STUDIES OF IONIC INTERACTIONS IN SOLUTIONS

A Thesis submitted to the
University of Glasgow
in candidature for the degree of

DOCTOR OF PHILOSOPHY

by

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Preface

The work described in this Thesis was performed in the Chemistry Department of the University of Glasgow during the period from October 1966 to September 1970. During this period, Professor J. Monteath Robertson was the Director of the Chemical Laboratories.

I should like to thank my supervisor, Dr. Helen S. Dunsmore for suggesting the research topic, and for many helpful discussions in connection with it. Discussions with my colleagues, Dr. R. Patterson, Mr. D. Midgley and Mr. C. McCallum have also been very useful, and I should like to take this opportunity of thanking them. I am grateful to Mr. I. Hainsworth of the Steroid Biochemistry Laboratory of the Glasgow Royal Infirmary for much advice concerning liquid scintillation counting.

Three years of the research were supported by the Science Research Council whose maintenance grant is gratefully acknowledged. I thank the University of Glasgow for the tenure of a Temporary Assistant Lectureship during the last year of the work.

G.M.A.
May, 1971.

SUMMARY

The object of the present work was to examine the interactions which occur in aqueous solutions which contain alkaline earth cations and anions of dicarboxylic acids. The calcium-oxalate system was to be examined in detail with special reference to the protonated complexes formed by the species hydrogen oxalate. In order to examine the calcium hydrogen oxalate system, reliable values of the dissociation constants of oxalic acid were required so that the concentrations of anionic species in the solutions could be calculated.

The thesis is divided into three parts. The first part describes the determination of the dissociation constants of oxalic acid in an ionic medium maintained at 0.1 molar by sodium perchlorate. A potentiometric titration method has been used and the results of the titrations are compared with earlier work on the dissociation constants of oxalic acid. Good agreement has been obtained.

The second and principal part of the thesis involves the determination of the stability constants of a number of complexes formed between alkaline earth cations and anionic dicarboxylic acid ligands. The cation exchange method has been used and the theory of the method is described. The experimental difficulties which were encountered are introduced and the methods which were used to overcome these difficulties are described. The systems which were examined were the following: calcium oxalate, calcium malonate, calcium succinate, calcium tartrate, strontium oxalate, strontium tartrate, calcium hydrogen oxalate and strontium hydrogen oxalate. Where comparison with other published work was possible, good agreement was found. A critical comparison was made of the stabilities of corresponding acetate and hydrogen oxalate complexes and use was made of such other data in the literature as were relevant. The denticity of the hydrogen oxalate ligand was examined and it was deduced that bidenticity was possible. Dissociation of the hydrogen oxalate complexes to the unprotonated complex and a hydrogen ion was considered in the light of a recent paper by some Russian workers and it was found that the empirical relationship which they had suggested was obeyed. The relative stabilities of all the complexes with the exception of the protonated complexes were considered in terms mainly of entropy contributions to the total free energy change in the reactions.

The effect of the cross linking of the cation exchanger on the stability constants obtained by the ion exchange method was examined in the third part of the thesis. A large number of experiments were performed on resins with cross linking of 8%, 10% and 12% DVB. The

results of the experiments were not conclusive because excellent agreement was observed between the results obtained for the 8% and 10% cross linked resins, but the 12% resin appeared to be out of line, but to an inconclusive extent. As far as can be seen this is in agreement with some earlier unpublished work on the same topic.

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Introductory Discussion

of

Ionic Association

Introductory Discussion of Ionic Association

The properties of electrolyte solutions depend upon the fact that they contain ions of opposite sign. Any analysis of the thermodynamic properties of solutions must take account of the forces involved between the ions. There are two principle types of force. The first of these is a long range effect, which arises from the charges on the ions; such effects are the coulombic forces. There are also interactions between ions and solvent molecules, which are short-range in character. Departures in the behaviour of electrolyte solutions from ideality may be ascribed to the formation round a given ion of an ionic atmosphere containing on average more ions of the charge-type opposite to that of the ion under consideration than of the same charge-type. This is the ionic cosphere. The concept of ionic association carries this idea to the point where the ions are so strongly influenced by each other that they are unable to move apart readily because the energy required to achieve this is now greater than their thermal energy of random motion. When this occurs, the approximations of the Debye-Hückel theory become invalid and a new species which is sufficiently stable to withstand the collisions of other species and of solvent molecules is formed. This new species is termed an ion pair. The equilibrium may be denoted thus:

$$M^{a+}_{aq.} + A^{b-}_{aq.} \rightleftharpoons MA^{(a-b)}_{aq.}$$

Bjerrum$^{(1)}$ considered ion association in terms of purely electrostatic forces between the ions. Ions were regarded as unpolarisable hard spheres contained in a medium of fixed finite dielectric constant. Non-polar quantum-mechanical bonds and ion-solvent interactions were excluded. A certain distance, q, was taken to be the distance from the ion within which a second ion was considered to be associated with it. In a solution of a symmetrical electrolyte the average distribution of negative ions, A, will be greater in the vicinity of positive ions, M, than in the bulk of the solution. The Boltzmann expression may be used to give the number of A ions round the M ion. The number of A ions in a shell of thickness dr is given by

$$\mathcal{N}_A = n_A \exp\{-Z_A e\psi_M/kT\}4\pi r^2 dr \text{ ,}$$

where n_A = overall concentration of the A species,

z_A = valency of the A species,

e = electronic charge

and $z_A e\psi_M$ = electrical potential energy of an A ion.

