70	5.60	5.60	5.18	5.07

The k_1 value at 25°C compares favourably with the conductimetric value of Darken,[88] 5.36×10^{-2}. Parton, Gibbons and Nicholson[43, 62] give values of 5.0×10^{-2} and 4.57×10^{-2}. Gane and Ingold,[64] using a potentiometric titration method and extrapolating to zero ionic strength obtained a k_1 of 5.90×10^{-2}.

The k_2 values used in the calculations were those of Pinching and Bates,[60] given by Robinson and Stokes,[5]

TABLE XIII(a)

Molal concentrations in oxalic acid experiments

Expt.	$10^3.m_4$	$10^3.m_1$	Expt.	$10^3.m_4$	$10^3.m_1$
1	2.39928	2.96409	7	4.97808	4.26498
2	2.40275	3.80068	8	4.27148	5.09005
3	4.00319	3.66685	9	3.89500	3.84672
4	4.13774	3.54144	10	1.32578	1.66255
5	5.57969	7.66096	11	1.56010	1.94423
6	4.25818	4.70956	12	2.55370	2.31017

TABLE XIII(b)

Results on oxalic acid

Expt.	$(E' - E^o)$	$10^3.[H^+]$	$10^3.I$	$10^5.[Ox^{2-}]$	$10^5.Y$	$10^4.X$
		Temp. = 0^oC.				
1	0.26935	5.1867	5.213	4.419	1.53	2.16
3	0.24969	7.3508	7.391	3.972	2.68	4.17
6	0.24507	8.5095	8.554	4.474	3.41	5.20
7	0.24062	8.8184	8.858	3.925	3.61	5.47
10	0.29580	2.9485	2.990	4.142	0.59	0.55
11	0.28868	3.4195	3.461	4.187	0.73	1.12
12	0.26984	4.7437	4.781	3.741	1.32	1.76

TABLE XIII(b) contd.

Expt.	$(E' - E^0)$	$10^3[H^+]$	$10^3.I$	$10^5[Ox^{2-}]$	$10^5.Y$	$10^4.X$
		Temp. = 15°C.				
1	0.28437	5.1554	5.197	4.134	1.46	2.49
2	0.28124	5.8961	5.943	4.686	1.82	3.19
4	0.26271	7.3421	7.378	3.585	2.61	4.46
5	0.24396	12.1111	12.160	4.877	5.58	9.96
7	0.25415	8.7410	8.778	3.651	3.38	6.26
11	0.31202	3.4214	3.461	3.942	0.74	1.08
12	0.30459	4.7155	4.750	3.493	1.26	2.12
		Temp. = 25°C.				
1	0.29430	5.1574	5.196	3.842	1.45	2.46
2	0.29102	5.9097	5.963	4.362	1.82	3.05
3	0.27297	7.3331	7.368	3.466	2.59	4.31
4	0.27192	7.3375	7.371	3.329	2.57	4.49
5	0.25245	12.1490	12.195	4.553	5.61	9.61
6	0.26780	8.4721	8.511	3.899	3.25	5.48
7	0.26295	8.7793	8.813	3.416	3.43	5.81
8	0.26681	8.8099	8.851	4.068	3.46	5.81
11	0.31524	3.4178	3.454	3.658	0.73	1.13

TABLE XIII(b)contd.

Expt.	$(E' - E^0)$	$10^3[H^+]$	$10^3.I$	$10^5[Ox^{2-}]$	$10^5.Y$	$10^4.X$
		Temp. = 35°C.				
1	0.30424	5.1564	5.191	3.419	1.44	2.45
2	0.30092	5.8926	5.931	3.874	1.78	3.19
3	0.28212	7.3018	7.333	3.067	2.50	4.62
4	0.28115	7.3285	7.358	2.958	2.52	4.56
5	0.26121	12.0530	12.093	4.022	5.33	10.21
6	0.27699	8.4294	8.464	3.451	3.13	5.83
8	0.27591	8.7866	8.823	3.612	3.37	5.97
9	0.28266	7.3596	7.392	3.201	2.54	4.61
		Temp. = 45°C.				
1	0.31427	5.1403	5.171	3.079	1.41	2.61
3	0.29140	7.2922	7.320	2.767	2.46	4.70
4	0.29047	7.3011	7.328	2.659	2.45	4.84
5	0.26976	12.0780	12.114	3.647	5.31	9.95
6	0.28611	8.4215	8.453	3.116	3.08	5.86
8	0.28509	8.7430	8.776	3.247	3.25	6.30
9	0.29202	7.3326	7.361	2.879	2.47	4.86

and are:-

Temp °C	0	15	25	35	45
$10^5.k_2$	6.299	5.877	5.420	4.874	4.287

In measurements using the cell

$$H_2, Pt \ / \ H_2Ox(m_1) \ , \ NaOH(m_2), \ MCl_2(m_3) \ / \ AgCl \ / \ Ag$$

if m_1, m_2 and m_3 are the molal concentrations of oxalic acid, sodium hydroxide and metal chloride respectively, the corrected e.m.f. of the cell, E', and the standard potential of the silver-silver chloride electrode, E^o, are combined in the relationship

$$E' = E^o - 2.303 \ ^{RT}/_F \log a_{H^+}.a_{Cl^-}$$

and the concentration of hydrogen ions is given by rearrangement of this equation (where $k = 2.303 \ ^{RT}/_F$)

$$\text{i.e.} \quad - \log \left[H^+\right] = {}^{(E' - E^o)}/_k + 2\log m_3 + \log \gamma_{H^+}\gamma_{Cl^-} \quad -(30)$$

The ionic concentrations of the species were obtained from the equations

$$m_1 = \left[H_2Ox\right] + \left[HOx^-\right] + \left[Ox^{2-}\right] + \left[MOx\right] \text{------------------}(31)$$

$$m_3 = \left[M^{2+}\right] + \left[MOx\right] \text{------------------------------}(32)$$

electroneutrality,

$$[H^+] + 2[M^{2+}] + m_2 = [HOx^-] + 2[Ox^{2-}] + 2m_3 \text{ ---(33)}$$

the dissociation constants k_1 and k_2 of oxalic acid and the ionic strength,

$$I = \tfrac{1}{2}\Big[[H^+] + 6m_3 + m_2 - 4m_1 + [HOx^-]\Big\{5 + \frac{8k_2}{[H^+].\gamma_2} + \frac{4[H^+].\gamma_1^2}{k_1}\Big\}\Big] \text{ --------(34)}$$

An approximate value of I ($6m_3 + m_2 - 4m_1$) and hence γ, was used to give first values of $[H^+]$ in equation (30) from activity coefficients using the Davies equation (2). Substitution in equations (31) - (33) gave ionic concentrations and using (34) a more accurate value of I obtained. Successive approximations were made until I and the ionic concentrations remained constant. Calculations were done using a T.I.P. programme on a high speed DEUCE computer and constancy in I to 0.1% was usually given after three cycles. The association constant was then calculated from equation (3).

In the case of the least soluble salt, cobalt oxalate, concentrations were about ten times lower than in the corresponding nickel and manganese systems. The results on nickel oxalate, cobalt oxalate and manganese oxalate are given in Tables XIV, XV, XVI respectively. It is seen that K values are constant over a range of concentrations indicating that only one complex is present in these solutions. There are no temperature data available in the literature for any of the complexes studied, but K values may be compared with those of other workers. Money and Davies,[6] using a conductivity method at 18°C, gave $K(NiOx) = 2.0 \times 10^5$, $K(CoOx) = 5.1 \times 10^4$ and $K(MnOx) = 8.1 \times 10^3$. These may be compared with the present values at 15°C of 1.4×10^5, 6.1×10^4 and 8.4×10^3 respectively and only in the case of nickel oxalate is the agreement poor. In their paper, however, Money and Davies indicate that in this case an increasing dissociation constant was given over the limited range of concentrations used. These authors also report a value of $K(MnOx) = 9.1 \times 10^3$ at 25°C using a solubility method[66] which compares excellently with the present value at 25°C.

[illegible] concentrations in nickel oxalate [illegible]

	1	2	3	4	5
	0.9346	1.9174	2.4034	1.5028	1.[illegible]
[illegible]	0.9150	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.3669

[illegible]

[illegible]

[illegible] 10^{-5} [illegible]

TABLE XIV.

[illegible]	[illegible]	21.4[illegible]	[illegible]	1.53
[illegible]	[illegible]	21.913	[illegible]	1.62
[illegible]	[illegible]	21.451	[illegible]	1.46
[illegible]	[illegible]	[illegible]	[illegible]	1.52
[illegible]	[illegible]	2[illegible].920	1.0248	1.43

Mean K = 1.51 ± 0.05

Temp. = 15°C.

[illegible]	[illegible]	12.634	1.9709	1.34
[illegible]	[illegible]	22.[illegible]1	2.3577	1.42
[illegible]	[illegible]	21.[illegible]	1.6914	1.32

Expt.	$(E' - E^{o})$	10^3.I
1	0.25048	9.630
2	0.24226	11.574
3	0.25808	8.298
4	0.24607	10.598
5	0.27336	8.467

1	0.26490	9.789
2	0.25630	11.781
3	0.27287	8.423
4	0.26008	10.717
5	0.28880	8.510

TABLE XIV(a)

Molal concentrations in nickel oxalate experiments

Expt.	1	2	3	4	5
$10^3.m_1$	2.9569	3.5174	2.4884	3.2920	1.4138
$10^3.m_2$	0.9450	1.1136	0.8777	1.0339	0.9226
$10^3.m_3$	3.6011	4.3440	3.1053	3.9512	3.1629

TABLE XIV(b)

Results on nickel oxalate

$10^3.[H^+]$	$10^4.[HOx^-]$	$10^5.[Ox^{2-}]$	$10^3.[NiOx]$	$10^{-5}.K$
		Temp. = 0°C.		
4.0397	8.282	1.914	2.0586	1.53
4.8259	9.570	1.913	2.4721	1.62
3.3479	6.809	1.851	1.7539	1.46
4.4763	9.461	2.006	2.2620	1.52
1.7207	1.750	0.929	1.2248	1.43
		Mean K =	1.51 ± 0.05	
		Temp. = 15°C.		
3.9568	9.038	2.014	1.9789	1.36
4.7179	10.553	2.041	2.3677	1.42
3.2842	7.404	1.936	1.6914	1.32
4.4136	10.036	2.038	2.2015	1.44
1.6996	1.953	0.988	1.2036	1.33
		Mean K =	1.37 ± 0.04	

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Temp. = 25°C.

[illegible]	[illegible]	1.919	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

TABLE XIV contd.

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Mean [illegible]

Temp. = 45°C.

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	1.921	[illegible]	1.60
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Expt.	$(E' - E^{\circ})$	$10^3.I$
1	0.27432	9.822
2	0.26539	11.808
3	0.28243	8.418
4	0.26940	10.772
5	0.29901	8.521

1	0.28403	9.920
2	0.27470	11.889
3	0.29240	8.499
4	0.27884	10.848
5	0.30941	8.553

1	0.29365	9.989
2	0.28406	11.981
3	0.30227	8.553
4	0.28829	10.920
5	0.31977	8.577

TABLE XIV(b) contd.

$10^3.[H^+]$	$10^4.[HOx^-]$	$10^5.[Ox^{2-}]$	$10^3.[NiOx]$	$10^{-5}.K$
	Temp. = 25°C.			
3.9374	9.222	1.919	1.9608	1.42
4.7014	10.707	1.932	2.3529	1.50
3.2839	7.409	1.798	1.6923	1.44
4.3831	10.319	1.962	2.1729	1.47
1.6932	2.014	0.950	1.1977	1.39
			Mean K = 1.44 ± 0.03	
	Temp. = 35°C.			
3.8795	9.706	1.826	1.9087	1.44
4.6499	11.113	1.806	2.3081	1.57
3.2369	7.814	1.713	1.6494	1.46
4.3349	10.703	1.833	2.1309	1.54
1.6756	2.178	0.923	1.1810	1.42
			Mean K = 1.49 ± 0.06	
	Temp. = 45°C.			
3.8401	10.058	1.728	1.8724	1.48
4.5978	11.572	1.721	2.2598	1.60
3.2060	8.094	1.619	1.6210	1.51
4.2933	11.070	1.731	2.0928	1.60
1.6627	2.300	0.887	1.1688	1.48
			Mean K = 1.53 ± 0.05	

TABLE XV

4	[illegible]	5.6[illegible]
5	2.[illegible]	6.26
6	2.[illegible]	5.6[illegible]
8	2.[illegible]	6.2[illegible]
9	3.[illegible]	5.9[illegible]

Mean k = 5.[illegible] ± 0.[illegible]

Temp. = 5°C.

4	2.7303	5.92
6	2.4152	5.70
8	2.9412	6.20

Molal concentrations

Expt.	1	2	3
$10^4.m_1$	10.6015	7.5201	9.9339
$10^4.m_2$	4.3378	4.8485	3.5936
$10^4.m_3$	7.1875	5.7084	5.3596

Expt.	$(E' - E^o)$	$10^3.I$
4	0.33709	1.723
5	0.33243	2.113
6	0.33877	2.367
8	0.33164	2.251
9	0.32831	2.565

4	0.34338	1.723
6	0.34513	2.369
8	0.33791	2.257
9	0.33445	2.567

TABLE XV(a)

in cobalt oxalate experiments

4	5	6	7	8	9
4.6320	4.4061	3.3415	4.3336	4.0907	4.4713
1.9813	2.2535	2.4126	2.5495	1.9679	2.6201
5.8845	7.5226	8.4511	7.4063	8.0331	9.1779

TABLE XV(b)

Results on cobalt oxalate

$10^4.[H^+]$	$10^4.[HOx^-]$	$10^5.[Ox^{2-}]$	$10^4.[CoOx]$	$10^{-4}.K$
	Temp. = 0°C.			
5.5981	1.6533	2.222	2.7409	5.60
5.3863	1.1516	1.638	3.0803	6.26
3.6818	0.5814	1.223	2.6342	5.60
5.2324	0.9642	1.420	2.9760	6.20
5.3095	0.9954	1.463	3.3207	5.95
			Mean K = 5.92 ± 0.26	
	Temp. = 5°C.			
5.5749	1.6768	2.094	2.7303	5.91
3.6613	0.6019	1.178	2.6182	5.78
5.1932	1.0031	1.27_8	2.9412	6.30
5.2848	1.0201	1.395	3.3029	6.21
			Mean K = 6.05 ± 0.21	

TABLE XV contd.

Expt.	(E' - E°)	10^3.I
1	0.33477	2.435
2	0.35283	1.848
3	0.34364	2.003
4	0.35568	1.719
5	0.35092	2.119
7	0.35302	2.075
8	0.34995	2.250
9	0.34660	2.572

1	0.34646	2.425
2	0.36519	1.841
3	0.35571	1.999
4	0.36843	1.733
5	0.36331	2.122
7	0.36580	2.095
8	0.36267	2.273

TABLE XV(b) contd.

$10^4.[H^+]$	$10^4.[HOx^-]$	$10^5.[Ox^{2-}]$	$10^4.[CoOx]$	$10^{-4}.K$
	Temp. =	15°C.		
10.8014	5.8534	3.946	4.2483	5.62
6.4859	3.6266	3.966	3.4573	5.64
10.0836	6.0320	4.293	3.3708	5.84
5.5921	1.6593	2.091	2.7479	6.03
5.3482	1.1892	1.597	3.0465	6.37
4.9883	1.1107	1.596	3.0539	6.54
5.2243	0.9722	1.344	2.9756	6.61
5.2674	1.0370	1.442	3.2811	5.99
		Mean K = 6.08 ± 0.32		
	Temp. =	25°C.		
10.7932	5.8618	3.659	4.2687	6.18
6.4688	3.6436	3.695	3.4674	6.13
10.0025	6.0680	4.010	3.3630	6.25
5.5157	1.7348	2.051	2.6759	5.89
5.3168	1.2202	1.526	3.0224	6.62
4.8970	1.2010	1.628	2.9599	6.14
5.1204	1.0747	1.405	2.8663	6.02
		Mean K = 6.18 ± 0.15		

TABLE XV contd.

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Temp. = [illegible]°C.				
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]				
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Expt.	$(E' - E^{o})$	$10^{3}.I$
1	0.35842	2.434
2	0.37786	1.847
3	0.36801	2.007
4	0.38115	1.740
5	0.37596	2.136
7	0.37842	2.102
8	0.37509	2.277
9	0.37125	2.586

1	0.37024	2.432
2	0.39050	1.852
3	0.38028	2.015
4	0.39386	1.746
5	0.38838	2.138
7	0.39117	2.113
8	0.38762	2.285
9	0.38352	2.588

TABLE XV(b) contd.

$10^4.[H^+]$	$10^4.[HOx^-]$	$10^5.[Ox^{2-}]$	$10^4.[CoOx]$	$10^{-4}.K$
	Temp. = 35°C.			
10.6757	5.9676	3.339	4.1892	6.52
6.3769	3.7309	3.400	3.4072	6.43
9.8810	6.1784	3.663	3.2818	6.47
5.4489	1.7992	1.909	2.6246	6.16
5.2338	1.3010	1.465	2.9466	6.67
4.8415	1.2548	1.525	2.9156	6.44
5.0795	1.1142	1.301	2.8365	6.45
5.1728	1.1294	1.312	3.2005	6.44
		Mean K = 6.45 ± 0.08		
	Temp. = 45°C.			
10.6254	6.0146	3.041	4.1702	7.14
6.3028	3.8033	3.155	3.3585	6.74
9.7853	6.2705	3.377	3.2164	6.72
5.3926	1.8543	1.788	2.5810	6.43
5.2032	1.3309	1.356	2.9272	7.18
4.7706	1.3246	1.470	2.8507	6.49
5.0261	1.1666	1.239	2.7898	6.65
5.1428	1.1588	1.219	3.1801	6.93
		Mean K = 6.79 ± 0.23		

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

TABLE XVI

[illegible]	[illegible]	[illegible]	[illegible]	10^{-3}.K
[illegible]	[illegible]	[illegible]	1.7367	6.37
[illegible]	[illegible]	[illegible]	[illegible]	9.50
[illegible]	[illegible]	[illegible]	[illegible]	6.17
[illegible]	[illegible]	11.530	1.4200	6.01
[illegible]	[illegible]	[illegible]	1.7736	6.33

Mean K = 6.[illegible] ± 0.15

Molal concentrations

Expt.	1	2
$10^3.m_1$	3.4320	4.7888
$10^3.m_2$	3.2776	4.4524
$10^3.m_3$	9.3107	10.5926

Expt.	$(E' - E^{\circ})$	$10^2.I$
1	0.24805	2.805
2	0.23893	3.233
3	0.24977	2.705
4	0.25855	2.329
5	0.22908	2.962

TABLE XVI(a)

in manganese oxalate experiments

3	4	5	6	7
3.0969	2.6820	6.0543	3.8573	4.5292
2.8542	2.7137	3.1920	5.3869	6.1270
8.9826	7.7665	9.0494	8.6069	8.6630

TABLE XVI(b)

Results on manganese oxalate

$10^3.[H^+]$	$10^3.[HOx^-]$	$10^5.[Ox^{2-}]$	$10^3.[MnOx]$	$10^{-3}.K$
	Temp. = 0°C.			
1.9402	1.5637	9.437	1.7327	8.37
2.5586	2.4025	11.402	2.1902	8.50
1.8609	1.4069	8.773	1.5663	8.17
1.4553	1.1485	8.830	1.4220	8.01
4.5000	3.9386	10.391	1.7728	8.33

Mean K = 8.28 ± 0.15

Temp. = 15°C.

[illegible]	[illegible]	Expt	10^3.[mole]	10^{-5}.K
[illegible]	[illegible]	1	1.6979	9.53
[illegible]	[illegible]	2	[illegible]	[illegible]
[illegible]	[illegible]	3	[illegible]	9.34
[illegible]	[illegible]	4	[illegible]	9.41
[illegible]	[illegible]	5	[illegible]	9.40
[illegible]	[illegible]	6	[illegible]	[illegible]
[illegible]	[illegible]	7	[illegible]	9.11

TABLE XVI contd. [illegible] 9.38

Temp. = 25°C.