If r is small the potential of the central ion becomes dominant and interionic forces may be neglected.

$$\psi_M = Z_M e/\epsilon r$$

where ϵ is the dielectric constant.

Substitution gives

$$\mathcal{N}_A = n_A \exp\left\{\frac{-Z_A Z_M e^2}{\epsilon kTr}\right\} 4\pi r^2 dr$$

If a series of such shells is considered, an estimation on a time average basis may be made of the number of ions in each shell. As r increases, the probability of finding an ion decreases in any unit of volume. If, however, equal steps outward are considered, the volume of each shell increases and introduces an opposing effect. At a certain critical distance there is a minimum probability of finding an A ion anywhere in the sphere surrounding an M ion. This is the distance q where the mutual potential energy of the ions is equal to 2kT, the energy required for random motion of the ions. In water at 25°C it may be shown that

$$q = \frac{|Z_A Z_M| e^2}{2kT}$$

so that

$$q = Z^2 |3.57| \mathring{A} .$$

Bjerrum (loc.cit.) showed how the equilibrium constant depends on the solvent dielectric constant, temperature, and ion size. At a distance greater than q the Debye-Hückel theory continues to be valid. In experiments at constant ionic strength activity coefficients may be disregarded and the corresponding stoichiometric stability constants are obtained.

Ion association may be studied by a number of methods, which include

(i) Conductivity.
(ii) E.M.F. and pH.
(iii) Freezing point studies.
(iv) Ion exchange.
(v) Solubility.
(vi) Solvent extraction.
(vii) Spectrophotometry.
(viii) Polarography.
(ix) N.M.R.

These methods and others have been discussed fully by Monk.(2) The conductivity method depends on the fact that symmetrical ion pairs have no net charge and therefore no conductivity contribution is made. There are therefore deviations from the Onsager limiting equation. In the solubility method the solubility of sparingly soluble salts in the presence of added electrolyte is studied. The spectrophotometric method uses the different extinction coefficients of ions and ion pairs. In the polarographic method the half-wave potential of a metal ion is shifted to a more negative value when association with an anion occurs. The amount of the shift depends on the number of electrons involved, and the number of anions associated with each cation.

Accurate values of stability constants are of importance in several applications. If all the stabilities of all the species present in a system are known, then the equilibrium concentrations of these species may be predicted; this is useful for the interpretation of optical, kinetic, partition and biological behaviour, and of great importance in an analytical and separative context. Further, the more information which is obtained on the stabilities of species in solution, the more readily will more comprehensive theories of the behaviour of electrolyte solutions be evolved.

In the present work the stability of some calcium and strontium complexes is examined by the ion exchange method, which has been used because of the very low solubility of some of the complexes, a fact which prevents the application of many of the more traditional methods of examining complexes in solution. These alkaline earth complexes are of some interest from both a chemical and biological standpoint.(122) Although the calcium and strontium oxalate complexes have been studied at 1.0 molar(3) and at infinite dilution(4,5,6) no study appears to have been made at 0.1 molar, or at a similar ionic strength. Although a few hydrogen-oxalate complexes of some other metals have been examined(7-16) the data in the literature are very sparse, and there is no information on the hydrogen-oxalate complexes of calcium and strontium. An examination of these complexes therefore seemed to be desirable. Such an examination requires reliable values for the dissociation constants of oxalic acid at the same ionic strength so that the concentrations of the ionic species present in solutions of these complexes may be calculated and it has been thought desirable to make a determination of these values; the results are compared with those of some earlier workers. Many experimental difficulties were overcome in the application of the method, which was then used to obtain precise data about certain related complex systems which have been characterised by other methods. These systems were the calcium malonate, calcium succinate, calcium tartrate and strontium tartrate systems. The effect of changing ionic strength on the stability of the calcium oxalate complex was examined, and it was found that at low ionic strengths experimental difficulties became more acute.