[illegible]	[illegible]	Expt	10^3.[mole]	10^{-5}.K
[illegible]	[illegible]	1	[illegible]	9.41
[illegible]	[illegible]	2	[illegible]	[illegible]
[illegible]	[illegible]	3	1.5599	9.43
[illegible]	[illegible]	4	1.4139	9.21
[illegible]	[illegible]	5	1.7334	9.44
[illegible]	[illegible]	6	2.3415	8.89
[illegible]	[illegible]	7	2.5583	8.89

Mean K = 9.28 ± 0.24

Expt.	$(E' - E^0)$	$10^2.I$
1	0.26232	2.811
2	0.25270	3.241
3	0.26410	2.711
4	0.27318	2.331
5	0.24208	2.970
6	0.28139	2.530
7	0.27745	2.574

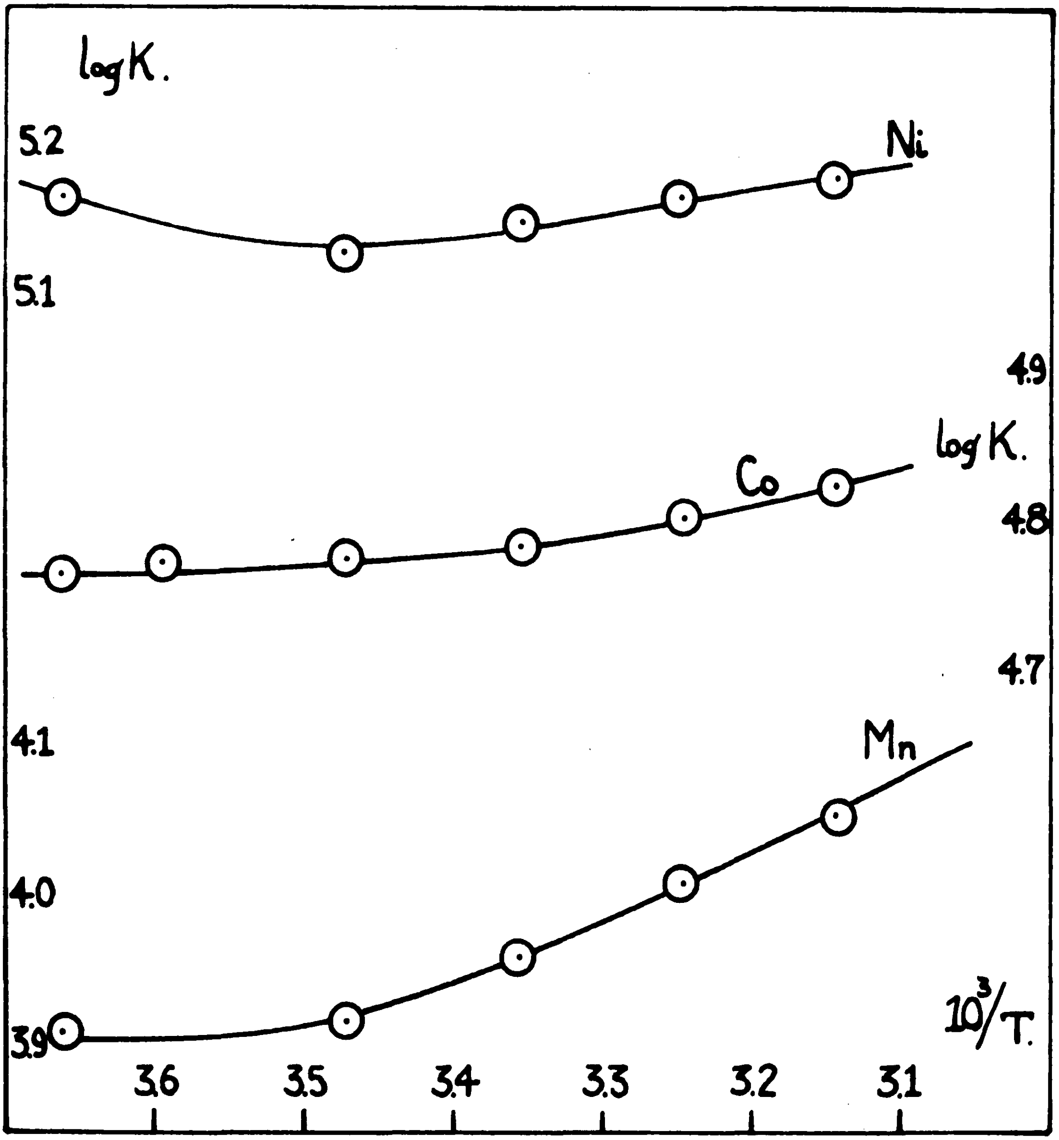
1	0.27154	2.808
2	0.26152	3.237
3	0.27321	2.706
4	0.28282	2.329
5	0.25066	2.969
6	0.29138	2.527
7	0.28727	2.570

Expt.	$(E' - E^o)$	$10^2.I$
1	0.28101	2.808
2	0.27065	3.236
3	0.28270	2.705
4	0.29271	2.329
5	0.25940	2.968
6	0.30162	2.524
7	0.29735	2.566

1	0.29055	2.809
2	0.27986	3.237
3	0.29222	2.705
4	0.30261	2.329
5	0.26817	2.971
6	0.31194	2.522
7	0.30741	2.564

TABLE XVI(b) contd.

$10^3.[H^+]$	$10^3.[HOx^-]$	$10^5.[Ox^{2-}]$	$10^3.[MnOx]$	$10^{-4}.K$
	Temp. = 35^oC.			
1.8905	1.6105	7.864	1.7002	1.06
2.5025	2.4539	9.407	2.1565	1.09
1.8296	1.4357	7.172	1.5524	1.06
1.4240	1.1781	7.276	1.4071	1.03
4.4221	4.0024	8.481	1.7210	1.06
0.9280	1.3638	13.192	2.3436	1.00
1.0852	1.7910	14.879	2.5618	1.00
			Mean K = 1.04 ± 0.03	
	Temp. = 45^oC.			
1.8735	1.6268	7.271	1.6894	1.16
2.4803	2.4749	8.690	2.1420	1.20
1.8179	1.4468	6.596	1.5467	1.18
1.4112	1.1905	6.723	1.4000	1.13
4.3939	4.0271	7.793	1.7015	1.17
0.9157	1.3760	12.226	2.3410	1.10
1.0736	1.8024	13.719	2.5619	1.11
			Mean K = 1.15 ± 0.03	



Metal Oxalates

Fig. 14.

DISCUSSION

Plots of log K against T^{-1} in Fig.14 show marked curvature indicating a non-zero ΔCp. Although this has been frequently found in precise measurements on weak acids and bases, it is uncommon to find finite ΔCp values in metal ion complexing reactions. The variation of log K with temperature may be described by equations of the form[67]:-

$$\log K = a + bT + CT^2 \quad (35)$$

$$\log K = a + bT + CT^2 + dT^3$$

$$\log K = a + bT + CT^2 + dT^3 + eT^4$$

$$\log K = a + bT + CT\log T \; (+ dT^2)$$

$$\log K = {}^{a}/_{T} + b + cT \; (+dT^2)$$

$$\log K = {}^{a}/_{T} + {}^{b}/T.\log T + {}^{c}/T.\log {}^{2}T + d$$

Equation (35) was found to interpret satisfactorily the data in the present work, although Feates and Ives[67] in their investigations into the ionisation of cyanoacetic acid used expressions involving higher terms in T. The parameters a, b and c were obtained by substituting known values of log K at temperatures 0°, 25° and 45°C and solving the three simultaneous equations. The equation for the curve was then checked by estimating log K at 15° and 35°C. The maximum difference between calculated and observed values was 3% but in most cases it was less than 1%. The parameters for the three curves in Fig.14 are given in Table XVII.

TABLE XVII

Parameters for the temperature dependence of log K

	a	$-10^2.b$	$10^5.c$
NiOx	9.065	2.655	4.512
CoOx	6.810	1.500	2.760
MnOx	8.141	3.146	5.857

The agreement is illustrated by the results for cobalt oxalate, the calculated log K being 4.780 compared with the experimental value of 4.784.

Thermodynamic data at 25°C were calculated from

$$-\Delta G = 2.303\ {}^{RT}/F\ \log K \tag{36}$$

Differentiation of equation (35) at constant pressure gives the Van't Hoff isochore,

$$\left(\frac{\partial \log K}{\partial T}\right)_p = \frac{-\Delta H}{2.303\ RT^2} = b + 2CT. \tag{37}$$

ΔS was calculated from the equation,

$$\Delta G = \Delta H - T.\Delta S, \tag{38}$$

ΔH from

$\Delta H = 2.303\ RT^2\ (b + 2cT)$ --------------------(39)

and ΔCp from $\frac{d\Delta H}{dT} = \Delta Cp = 4.606\ RT\ (b + 3cT)$------(40)

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

TABLE XVIII

Thermodynamic properties for metal oxalates

Reaction	$Ni^{2+} + Ox^{2-}$	$Co^{2+} + Ox^{2-}$	$Mn^{2+} + Ox^{2-}$
ΔH (k.cal./mole)	0.30 ± 0.05	0.59 ± 0.07	1.42 ± 0.20
ΔG (k.cal./mole)	7.05 ± 0.02	6.54 ± 0.02	5.41 ± 0.02
ΔS (cal.deg./mole)	24.7 ± 0.20	23.9 ± 0.30	22.9 ± 0.70
ΔCp (cal.deg.$^{-1}$)	38 ± 12	26 ± 10	65 ± 15

The values of ΔCp may be compared with 35 - 45 cal. deg.$^{-1}$ for a number of reactions in which the association of hydrogen ion with a univalent anion has been studied.[67, 68] Postmus and King[69] found a ΔCp of

70 cal.deg.$^{-1}$ for the association of trivalent chromium with the thiocyanate ion and thought the larger value reasonable in view of the greater charge of the chromic ion. ΔS varies with the reciprocal of the cationic radius, but a fuller discussion of this will be given in the General Discussion.

[illegible]

[illegible] strength of 0.2M, at which activities may be [illegible] constant.

It was first necessary to measure the dissociation constants, $K_1' = [H^+].[HSucc^-] / [H_2Succ]$ and $K_2' = [H^+][Succ^{2-}] / [HSucc^-]$ at this ionic strength, in solutions containing succinic acid and sodium hydroxide together with the calculated amount of sodium perchlorate to give an ionic strength of 0.2M were investigated using a glass electrode cell, both with and without liquid junction. $[H^+]$'s were obtained [illegible]

METAL SUCCINATES

RESULTS

A series of e.m.f. measurements were made on solutions containing succinic acid, sodium hydroxide and metal chlorides.

Using a method of calculation exactly similar to that in the metal oxalates, it was found that interpretation in terms of only one complex, MSucc, was not satisfactory. Values of K for NiSucc are given in Table XIX.

In order to identify the species present, pH measurements were made on solutions at a constant ionic strength of 0.2M, at which activities may be assumed constant.

It was first necessary to measure the dissociation constants, $k_1' = [H^+] . [HSucc^-] / [H_2Succ]$ and $k_2' = [H^+][Succ^{2-}] / [HSucc^-]$ at this ionic strength, and solutions containing succinic acid and sodium hydroxide together with the calculated amount of sodium perchlorate to give an ionic strength of 0.2M were investigated using a glass electrode cell, both with and without liquid junction. $[H^+]$'s were obtained using the mean activity coefficient data of Robinson and Stokes.[5] A graphical method was used similar to that

TABLE XIX

Association constants for nickel succinate, at 25°C, assuming only NiSucc present.

$10^3.m_1$	$10^3.m_2$	$10^3.m_3$	$10^3.I$	K
2.89192	4.24577	3.95576	16.59	155
7.16050	6.90610	2.56313	15.02	156
9.15003	8.58724	5.61057	25.42	252
5.82184	8.93603	8.45457	33.87	212
5.21188	8.03486	7.24212	31.69	207
6.24147	6.25450	4.26849	19.23	204
2.61898	2.22955	5.08036	17.44	253
11.76196	9.92814	10.62220	36.09	257
2.64671	3.48187	3.97423	15.63	183

TABLE XX

Dissociation constants of succinic acid at 25°C, I = 0.2M

Expt.	$10^3.T_a$	$10^3[Na^+]$	$10^4[H^+]$	$10^4.X$	$10^8.Y$
1	7.099	0.620	6.711	3.02	4.51
2	7.099	0.692	6.237	2.60	3.97
3	7.099	1.261	4.464	1.93	2.72
4	7.099	1.358	4.196	1.80	2.52
5	7.099	1.383	4.110	1.76	2.44
6	7.099	1.582	3.730	1.57	2.22
7	7.099	2.192	2.647	1.05	1.47
8	7.099	2.543	2.271	0.86	1.25
9	7.099	2.456	2.295	0.88	1.23
10	7.099	2.731	2.064	0.76	1.11
11	7.099	3.245	1.602	0.55	0.81
12	12.660	7.084	1.156	0.35	0.53
13	12.660	14.722	0.181	-0.036	0.045
14	12.660	20.543	0.0437	-0.072	0.008

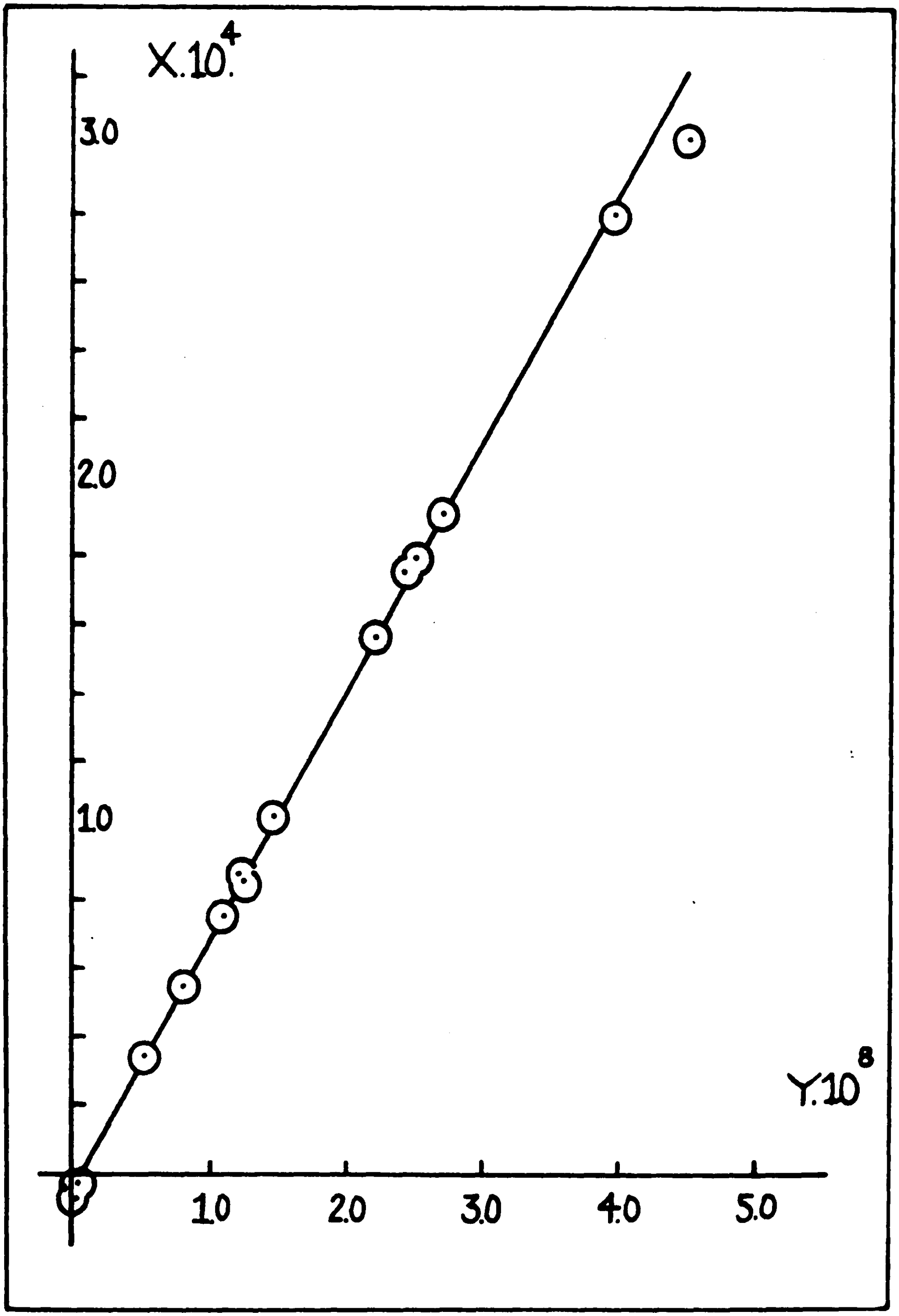


Fig. 15.

of Speakman,[65] leading to the equation

$$X = k_1'.Y + k_1'.k_2'$$

where

$$X = \frac{[H^+]^2\{[HSucc^-] + 2[Succ^{2-}]\}}{2[H_2Succ] + [HSucc^-]}$$

and

$$Y = \frac{[H^+]\{[H_2Succ] - [Succ^{2-}]\}}{2[H_2Succ] + [HSucc^-]}$$

The results are summarised in Table XX and a plot of X against Y is shown in Fig.15. The slope of the line is $k_1' = 1.38 \times 10^{-4}$ and the intercept $k_1'k_2'$ gives a k_2' value of 6.9×10^{-6}.

Since the ratio k_2/k_1 of the dissociation constants of succinic acid is much less than that for oxalic acid, the concentration of $HSucc^-$ in solution is much larger leading to a greater possibility of complexes of the type $MHSucc^+$. In experiments conducted at an ionic strength of 0.2M, two ion-pairs MSucc and $MHSucc^+$ were taken into account and stability constants were calculated from equations for the total metal ion concentration,

$$T_m = [M^{2+}] + [MSucc] + [MHSucc^+] \text{ ----------(41)}$$

the total succinic acid concentration,

$$T_a = [H_2Succ] + [HSucc^-] + [Succ^{2-}] + [MSucc] + [MHSucc^+] \quad \text{------(42)}$$

electroneutrality,

$$[Na^+] + [H^+] + 2[M^{2+}] + [MHSucc^+] = [HSucc^-] + 2[Succ^{2-}] + 2m_3 \quad \text{---(43)}$$

and the dissociation constants k_1' and k_2' of succinic acid. Equilibrium constants for the complex formation at this ionic strength may be written:-

$$K' = [MSucc] / [M^{2+}].[Succ^{2-}] \quad \text{----------(44)}$$

and

$$K_1' = [MHSucc^+] / [M^{2+}].[HSucc^-]. \quad \text{-------(45)}$$

Equations (41) - (45) yielded the quadratic

$$K_1'.[HSucc^-]^2 \left\{ \frac{[H^+]}{k_1'} + 1 + \frac{k_2'}{[H^+]} \right\} + [HSucc^-] \left\{ 1 + \frac{2[H^+]}{k_1'} + K_1' (Tm-Ta) \right\} + [Na^+] + [H^+] - 2T_a = 0 \quad \text{--(46)}$$

and insertion of approximate K_1' values in (46) gave $[HSucc^-]$. pH measurements were made with manganese succinate over a range of concentrations of metal ion and base. Various values of K_1' were inserted in

TABLE XXI

Manganese succinate at 25°C, $I = 0.2M$, using $K'_1 = 5$ l./mole

Expt.	$10^3.T_m$	$10^3.T_a$	$10^3[Na^+]$	$10^4[H^+]$	$10^3[HSucc^-]$
1	18.310	12.660	7.084	1.308	5.711
2	7.324	12.660	14.772	0.2079	7.744
3	18.310	12.660	14.772	0.2414	7.215
4	36.620	12.660	14.772	0.2740	6.566
5	18.310	12.660	20.543	0.0566	4.076
6	36.620	12.660	20.790	0.06528	3.562

Expt.	$10^3[Succ^{2-}]$	$10^3[MnSucc]$	$10^3[MnHSucc^+]$	K'_1	K'
1	0.330	0.154	0.536	5.3	26.5
2	2.809	0.552	0.277	5.5	30.3
3	2.254	1.214	0.595	5.0	32.6
4	1.807	1.710	1.149	5.2	28.0
5	5.430	2.642	0.329	5.3	31.7
6	4.114	4.208	0.591	5.2	32.1

equation (46) and a constant K' was obtained over a 23 fold variation in $[H^+]$ when $K = 5$ $l.mole^{-1}$, providing confirmatory evidence that the second complex present in these solutions was $MHSucc^+$. The results are summarised in Table XXI.

Having established the existence of the two species in solution, precise e.m.f. measurements were made at 0° to 45°C at low concentrations using nickel, cobalt and manganous chlorides. The cell used was

$$H_2, Pt / H_2Succ (m_1), NaOH (m_2), MCl_2 (m_3) / AgCl, Ag$$

and the hydrogen ion concentration of the solution was obtained from

$$-\log [H^+] = (E' - E^o)/k + 2 \log m_3 + \log\gamma_{H^+} . \gamma_{Cl^-}$$

where $k = 2.303RT/F$. The concentrations of the ionic species were derived using

$$m_1 = [H_2Succ] + [HSucc^-] + [Succ^{2-}] + [MSucc] + [MHSucc^+]$$

$$m_3 = [M^{2+}] + [MSucc] + [MHSucc^+] ,$$

electroneutrality

$$m_2 + [H^+] + 2[M^{2+}] + [MHSucc^+] = [HSucc^-] + 2[Succ^{2-}] + 2m_3,$$

the ionic strength

TABLE XXII

Dependence of K on K_1 values for nickel succinate at 25°C

K_1	0	5	10	15
Expt.	K	K	K	K
1	180	189	197	206
3	249	242	234	227
4	197	202	207	209
5	177	190	203	216
6	204	206	209	211
7	223	223	223	223
8	260	252	243	235
Mean K	213	215	217	219
Dev. in K	±12.5%	± 9.6%	± 6.6%	± 3.9%

K_1	20	25	30	40
Expt.	K	K	K	K
1	215	223	232	249
3	220	212	205	191
4	218	223	229	240
5	228	241	254	279
6	214	217	219	224
7	223	223	223	223
8	227	219	210	193
Mean K	221	223	225	229
Dev. in K	± 2.3%	± 2.7%	± 5.3%	±10.4%

TABLE XXIII

Association constants at 25°C.

K_1	Nickel		Cobalt		Manganese	
	K	Dev(%) in K.	K	Dev.(%) in K.	K	Dev.(%) in K.
0	213	12.5	165	3.6	179	15.6
2	-	-	167	4.5	-	-
5	215	9.6	172	5.4	180	10.0
10	217	6.6	179	6.6	182	4.7
15	219	3.9	185	8.8	184	2.2
20	221	2.3	192	10.5	186	5.5
25	223	2.7	199	12.1	187	10.8
30	225	5.3	-	-	-	-
40	229	10.4	-	-	-	-

Underlined values adopted at 25°C.

$I = 3m_3 - m_1 + 4[\mathrm{Succ}^{2-}] + [H_2\mathrm{Succ}] + 2[\mathrm{HSucc}^-]$, and activity coefficients from equation (2). The thermodynamic association constants

$$K = [\mathrm{MSucc}] / [M^{2+}].[\mathrm{Succ}^{2-}].\gamma_2^2$$

and

$$K_1 = [\mathrm{MHSucc}^+] / [M^{2+}].[\mathrm{HSucc}^-].\gamma_2$$

were calculated at 25°C using a T.I.P. programme on a DEUCE electronic computer. K's were obtained by inserting various K_1 values. When $K_1 = 0$, there is a wide variation in K but as K_1 increases, the deviations become less and pass through a minimum. Further increase in K_1 leads to larger deviations in K. The K_1 value giving the smallest deviation in K was taken as the correct one. Table XXII, shows the dependence of K on K_1 for experiments on nickel succinate. It is seen that the mean deviation in K passes through a minimum at $K_1 = 20$. Table XXIII summarises the data, and the best K_1 values for cobalt and manganese succinates are seen to be 0 and 15 respectively. Calculations at other temperatures showed that there were the best value throughout. In the case of cobalt where the best fit is obtained with only one complex present, the experimental conditions were designed so as to limit the amount of MHSucc^+ present. Using the

K_1 values, K was calculated at each temperature and Tables XXIV, XXV, and XXVI show the good constancy obtained. The values may be compared with those as given by Davies[19] of K (CoSucc = 2.7×10^2), K(NiSucc = 2.46×10^2) and K(MnSucc = 1.78×10^2). The agreement with the present values is good except in the case of cobalt.