THE EVALUATION OF THE DISSOCIATION CONSTANTS OF OXALIC ACID FROM POTENTIOMETRIC DATA

The Evaluation of the Dissociation Constants of Oxalic Acid from Potentiometric Data

General

In the experiments on oxalic acid, the apparatus comprised a titration cell which was basically a five-necked round-bottomed flask, with an inlet in the bottom to allow nitrogen to be bubbled through the contents of the cell. A bridge of the design suggested by Forsling et al.(121) and illustrated below (Figure 1) was used, and this formed a liquid junction with the solution in the cell. The reference electrode was a silver/silver chloride electrode and the hydrogen ion activity in the titration cell was measured by means of a Beckman glass electrode. The scheme, therefore, was as follows.

$$\begin{array}{c|c:c:c|c|c} \text{glass electrode} & \text{soln. titrated} & 0.1\ \text{M NaClO}_4 & 0.1\ \text{M NaCl, AgCl.} & \text{Ag} & \text{AgCl} \end{array}$$

Into the titration cell were run from calibrated pipettes various proportions of oxalic acid solutions and sodium perchlorate solutions so that the total ionic strength was always 0.1 molar. A new liquid junction was made at the beginning of each titration, and between readings the three-way tap was closed to prevent excessive diffusion from one solution to the other.

To the solution in the titration cell, sodium hydroxide solution was added from a calibrated burette. Sodium perchlorate had been added to the sodium hydroxide solutions in concentrations sufficient to maintain an ionic strength of 0.1 after the addition had been made. The resulting hydrogen ion activity was measured by a glass electrode after the circuit had been standardised.

In some of the titrations additions were made to the cell in even steps throughout the course of the titration; in others a larger number of additions were made in the regions of a quarter and three-quarters neutralisation. The experimental data were analysed by a method devised by Speakman(17), and the calculations on the data were performed on a KDF 9 computer. Programs written by Dr. H.S. Dunsmore of this Department were employed. These programs refined the results by the application of least-squares treatments, and by successive approximations. If the experiments are performed in a medium of constant ionic strength the activity coefficients may be omitted from the calculations as they may then be assumed to be constant, and the corresponding stoichiometric dissociation constants will be obtained.

Theory

In the following analysis(17) the dibasic acid is denoted by H_2A. The acid is assumed to dissociate in two stages according to the following scheme

$$H_2A \rightleftharpoons H^+ + HA^- ,$$
$$HA^- \rightleftharpoons H^+ + A^{2-} .$$

The dissociation constants, K_1 and K_2 are expressed

$$K_1 = \{H^+\}\{HA^-\}/\{H_2A\} ,$$
$$K_2 = \{H^+\}\{A^{2-}\}/\{HA^-\} .$$

Since they involve activities rather than concentrations, these constants are referred to as <u>thermodynamic dissociation constants</u>. The curly brackets denote activities. If activity coefficients are included,

$$K_1 = \{H^+\}[HA]f_1/[H_2A]f_0 ,$$
$$K_2 = \{H^+\}[A^{2-}]f_2/[HA]f_1 .$$

The square brackets denote concentrations. Let the total acid concentration be

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

Suppose that a stronge monoacid base is added, for example, sodium hydroxide, to give a molar concentration b, then, from considerations of electro-neutrality

$$b + \{H^+\} = [HA^-] + 2[A^{2-}] + [OH^-] .$$

Now let $L = b + \{H^+\} - [OH^-]$

and let $M = a - b - \{H^+\} + [OH^-]$

i.e. $M = [H_2A] + [HA^-] + [A^{2-}] - b - \{H^+\} + \{OH^-\}.$

Let $N = 2a - b - \{H^+\} + \{OH^-\}$

i.e. $N = 2[H_2A] + 2[HA^-] + 2[A^{2-}] - b - \{H^+\} .$

It may then be shown that

$$\{H^+\}^2Lf_2/Nf_0 = K_1\{H^+\}Mf_2/Nf_1 + K_1K_2 .$$

An equation of the general type

$$X = MY + C$$

has thus been obtained. If X and Y are calculated from the experimental data, it is possible to obtain a value for K_1 and hence a value for K_2. The value of K_1 is obtained from the slope of the X values against the corresponding positive Y values, and this K_1 is used to calculate a value of K_2 for each point corresponding to a negative value of Y.

Experimental

General

All the glassware used in the course of the distillation and indeed in all of the operations involved in all of the subsequent work was cleaned by prolonged immersion in a solution of Pyroneg , followed by washing in dilute hydrochloric acid, rinsing with tap water, distilled water and finally by washing with "AnalaR" grade acetone. The glassware was then dried by the passage of dried filtered air through and over the apparatus. All the apparatus and solutions were used at 25°C. Where appropriate, glassware was calibrated.