TABLE XXIV

Molal concentrations

Expt.	1	2	3
$10^3.m_1$	2.64432	2.89030	2.61753
$10^3.m_2$	3.48105	4.24597	2.22955
$10^3.m_3$	3.97073	3.95576	5.08036

Results on

Expt.	$(E' - E^0)$	$10^6[H^+]$	$10^2.I$
1	0.40142	6.361	1.548
2	0.41305	3.874	1.642
6	0.37687	16.960	1.899
7	0.36519	21.889	2.503
8	0.34184	33.181	4.038

TABLE XXIV(a)

in nickel succinate experiments

4	5	6	7	8
2.86422	5.21511	6.24147	9.15003	11.76920
3.20346	7.99195	6.25450	8.58724	9.92814
4.26079	7.24212	4.26849	5.61057	10.62220

TABLE XXIV(b)

nickel succinate, using K_1 = 20 l.mole.$^{-1}$

$10^3.[HSucc^-]$	$10^4.[Succ^{2-}]$	$10^3.[Ni^{2+}]$	$10^4.[NiSucc]$	$10^{-2}.K$
	Temp. = 0°C.			
1.458	7.863	3.712	1.954	1.76
1.319	11.824	3.643	2.539	1.59
4.014	8.482	3.896	1.855	1.64
5.759	10.055	5.031	2.591	1.67
6.832	8.913	9.628	3.519	1.71

Mean K = 1.67 ± 0.05

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE XXIV contd.

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	5	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	6	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	7	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	8	[illegible]	[illegible]

Mean [illegible]

Expt.	$(E' - E^0)$	$10^6[H^+]$	$10^2.I$
3	0.37908	29.899	1.732
4	0.40359	13.155	1.589
5	0.42051	4.211	2.938
6	0.39479	19.079	1.893
7	0.38238	24.730	2.495
8	0.35768	37.645	4.031

		$10^5[H^+]$	
1	0.43442	0.737	1.538
3	0.39088	3.157	1.729
4	0.41660	1.373	1.585
5	0.43388	0.444	2.910
6	0.40734	2.004	1.885
7	0.39441	2.608	2.484
8	0.36873	3.994	4.019

TABLE XXIV(b) contd.

10^3[HSucc$^-$]	10^4[Succ^{2-}]	10^3[Ni^{2+}]	10^4[NiSucc]	10^{-2}.K
	Temp. = 15°C.			
1.616	2.072	4.918	0.674	1.87
1.799	5.146	4.022	1.507	1.98
2.080	21.512	6.366	7.376	1.96
4.032	8.267	3.863	2.038	1.86
5.782	9.767	5.014	2.798	1.91
6.859	8.649	9.617	3.716	1.93

Mean K = 1.92 ± 0.04

10^3[HSucc$^-$]	10^4[Succ^{2-}]	10^3[Ni^{2+}]	10^4[NiSucc]	10^{-2}.K
	Temp. = 25°C.			
1.648	0.758	3.689	2.202	2.15
1.617	1.999	4.912	0.752	2.20
1.805	5.030	4.014	1.595	2.18
2.083	20.800	6.297	8.085	2.28
4.043	8.028	3.865	2.226	2.15
5.794	9.447	4.989	3.088	2.24
6.861	8.322	9.589	4.087	2.27

Mean K = 2.21 ± 0.05

[illegible]

Temp. = 25°C.

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]

TABLE XXIV contd.

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Mean K = [illegible]

Expt.	$(E' - E^{o})$	$10^{5}.[H^{-}]$	$10^{2}.I$
1	0.44860	0.751	1.530
3	0.40334	3.260	1.726
4	0.43000	1.408	1.579
5	0.44801	0.453	2.888
6	0.42043	2.056	1.877
7	0.40698	2.685	2.494
8	0.38029	4.141	4.008

1	0.46313	0.749	1.522
3	0.41617	3.304	1.723
4	0.44374	1.426	1.571
5	0.46249	0.456	2.856
6	0.43403	2.069	1.868
7	0.42011	2.708	2.464
8	0.39235	4.212	3.996

TABLE XXIV(b) contd.

$10^3.[HSucc^-]$	$10^4.[Succ^{2-}]$	$10^3.[Ni^{2+}]$	$10^4.[NiSucc]$	$10^{-2}.K$
	Temp. = 35°C.			
1.472	7.366	3.670	2.395	2.46
1.621	1.919	4.905	0.821	2.55
1.811	4.863	4.001	1.737	2.51
2.088	20.221	6.243	8.649	2.59
4.060	7.767	3.848	2.413	2.46
5.816	9.117	4.969	3.324	2.56
6.877	7.982	9.565	4.397	2.62
		Mean K = 2.53 ± 0.05		
	Temp. = 45°C.			
1.478	7.134	3.650	2.603	2.82
1.625	1.830	4.899	0.895	2.98
1.814	4.633	3.980	1.956	3.03
2.093	19.389	6.164	9.471	3.05
4.078	7.469	3.828	2.632	2.85
5.842	8.761	4.947	3.569	2.94
6.892	7.608	9.540	4.737	3.04
		Mean K = 2.96 ± 0.08		

[illegible]

TABLE XXV

[illegible]

Molal concentrations

Expt.	1	2
$10^3.m_1$	4.5096	5.0085
$10^3.m_2$	4.5314	4.8902
$10^3.m_3$	6.5698	7.0268

Results on

Expt.	$(E' - E^o)$	$10^5.[H^+]$
1	0.36658	1.757
2	0.36272	1.952
3	0.39994	0.505
4	0.39579	0.569
5	0.39025	0.710
6	0.39012	0.757
3	0.41944	0.561
4	0.41502	0.634
5	0.40924	0.789
6	0.40877	0.852

TABLE XXV(a)

in cobalt succinate experiments

3	4	5	6
3.6668	3.7054	3.8596	3.7091
5.1766	5.1137	5.0583	4.7523
5.4807	5.8234	5.9076	5.5273

TABLE XXV(b)

cobalt succinate, using $K_1 = 0$

$10^2.I$	$10^3.[HSucc^-]$	$10^3.[Succ^{2-}]$	$10^4.[CoSucc]$	$10^{-2}.K$
	Temp. = 0°C.			
2.446	2.971	0.643	1.465	1.15
2.615	3.282	0.650	1.640	1.23
2.219	1.877	1.381	2.711	1.16
2.304	1.968	1.296	2.803	1.23
2.314	2.202	1.163	2.686	1.29
2.172	2.178	1.063	2.285	1.24

Mean K = 1.24 ± 0.04

	Temp. = 15°C.			
2.212	1.883	1.362	2.880	1.29
2.297	1.974	1.276	2.977	1.36
2.310	2.211	1.149	2.782	1.39
2.161	2.182	1.033	2.562	1.47

Mean K = 1.37 ± 0.05

TABLE XXV contd.

[illegible]

[illegible]	[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]

TABLE XXV contd.

[illegible]

[illegible]	[illegible]	1	[illegible]	[illegible]
[illegible]	[illegible]	2	[illegible]	[illegible]
[illegible]	[illegible]	3	[illegible]	[illegible]
[illegible]	[illegible]	4	[illegible]	[illegible]
[illegible]	[illegible]	5	3.016	[illegible]
[illegible]	[illegible]	6	[illegible]	[illegible]

Mean N = [illegible]

[illegible]

[illegible]	[illegible]	1	[illegible]	[illegible]
[illegible]	[illegible]	2	[illegible]	[illegible]
[illegible]	[illegible]	3	[illegible]	[illegible]

Expt.	$(E' - E^{o})$	$10^{5}[H^{+}]$
1	0.39599	2.089
2	0.39183	2.316
3	0.43279	0.590
4	0.42809	0.670
5	0.42203	0.837
6	0.42192	0.891
1	0.40864	2.150
2	0.40426	2.391
3	0.44678	0.604
4	0.44201	0.684
5	0.43564	0.858
6	0.43547	0.916
1	0.42137	2.202
2	0.41700	2.436
3	0.46114	0.610
4	0.45608	0.694
5	0.44959	0.868
6	0.44945	0.925

TABLE XXV(b) contd.

10^2.I	10^3.[HSucc$^-$]	10^3.[Succ^{2-}]	10^4.[CoSucc]	10^{-2}.K
	Temp. = 25°C.			
2.433	2.986	0.605	1.787	1.56
2.603	3.302	0.614	1.918	1.60
2.194	1.884	1.316	3.331	1.58
2.278	1.974	1.226	3.472	1.69
2.291	2.210	1.101	3.274	1.75
2.151	2.187	1.007	2.799	1.69
		Mean K = 1.65 ± 0.06		
	Temp. = 35°C.			
2.426	2.995	0.584	1.954	1.81
2.595	3.310	0.590	2.121	1.88
2.177	1.887	1.273	3.752	1.89
2.264	1.978	1.191	3.806	1.96
2.277	2.215	1.064	3.616	2.05
2.137	2.191	0.972	3.140	2.01
		Mean K = 1.93 ± 0.07		
	Temp. = 45°C.			
2.411	2.990	0.548	2.338	2.37
2.582	3.310	0.559	2.437	2.35
2.154	1.889	1.215	4.321	2.34
2.240	1.979	1.130	4.405	2.45
2.257	2.217	1.015	4.102	2.50
2.120	2.194	0.928	3.562	2.45
		Mean K = 2.41 ± 0.06		

TABLE XXVI

[illegible]

molal concentrations

Expt.	1	2	3
$10^3 . m_1$	3.87732	3.58060	4.10579
$10^3 . m_2$	2.72403	3.64612	3.40891
$10^3 . m_3$	4.89258	5.65596	4.90255

Results on

Expt.	(E' - E°)	$10^5 . [H^+]$	$10^2 . I$
1	0.35267	4.096	1.731
2	0.37151	1.620	2.060
3	0.36168	2.822	1.802
5	0.36559	1.274	3.359
7	0.36851	1.098	3.915
8	0.36778	1.200	3.832

1	0.36921	4.617	1.730
5	0.38291	1.437	3.353
6	0.38621	1.436	2.927
7	0.38543	1.264	3.882
8	0.38453	1.388	3.791

TABLE XXVI(a)

in manganese succinate experiments

4	5	6	7	8
3.73456	3.84355	3.70642	7.12848	8.07886
3.65978	4.42001	4.20629	8.56922	9.41907
3.54878	9.63515	8.44751	10.28948	9.68893

TABLE XXVI(b)

manganese succinate, using $K_1 = 15$ l.mole.$^{-1}$

$10^3.[HSucc^-]$	$10^4.[Succ^{2-}]$	$10^3.[Mn^{2+}]$	$10^4.[MnSucc]$	$10^{-2}.K$
	Temp. = 0°C.			
2.201	1.888	4.753	0.458	1.41
2.290	5.182	5.438	1.092	1.16
2.537	3.186	4.718	0.777	1.45
2.285	7.386	9.417	2.523	1.38
4.151	16.220	9.550	4.460	1.19
4.833	17.188	8.948	4.194	1.11
		Mean K = 1.28 ± 0.13		
	Temp. = 15°C.			
2.213	1.838	4.752	0.476	1.54
2.293	7.201	9.403	2.686	1.55
2.253	6.825	8.075	2.297	1.52
4.148	15.407	9.470	5.332	1.55
4.822	16.211	8.848	5.278	1.54
		Mean K = 1.54 ± 0.02		

TABLE XXVI contd.

Expt.	$(E' - E^o)$	$10^5.[H^+]$	$10^2.I$
1	0.38077	4.869	1.729
5	0.39468	1.531	3.340
6	0.39817	1.527	2.916
7	0.39730	1.348	3.854
8	0.39666	1.463	3.773
3	0.40296	3.435	1.795
4	0.42438	2.066	1.424
5	0.40702	1.592	3.327
6	0.41074	1.581	2.905
7	0.41010	1.383	3.839
8	0.40925	1.511	3.751
4	0.43792	2.093	1.417
5	0.41962	1.637	3.310
6	0.42334	1.633	2.887
7	0.42309	1.407	3.812
8	0.42212	1.534	3.719

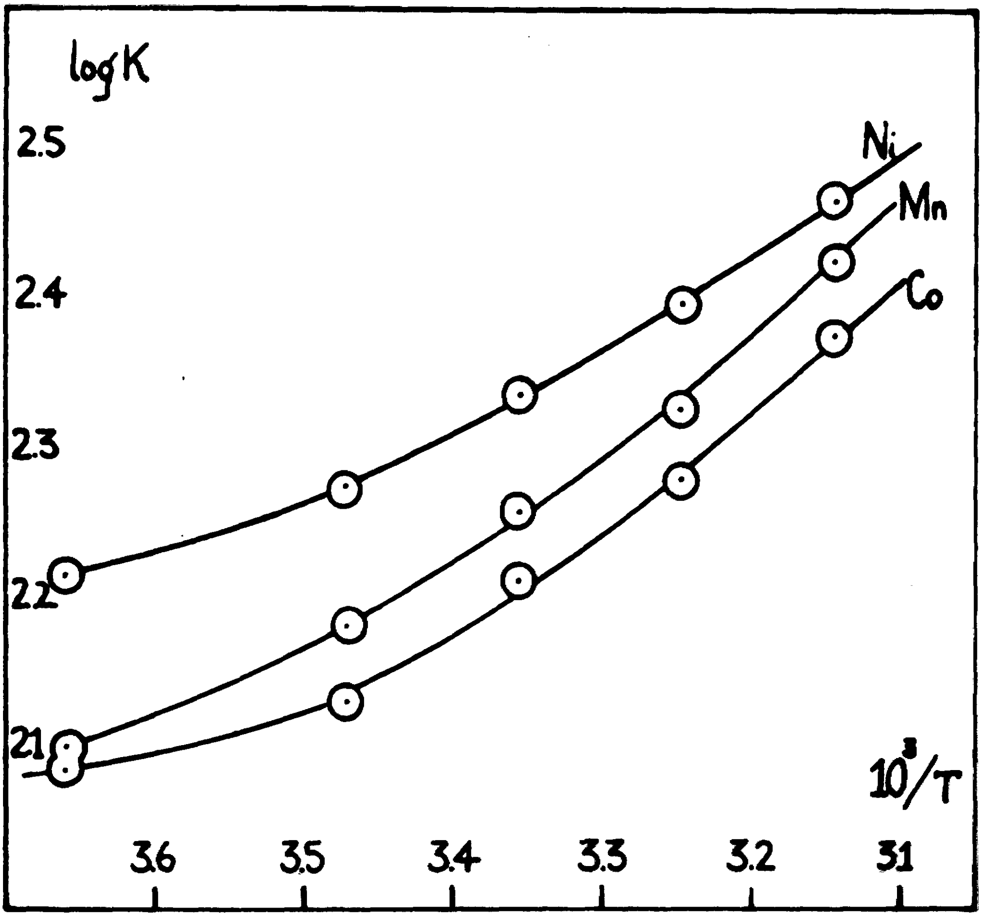
TABLE XXVI(b) contd.

$10^3.[\mathrm{HSucc}^-]$	$10^4.[\mathrm{Succ}^{2-}]$	$10^3.[\mathrm{Mn}^{2+}]$	$10^4.[\mathrm{MnSucc}]$	$10^{-2}.K$
	Temp. = 25°C.			
2.218	1.777	4.747	0.532	1.81
2.292	6.884	9.371	3.029	1.88
2.252	6.539	8.046	2.602	1.83
4.145	14.718	9.402	6.065	1.90
4.832	15.708	8.804	5.759	1.78
		Mean K = 1.84 ± 0.04		
	Temp. = 35°C.			
2.570	2.913	4.705	0.926	2.01
2.471	4.422	3.349	1.246	2.26
2.293	6.566	9.341	3.356	2.23
2.255	6.264	8.021	2.872	2.16
4.161	14.286	9.368	6.434	2.13
4.843	15.109	8.752	6.326	2.09
		Mean K = 2.15 ± 0.07		
	Temp. = 45°C.			
2.476	4.211	3.330	1.439	2.80
2.289	6.154	9.299	3.800	2.78
2.249	5.836	7.976	3.347	2.78
4.167	13.572	9.302	7.147	2.57
4.846	14,298	8.675	7.154	2.58
		Mean K = 2.70 ± 0.10		

DISCUSSION

It is seen that the association constants for metal succinates do not follow the Irving-Williams order. This has also been observed for transition metal sulphates, the small free energy changes on association being accounted for in terms of heat and entropy effects. The Irving-Williams sequence will be adhered to only when the ligands interact with protons more strongly than does water. The association constants for the sulphates and succinates are similar and in the case of these less stable complexes the association with water molecules is greater than with the ligands. The stabilities of the succinates are much lower than those of the oxalates due to the formation of the seven membered ring. Davies suggested that the influence of chelation is diminished in a ring of this size and that there is also some electrostatic attraction between the ions. Guggenheim[74] has supported this by showing that for 2:2 electrolytes any kind of association stronger than that due to electrostatic forces would be revealed by K values greater than 2×10^2 kg. mole.^{-1}

Estimating γ_1 and γ_2 from the Davies equation at an ionic strength of 0.2M, the stability constant values for manganese succinate reduced to $I \rightarrow 0$ become K = 20



METAL SUCCINATES

Fig. 16

and $K_1 = 13$, which are in excellent agreement with 184 and 15 respectively in Tables XXIII and XXVI.

Plots of log K against T^{-1} in Fig.16 again show marked curvature indicating a positive ΔCp. The curves may be represented by the equation

$$\log K = a + bT + cT^2$$

the maximum difference in calculated and observed K values being about 3%. The parameters a, b and c were evaluated as in the case of the oxalates, and the values for the different systems are given in Table XXVII.

TABLE XXVII

Parameters for temperature dependence of log K

	a.	-10^2b.	10^5c.
NiSucc	3.560	1.384	3.274
CoSucc	6.041	3.255	6.615
MnSucc	4.006	1.912	4.453

Thermodynamic properties were evaluated using equations (36) - (40) and are given in Table XXVIII together with the deviations. The K values at all temperatures are lower than those of the oxalates and malonates,[38] confirming the suggestion that the stability of the complex decreases as the ring size increases. The order is oxalate > malonate > succinate.

TABLE XXVIII

Thermodynamic properties

Reaction	Ni^{2+} + $Succ^{2-}$	Co^{2+} + $Succ^{2-}$	Mn^{2+} + $Succ^{2-}$
ΔH (k.cal.mole^{-1})	2.23 ± 0.2	2.81 ± 0.1	2.95 ± 0.1
ΔG (k.cal.mole^{-1})	3.20 ± 0.02	3.02 ± 0.02	3.09 ± 0.02
ΔS (cal.deg.$^{-1}$mole)	18.2 ± 0.7	19.6 ± 0.1	20.3 ± 0.2
ΔCp (cal.deg.$^{-1}$)	42 ± 20	72 ± 20	62 ± 15.

PART III
GENERAL DISCUSSION

[illegible] ate determinations of association [illegible] been made at only one temperature. [illegible] have been discussed only in the [illegible] solutions [illegible] al. If [illegible] completely, [illegible] ken into [illegible] to gain an [illegible] quilibria, [illegible] d as a [illegible] since [illegible] entropy [illegible] others where [illegible] entropy conditions.

Gurney[77] has introduced the idea that between a pair of oppositely charged ions the forces of attraction will be of two kinds; long range or electrostatic, and short range or quantum mechanical. For association reactions such as

$$M^{z+} + A^{z-} \rightleftharpoons MA \quad \text{--------------} (47)$$

It is well known that for a large number of ion-pairs, accurate determinations of association constants have been made at only one temperature. These reactions have been discussed only in the light of free energy changes and any correlations with ionic properties are rather empirical. If the association process is to be studied completely, heat and entropy changes must also be taken into account. It has been suggested[15] that to gain an insight into the factors affecting the equilibria, the free energy change should be regarded as a consequence of heat and entropy changes since reactions are known in which favourable entropy factors have overcome endothermicity and others where positive heat changes offset unfavourable entropy conditions.

Gurney[79] has introduced the idea that between a pair of oppositely charged ions the forces of attraction will be of two kinds, long range or electrostatic, and short range or quantum mechanical. For association reactions such as

$$M^{x+} + A^{x-} \rightleftharpoons MA \quad \text{-------------}(47)$$

the work, W, done in the formation of an ion-pair from the separate ions in solution is given by

$$W = \Delta G/N - kT \ln 55.5 \quad \text{--------}(48)$$

where N is Avogadro's number and k the Boltzmann constant. The importance of the $-kT \ln 55.5$ term has been stressed since it is characteristic of a reaction in which the number of solute particles decreases by unity, and its inclusion results in dimensionless K values, 55.5 being the number of moles in 1000 grams of water. W may be regarded as consisting of two parts, W_{env} and W_{non} representing respectively the long range electrostatic forces dependent on environment and temperature, and the (short range) quantum mechanical forces due to rapid movement of the electrons, independent of temperature and insensitive to environment.

$$W = W_{env} + W_{non} = -kT\left[\ln K + \ln 55.5\right] = -kT\ln K_x \quad \text{--(49)}$$

The dependence of K values on these two quantities has been illustrated by Davies[80] who showed that for the hydroxide complexes of the Na^+, Li^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, and La^{3+} ions where the only short range forces were those of repulsion due to completed electronic shells, K was governed mainly by W_{env}, and Nancollas[15] has shown that for Fe^{3+}, V^{3+} and U^{4+} complexes, quantum mechanical forces as well as electrostatic attractive forces lead to much larger K values.

The variation of the association constant with temperature may be represented in terms of W_{env} and W_{non}. Since W_{non} is independent of temperature, the behaviour should be simple when W_{env} is zero or near zero. In this case the increase may be represented by

$$W = W_{non} + \alpha T$$

where α is a small parameter, so that

$$-\ln K_x = \frac{W_{non}}{kT} + \frac{\alpha}{k} = \frac{A}{T} + B \quad ---(50)$$

where A and B are constants. Thus, if W is of this form, a linear plot will be given of lnK against T^{-1} and this has been found in several instances.

In the cases where environmental factors are involved, since W_{env} is almost entirely electrostatic in origin, it may be replaced by W_{el} which is dependent on temperature and inversely proportional to ε, the dielectric constant of the medium. This will not, however, be a strict proportionality due to the dielectric saturation effect in the neighbourhood of the ion. W is thus composed of W_{el} which increases with temperature and W_{non}. Using this theory, Gurney has shown that it is possible to account for the temperature variation of K in many systems. It is implied in the theory that the value of W (i.e., $kT \ln K_x$)

should in no case pass through a maximum or minimum or decrease and a study of the weak organic acids has confirmed this, W increasing throughout the temperature range in every instance. It can be shown that for common solvents, $1/\varepsilon$ may be expressed in the form

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

where θ is a temperature characteristic of the solvent. Now, since W_{el} is inversely proportional to ε, we may write

$$\ln K_x = -C\left(\frac{a + e^{T/\theta}}{T}\right) \text{-----------------} (51)$$

where $Ca = W_{non}/k$ and $Ce^{T/\theta} = W_{el}/k$.
Differentiation of (51) and equation to zero gives the temperature T^* at which the association constant passes through a minimum.