Preparation of materials

Constant boiling hydrochloric acid

AnalaR hydrochloric acid was diluted to a specific gravity of approximately 1.14 with conductivity water. The distillation was performed in a three litre "Quickfit" flask fitted by a still head to a fifty centimetre long Liebig condenser, tapering in diameter from two centimetres to one centimetre. An "Electrothermal" heating mantle was used to provide heat, and was controlled by a "Sunvic" regulator. The flask and still-head were enclosed in cellulose wadding which ensured a gentle heat gradient to the top of the flask. The thermometer was a "Quickfit" 0°C - 360°C range instrument. Bumping was prevented by the addition of a few glass beads cleaned in the same manner as the rest of the apparatus. A length of rubber tubing led from the receiver adaptor to the sink to prevent the escape of hydrochloric acid gas or vapour to the laboratory. The atmospheric pressure was measured on a Fortin barometer before, during and after the distillation.

On the basis of work performed by Titus and Smith(18) it was decided to take three fractions. Of the initial 1300 ml the first 800 were rejected; the fraction 800 ml to 1050 ml was collected as was the fraction 1050 ml to 1200 ml. The commencing specific gravity of 1.14 was chosen on the basis of the work of Titus and Smith,(loc.cit.) who suggested that the equilibrium should be attained more rapidly from the more concentrated side. The rate of distillation, 5 ml per minute, was controlled carefully, since the work of Foulk and Hollingsworth(19) indicates that the percentage of hydrogen chloride in the constant boiling mixture is reduced as the rate of distillation is increased. The theoretical concentration of the constant boiling mixture was obtained from the work of Foulk and Hollingworth.(loc.cit.) The constant boiling acid was stored in "Pyrex" glass flasks; the stability of such solutions in glass vessels has been studied by Shaw(20) who showed that constant boiling hydrochloric acid was stable in glassware over long periods of time.

Preparation of Pure Sodium Hydroxide

A saturated solution of sodium hydroxide was made as follows. AnalaR grade sodium hydroxide sticks were added to a one litre conical flask containing boiled-out distilled water. Nitrogen was bubbled through to exclude carbon dioxide, and the solution was stirred by a Teflon covered magnetic stirrer. When saturation was complete an approximately 0.1 molar solution of sodium hydroxide was made by adding 5 ml of the saturated solution to a one litre graduated flask, and by making the volume up to one litre by the addition of boiled-out distilled water.

Preparation of Pure Potassium Hydrogen Phthalate

AnalaR potassium hydrogen phthalate was recrystallised from distilled water and filtered under vacuum through a Gooch funnel or a 5 micron "Millipore" filter. It was dried in an oven at 130°C and was stored in a desiccator over silica-gel. Since the material was more than 99.9% pure before recrystallisation it was assumed that after recrystallisation its purity would be in excess of this figure.

In the potentiometric measurements a buffer solution consisting of a 0.05 molar solution of potassium hydrogen phthalate was used. To make this solution, the correct weight of the salt was added to a grade A flask, and distilled water was added up to the mark. This solution was taken to have a pH value of 4.008.(21)

Preparation of Pure Sodium Carbonate

AnalaR sodium bicarbonate was heated for two hours in a platinum crucible in an oven set at 270°C. Temperature control was rigorous in order to prevent decomposition of the carbonate. The product was stored in a platinum crucible over silica-gel in a desiccator.

Preparation of Pure Sodium Perchlorate

B.D.H. sodium perchlorate with a chloride content of 0.002 % was used. About 400 g of the salt were dissolved in 220 ml of distilled water in a 500 ml "Quickfit" conical flask. Some of the water was boiled off, and the solution was filtered with Millipore apparatus. After being cooled the filtered solution was seeded and the recrystallised material was filtered off in a Gooch funnel. The material was dried for a week under vacuum, over phosphorus pentoxide. On the assumption that the material was anhydrous a solution of approximate concentration 0.2 molar was made up. This solution was analysed by an ion exchange method. A column containing about 10 ml of Amberlite 120 cation exchanger in the hydrogen form was regenerated with 0.1 molar hydrochloric acid and washed with distilled water until the washings were of pH 5-6, that is, the pH of distilled water at equilibrium with the atmosphere. 5 ml of the sodium perchlorate solution were passed through the column and this was washed through with 50 ml of distilled water. The acid solution was titrated with standard sodium hydroxide solution and phenolphthalein was used as an indicator.

The results of the titrations indicated that the sodium perchlorate which had been obtained was anhydrous.

Preparation of Pure Oxalic Acid

200 g of AnalaR oxalic acid were dissolved in about 600 ml of distilled water at 80°C. This solution was filtered through a Hirsch funnel into a filter flask which had previously been heated to 80°C in an oven. After filtration the solution was allowed to cool to about 25°C and the resulting yield of needle-shaped crystals was collected by means of a Whatman No. 1 filter paper in a Hirsch funnel. The material was recrystallised twice, and the product was stored in a desiccator over silica-gel.