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

where W_{el}^* is the value of W_{el} at temperature T^*.
Thus the position of the minimum depends not on the value of $(W_{non} + W_{el})$ but on their ratio. It may also be noted that if T^* is below the freezing point of the solvent, then K will rise over the whole temperature range studied. Nancollas (loc.cit.) has shown that

in the case of the alkaline earth hydroxide ion-pairs where W_{non}/W_{el} is small there will be a mutual potential energy decrease when the temperature is raised causing K to increase. For other ion-pairs involving the OH^- ion, however, W_{non} becomes important and W_{non}/W_{el} may be large so that the predominant effect will be the tendency for thermal agitation to dissociate the ion-pairs. Values of T^* have been found for the oxalate systems since at each minimum ΔH is zero. It was found that T^* fell along the series Ni, Co, Mn, the values being 292°, 272° and 268°K respectively.

In reactions corresponding to equation(47), the free energy change may be written

$$\Delta G = - RT\ln K_a = G_{(MA)aq} - G_{(M^{x+})aq} - G_{(A^{x-})aq}$$

where G is the standard molar free energy of the species denoted by the subscript. Duncan and Kepert[40] plotted ΔG against $G_{(M^{2+})aq}$ for a series of ions with A^{2-} constant (oxine) and recognised two types of behaviour, (a) metal ion complexes in which $RT\ln K_a$ fell with decreasing values of $G_{(M^{2+})aq}$ and where there is covalent bonding between the ions, and (b) ion-pairs where ΔG was almost independent of $G_{(M^{2+})aq}$. In (b) the ions interact without seriously distorting their hydration sheaths. Smithson and Williams[78] have proposed a

TABLE XXIX

Thermodynamic Properties

Reaction	K_{298} (l./mole)	ΔG (k.cal./mole)	ΔH (k.cal./mole)	ΔS (cal./deg./mole)	Ref.
$Ag^{+} + IO_3^{-}$	6.8	-1.13	5.14	20.3	71.
$Ag^{+} + Cl^{-}$	$2x10^3$	-4.5	-2.7	6.0	71.
$Tl^{+} + OH^{-}$	6.7	-1.12	0.37	5.1	8.
$Zn^{2+} + Mal^{2-}$	-	-5.10	2.57	25.8	99.
$Mg^{2+} + SO_4^{2-}$	179	-3.07	4.84	26.2	11.
$Zn^{2+} + SO_4^{2-}$	240	-3.25	4.01	24.4	11.
$Ni^{2+} + SO_4^{2-}$	210	-3.16	3.31	21.7	11.
$Co^{2+} + SO_4^{2-}$	232	-3.21	1.74	16.6	11.
$Mn^{2+} + SO_4^{2-}$	181	-3.07	3.37	22.6	11.
$La^{3+} + Fe(CN)_6^{3-}$	$5.5x10^3$	-5.09	2.0	23.9	72.
$La^{3+} + Co(CN)_6^{3-}$	$5.8x10^3$	-5.13	1.33	21.7	73.

distinction between complexes and ion-pairs in that in the former the ions are adjacent whereas in the latter they are separated by solvent molecules.

The entropy change in (47) is composed of two parts since there is a decrease in entropy due to the reduction in the number of particles in solution, but there is an accompanying increase since in the neutralisation of charge solvent molecules are released from the fields of the ions. Frank and Evans[70] have suggested that in aqueous solutions, water molecules are orientated around the ions forming an "iceberg", the process being similar to the partial freezing of a liquid. When a complex is formed, there is a breakdown of this structure and a resulting entropy change favouring complex formation. Entropy may be regarded as a measure of the disorder of the system and the positive entropy change in reaction (47) is illustrated in Table XXIX where data are given for uni-univalent, di-divalent and tri-tri-valent associations. Williams[81] has shown that for reactions such as those depicted above and in the formation of complexes between charged ions and neutral molecules where the sum of positive and negative charges in the solution remains the same throughout, in almost all cases examined the entropy change was favourable. Comparisons between reactions can only be made when there is the same change in the number of solute species, a factor which was not taken into account by Williams.

For equilibrium (47) the entropy change may be expressed in terms of a cycle[82]

$$\begin{tikzcd}
\underset{(g)}{M^{a+}} & + & \underset{(g)}{X^{b-}} \arrow[r, "\Delta S_g(3)"] & \underset{(g)}{MX^{(a-b)+}} \arrow[d, "\Delta S_{Hyd}(4)"] \\
\underset{(aq)}{M^{a+}} \arrow[u, "\Delta S_{Hyd(1)}"] & + & \underset{(aq)}{X^{b-}} \arrow[u, "\Delta S_{Hyd}(2)"] & \underset{(aq)}{MX^{(a-b)+}} \arrow[l, "-\Delta S_{assoc}"]
\end{tikzcd}$$

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 $\Delta S_g(3)$ is the change on a association in the gas phase. The observed entropy change on association in solution may be written:-

$$\Delta S_{assoc} = \Delta S_{Hyd(1)} + \Delta S_{Hyd(2)} + \Delta S_g(3) + \Delta S_{Hyd(4)} \qquad (52)$$

In the gas phase, the entropy change includes both rotational and translational terms

$$\Delta Sg(3) = S_{trans}(MX^{(a-b)+}) + S_{rot}(MX^{(a-b)+}) - S_{trans}(M^{a+}) - S_{trans}(X^{b-}) - S_{rot}(X^{b-}) \text{ ----------}(53)$$

S_{trans} for monatomic ions and diatomic molecules may be obtained 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 (or molecular) weight of the ion. For symmetrical non-linear anions, (e.g. SO_4^{2-}), $S_{rot}(X^{b-})$ may be obtained from the equation[83]

$$S_{rot}(X^{b-}) = 2.2868\ (3 \log T + 3 \log I_A - 2 \log \sigma) + 267.52$$

where I_A is the moment of inertia about the bonds (S - O in this case) and σ is the symmetry number. For an ion-pair which can be considered as a linear molecule,

$$S_{trans}(MX^{(a-b)+}) + S_{rot}(MX^{(a-b)+})$$

$$= 2.2868\ (7 \log T + 3 \log M + 2 \log I_B - 2 \log \sigma) - 6.661$$

where I_B is the moment of inertia about its axis. For rigid molecules which are not linear, the equation used is

$$S_{trans}\,(MX^{(a-b)+}) \;+\; S_{rot}(MX^{(a-b)+})$$

$$= 2.2868\ (8 \log T + \log I_A I_B I_C + 3 \log M - 2 \log \sigma) - 7.697 \text{ -------------} (54)$$

The product $I_A I_B I_C$ of the principal moments may be evaluated by solving the determinant

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

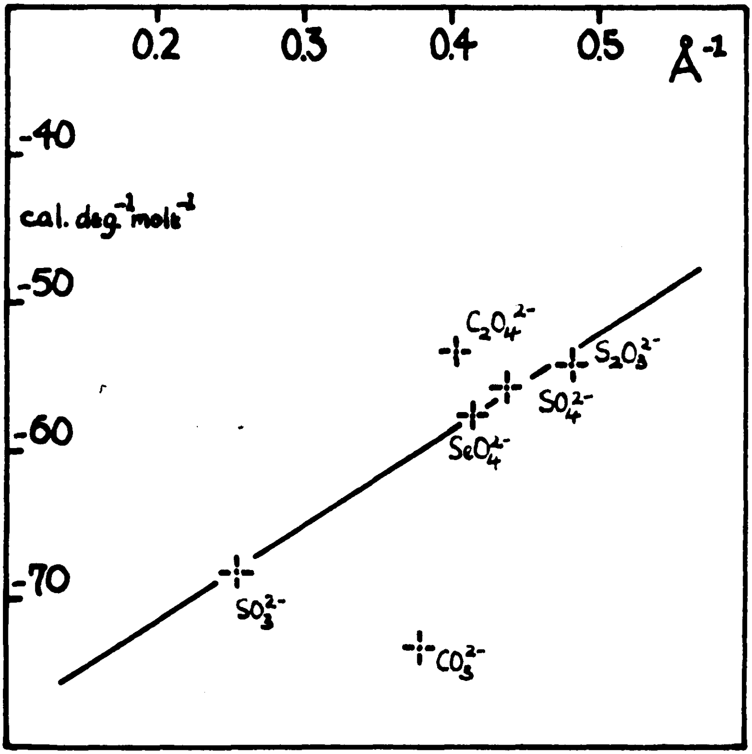
Where I_{xx} and I_{xy} etc. are the moments and products of inertia with respect to a co-ordinate system having the centre of mass as origin, i.e.

$$I_{xx} = \sum_i m_i \quad (y_i^2 + z_i^2) \text{ ----}$$

$$I_{xy} = \sum_i m_i \quad x_i \cdot y_i \text{ ----}$$

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

In the case of the oxalate and succinate anions,



PLOT OF $\Delta S_{Hyd}(2)$ AGAINST r_{-Hyd}^{-1}

Fig. 17

the ions were assumed to be planar and the interatomic distances used in calculations were those in the solid phase.[85] Values of the entropies of free ions required in the calculation of $\Delta S_{Hyd}(1)$ and $\Delta S_{Hyd}(2)$ were obtained from Latimer, " Oxidation Potentials ", Prentice-Hall, New York, 1952. To evaluate $\Delta S_{Hyd}(2)$ for the succinate anion a plot was used of $\Delta S_{Hyd}(2)$ against the reciprocal of the hydrated anionic radius (r^{-1}_{-Hyd}) for a series of divalently charged anions. r^{-1}_{-Hyd} was obtained using the formula of Jenkins and Monk[84], $r^{-1}_{-Hyd} = 9.16 \times 10^{7}.z/\Lambda^{o}_{1}$ at 25°C, where Λ^{o}_{1} is the limiting ionic mobility of the ion. $S_{(g)}(A^{=})$ was found using the Sackur-Tetrode equation for SO_4^{2-}, CO_3^{2-}, $C_2O_4^{2-}$, SeO_4^{2-}, SO_3^{2-} and $S_2O_3^{2-}$ ions. The corresponding conductivity data for the ions are given in references 86-91 respectively. Latimer's values of $S^{o}_{(aq)}(A^{2-})$ were used to calculate $\Delta S_{Hyd}(2)$ from $S^{o}_{(aq)}(A^{2-}) - S_{(g)}(A^{2-})$. The plot of $\Delta S_{Hyd}(2)$ against r^{-1}_{-Hyd} is shown in Fig. 17 and a value of 62.9 cal./deg./mole for $\Delta S_{Hyd}(2)$ for the succinate anion was interpolated using ionic mobility data.[92] In the calculations involving the nickel and cobalt ions, Latimer's values of -38.0 and -27.0 for $S^{o}_{(aq)}(M^{2+})$ have been replaced by those of Staveley

TABLE XXX

Thermodynamic Properties ^{x}

Ion-pair	S_g(MA)	ΔS_{assoc}	S^o(MA)	$-\Delta S_{Hyd}$(4)	r_+^{-1} (Å^{-1})
NiOx	70.0	24.7	13.9	56.1	1.37
CoOx	70.0	23.9	14.1	55.8	1.35
MnOx	69.9	22.9	15.1	54.8	1.28
NiMal	70.3	24.8	7.3	63.0	1.37
CoMal	70.3	25.8	9.3	61.0	1.35
MnMal	70.2	26.8	12.3	57.9	1.28
NiSucc	70.6	18.2	1.1	69.5	1.37
CoSucc	70.6	19.5	3.5	67.1	1.35
MnSucc	70.5	20.3	6.2	64.4	1.28

x Entropies in cal./deg./mole.

Malonate data from reference 38.

TABLE XXXI

Thermodynamic Properties [x]

Ion-pair	S_g(MA)	ΔS_{assoc}	S^o(MA)	$-\Delta S_{Hyd}$(4)	$(r_+ + r_-)^{-1}$ ($\mathring{A}^{-1}$)
$CaOH^+$	53.8	10.8	-4.8	58.6	0.397
$SrOH^+$	56.0	7.6	-4.3	60.3	0.376
$BaOH^+$	58.4	8.8	9.3	49.1	0.347
VOH^{2+}	53.7	45.5	-22.0	75.7	0.457
$FeOH^{2+}$	53.9	44.0	-23.2	77.1	0.469
$CrOH^{2+}$	53.8	-	-16.4	70.2	0.462
TlOH	58.8	5.1	33.0	25.8	0.352
TlCl	60.9	-1.7	41.9	19.0	0.308
TlBr	62.8	-4.2	45.5	17.3	0.295
$TlNO_3$	80.4	-1.0	64.4	16.0	0.289
AgCl	58.9	6.0	36.5	22.4	0.326
$MgSO_4$	68.2	26.1	2.0	66.2	0.26
$CaSO_4$	69.5	16.1	7.0	62.5	0.24
$MnSO_4$	70.1	22.6	6.7	63.4	0.25
$CoSO_4$	70.2	16.6	-1.0	71.0	0.255
$NiSO_4$	70.2	21.7	3.0	67.0	0.256
$ZnSO_4$	70.3	24.4	3.0	67.3	0.257

[x] Entropies in cal./deg./mole.

and Randall[39] of -23.0 and -22.0 respectively. In evaluating $S_{(g)}$(MA) for the oxalates, a non planar model was used for the complex species in which the M--O and oxalate planes were at an angle of 101°. In the case of the succinates, a seven membered planar ring was used to simplify calculations. Substitution of entropy values in equation (52) gave ΔS_{Hyd}(MA) the hydration entropy of the ion-pair. Entropy data are given in Tables XXX and XXXI.

Powell and Latimer[93] have shown that since there is an entropy decrease when water molecules are held in the field of an ion, there is a relationship between the partial molar entropy S^o of the ions and their size and charge. For a large number of simple monatomic ions, this behaviour may be described by the equation

$$S^o = 3/2 \; R \ln M + 37 - 270z/r_e^2 \qquad (55)$$

Where z is the ionic charge, M the atomic weight and r_e the "effective ionic radius" which includes corrections for the hydration sheaths of the ions. The correlation of S with the first power of z is in disagreement with the Born electrostatic picture which requires dependence on z^2/r. Recently, Laidler[94] has shown that Gurney's value $S^o_H = -5.5$ cal.deg.$^{-1}$mole^{-1} is better than the normally assumed value of zero. He found that for all monatomic cations

$$S^o_{(abs)} = 3/2 \ R \ln M + 10.2 - 116z^2/r. \quad \text{-----(56)}$$

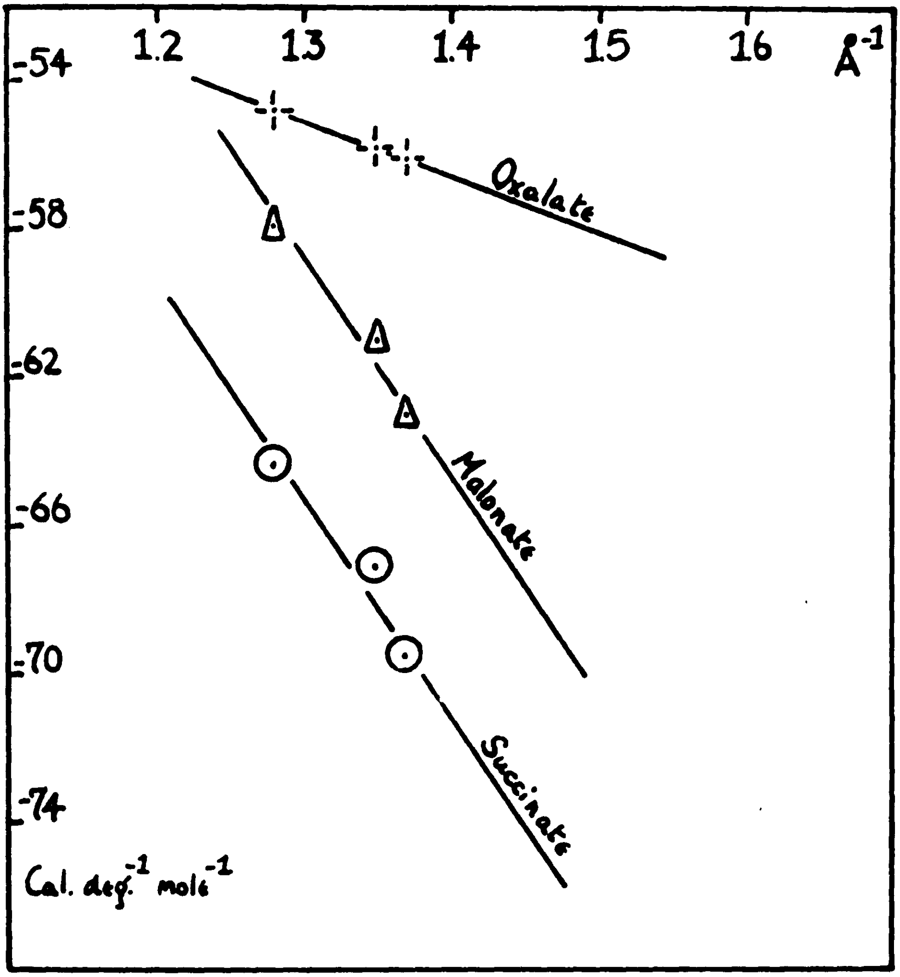
Cobble[95] has extended the method to complex inorganic ions by taking into account the number of water molecules displaced from the hydration shell of the cation on ion association and by introducing a factor arising from the open structure of the complexes.

Much of the thermodynamic data available in the literature deals with the reactions between weak acid anions and protons and there is seen to be some regularity in ΔS values which are of the order of 20 cal.deg.$^{-1}$mole^{-1}. The value for the association of hydrogen and glycine ions is somewhat less due to the neutral zwitterion structure which exerts a strong effect on the solvent molecules. Although complexing reactions have been much less studied, it may be noted that there is the expected trend towards larger ΔS values as the charge on the ions increases. The values found for divalent transition metal sulphates[11] lie between 16 and 26 cal.deg.$^{-1}$mole^{-1} and values obtained in this work for both oxalates and succinates are within these limits. The smaller ΔS values for succinates confirm the view of Davies[19] that in larger membered rings there may be some residual electrostatic charges which would cause some ordering of the water molecules. This effect is not seen in the oxalates where the stable chelated five membered ring is formed, the almost complete neutralisation of charge being reflected in the higher entropy changes.

If a series of similar reactions is considered then $\Delta S_g(3)$ may be considered as constant, so that the observed S_{assoc} would then depend on differences in hydration effects. i.e. $\Delta S_{Hyd}(1) + \Delta S_{Hyd}(2) + \Delta S_{Hyd}(4)$. If a single cation associates with various simple anions then $\Delta S_{Hyd}(1)$ is constant and $\Delta S_{Hyd}(4)$ remains approximately the same so that a relationship might be expected between the hydration entropy of the anion and the observed entropy. In their study of the ethylenediaminetetraacetates, Stavely and Randall showed that differences in ΔS_{assoc} were due to variations in $\Delta S_{Hyd}(4) - \Delta S_{Hyd}(1)$ and that $\Delta S_{Hyd}(1)$ could arise from interactions of the ions and water molecules in two ways; (a) between the ion and the molecules displaced when the complex is formed and (b) between the ion and more remote solvent molecules. Entropy effects due to (a) will however be independent of ionic size and electronic structure whereas those from (b) will vary from ion to ion so that a relationship between ΔS and ionic radius might result. They observed a direct linear relationship for divalent metal ethylenediaminetetraacetates, but one which was curved for trivalent ions.

Nancollas[15], using the data of Staveley and Randall, plotted ΔS against $-\Delta S_{Hyd}(1)$ and obtained a single reasonable linear relationship which included all charge types.

Latimer[96] has found that a plot of ΔS_{Hyd} against z/r' for various cations and anions gave a curve consisting of two linear relationships, one for univalent ions and the other for ions of higher charge. r' is a corrected radius which for cations is $r_{cryst} + 0.85\text{Å}$ and for anions in $r_{cryst} + 0.1\text{Å}$. Duncan,[97] in a paper in which the relationships between ionic parameters and standard thermodynamic quantities are discussed in detail, has shown that under certain conditions ΔS varies with r_{M+}^{-1}



Plots of $\Delta S_{Hyd}(4)$ against r_+^{-1}

Fig. 18

although enthalpy changes yield no systematic dependence of this kind.

George[98] has recently indicated that good linearity is derived using the equation

$$\Delta S = \Delta S_{Hyd}(2) + \text{Constant}$$

the value of the constant changing from +10 in the case of ferric ion association with univalent anions to -40 for acetate ion reacting with divalent alkaline earth cations. Nair and Nancollas[11] calculated $\Delta S_{Hyd}(4)$ and found that a linear relationship was given for uni-univalent ion pairs when plotted against $(r_+ + r_-)^{-1}$ and similar plots for other hydroxide complexes carrying a residual positive charge confirmed this. Using entropy data from the present work, it is seen (Fig.18) that linear plots of $\Delta S_{Hyd}(4)$ against r_+^{-1} for both oxalates and succinates were obtained. The variation of ΔS_{assoc} with r_+^{-1} is however important in that for the oxalates the observed entropy change decreases in the expected direction with the reciprocal of the cationic radius whereas with the succinates there is an increase. As far as this is significant it would seem that $\Delta S_{Hyd}(4)$ and not ΔS_{assoc} should be used in correlations with the ionic radius. In each system studied, ΔS_{assoc} increased with temperature reflecting the greater freedom of the solvent molecules when released from the ions at higher temperatures. The values at 0°C and 45°C are

Complex	ΔS_{assoc}	
	0°C	45°C
NiOx	21.0	28.2
CoOx	22.0	25.8
MnOx	18.6	27.0
NiSucc	15.2	21.5
CoSucc	14.1	24.8
MnSucc	16.1	24.5

the entropy units being in cal.deg.$^{-1}$mole^{-1}.

Association entropies can yield qualitative information about the reactions. When an ion-pair if formed without the elimination of water molecules ΔS_{assoc} is less positive than expected. This is seen for certain 3 : 3 - valent ion-pairs in that a greater entropy change would be expected (see Table XXIX). The smaller values for the formation of lanthanum ion-pairs may be understood if solvent molecules in the first co-ordination sphere of the cation are not released.

Heat changes in complex formation are dependent on the hydrated nature of the complex and ions involved. Williams[81] has shown that the heat of formation of a complex can be described by the equation

$$\Delta H = Az/r_+ + BI_{02} - C/r_+^3$$

where I_{02} is the ionisation potential of the cation. If comparisons are made between K values at a given temperature it is implied that the free energy change is dominated by the heat term and that $T.\Delta S$ may be neglected. This may be taken to be the case for complexes involving uncharged ligands where the influence of the entropy term is small. For charged ligands, however, the entropy change becomes significant (Table XXIX) and the heat of reaction opposes complex formation, the complex being stabilised by the entropy term. In all the present results heat changes also oppose the association reactions and account for the wide variations in K. Cotton and Harris[101] have compared heat changes in the formation of five and six membered chelate rings and have shown that for the latter there is a relatively higher heat contentdue to distortion from a sterically ideal structure. This has been confirmed in the present study where an increase is seen on comparison of ΔH values for corresponding oxalates and succinates.

Irving [21a] has also shown that the heats of formation of complex diamines are dependent on the chain length of the ligand and the nature of the metal atom and contribute as substantially to the free energy change as do the various entropy terms.

A cycle similar to that used in the entropy calculations has been proposed to describe the heat changes on complex formation. No simple relationships have, however, been found between the heats of hydration of the ions and ionic parameters as was done for the entropies. Subsequent work using direct calorimetric method,[17, 101, 39] has shown that there are no obvious regularities in the values. ΔH values seem to be dependent on covalent and electrostatic interactions between the ions together with some stabilisation due to the different available bonding orbitals of the cation.

Plots of log K against T^{-1} for both the oxalates and succinates showed marked curvature indicating a non zero ΔCp. Values have been derived from ΔH measurements and since these are subject to a degree of uncertainty, ΔCp's are even less reliable although it is possible to obtain their order of magnitude. Studies on the variations of weak acid dissociation constants with temperature have frequently indicated positive ΔCp values but these are the first instances of this occurring in metal complexing equilibria, although Postmus and King[69] obtained a value of ΔCp = 70 cal.deg.$^{-1}$ for the association in acid solutions of tervalent chromium with the thiocyanate ion. This value may be compared with 35 to 45 cal.deg.$^{-1}$ for a number of reactions between hydrogen ions and acid anions, the difference probably being due to the higher charge of the cation. In the oxalates and succinates the values are intermediate indicating a trend towards greater ΔCp with increasing charge although cobalt oxalate seems to be anomalous in this respect.

PART IV

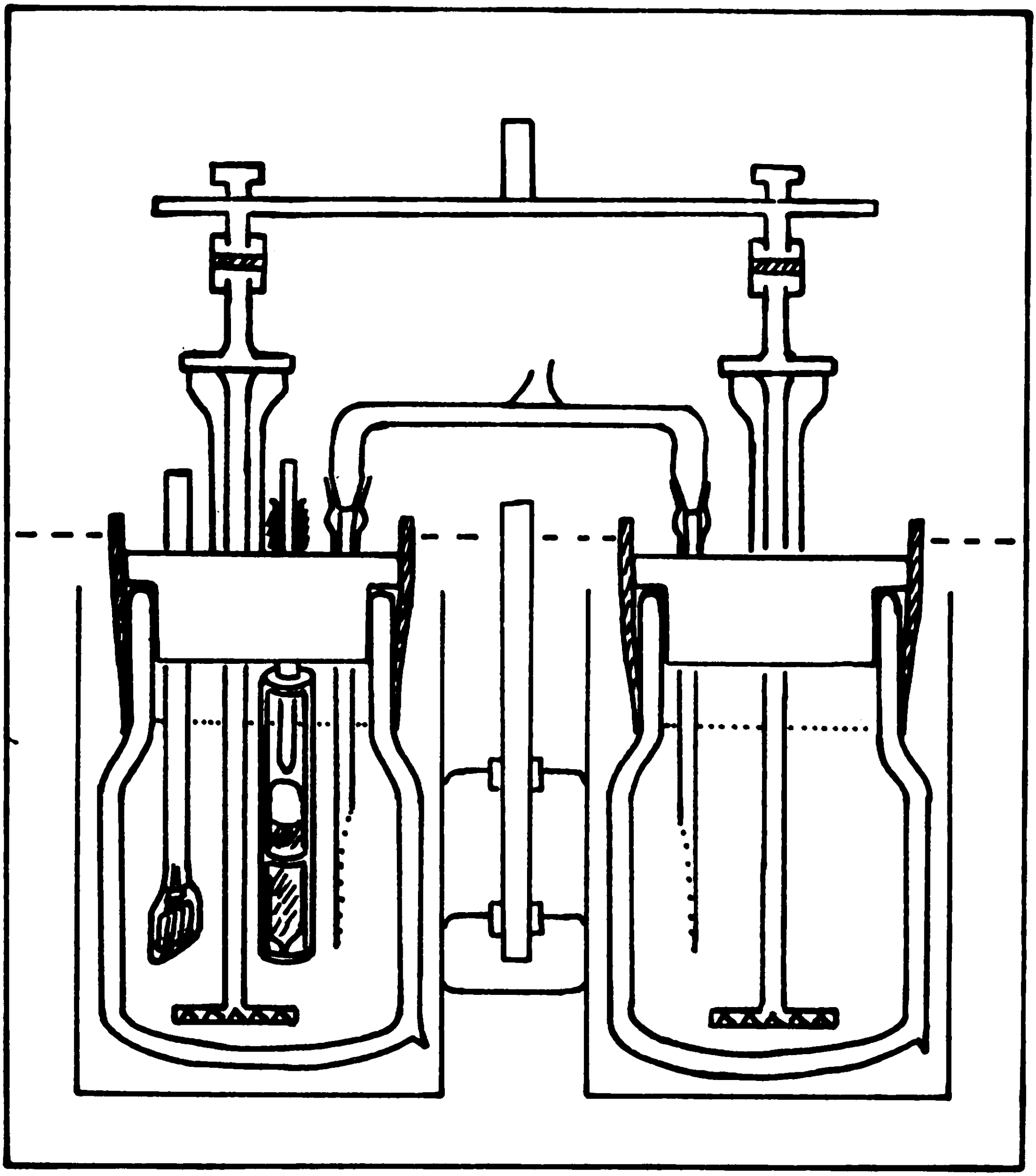
THE HEAT OF FORMATION OF MANGANESE MALONATE

It has long been recognised that if a true picture of the energy changes involved in complex formation is to be given, accurate values of heat and entropy changes are essential. There are two methods of determining ΔH: (a) by direct calorimetry and (b) using temperature coefficient data. In part II the latter method was used to evaluate heat changes for metal oxalates and succinates. This method has been employed much more widely than (a) although it is less reliable. The use of a large temperature range reduces to some extent the errors involved and good agreement has been obtained between e.m.f. and calorimetric determinations of the heat of formation of the bisulphate ion.[11, 68]

Heat changes in complex formation are important since they depend both on the nature of the final complex and on the nature of the hydration of the ions involved in the reaction. Relationships have been introduced[81] in which heats of formation have been described in terms of ionisation potentials and ionic radii.

Various methods of determination have been used. Rossini, Pitzer et al,[102] (as part of the American Petroleum Institute Research Project No.44) derived much thermodynamic data for the hydrocarbons using bomb calorimetry which has now advanced to a high degree of accuracy. For ionic reactions in solution, Staveley and his associates[101] have used a Dewar vessel, with a resistance thermometer and a rotating stirrer, containing a small phial of solution. Ciampolini and Sacconi[17] have extended this method in their study of diamine complexes. Lange[103] has introduced a system of twin adiabatic calorimeters designed to detect minute heat changes, having in each vessel a section of a 1500 junction thermocouple. This instrument was maintained in a water bath controlled to ± 0.0002°C and was used to yield information on heats of dilution. The design used in the present investigation was similar to that of Lange although the stirring was vibro-rotatory with both calorimeters being stirred at exactly the same speed. One calorimeter held the solution and the phial whilst the other contained an exactly equivalent weight of water.

The heat of solution of potassium chloride has been measured to test the accuracy of the apparatus and the heat of formation of manganese malonate has been determined at low concentrations. Comparison is made between this result and that obtained from temperature measurements by Nair and Nancollas.[38]



CALORIMETER WITH FITTINGS

Fig. 19.

APPARATUS

The calorimeter consisted of two Dewar Flasks, held in a metal cradle. Into one was fitted a phial of solution (or solid), a heater, a stirrer, and one end of a thermocouple and in the other an exactly similar stirrer and the other thermocouple junction. (Fig. 19) A special stirring head was constructed such that both vessels were stirred at exactly the same speed and the thermocouple e.m.f. was read using a sensitive galvanometer to ± 0.05 microvolts.

The Dewar Flasks

These were silvered vessels of 500 c.c. capacity. A tightly fitting rubber sheath was attached with Araldite to the outside of each, so that about two inches of sheathing overlapped the rim; each Dewar was fitted with a tightly fitting polythene bung. Four holes accomodated the tube attached to the heater, the stirrer diaphragm, the neck of the phial cradle and a glass tube having a B.19 socket attached to it, into which was fitted one arm of the thermocouple. The bung was usually smeared with vaseline to ensure a perfect water seal. When in position, the sheathing covered the stopper by abcut ½" and the vessels and stoppers were totally immersed in the thermostat.

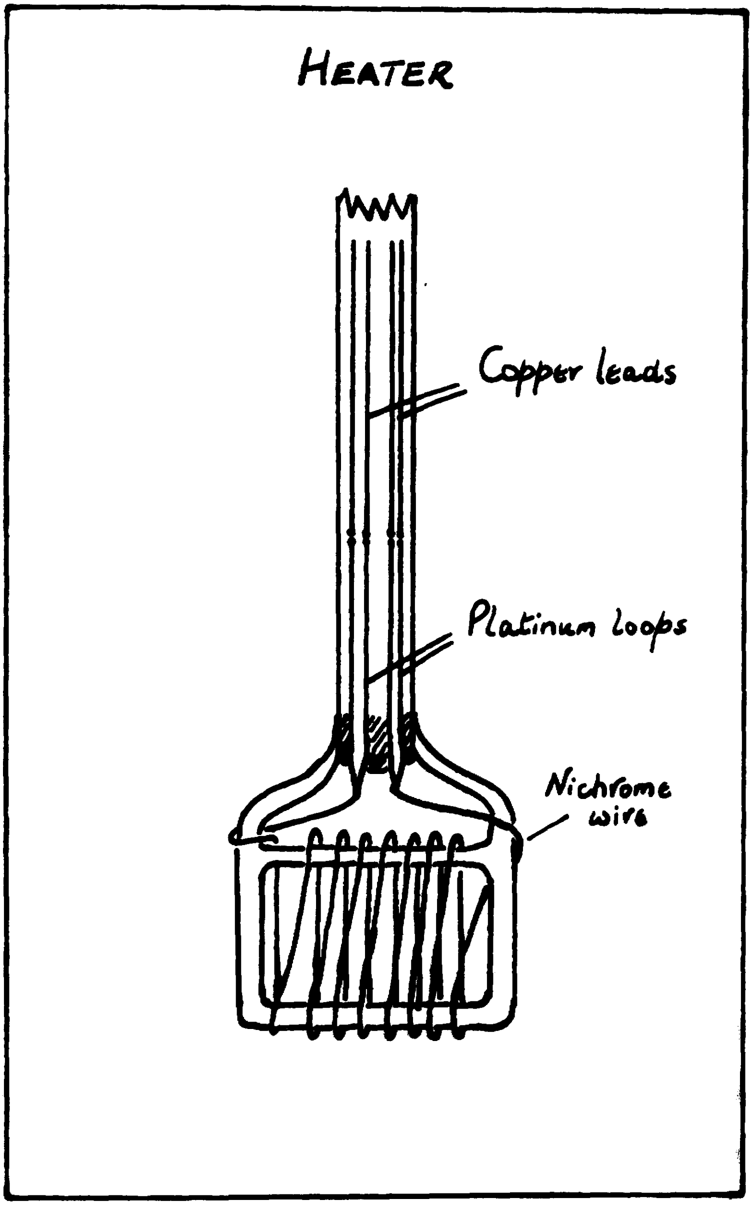


Fig. 20.

The Thermocouple.

This consisted of 30 junctions of cloth-covered constantan wire, 20 S.W.G., and enamelled copper wire 34 S.W.G. The copper was wrapped round the constantan and the junctions, which were made by soft soldering, were arranged alternately in the two vessels so as to be at about ½ cm. intervals throughout their depths.[104] The wires and thermojunctions were insulated by coating with Araldite, and nylon thread was used to bind them together before a further coating of Araldite was applied. The rest of the thermopile was bound with P.V.C. tape and a B.19 ground glass joint was affixed to each arm such that when these were fitted into the sockets on the calorimeter bungs the thermocouple was at the correct height in the vessel.

The Heater.

A pyrex glass tube 8 mm. in diameter was flattened at one end and a small glass former 1" x 1½" was sealed to it. Two 'U' shaped pieces of platinum wire soft soldered at their ends to copper leads were placed in position at the constricted end of the tubes (Fig.20). About twenty windings of nichrome wire (8 ohms per foot) were wound round the former, the ends being spot welded to the platinum loops.

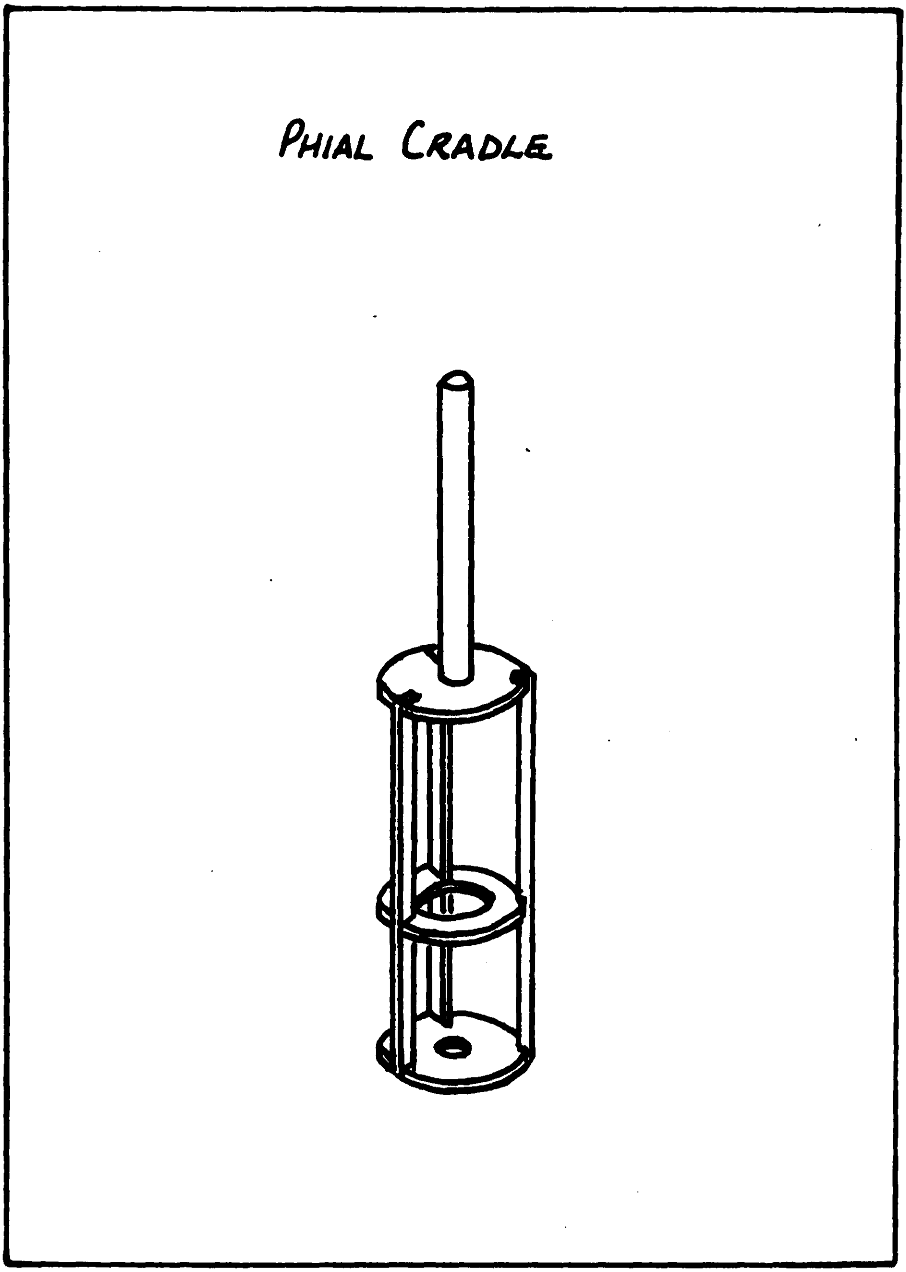
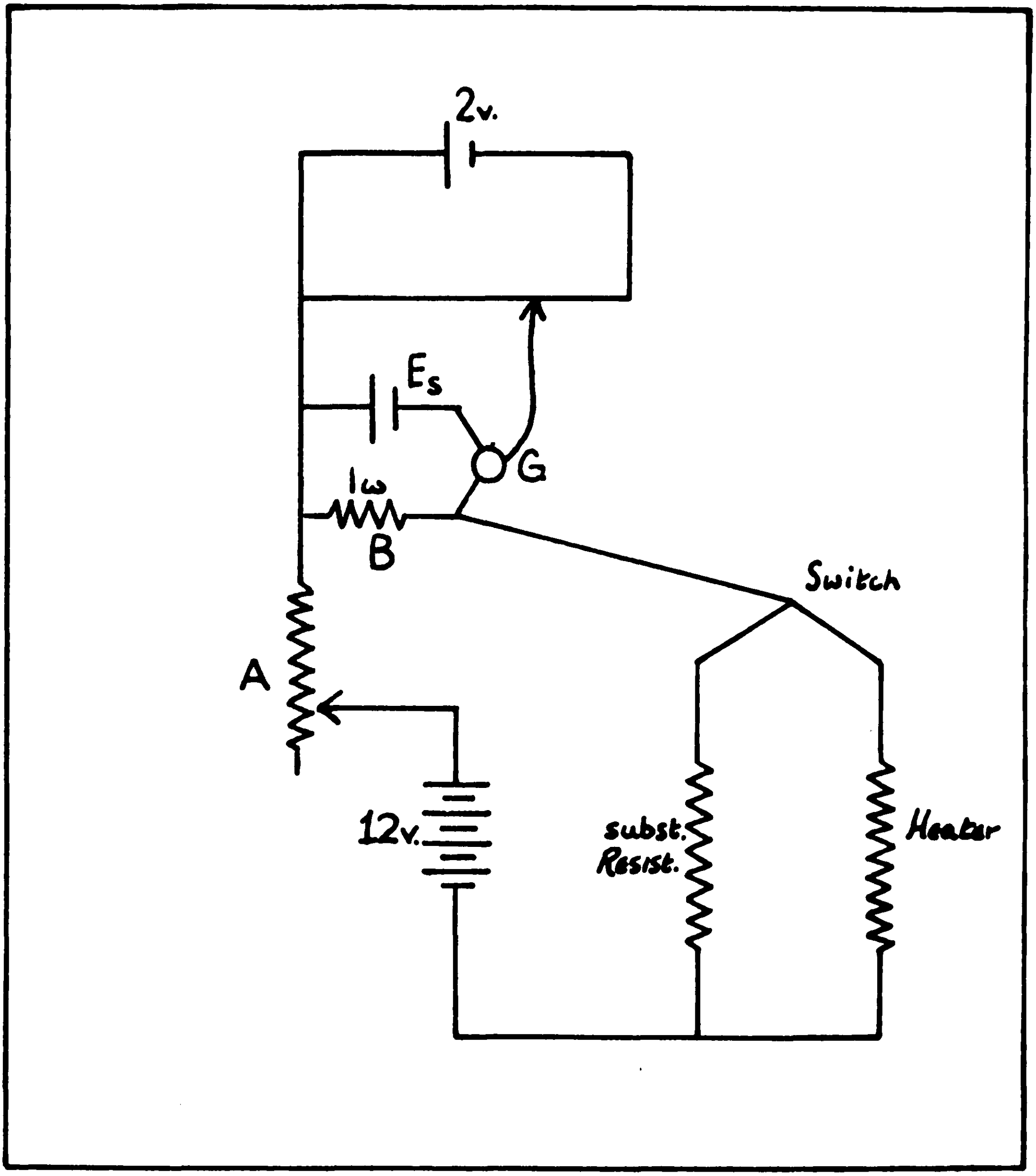


Fig. 21.



HEATER CIRCUIT

Fig. 22.

The whole was then coated with a dilute Araldite solution (Araldite 123A and hardener B.951) and finally waterproofed with a coating of "Formvar" in ethylene dichloride. The resistance of the heater was found to be about 15 ohms. (Table XXXII).

Phial Cradle

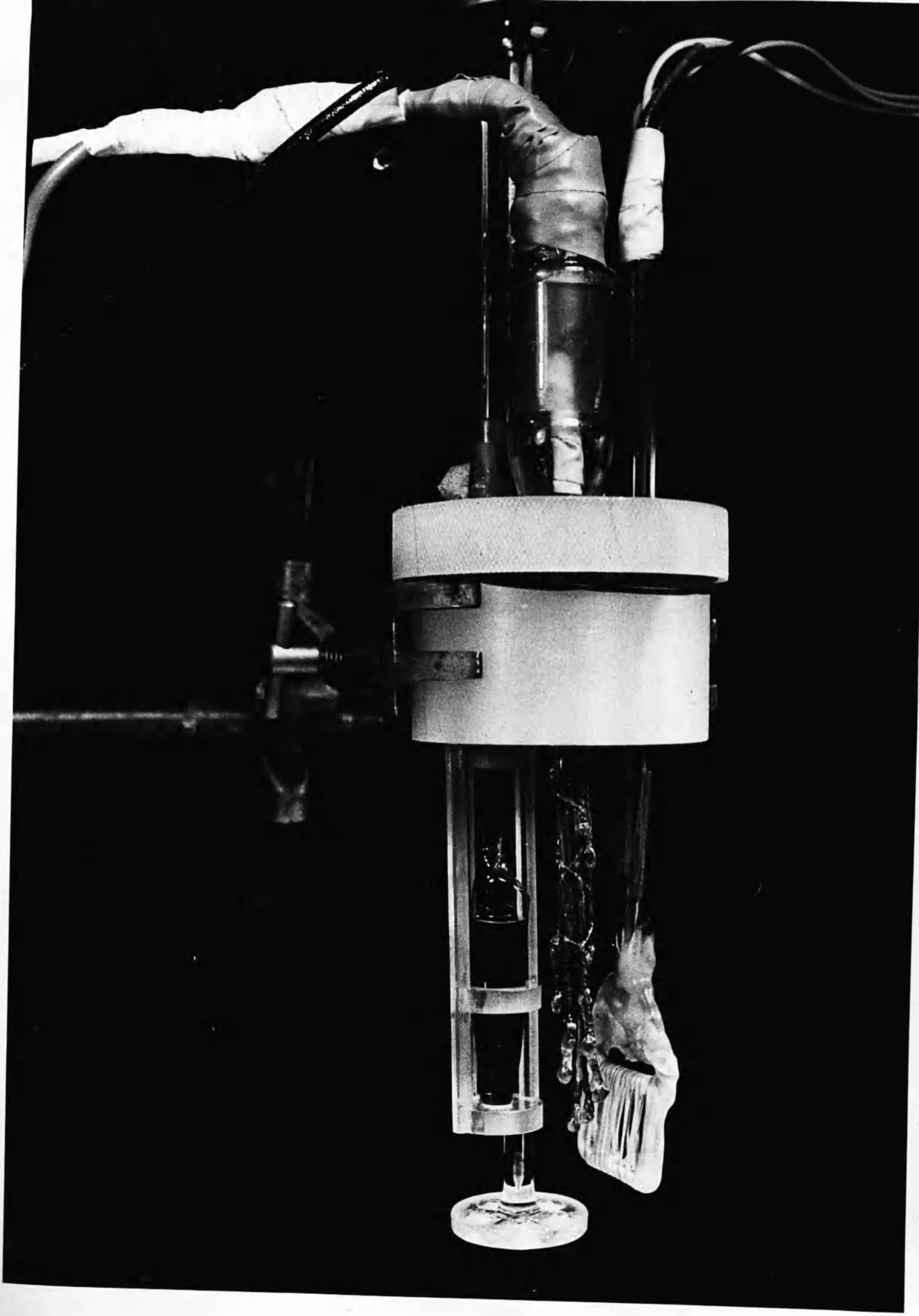
This was made of perspex and is shown in Fig.21. The neck of polythene tubing was 8 cms. long and 4mm. internal bore. The supports and discs were held in position using a solution of perspex in chloroform. Small glass phials about 2½" long and ⅝" diameter and about 5cc. capacity were made by drawing out very thin glass tubing. The phial crusher was a piece of glass rod 3mm. in diameter, operated through the central perspex tube, slightly tapered at one end.