The above procedure is reported to result in a dihydrate.(22) When the product was dry it was ground to a fine powder in an agate mortar. Weighed samples of the acid were titrated against standard caustic soda solutions, and the results indicated that a pure dihydrate had been obtained. The melting point of the product was 100°C - 102°C.(literature; 101°C)

Analysis of the constant boiling hydrochloric acid

Since constant boiling hydrochloric acid was the standard to which other solutions used in this section of the work would ultimately be referred it was necessary that the concentration of this reagent should be known accurately. The concentration of the acid, therefore, was found by a number of methods, and the results were compared with each other.

Gravimetric method

A stock solution of hydrochloric acid was prepared by the addition of 20 ml of the constant-boiling acid from a pipette to a one litre flask, and by making the volume up to the mark by the addition of distilled water. Chloride was estimated as silver chloride according to the method described by Vogel.(23) To about 20 ml of the approximately 0.12 molar solution in a 250 ml beaker, 100 ml of distilled water and 2 ml of 0.02 molar nitric acid were added to prevent precipitation of silver phosphate or silver carbonate. A slight excess of silver nitrate solution was added to the mixture and a colloidal suspension of silver chloride which was coagulated into curds by being heated to 90°C and stirred was formed. The entire procedure was performed in the dark to prevent photoreduction of the silver ions. The precipitate was collected by vacuum pump filtration on a sintered glass crucible (pore size 5-10 microns) and washed with dilute nitric acid. The crucibles which had been weighed empty were dried in an oven for one hour at 140°C and weighed when cool. The process was repeated until consecutive weighings gave the same result. About a dozen determinations in all were made.

Volumetric method

Sodium hydroxide solution which was prepared by the method described above was standardised by titration against recrystallised potassium hydrogen phthalate. Weighed quantities of potassium hydrogen phthalate were added to clean, dry 200 ml conical flasks and about 70 ml of distilled water were added. A hot plate was used to raise the temperature of the solution to near boiling point to help exclude carbon dioxide uptake at the end point. Two drops of fresh phenolphthalein solution were used as the indicator. Sodium hydroxide was added from a burette until a faint but permanent pink coloration was observed. A blank was then performed.

The standardised sodium hydroxide solution was then used to standardise the stock solution of hydrochloric acid prepared as described in the foregoing section. The method of titration was identical, except that instead of weighed quantities of potassium hydrogen phthalate, volumes of acid were delivered to the conical flasks from pipettes.

Titration against sodium carbonate

Weighed samples of sodium carbonate prepared as described above were added to conical flasks and about 70 ml of distilled water were added. Two drops of screened methyl orange were used as an indicator, and hydrochloric acid was added from a burette until the end point was reached. A blank was then performed.

Results of the Hydrochloric Acid Analyses

The results of the analyses are shown in the following summary.

Method	Calculated Molarity	No. of Determinations
silver chloride precipitation	0.12241	7 (best of 12)
sodium hydroxide titration	0.12224	5
sodium carbonate titration	0.12246	3
average	0.12237	
literature value(19)	0.12161	