Heating Circuit

This is similar to that of Pitzer[68] and is shown in Fig.22. The current in the circuit was regulated using a pre-set wire wound 100 ohm potentiometer A. The standard 1 ohm resistance B, and the standard cell, E_s, were maintained in an oil bath at 25°C. A 'Scalamp' galvanometer, G, was used in conjunction with the Croydon Vernier potentiometer to measure the voltage drop across the resistance standard. A small switch box was constructed so that by means of a two-pole

PLATE II

CALORIMETER BUNG WITH FITTINGS



three way switch the heater or substitute resistance could be put in circuit. The 'dummy' resistance was the same as that of the heater, and was made from the same nichrome wire wound on a 'paxolin' former. In use, the current was allowed to flow for three hours before each run with the 'dummy' resistance in series to allow the 12 volt battery to settle.

A holder was constructed (Fig.19) into which the calorimeters were placed during the run. This consisted of two aluminium cylinders, with holes punched in the sides to allow circulation of the thermostat water around the Dewars. The holder was clamped in position in the tank to the level shown in the figure. The stirring rods were connected to a specially constructed dual chuck which allowed both stirrers to be used under exactly the same conditions, so that any heating effects from this source were balanced. The stirrer was of the vibro-rotatory type (Vibro-Mischer, Messrs.Shandon and Co. Ltd., England.) The thermostat used was that described in Part II. the temperature control being ± 0.005°C.

A precision Vernier potentiometer (Cambridge Instrument Co. Ltd., Cambridge, England) having a three dial system was used to measure e.m.f.s. The overall range of the instrument was 1.9v to 0.1 microvolts, in three ranges, each of which had a separate standard cell calibration.

Using a sensitive, spot reflecting moving coil galvanometer of 25 ohm resistance, in conjunction with a lamp and scale at a distance of one metre, it was possible to detect changes of ± 0.05 microvolts.

In some early experiments, two platinum resistance thermometers were used as part of a Wheatstone bridge circuit but these were neither as stable nor as sensitive as the thermocouples.

		voltage	resistance
100 ohms	[illegible]	1.7[illegible]	100.000
ohm		[illegible]	1.00097
[illegible] (standard)		0.[illegible]	1.0082
[illegible]ster		[illegible]	15.620
100 ohms	[illegible]	[illegible].71169	100.000
[illegible]		0.017127	1.000[illegible]
[illegible] (standard)		0.017147	1.0081
[illegible]		0.26842	15.607

EXPERIMENTAL

Calibration of standard and heater resistances.

Two N.P.L. checked resistances of 1 and 100 ohms respectively, known to better than 0.05%, were used in accurate determinations of the heater and standard resistances. The current used was varied over a range from 10 to 100 mamps and a typical experiment is summarised in Table XXXII. The 100 ohms resistance was taken to be exactly 100.0000 ohms and values corresponding to this were used.

TABLE XXXII

1 = 0.0171 amp.

		voltage	resistance
100 ohms	tested	1.71153	100.0000
1 ohm		0.017132	1.00097
1 ohm (standard)		0.017152	1.0022
heater		0.26851	15.688
100 ohms	tested	1.71109	100.0000
1 ohm		0.017127	1.00094
1 ohm (standard)		0.017147	1.0021
heater		0.26842	15.687

The mean values for the 1 ohm standard and the heater resistances were 1.0021 and 15.687 ohms respectively.

Heat Measurements

The potassium chloride, manganese chloride and malonic acid used were of 'AnalaR' quality. Preparation and analysis of stock solutions of the metal chloride, sodium hydroxide and malonic acid have been described in Part II. All solutions were made using distilled water.

In experiments to determine the heat of solution of potassium chloride, equal portions of distilled water which had previously been allowed to equilibrate at 25°C for some hours were weighed into each vessel. A small phial containing 1 - 3 grams of solid potassium chloride was sealed by drawing out in a flame and the calorimeters were set up as shown in Fig.19. After being allowed to settle at 25°C overnight, and after the current in the 'dummy' heating circuit had become steady, e.m.f. readings were taken at minute intervals and the experiment was started when readings had been constant for at least ten minutes. First the water equivalent of the calorimeter was determined by heating for about 2½ - 3 minutes, the voltage drop across the standard 1 ohm resistance being read every 30 seconds to ensure that a steady heating current was flowing. Timing of the current was done using a stop-watch accurate to ± 0.1 sec. The change in thermocouple e.m.f. was noted and when the readings became

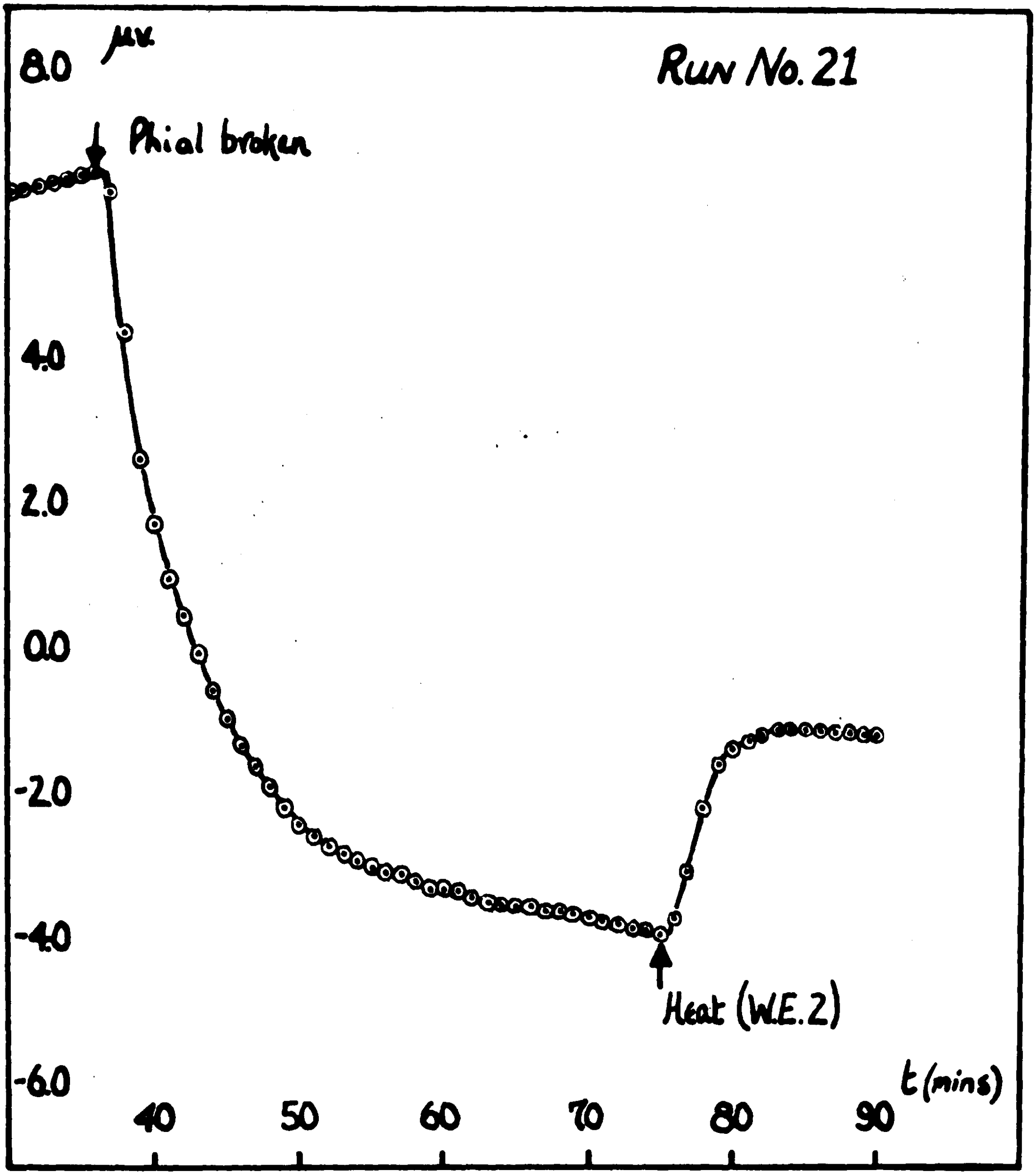

μv.
8.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
Run No. 21
Phial broken
Heat (W.E.2)
t (mins)
40
50
60
70
80
90

Fig. 23.

steady again (usually after about 8 minutes) the phial was crushed, and the time for complete dissolution of the solid varied with the quantity present. A further determination of the water equivalent was made after the e.m.f. had become steady again. A typical graph of the voltage against time is given in Fig.23.

For the heat of formation of manganese malonate, about 3 - 4 grams of metal chloride stock solution were placed in the phial which was then sealed, and the calorimeters, one containing known quantities of malonic acid and sodium hydroxide solutions, and the other the equivalent weight of water, were set up as before. The heat change and water equivalent were then measured as described above.

The effect of the dilution of the manganese chloride stock solution was examined in an experiment in which the heat of dilution was measured; this was found to be negligible. Following Sacconi et al[17] the heat of dilution of the malonic acid solution by the water in the metal chloride solution was taken to be zero. In some early potassium chloride runs it was found that there was a slight heating effect on crushing the phial and the extent of the correction to be applied was found from blank experiments in which water alone was used.

Method of calculation

Evaluations of water equivalents and heats of solution were made using the procedure of Eitel.[105] In Fig.24, the graphical reproduction of part of the course of heat of solution of potassium chloride experiment is shown and corrections for heat loss ('leakage') are made on the basis of the Regnault-Pfaundler formula. The small scatter of experimental points is seen and temperature changes (expressed in microvolts) are recorded as a function of time (abscissae) measured from the start of the recorded readings.

A heat change was subdivided into three parts, the "Anterior", "Experimental" and "Rating" periods, the corresponding time and temperature variables being indicated by suffixes a, x and r. The first temperature reading θ_o was at time, T_o, and the substance was dropped into the solution at T_1, at which the temperature was θ_1. The cooling rate in the anterior period, v_a, was given by $(\theta_o - \theta_1)/T_a$, and the average temperature of the period was $\frac{1}{2}(\theta_o + \theta_1) = \theta_a$. The heat effect was given by the rise in temperature from θ_1 to the value θ_e at which the effect was exhausted, i.e., the curve of the temperature increase began to fade into the straight-lined rating period. The time interval

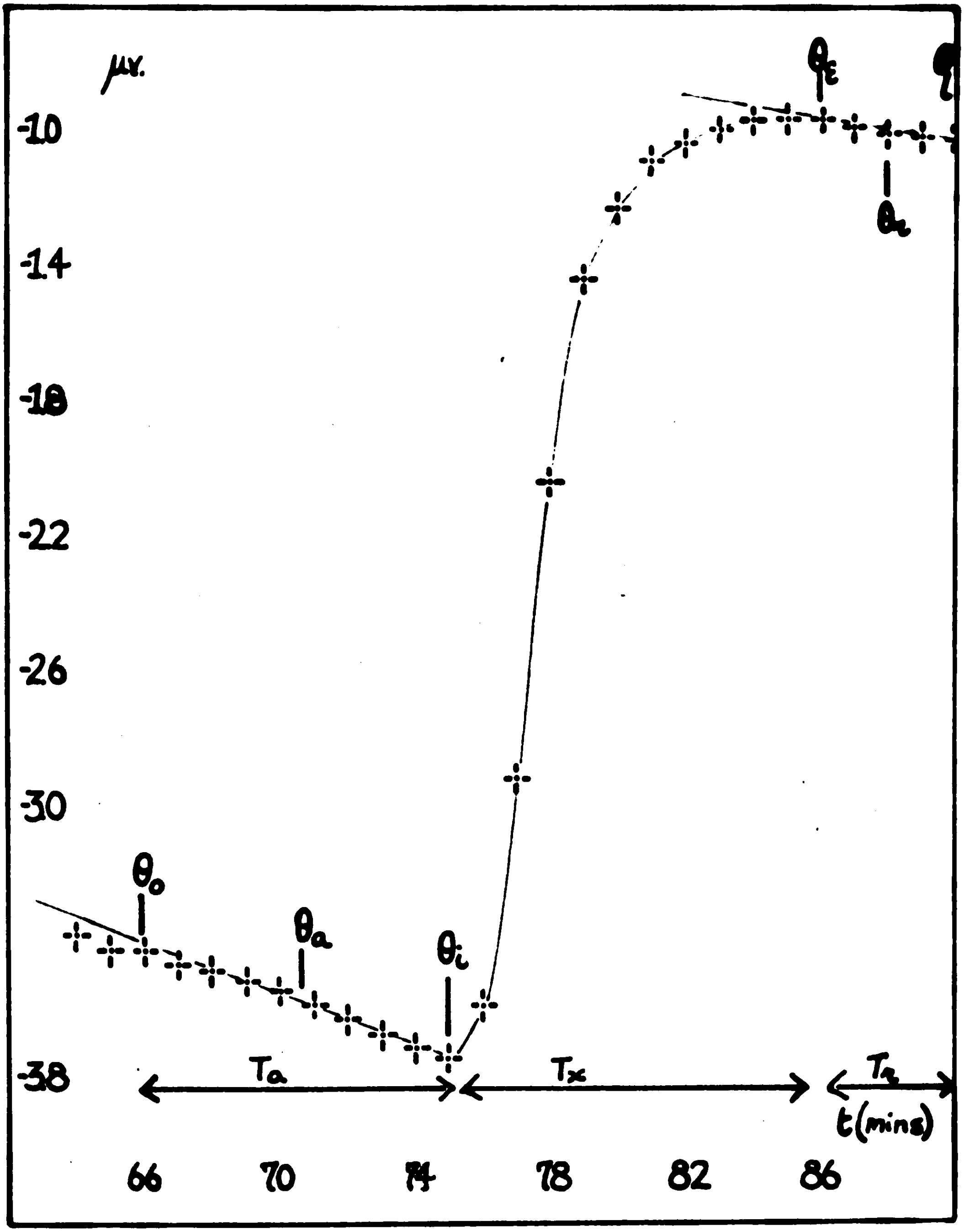


Fig. 24.

over this period was T_x. The rate of cooling, and the average temperature in the rating period were $(\theta_e - \theta_1)/T_r$ and $\theta_r = \frac{1}{2}(\theta_e + \theta_1)$ respectively.

The Regnault-Pfaundler formula for the correction for the observed rise in temperature, $\theta_e - \theta_1$, is given by

$$\partial\theta = T_x v_a + \frac{(v_r - v_a)}{(\theta_r - \theta_a)} \left[\tfrac{1}{2}(\theta_e + \theta_1) + \sum_{1}^{T_x - 1} \theta - T_x \theta_a \right]$$

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

and the corrected temperature increase,

$$\Delta\theta' = \partial\theta + \theta_e - \theta_1 .$$

The usual anterior and rating periods were of the order of ten minutes. The experimental periods were about twenty minutes for the solution of potassium chloride and about one minute for the formation of the complex.

RESULTS AND DISCUSSION

The heat of solution of potassium chloride has long been used as a standard in calorimetry, but although many values exist in the literature,[106, 107] they refer to experiments carried out at a wide variety of concentrations and temperatures. Staveley,[101] however, has recalculated some of the data, correcting it to a dilution of 1 mole of potassium chloride in 167 moles of water. In the present study, solutions contained 600 to 800 moles of water per mole of salt and corrections have been made, using Rossini's data[107] to Staveley's dilution. The values obtained are given in Table XXXIII; the mean, 4060 cals./mole, is about 3% lower than Staveley (4184), Rossini (4194) and Miscenko and Kaganovich[108] (4187).

TABLE XXXIII

Heat of solution of potassium chloride

Expt.	Wt.KCl	$\frac{\text{moles } H_2O}{\text{mole KCl}}$	$\Delta\theta'$ (μv.)	W.E.	ΔH	ΔHcorr.
7.	1.8012	789.4	8.32	11.57	3985	4014
10.	1.9840	709.6	8.70	12.40	4054	4064
11.	2.2485	627.3	10.18	11.98	4030	4030
15.	2.8991	454.9	10.95	14.56	4100	4060
21.	2.4106	548.2	9.58	14.03	4156	4126

Mean ΔH corr. = 4059 cal/mole.

In the manganese malonate experiments, the concentration of the complex was found from the total acid concentration, (where $A = C_3H_2O_4{}^{2-}$)

$$m_1 = [H_2A] + [HA^-] + [A^{2-}] + [MnA] \text{-----------} (57)$$

the total metal concentration,

$$m_3 = [Mn^{2+}] + [MnA] \text{-----------------------------} (58)$$

and the electroneutrality

$$[H^+] + [Na^+] + 2[Mn^{2+}] = 2[A^{2-}] + [HA^-] + 2m_3, \text{ --} (59)$$

the association constant $K = [MnA]/[Mn^{2+}].[A^{2-}].f_2^2$ and the dissociation constants k_1^a and k_2^a of malonic acid.[38, 42] In the calculation, the cubic equation

$$\frac{[H^+]^3 \, f_1^2.f_2}{k_1^a.k_2^a} + [H^+]^2 \left\{ \frac{f_1^2.f_2}{k_1^a.k_2^a} \left(\frac{2m_3}{1 + K[A^{2-}].f_2^2} + m_2 - 2m_3 \right) + \frac{f_2}{k_2^a} \right\}$$

$$+ [H^+] \left\{ \frac{m_3}{1 + K[A^{2-}].f_2^2} \left[\frac{2f_2}{k_2^a} + Kf_2^2 \right] + 1 + \frac{f_2(m_2 - m_1 - 2m_3)}{k_2^a} \right\}$$

$$+ \frac{m_3}{1 + K[A^{2-}].f_2^2} \left\{ 2 + \frac{2m_3.f_2^2}{1 + K[A^{2-}].f_2^2} + K.f_2^2.m_2 - 2Kf_2^2 \right\}$$

$$+ m_2 - 2m_1 - 2m_3 = 0$$

was given. Assuming in the denominators that $K.[A^{2-}].f_2^2$

can be neglected, $[H^+]$ was calculated and hence $[MnA]$. The results are shown in Table XXXIV.

TABLE XXXIV

Heat of formation of manganese malonate

Expt.	$10^3.m_1$	$10^3.m_2$	$10^3.m_3$	$\Delta\theta'(\mu v.)$	W.E.
3.	11.0693	11.0793	14.3754	0.42	9.4
5.	8.3879	11.8059	11.0393	0.81	8.02
8.	5.5882	7.4345	11.5589	0.42	9.44
9.	5.3152	7.9169	11.6169	0.53	9.4
10.	5.6596	8.2543	10.2989	0.44	10.43

Expt.	$10^5[H^+]$	$10^4[A^{2-}]$	$10^3[MnA]$	$10^3[HA^-]$	ΔH_f
3.	24.0	1.502	1.12	8.7708	3.53
5.	2.25	10.452	2.01	5.7214	3.23
8.	2.00	7.499	1.15	3.6489	3.45
9.	0.85	12.97	1.32	2.6822	3.76
10.	0.90	13.23	1.30	3.0283	3.54

Mean ΔH_f = 3.50 ± 0.13 k.cal./mole.

The overall limits of accuracy are probably about ±0.5 k.cal/mole due to the small concentration of complex, MnA, and the somewhat inaccurate $[H^+]$ values. ΔH, however, agrees well with 3.53 ± 0.2 k.cal./mole of Nair and Nancollas from e.m.f. measurements.[38]

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[illegible] SOLUTIONS OF
[illegible] ATE

[illegible] PANCHOLI [illegible]

[illegible] Glasgow, W.2

[illegible] 1960

[illegible] radio[illegible] copper of [illegible] have been used [illegible] of the copper species present in a number of [illegible] concentrations as possible. Further measurements [illegible] the thermodynamic [illegible] constants. The [illegible] polarographically.

[illegible] copper species present in solutions of copper oxalate [illegible] extremely small solubility of the salt (1.6 × 10⁻⁴ M at 18°) [illegible] in the presence of excess oxalate ions [illegible] The result [illegible] concentration of excess oxalate and the stability [illegible] the reaction

$$[illegible] + 2C_2O_4^{2-} \rightleftharpoons Cu(C_2O_4)_2^{2-}.$$

[illegible] in which a single oxalate is associated with the [illegible] already exist for most other [illegible] metal oxalates. [illegible] which has an appreciably greater solubility, has been [illegible] by a number of methods [illegible] containing the [illegible] chelate rings. [illegible] has been found possible [illegible] technique to prepare [illegible] of copper oxalate which [illegible] stable for at least [illegible]. This has enabled [illegible] to be made over a much wider range of concentra[illegible] thought possible [illegible] are interpreted in terms of three

$$[illegible] Cu(C_2O_4) \quad (1)$$

$$[illegible] O_4 \quad (2)$$

$$[illegible] (C_2O_4)_2^{2-} \quad (3)$$

[illegible] and thermodynamic equilib[illegible] have been determined. At the low pH [illegible] the presence of [illegible] [illegible] at higher [illegible] concentrations are also reported [illegible]

EXPERIMENTAL

[illegible] reagents were used where available. Copper perchlorate [illegible] cupric oxide and perchloric acid and analysed [illegible] solutions were prepared from the recrystallised [illegible] solution of Analar [illegible]. pH [illegible] glass electrode in a cell of the type

[illegible]

Offprinted from the *Transactions of the Faraday Society*,
No. 452, Vol. 56, Part 8, August, 1960

COMPLEX FORMATION IN SOLUTIONS OF COPPER OXALATE

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Received 8th February, 1960

Potentiometric measurements at a constant ionic strength of 0·1 M have been used to identify and determine the stabilities of the complex species present in solutions of copper oxalate over as wide a range of concentration as possible. Further measurements at low concentrations have then yielded the thermodynamic association constants. The results are compared with those obtained polarographically.

The identification of complex species present in solutions of copper oxalate is difficult owing to the extremely small solubility of the salt ($1{\cdot}6\times10^{-4}$ M at 18°).[1] It is, however, appreciably soluble in the presence of excess oxalate ions due to the formation of increasing quantities of the complex $Cu(C_2O_4)_2^{2-}$. The result is that all the published data refer to conditions of excess oxalate and the stability constants are the overall constants for the reaction

$$Cu^{2+}+2C_2O_4^{2-}\rightleftharpoons Cu(C_2O_4)_2^{2-}.$$

We are interested in complexes in which a single anion is associated with the copper ion since accurate data already exist for most other divalent metal oxalates. Also copper malonate, which has an appreciably greater solubility, has been studied rather carefully by a number of methods [2] and it is of interest to compare the stabilities of complexes containing the five- and six-membered chelate rings.

In the present work it has been found possible, by careful control of concentrations and experimental technique, to prepare solutions of copper oxalate which are appreciably supersaturated and stable for at least 3-4 h. This has enabled potentiometric measurements to be made over a much wider range of concentration than was previously thought possible. Data are interpreted in terms of three equilibria:

$$Cu^{2+}+HC_2O_4^{-}\rightleftharpoons CuHC_2O_4^{+}, \tag{1}$$

$$Cu^{2+}+C_2O_4^{2-}\rightleftharpoons CuC_2O_4, \tag{2}$$

$$CuC_2O_4+C_2O_4^{2-}\rightleftharpoons Cu(C_2O_4)_2^{2-}, \tag{3}$$

and equilibrium quotients at constant ionic strength and thermodynamic equilibrium constants for these three reactions have been determined. At the low pH values employed, the presence of $CuOH^+$ was avoided.

Polarographic measurements at higher oxalate concentrations are also reported and they support the potentiometric values.

EXPERIMENTAL

Grade A glassware and A.R. reagents were used where available. Copper perchlorate solutions were prepared from cupric oxide and perchloric acid and analyzed iodometrically for copper. Sodium perchlorate solutions were prepared from the recrystallized material and analyzed on an ion-exchange resin column of Amberlite IR 120. pH measurements were made with a glass electrode in a cell of the type

Ag/AgCl, HCl (0·2 M)/glass/solution under study/sat. KCl/calomel electrode.

Glass electrodes were made from Corning 015 glass and had a resistance of about 10^7 Ω. Reproducible liquid-junction potentials were ensured by using the apparatus designed by Dunsmore and Speakman.[3] The cell was maintained at 25° in an oil bath even when not in use to prevent fluctuating calomel electrode potentials. E.m.f. measurements were made using a Tinsley potentiometer and a Vibron electrometer (E.I.L. model 33B) as a null indicator; readings were reproducible to $\pm 0{\cdot}1$ mV. For the constant ionic strength measurements, the electrode system was standardized before and after each set of measurements with solutions containing hydrochloric acid and sodium perchlorate at a constant ionic strength of 0·1 M. Calibration curves of e.m.f. against log $[H^+]$ showed good linearity with slopes of 0·058 to 0·060 and unknown log $[H^+]$ could be obtained with an accuracy of $\pm 0{\cdot}003$. At low concentrations, the electrodes were standardized with hydrochloric acid solutions, using the activity data given by Robinson and Stokes,[4] with 0·01 M hydrochloric acid+0·09 M potassium chloride which has a pH = 2·078,[5] and with 0·05 M potassium hydrogen phthalate, pH = 4·005 : [6] the definition of pH being $\text{pH} = -\log a_{\text{H}^+}$. The procedure consisted in determining the pH of solutions containing known concentrations of oxalic acid, sodium hydroxide and copper perchlorate, with and without sufficient sodium perchlorate to maintain an ionic strength of 0·1 M. Some runs were made with copper chloride in place of the perchlorate with no detectable difference. Solutions were prepared immediately before use, and the copper solution was added very slowly only when the other ingredients had been made up nearly to the required volume.

Polarographic measurements were mde as described previously [7] with a Tinsley pen-recording polarograph and dropping mercury electrode. An expanded potential scale enabled the determination of half-wave potentials to within 1 mV. Cell resistances ranged from 4000 to 7000 Ω and corrections for iR drop amounted to 2 to 3 mV. The capillary was made from marine barometer tubing (0·04 mm int. diam.) and had a drop time of $3{\cdot}3 \pm 0{\cdot}3$ sec. Before each polarogram, nitrogen, freed from oxygen by means of vanadium sulphate solution, was bubbled through the cell for 15 min. 0·005 % Polaritan gelatine was used as maximum suppressor and measurements were made at 25°.

RESULTS AND DISCUSSION

It was first necessary to obtain the dissociation constants of oxalic acid at an ionic strength of 0·1 M :

$$k_1' = [H^+][HC_2O_4^-]/[H_2C_2O_4] \text{ and } k_2' = [H^+][C_2O_4^{2-}]/[HC_2O_4^-].$$

Since the first dissociation is rather extensive, k'_2 was obtained from log $[H^+]$ measurements with solutions containing oxalic acid and sodium hydroxide together with sufficient sodium perchlorate to raise the ionic strength to 0·1 M. At these higher log $[H^+]$, $[H_2C_2O_4]$ could be neglected and the concentrations of ionic species were obtained from equations for total acid,

$$T_a = [HC_2O_4^-]+[C_2O_4^{2-}]$$

and for electroneutrality,

$$[Na^+]+[H^+] = [HC_2O_4^-]+2[C_2O_4^{2-}].$$

The results are given in table 1.

In order to obtain k_1', measurements were made on solutions containing oxalic acid, hydrochloric acid and sodium perchlorate. At sufficiently low log $[H^+]$, the

TABLE 1.—SECOND DISSOCIATION CONSTANT FOR OXALIC ACID AT $I = 0{\cdot}1$

$Ta \times 10^3$	$[Na^+] \times 10^3$	$[H^+] \times 10^4$	$[C_2O_4^{2-}] \times 10^3$	$[HC_2O_4^-] \times 10^3$	$k_2' \times 10^4$
1·978	1·852	5·56	0·430	1·548	1·54
1·974	2·040	4·52	0·518	1·456	1·61
1·968	2·305	3·24	0·661	1·307	1·64
1·962	2·575	2·16	0·829	1·133	1·58
1·956	2·879	0·135	1·058	0·898	1·59
0·381	0·351	1·95	0·165	0·216	1·49
0·374	0·461	1·19	0·206	0·168	1·46

mean $k_2' = 1{\cdot}56$

contribution made by $[C_2O_4^{2-}]$ could be neglected and the expressions for total acid and electroneutrality become

$$T_a = [H_2C_2O_4]+[HC_2O_4^-] \text{ and } [H^+] = [HC_2O_4^-]+[Cl^-].$$

The results are given in table 2.

TABLE 2.—FIRST DISSOCIATION CONSTANT OF OXALIC ACID AT $I = 0{\cdot}1$

$T_a \times 10^3$	$[H^+] \times 10^3$	$[Cl^-] \times 10^3$	$[H_2O_2O_4] \times 10^3$	$k^1 \times 10^2$
4·058	8·035	4·657	0·680	4·1
7·596	10·5	4·371	1·497	4·2
10·926	12·6	4·102	2·438	4·3
12·902	13·8	3·943	3·045	4·5
14·106	14·45	3·845	3·501	4·4
				mean $k_1' = 4{\cdot}3$

The ionic species possible in solutions containing copper perchlorate, oxalic acid and sodium hydroxide are $CuHC_2O_4^+$, CuC_2O_4, $Cu(C_2O_4)_2^{2-}$ and a comprehensive treatment at low concentrations would involve equations for total metal ion concentration

$$T_m = [Cu^{2+}]+[CuC_2O_4]+[CuHC_2O_4^+]+[Cu(C_2O_4)_2^{2-}], \tag{4}$$

for total oxalic acid concentration

$$T_a = [H_2C_2O_4]+[HC_2O_4^-]+[C_2O_4^{2-}]+[CuC_2O_4]+[CuHC_2O_4^+] +2[Cu(C_2O_4)_2^{2-}] \tag{5}$$

for electroneutrality,

$$[Na^+]+[H^+]+2[Cu^{2+}]+[CuHC_2O_4^+] = [HC_2O_4^-]+2[C_2O_4^{2-}] +2[Cu(C_2O_4)_2^{2-}]+2T_m, \tag{6}$$

and for the thermodynamic dissociation constants of oxalic acid

$$k_1 = [H^+][HC_2O_4^-]f_1^2/[H_2C_2O_4], \tag{7}$$

and

$$k_2 = [H^+][C_2O_4^{2-}]f_2/[HC_2O_4^-]. \tag{8}$$

If the required association constants are for eqn. (1),

$$K_1 = [CuHC_2O_4^+]/[Cu^{2+}][HC_2O_4^-]f_2, \tag{9}$$

eqn. (2),

$$K_2 = [CuC_2O_4]/[Cu^{2+}][C_2O_4^{2-}]f_2^2, \tag{10}$$

and eqn. (3),

$$K_3 = [Cu(C_2O_4)_2^{2-}]/[C_2O_4^{2-}][CuC_2O_4], \tag{11}$$

the ionic strength becomes

$$I = 3T_a - T_m - 3[H_2C_2O_4] - 2[HC_2O_4^-] + \frac{4(2T_a-[Na^+]-[H^+]-2[H_2C_2O_4]-[HC_2O_4^-])}{K_1[HC_2O_4^-]f_2}. \tag{12}$$

At constant ionic strength, activity coefficients are omitted and the corresponding stability constants are written K_1', K_2' and K_3'. Three series of measurements were made. (i) T_a was much smaller than T_m, and a low [NaOH] enabled the analysis of the data in terms of only two complexes $CuHC_2O_4^+$ and CuC_2O_4. Concentrations and values of K_1' and K_2' are given in table 3.

Polarograms of solutions containing copper perchlorate in 0·1 M KNO_3 showed a reversible two-electron wave with a half-wave potential $E^{\mathrm{s}}_{\frac{1}{2}} = 0{\cdot}014$ V relative to the saturated calomel electrode; in 0·4 M $NaClO_4$, $E^{\mathrm{s}}_{\frac{1}{2}}$ was 0·017V.

TABLE 7.—pH DETERMINATIONS

$T_a \times 10^3$	$T_m \times 10^3$	$[Na^+] \times 10^3$	$[H^+] \times 10^3$	$I \times 10^3$	$K_1 \times 10^{-3}$	$K_2 \times 10^{-6}$	$K_3 \times 10^{-4}$
3·829	2·165	3·807	2·541	7·16	1·50	1·45	1·0
3·829	2·165	4·715	1·773	7·39	1·50	(1·05)	0·9
3·829	2·165	5·710	1·048	7·71	1·50	1·49	0·9
3·829	4·328	5·941	1·520	10·28	1·52	1·50	1·4
3·829	4·328	6·446	1·069	10·32	1·50	1·50	1·3
				mean	1·50	1·49	1·1

Half-wave potentials were obtained from the intercept of the plot of log $[i/(i_d - i)]$ against the applied voltage, where i is the current corresponding to an applied voltage E, and i_d is the diffusion current. The equation for the wave

$$E = E_{\frac{1}{2}} - (RT/nF) \ln [i/(i_d - i)]$$

requires a slope of 0·0296 for a two-electron reduction at 25°.

Measurements were made in the presence of a large excess of sodium oxalate and these are summarized in table 8. It is seen from the values for the slopes that all the waves were reversible.

TABLE 8.—POLAROGRAPHIC MEASUREMENTS

$T_m \times 10^4$	$[C_2O_4^{2-}] \times 10$	$E_{\frac{1}{2}}$	slope	$\Delta E_{\frac{1}{2}}$
		IN 0·1 M KNO_3		
4·95	5·00	−0·245	0·030	−0·259
4·95	4·00	−0·240	0·029	−0·254
4·95	3·00	−0·233	0·030	−0·247
4·95	2·00	−0·225	0·029	−0·239
4·95	1·00	−0·206	0·029	−0·220
		IN 0·4 M $NaClO_4$		
5·90	0·576	−0·187	0·031	−0·204
5·90	0·480	−0·183	0·031	−0·200
5·90	0·384	−0·178	0·030	−0·195
5·90	0·288	−0·171	0·030	−0·188
5·90	0·192	−0·159	0·031	−0·176
5·90	0·0961	−0·141	0·030	−0·158

When the oxalate ion is in large excess, the concentrations of free oxalate ion in the solution and on the surface of the mercury drops may be assumed equal. The shift in half-wave potential may then be written[11]

$$\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}} - E^{\mathrm{s}}_{\frac{1}{2}} = -(RT/nF) \ln K - (pRT/nF) \ln [C_2O_4^{2-}],$$

where n is the number of electrons involved in the reduction, p is the number of oxalate ions associated with each Cu^{2+} ion, and K is the overall stability constant.

Although the ionic strength varies from about 0·6 to 0·3, it is seen from fig. 2 that there is a good linear relationship between $\Delta E_{\frac{1}{2}}$ and log $[C_2O_4^{2-}]$ for all the solutions. The slope of the line, 0·06, corresponds to $p = 2$ and the complex is therefore predominantly $Cu(C_2O_4)_2^{2-}$. The intercept gives $K = 2{\cdot}5 \times 10^9$. The linear relationship implies an insensitivity of K to changes in ionic strength at these high values and this has often been observed in polarographic measurements. In this connection it may be noted that f_2 values, calculated from the mean activity coefficient data for divalent metal chlorides and hydrochloric acid,[4] change by only 15 to 20 % in this range of ionic strength.

The constants derived in the present work are summarized below.

	K_1	K_2	K_3	K_2K_3
$I\to 0$	$1{\cdot}5\times 10^3$	$1{\cdot}54\times 10^6$	$1{\cdot}1\times 10^4$	$1{\cdot}7\times 10^{10}$
	K'_1	K'_2	K'_3	$K'_2K'_3$
$I = 0{\cdot}1$	$3{\cdot}1\times 10^2$	$7{\cdot}0\times 10^4$	$2{\cdot}3\times 10^4$	$1{\cdot}6\times 10^9$
$I = 0{\cdot}2$-$0{\cdot}6$				$2{\cdot}5\times 10^9$

Assuming an f_2 of about 0·2 at $I = 0{\cdot}1$,[4] K' values, reduced to $I\to 0$, become

$$K_1 = 1{\cdot}6\times 10^3, \qquad K_2 = 1{\cdot}7\times 10^6, \qquad K_3 = 2{\cdot}3\times 10^4:$$

the agreement with the measured values is good. The polarographic stability constant also shows the expected trend with ionic strength. Meites[12] obtained an overall $K = 2{\cdot}08\times 10^{10}$ for $Cu(C_2O_4)_2^{2-}$ from polarographic measurements but this was based on only two solutions having ionic strengths of 0·09 and 0·95. This is rather a large range of I in which to expect constancy of K.

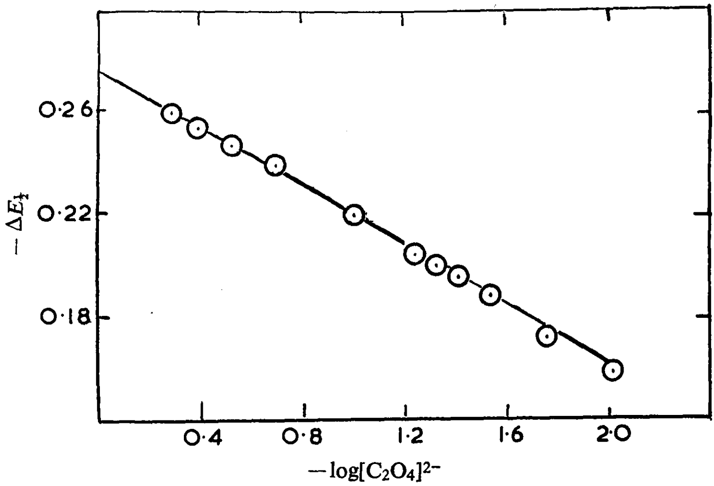

FIG. 2.—Plots of $-\Delta E_{\frac{1}{2}}$ against $-\log [C_2O_4^{2-}]$.

The value, $\log K = 6{\cdot}19$, for the formation of CuC_2O_4 may be compared with 5·75 for the corresponding malonate complex and reflects the normal increased stability of the five-membered ring. It also fits in with the expected order of transition-metal oxalate stabilities.[13]

We thank the D.S.I.R. for a grant to A. McA.

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PRINTED IN GREAT BRITAIN AT
THE UNIVERSITY PRESS
ABERDEEN

Preprinted from the Journal of the Chemical Society,
May, 1961, (420), pages 2215—2221.

420. *Thermodynamics of Ion Association. Part VII.*[1] *Some Transition-metal Oxalates.*

By A. McAuley and G. H. Nancollas.

Thermodynamic equilibrium constants for the association, in aqueous solution, of nickel, cobalt, and manganese ions with the oxalate ion have been determined by a precise e.m.f. method between 0° and 45°. ΔG, ΔH, and ΔS for the reaction $M^{2+} + C_2O_4^{2-} \rightleftharpoons MC_2O_4$ have been calculated and ΔC_p has been estimated from the variation of ΔH with temperature. The thermodynamic quantities are discussed.

Previous parts of this series have been concerned mainly with ion pairs of only moderate stability. The present work extends the available thermodynamic data to the much more stable oxalate complexes of bivalent transition-metal ions which are known to follow the Irving–Williams order of stability. The identification of complex species present in such solutions is made difficult by the low solubility of the salts. In the presence of an excess of oxalate the solubility increases owing to the formation of increasing amounts of $M(C_2O_4)_2^{2-}$, but we are interested in complexes in which a single anion is associated with each metal ion. Studies of copper oxalate have shown that, with careful control of experimental conditions, supersaturated solutions may be prepared which are stable for long periods.[2] This technique has been extended to cobalt, nickel, and manganese oxalate in the present work, and measurements have been made by using the cell

$$H_2\text{–}Pt|MCl_2,H_2C_2O_4,NaOH|AgCl\text{–}Ag$$

Only in the case of cobalt was it necessary seriously to limit the concentrations to prevent precipitation.

Experimental

Concentrations of stock solutions prepared from "AnalaR" metal chlorides were determined by gravimetric analysis of the chloride as silver chloride; duplicate determinations agreed to within 0·02%. "AnalaR" oxalic acid was recrystallised three times from conductivity water (analysis, 99·9% pure). Hydrochloric acid was constant-boiling material. Carbonate-free sodium hydroxide, prepared from a saturated solution suitably diluted with carbon dioxide-free conductivity water, was standardised both by volume- and by weight-titration against weighed samples of potassium hydrogen phthalate. The apparatus and experimental technique have been described previously.[3] Measurements were made with solutions, stable for at least 24 hr., containing known concentrations of oxalic acid, sodium hydroxide, and the metal chloride. To prevent precipitation, the metal chloride was added slowly only when the other ingredients had been made up nearly to the required volume. E.m.f. readings were constant to within 20 μv.

Results and Discussion

Since only the second thermodynamic dissociation constant of oxalic acid, $K_2 = a_{H^+}a_{C_2O_4^{2-}}/a_{HC_2O_4^-}$, had been determined accurately over a range of temperature,[4] it was necessary to obtain the corresponding values of $K_1 = a_{H^+}a_{HC_2O_4^-}/a_{H_2C_2O_4}$. The first dissociation is rather extensive and measurements were made with a mixed acid cell

$$\mathrm{H_2\text{–}Pt|H_2C_2O_4(m_1),\ HCl(m_4)|AgCl\text{–}Ag}$$

the e.m.f. of which is given by

$$E' = E^0 - k \log a_{\mathrm{H}^+}a_{\mathrm{Cl}^-}$$

or
$$-\log [\mathrm{H}^+] = (E' - E^0)/k + \log \mathrm{m}_4 + \log \gamma_{\mathrm{H}^+}\gamma_{\mathrm{Cl}^-}$$

where m represents molality, γ activity coefficient, and $k = 2{\cdot}3026\ \boldsymbol{RT/F}$. By using expressions for total oxalate $\mathrm{m_1 = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]}$, electroneutrality $\mathrm{[H^+] = [HC_2O_4^-] + 2[C_2O_4^{2-}] + m_4}$, and ionic strength $I = \mathrm{[H^+] + [C_2O_4^{2-}]}$, a graphical solution similar to that described by Speakman [5] was applied, leading to an equation

TABLE 1. *Dissociation constant of oxalic acid.*

$10^3\mathrm{m}_1$	$10^3\mathrm{m}_4$	$(E' - E^\circ)$	$10^3[\mathrm{H}^+]$	$10^3 I$	$10^5[\mathrm{C_2O_4^{2-}}]$	$10^4 X$	$10^5 Y$
2·9641	2·3993	0·29430	5·1574	5·196	3·842	2·457	1·454
3·8007	2·4028	0·29102	5·9097	5·953	4·362	3·048	1·824
3·6686	4·0032	0·27279	7·3331	7·368	3·466	4·309	2·591
3·5414	4·1377	0·27192	7·3375	7·371	3·329	4·488	2·572
7·6610	5·5797	0·25245	12·1490	12·195	4·553	9·614	5·606
4·7096	4·2582	0·26780	8·4721	8·511	3·899	5·475	3·249
4·2650	4·9781	0·26295	8·7793	8·813	3·416	5·808	3·433
5·0901	4·2715	0·26681	8·8099	8·851	4·068	5·806	3·456
1·9442	1·5601	0·31524	3·4178	3·454	3·658	1·126	0·727

Temp.	0°	15°	25°	35°	45°
$10^2 k_1$	5·70	5·60	5·60	5·18	5·07

$$Y = XK_1 + K_1K_2$$

in which
$$X = \frac{[\mathrm{H}^+]\gamma_2(\mathrm{m}_1 - [\mathrm{H}^+] - \mathrm{m}_4)}{2\mathrm{m}_1 - [\mathrm{H}^+] + \mathrm{m}_4}$$

and
$$Y = \frac{([\mathrm{H}^+] - \mathrm{m}_4)[\mathrm{H}^+]^2\gamma_1^2\gamma_2}{2\mathrm{m}_1 - [\mathrm{H}^+] + \mathrm{m}_4}$$

Activity coefficients were obtained from the Davies equation [6]

$$-\log \gamma_z = Az^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I] \quad . \ . \ . \ . \ . \ . \quad (1)$$

Fig. 1 shows the good linear relation between X and Y at each temperature. The results at 25° are detailed in Table 1, which includes only the K_1 values at the other temperatures. At 25°, the value agrees very well with $5{\cdot}36 \times 10^{-2}$, obtained from conductivity measurements.[4]

The concentration of hydrogen ions in the cell

$$\mathrm{H_2\text{–}Pt|H_2C_2O_4(m_1),\ NaOH(m_2),\ MCl_2(m_3)|AgCl\text{–}Ag}$$

is given by

$$-\log [\mathrm{H}^+] = (E' - E^0)/k + \log 2\mathrm{m}_3 + \log \gamma_{\mathrm{H}^+}\gamma_{\mathrm{Cl}^-}$$

The concentrations of ionic species were obtained from: $\mathrm{m_1 = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}] + [MC_2O_4]}$, $\mathrm{m_3 = [M^{2+}] + [MC_2O_4]}$, the electroneutrality condition $\mathrm{[H^+] + 2[M^{2+}] + m_2 = [HC_2O_4^-] + 2[C_2O_4^{2-}] + 2m_3}$, and K_1 and K_2 for oxalic acid. Studies on the association between the nickel ion and the malonate and substituted malonate anions both at low concentration and at a number of constant ionic strengths up to $I = 0{\cdot}2$ have shown that equation (1) represents the activity coefficients very satisfactorily.[7] The same equation has been used in the present work. T.I.P. programmes were constructed for a high-speed DEUCE electronic computer leading to the calculation of thermodynamic association constants $K = \{\mathrm{MC_2O_4}\}/\{\mathrm{M^{2+}}\}\{\mathrm{C_2O_4^{2-}}\}$ by successive approximations of I.