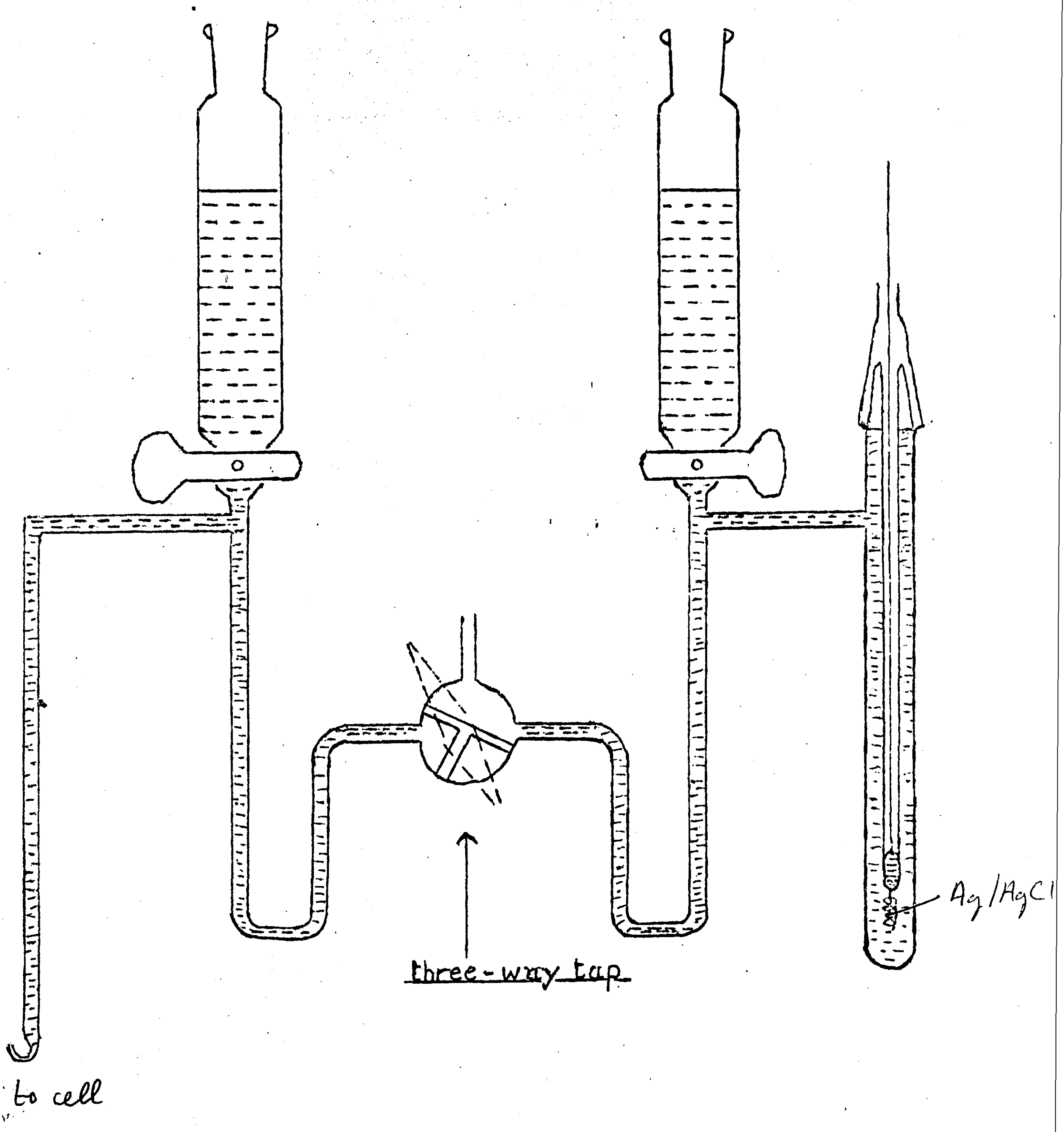
It was decided to adopt as the value of the concentration of the acid the average of the figures found by experiment as there was very good agreement between the values found by different methods, and poorer agreement with the literature value. The molarity of the constant boiling hydrochloric acid was therefore taken as 6.1188.

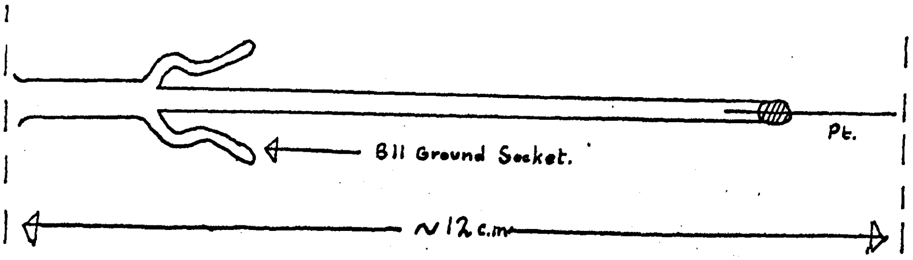
The Apparatus

The Bridge

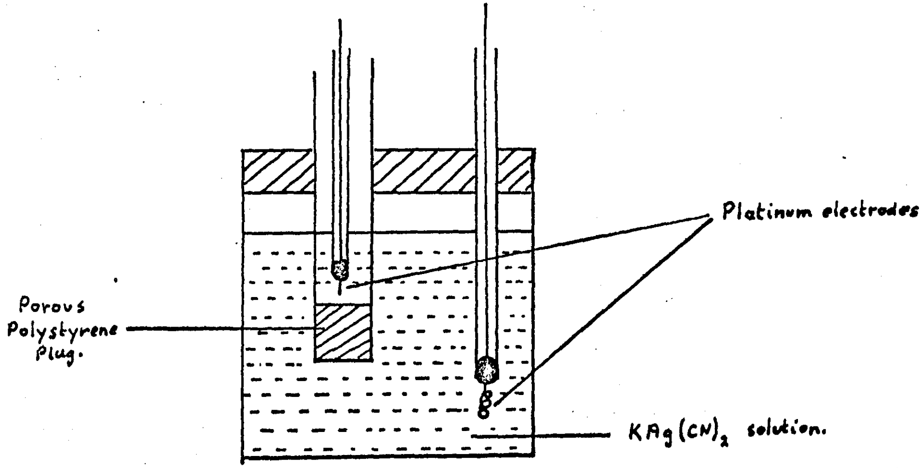
The bridge used is shown in diagram form in figure I. In order to use this apparatus it was necessary to construct silver-silver chloride electrodes of suitable dimensions. These were prepared by the following method. Platinum electrodes were constructed as illustrated below (figure II). The platinum wire was sealed into the end of the glass tube with "Araldite" epoxy resin, of which a few grains were placed inside the end of the tube. The tubes were then placed in an oven at room temperature and heated slowly to 130°C to avoid uneven heating with resultant poor sealing. The electrodes were plated with silver, use being made of the system illustrated below. The circuit which was used is also shown in figure II. The "Solartron" was set to give constant voltage, and the rheostat to give 0.1 M ohm. Potassium argentocyanide was used as the plating solution. At the beginning, a few drops of silver nitrate solution were added to remove any free cyanide as silver

The Bridge.