TABLE 2. *E.M.F. measurements.*

Nickel oxalate

Experiment	1	2	3	4	5
10^3m_1 …………	2·9569	3·5174	2·4884	3·2920	1·4138
10^3m_2 …………	0·9450	1·1136	0·8777	1·0339	0·9226
10^3m_3 …………	3·6011	4·3440	3·1053	3·9512	3·1629

Expt.	$(E' - E^\circ)$	10^3I	$10^3[H^+]$	$10^4[HC_2O_4^-]$	$10^5[C_2O_4^{2-}]$	$10^3[MC_2O_4]$	$10^{-5}K$
			Temp. = 0°				
1	0·25048	9·630	4·0397	8·282	1·914	2·0586	1·53
2	0·24226	11·574	4·8259	9·570	1·913	2·4721	1·62
3	0·25808	8·298	3·3479	6·809	1·851	1·7539	1·46
4	0·24607	10·598	4·4763	9·461	2·006	2·2620	1·52
5	0·27336	8·467	1·7207	1·750	0·929	1·2248	1·43
						Mean K = 1·51 ± 0·05	
			Temp. = 15°				
1	0·26490	9·789	3·9568	9·038	2·014	1·9789	1·36
2	0·25630	11·781	4·7179	10·553	2·041	2·3677	1·42
3	0·27287	8·423	3·2842	7·404	1·936	1·6914	1·32
4	0·26008	10·717	4·4136	10·036	2·038	2·2015	1·44
5	0·28880	8·510	1·6996	1·953	0·988	1·2036	1·33
						Mean K = 1·37 ± 0·04	
			Temp. = 25°				
1	0·27432	9·822	3·9371	9·222	1·919	1·9608	1·42
2	0·26539	11·808	4·7014	10·707	1·932	2·3529	1·50
3	0·28243	8·418	3·2839	7·409	1·798	1·6923	1·44
4	0·26940	10·772	4·3831	10·319	1·962	2·1729	1·47
5	0·29901	8·521	1·6932	2·014	0·950	1·977	1·39
						Mean K = 1·44 ± 0·03	
			Temp. = 35°				
1	0·28403	9·920	3·8795	9·706	1·826	1·9087	1·44
2	0·27470	11·889	4·6499	11·113	1·806	2·3081	1·57
3	0·29240	8·499	3·2369	7·814	1·713	1·6494	1·46
4	0·27884	10·848	4·3349	10·703	1·833	2·1309	1·54
5	0·30941	8·553	1·6756	2·178	0·923	1·1810	1·42
						Mean K = 1·49 ± 0·06	
			Temp. = 45°				
1	0·29365	9·989	3·8401	10·058	1·728	1·8724	1·48
2	0·28406	11·981	4·5978	11·572	1·721	2·2598	1·60
3	0·30227	8·553	3·2060	8·094	1·619	1·6210	1·51
4	0·28829	10·920	4·2933	11·070	1·731	2·0928	1·60
5	0·31977	8·577	1·6627	2·300	0·887	1·1688	1·48
						Mean K = 1·53 ± 0·05	

Cobalt oxalate

Expt.	1	2	3	4	5	6	7	8	9
10^4m_1……	10·6015	7·5201	9·9339	4·6320	4·4061	3·3415	4·3336	4·0907	4·4713
10^4m_2……	4·3378	4·8485	3·5936	1·9813	2·2535	2·4126	2·5495	1·9679	2·6201
10^4m_3……	7·1875	5·7084	5·3596	5·8845	7·5226	8·4511	7·4063	8·0331	9·1779

Expt.	$(E' - E^\circ)$	10^3I	$10^4[H^+]$	$10^4[HC_2O_4^-]$	$10^5[C_2O_4^{2-}]$	$10^4[MC_2O_4]$	$10^{-4}K$
			Temp. = 0°				
4	0·33709	1·723	5·5981	1·6533	2·222	2·7409	5·60
5	0·33243	2·113	5·3863	1·1516	1·638	3·0803	6·26
6	0·33877	2·367	3·6818	0·5814	1·223	2·6342	5·60
8	0·33164	2·251	5·2324	0·9642	1·420	2·9760	6·20
9	0·32831	2·565	5·3095	0·9954	1·463	3·3207	5·95
						Mean K = 5·92 ± 0·26	
			Temp. = 5°				
4	0·34338	1·723	5·5749	1·6768	2·094	2·7303	5·91
6	0·34513	2·369	3·6613	0·6019	1·178	2·6182	5·78
8	0·33791	2·257	5·1932	1·0031	1·378	2·9412	6·30
9	0·33445	2·567	5·2848	1·0201	1·395	3·3029	6·21
						Mean K = 6·05 ± 0·21	

TABLE 2. (*Continued.*)

Expt.	$(E' - E^\circ)$	$10^3 I$	$10^4[H^+]$	$10^4[HC_2O_4^-]$	$10^5[C_2O_4^{2-}]$	$10^4[MC_2O_4]$	$10^{-4}K$
			Temp. = 15°				
1	0·33477	2·435	10·8014	5·8534	3·946	4·2483	5·62
2	0·35283	1·848	6·4859	3·6266	3·966	3·4573	5·64
3	0·34364	2·003	10·0386	6·0320	4·293	3·3708	5·84
4	0·35568	1·719	5·5921	1·6593	2·091	2·7479	6·03
5	0·35092	2·119	5·3482	1·1892	1·597	3·0465	6·37
7	0·35302	2·075	4·9883	1·1107	1·596	3·0539	6·54
8	0·34995	2·250	5·2243	0·9722	1·344	2·9756	6·61
9	0·34660	2·572	5·2674	1·0370	1·442	3·2811	5·99
						Mean $K = 6·08 \pm 0·32$	
			Temp. = 25°				
1	0·34646	2·425	10·7932	5·8618	3·659	4·2687	6·18
2	0·36519	1·841	6·4688	3·6436	3·695	3·4674	6·13
3	0·35571	1·999	10·0025	6·0680	4·010	3·3630	6·25
4	0·36843	1·733	5·5157	1·7348	2·051	2·6759	5·89
5	0·36331	2·122	5·3168	1·2202	1·526	3·0224	6·62
7	0·36580	2·095	4·8970	1·2010	1·628	2·9599	6·14
8	0·36267	2·273	5·1204	1·0747	1·405	2·8663	6·02
						Mean $K = 6·18 \pm 0·15$	
			Temp. = 35°				
1	0·35842	2·434	10·6757	5·9676	3·339	4·1892	6·52
2	0·37786	1·847	6·3769	3·7309	3·400	3·4072	6·43
3	0·36801	2·007	9·8810	6·1784	3·663	3·2818	6·47
4	0·38115	1·740	5·4489	1·7992	1·909	2·6246	6·16
5	0·37596	2·136	5·2338	1·3010	1·465	2·9466	6·67
7	0·37842	2·102	4·8415	1·2548	1·525	2·9156	6·44
8	0·37509	2·277	5·0795	1·1142	1·301	2·8365	6·45
9	0·37125	2·586	5·1728	1·1294	1·312	3·2005	6·44
						Mean $K = 6·45 \pm 0·08$	
			Temp. = 45°				
1	0·37024	2·432	10·6254	6·0146	3·041	4·1702	7·14
2	0·39050	1·852	6·3028	3·8033	3·155	3·3585	6·74
3	0·38028	2·015	9·7853	6·2705	3·377	3·2164	6·72
4	0·39386	1·746	5·3926	1·8543	1·788	2·5810	6·43
5	0·38838	2·138	5·2032	1·3309	1·356	2·9272	7·18
7	0·39117	2·113	4·7706	1·3246	1·470	2·8507	6·49
8	0·38762	2·285	5·0261	1·1666	1·239	2·7898	6·65
9	0·38352	2·588	5·1428	1·1588	1·219	3·1801	6·93
						Mean $K = 6·79 \pm 0·23$	

Manganese oxalate

Expt.	1	2	3	4	5	6	7
$10^3 m_1$ …	3·4320	4·7888	3·0967	2·6820	6·0543	3·8573	4·5292
$10^3 m_2$ …	3·2776	4·4524	2·8542	2·7137	3·1920	5·3869	6·1270
$10^3 m_3$ …	9·3107	10·5926	8·9826	7·7665	9·0494	8·6069	8·6630

Expt.	$(E' - E^\circ)$	$10^2 I$	$10^3[H^+]$	$10^3[HC_2O_4^-]$	$10^5[C_2O_4^{2-}]$	$10^3[MC_2O_4]$	$10^{-3}K$
			Temp. = 0°				
1	0·24805	2·805	1·9402	1·5637	9·437	1·7327	8·37
2	0·23893	3·233	2·5586	2·4025	11·402	2·1902	8·50
3	0·24977	2·705	1·8609	1·4069	8·773	1·5663	8·17
4	0·25855	2·329	1·4553	1·1485	8·830	1·4220	8·01
5	0·22908	2·962	4·5000	3·9386	10·391	1·7728	8·33
						Mean $K = 8·28 \pm 0·15$	
			Temp. = 15°				
1	0·26232	2·811	1·9043	1·5999	9·320	1·6979	8·53
2	0·25270	3·241	2·5125	2·4497	11·229	2·1453	8·69
3	0·26410	2·711	1·8288	1·4391	8·649	1·5354	8·34
4	0·27318	2·331	1·4400	1·1639	8·556	1·4094	8·41
5	0·24208	2·970	4·4585	3·9828	10·052	1·7333	8·64
6	0·28139	2·530	0·9430	1·3499	15·461	2·3354	8·13
7	0·27745	2·574	1·1004	1·7775	17·523	2·5497	8·11
						Mean $K = 8·41 \pm 0·18$	

TABLE 2. (*Continued.*)

Expt.	$(E' - E^\circ)$	$10^2 I$	$10^3[H^+]$	$10^3[HC_2O_4^-]$	$10^5[C_2O_4^{2-}]$	$10^3[MC_2O_4]$	$10^{-4}K$
			Temp. = 25°				
1	0·27154	2·808	1·9060	1·5986	8·672	1·7058	0·941
2	0·26152	3·237	2·5218	2·4413	10·396	2·1625	0·969
3	0·27321	2·706	1·8423	1·4261	7·927	1·5559	0·943
4	0·28282	2·329	1·4384	1·1658	7·991	1·4133	0·921
5	0·25066	2·969	4·4532	3·9904	9·402	1·7334	0·944
6	0·29138	2·527	0·9396	1·3536	14·500	2·3415	0·889
7	0·28727	2·570	1·0978	1·7805	16·390	2·5583	0·889
					Mean $K = 0·928 \pm 0·024$		
			Temp. = 35°				
1	0·28101	2·808	1·8905	1·6105	7·864	1·7002	1·06
2	0·27065	3·236	2·5025	2·4539	9·407	2·1565	1·09
3	0·28270	2·705	1·8296	1·4357	7·172	1·5524	1·06
4	0·29271	2·329	1·4240	1·1781	7·276	1·4071	1·03
5	0·25940	2·968	4·4221	4·0024	8·481	1·7210	1·06
6	0·30162	2·524	0·9280	1·3638	13·192	2·3436	1·00
7	0·29735	2·566	1·0852	1·7910	14·879	2·5618	1·00
					Mean $K = 1·04 \pm 0·03$		
			Temp. = 45°				
1	0·29055	2·809	1·8735	1·6268	7·271	1·6894	1·16
2	0·27986	3·237	2·4803	2·4749	8·690	2·1420	1·20
3	0·29222	2·705	1·8179	1·4468	6·596	1·5467	1·18
4	0·30261	2·329	1·4112	1·1905	6·723	1·4000	1·13
5	0·26817	2·971	4·3939	4·0271	7·793	1·7015	1·17
6	0·31194	2·522	0·9157	1·3760	12·226	2·3410	1·10
7	0·30741	2·564	1·0736	1·8024	13·719	2·5619	1·11
					Mean $K = 1·15 \pm 0·03$		

Three such approximations were usually carried through, giving 0·1% reproducibility in I. Table 2 shows the good constancy of K at each temperature.

The K values at 25° may be compared with those obtained from conductivity measurements:[8] $K(NiC_2O_4) = 2 \times 10^5$; $K(CoC_2O_4) = 5·1 \times 10^4$; and $K(MnC_2O_4) = 8·1 \times 10^3$; and, from solubilities, $K(MnC_2O_4) = 9·1 \times 10^3$. Plots of log K against T^{-1} in Fig. 2 are curved, indicating a non-zero ΔC_p. This has often been observed in precise measurements on the dissociation of weak acids, but the present is one of the few cases in which detectable values of ΔC_p have been found for reactions involving metal-ion complexes. The variation of log K with temperature may be expressed by the equation $\log K = a + bT + cT^2$, in which the values of the three parameters are as in Table 3. The calculated K values have a maximum difference of 3% from the observed values.

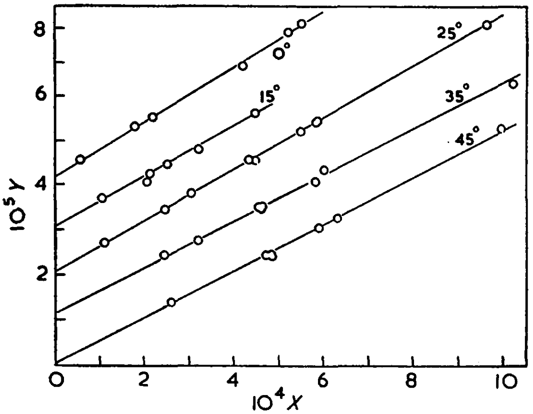

FIG. 1. *Plots of X against Y. (The lines are displaced along the y-axis for clarity.)*

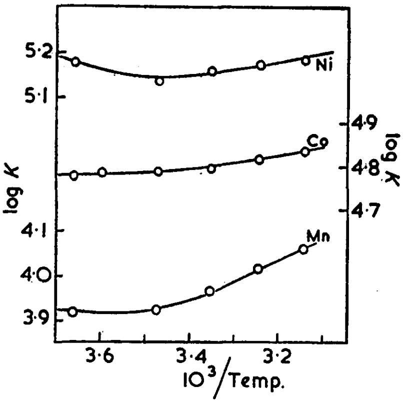

FIG. 2. *Plots of* log K *against* T^{-1}. *(Right-hand ordinates refer to* CoC_2O_4.)

ΔH, ΔC_p, and ΔS calculated from the equations $\Delta H = 2·303\boldsymbol{R}T^2(b + 2cT)$, $\Delta C_p = 4·606\boldsymbol{R}T(b + 3cT)$, and $\Delta S = (\Delta H - \Delta G)/T$, are given in Table 4. The mean deviations have been estimated by using different combinations of experimental points at three temperatures for the calculation of *a*, *b*, and *c*.

The values of ΔC_p may be compared with 35—45 cal. deg.$^{-1}$ for a number of reactions in which hydrogen ion associates with an anion.[9] $\Delta C_p(CoC_2O_4)$ appears to be rather low, but the larger values for NiC_2O_4 and MnC_2O_4 reflect the trend with charge type observed in proton-transfer reactions. A ΔC_p of 70 cal. deg.$^{-1}$ has been found for the association of tervalent chromium with thiocyanate ion.[10]

The entropy of association may be written:

$$\Delta S = \Delta S_g + \Delta S_{hyd}(MC_2O_4) - \Delta S_{hyd}(M^{2+}) - \Delta S_{hyd}(C_2O_4{}^{2-}) \quad . \quad . \quad (2)$$

where ΔS_g and ΔS_{hyd} are respectively gaseous and hydration entropies. ΔS_g has been calculated as described previously,[11] by using a non-planar model for the complex species with the M-O and oxalate planes at an angle of 101°. $\Delta S_{hyd}(MC_2O_4)$ obtained from equation (2) is given in Table 5. The values are lower than the 63—71 cal. deg.$^{-1}$ mole^{-1} observed for the corresponding sulphate ion pairs; this may be due to a greater neutralisation of charge accompanying the formation of oxalate complexes. The change in

TABLE 3. *Parameters for temperature-dependence of* log *K*.

	a	$-10^2 b$	$10^5 c$
NiC_2O_4	9·065	2·655	4·512
CoC_2O_4	6·810	1·500	2·760
MnC_2O_4	8·141	3·146	5·857

The calculated *K* values have a maximum difference of 3% from the observed values.

TABLE 4. *Thermodynamic properties*

Reaction	ΔH (kcal. mole^{-1})	ΔG_{298} (kcal. mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})	ΔC_p (cal. deg.$^{-1}$)
$Ni^{2+} + C_2O_4{}^{2-}$	$0·15 \pm 0·10$	$-7·05 \pm 0·02$	$24·2 \pm 0·4$	35 ± 12
$Co^{2+} + C_2O_4{}^{2-}$	$0·59 \pm 0·07$	$-6·54 \pm 0·02$	$23·9 \pm 0·3$	20 ± 10
$Mn^{2+} + C_2O_4{}^{2-}$	$1·42 \pm 0·20$	$-5·41 \pm 0·02$	$22·9 \pm 0·7$	65 ± 15

TABLE 5. *Thermodynamic properties*

Ion pair	$S_g(MC_2O_4)$ (cal. deg.$^{-1}$ mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})	$S^\circ(MC_2O_4)$ (cal. deg.$^{-1}$ mole^{-1})	$-\Delta S_{hyd}(MC_2O_4)$ (cal. deg.$^{-1}$ mole^{-1})	r_+^{-1} (Å^{-1})
NiC_2O_4	70·0	24·7	13·9	56·1	1·37
CoC_2O_4	70·0	23·9	14·1	55·8	1·35
MnC_2O_4	69·9	22·9	15·1	54·8	1·28

$\Delta S_{hyd}(MC_2O_4)$ is small but, as far as differences are significant, it varies in the expected direction with the reciprocal of the cationic radius. The entropy of association increases with temperature and the values at 0° and 45° are respectively; NiC_2O_4, 21·0 and 28·2; CoC_2O_4, 22·0 and 25·8; MnC_2O_4, 18·6 and 27·0 cal. deg.$^{-1}$ mole^{-1}. This increase reflects the greater freedom of the " frozen " solvent molecules when released from the fields of the ions at the higher temperatures.

The heat changes, ΔH, oppose the association reactions and it is these terms which account for the considerable differences of stability over the series of cations. This is to be expected for transition-metal ion complexes, and it has also been claimed that equations of the form

$$\Delta H = Az/r_+ + BI_{02} - C/r_+{}^3$$

may be used to represent the data.[12] The ΔH values of Table 4 follow the reverse of this order, decreasing with increasing $r_+{}^{-1}$ and ionization potential I_{02}. When ΔH is expressed by an equation analogous to (2), and all other terms are assumed to be approximately constant, ΔH should increase with $-\Delta H_{hyd}(M^{2+})$; the opposite order is observed: more results are required to explain this.

We thank Dr. H. S. Dunsmore for advice on computer programmes, and the D.S.I.R. for a grant to A. McA.

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[*Received, November 7th,* 1960.]

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PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.

SUMMARY

The association in aqueous solutions between divalent transition metal cations and the anions of dicarboxylic acids has been studied.

The thesis is divided into four parts.

Part I describes studies of association in copper oxalate solutions at 25°C. Potentiometric measurements, using a glass electrode system with a saturated calomel reference electrode, at an ionic strength of 0.1M were used to identify the species present in these solutions. These were found to be $CuHC_2O_4^+$, CuC_2O_4 and $Cu(C_2O_4)_2^{2-}$ and stability constants at this ionic strength were derived. Subsequent work at low concentrations yielded the thermodynamic association constants. Using a polarographic technique at ionic strengths varying from 0.2 to 0.6M, a value for the stability constant of the doubly charged anionic complex was obtained and this is compared with the potentiometric result.

Part II is devoted to a study of 2:2 electrolytes. The thermodynamic equilibrium constants for the association of divalent nickel, cobalt and manganese

ions with oxalate and succinate anions have been determined over the temperature range 0° to 45°C using the cell,

H_2, Pt / H_2A, NaOH, MCl_2 / AgCl, Ag,

in which e.m.f.s were measured to ±0.01m.v. Thermodynamic properties for each association have been derived. The first dissociation constant of oxalic acid was also measured over this temperature range using the cell,

H_2, Pt / H_2Ox, HCl / AgCl, Ag.

Results are compared with those in the literature. It was thought that in metal succinate solutions, due to the high concentrations of $HSucc^-$ present, there might exist in solution, along with the 2:2 electrolyte, a complex of the form $MHSucc^+$. E.m.f. measurements on manganese succinate solutions at 0.2M using the glass electrode system of Part I confirmed this and stability constants were obtained.

Part III consists of a general discussion of the results. The entropies of the ion-pairs have been calculated and correlations between ΔG, ΔH and ΔS with ionic parameters are investigated.

Part IV deals with a calorimetric study of the

heat of formation of manganese malonate at 25°C. The heat of solution of potassium chloride was also measured. Results are compared with existing data.