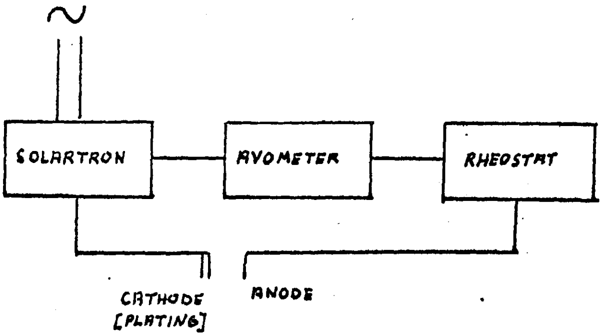




Platinum electrode.



Plating cell.



Plating circuit.

cyanide. The electrodes were first cleaned by immersion in concentrated nitric acid. When they were in the plating solution, the electrodes were subjected to a current density of 0.4 mA per square centimetre for six hours. The silver plated electrodes were then washed in distilled water and allowed to stand in a dilute solution of ammonium hydroxide for two hours.

Chloridisation was performed by electrolysis of 0.1 molar hydrochloric acid for thirty minutes at a current of 2 mA per square centimetre. Platinum anodes were used, because silver anodes polarise readily. The polystyrene plug was employed to prevent cyanide ions from diffusing towards the cathode, and contaminating the silver plating with silver cyanide (figure II).

This procedure produced a pair of silver-silver chloride electrodes the potential of which, in 0.1 molar hydrochloric acid, differed by 2×10^{-4} volt. One of these electrodes was incorporated into the bridge system which was used for the measurements.

Temperature control

Since dissociation constants and temperature dependent, rigorous temperature control was necessary. The bridge and the titration cell, therefore, were immersed during the titrations, and for some time before, in a water-bath, the temperature of which was regulated by a conventional mercury-toluene thermoregulator, which contained a large volume of toluene. The regulator was connected via a Sunvic proportioning head and a "Sunvic" relay (A.E.I. EH4T) to a heating element in the water-bath.

The water bath was cooled by twelve feet of copper tubing bent into a cooling element through which cold water was permitted to pass at a carefully controlled rate. Uniform temperature was maintained in the tank by a stirrer attached to a "Citenco" electric motor. The temperature was monitored by means of a Beckman thermometer. By the correct balance of heating and cooling, temperature control of better than 0.10° was maintained throughout the experiments. It was necessary to ensure that the needle of the thermoregulator and the surface of the mercury were clean so that the circuit could be opened and closed decisively.

The Assembly

The bridge and the cell were immersed in the bath described above. The bridge was attached to an aluminium frame and the cell was supported by a polythene base, which in turn sat in a hammock of copper gauze in order to screen the electrodes and their leads to the maximum possible extent.

emf values were measured on a "Pye" potentiometer connected to a "Vibron" electrometer as a null-detector. A junction-box used in the circuit allowed the use of two glass electrodes and/or two reference electrodes at the same time. The setting at which no current flowed in the circuit was detected by a "Scalamp" galvanometer at maximum sensitivity.

Calibration of the Glass Electrode

The response of the glass electrode to changes in pH is not in general 5.916×10^{-2} volts per pH unit at 25°C but is usually somewhat smaller as a result of the asymmetry potential.(24) This is usually accounted for as being the result of strains in the electrode surface so that the surface characteristics of the inner and outer surfaces are not identical. This fact results in the necessity of calibrating the electrode system prior to its use.

Titrations of standard hydrochloric acid with standard sodium hydroxide were performed so that measured emf values corresponding to calculated pH values could be obtained. The titrations were performed at an ionic strength of 0.1 molar, maintained by sodium perchlorate as a supporting electrolyte.

It was found that with the apparatus a serious and reproducible non-linear response at low values of pH was obtained. Checks on the concentrations of the acid and the base used showed no discrepancy that could account for the large deviations from linearity which were observed. Application of the correction for liquid junction potentials suggested by Biedermann and Sillen(25) reduced the discrepancy, but did not remove it. It was decided to use a calibration graph to convert the measured emf values to pH, but it was later found more convenient to incorporate the calibration into the computer program which was used for the calculation of the dissociation constants. The electrode response is shown plotted in figure III.

Results

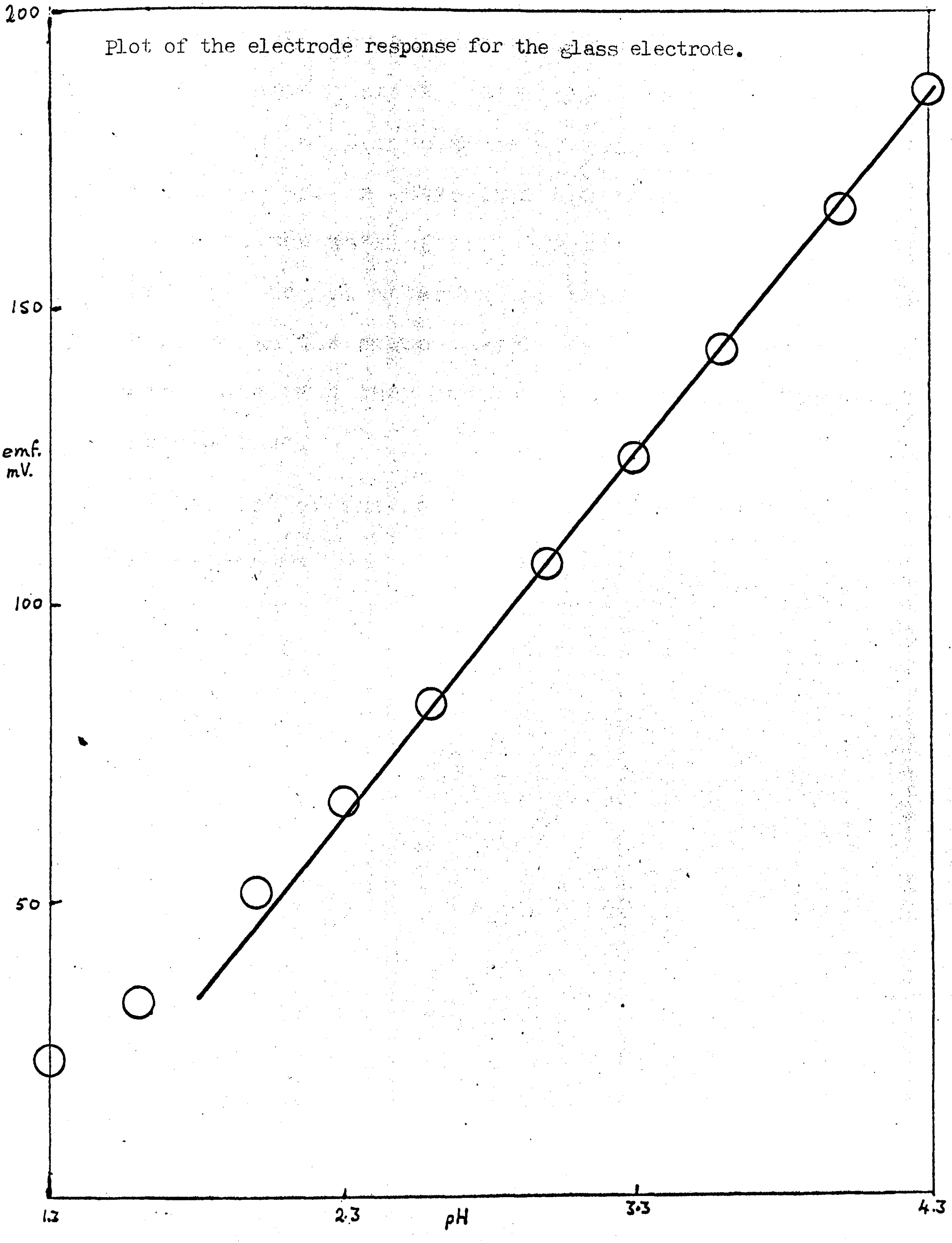
The experimental data and the positive X and Y values are listed in Appendix I, Tables I and II.

Summary of the K_1 and average K_2 values obtained from the experiments

Run	Points	K_1	Average K_2
1	1 - 22	4.63×10^{-2}	1.54×10^{-4}
2	23 - 45	5.11×10^{-2}	1.56×10^{-4}
3	46 - 70	4.91×10^{-2}	1.52×10^{-4}
4	71 - 92	5.20×10^{-2}	1.58×10^{-4}
5	93 - 117	5.09×10^{-2}	1.56×10^{-4}
6	118 - 141	5.03×10^{-2}	1.50×10^{-4}
7	142 - 158	4.79×10^{-2}	1.61×10^{-4}
8	159 - 175	4.43×10^{-2}	1.55×10^{-4}

The average value of K_1 is 4.90×10^{-2} with a standard deviation of 0.25, and the average value of K_2 is 1.55×10^{-4} with a standard deviation of 0.03. The standard deviations were calculated by the following formula.

$$\sigma = \left\{\frac{\Sigma k^2 - n\bar{k}^2}{n}\right\}^{\frac{1}{2}}$$



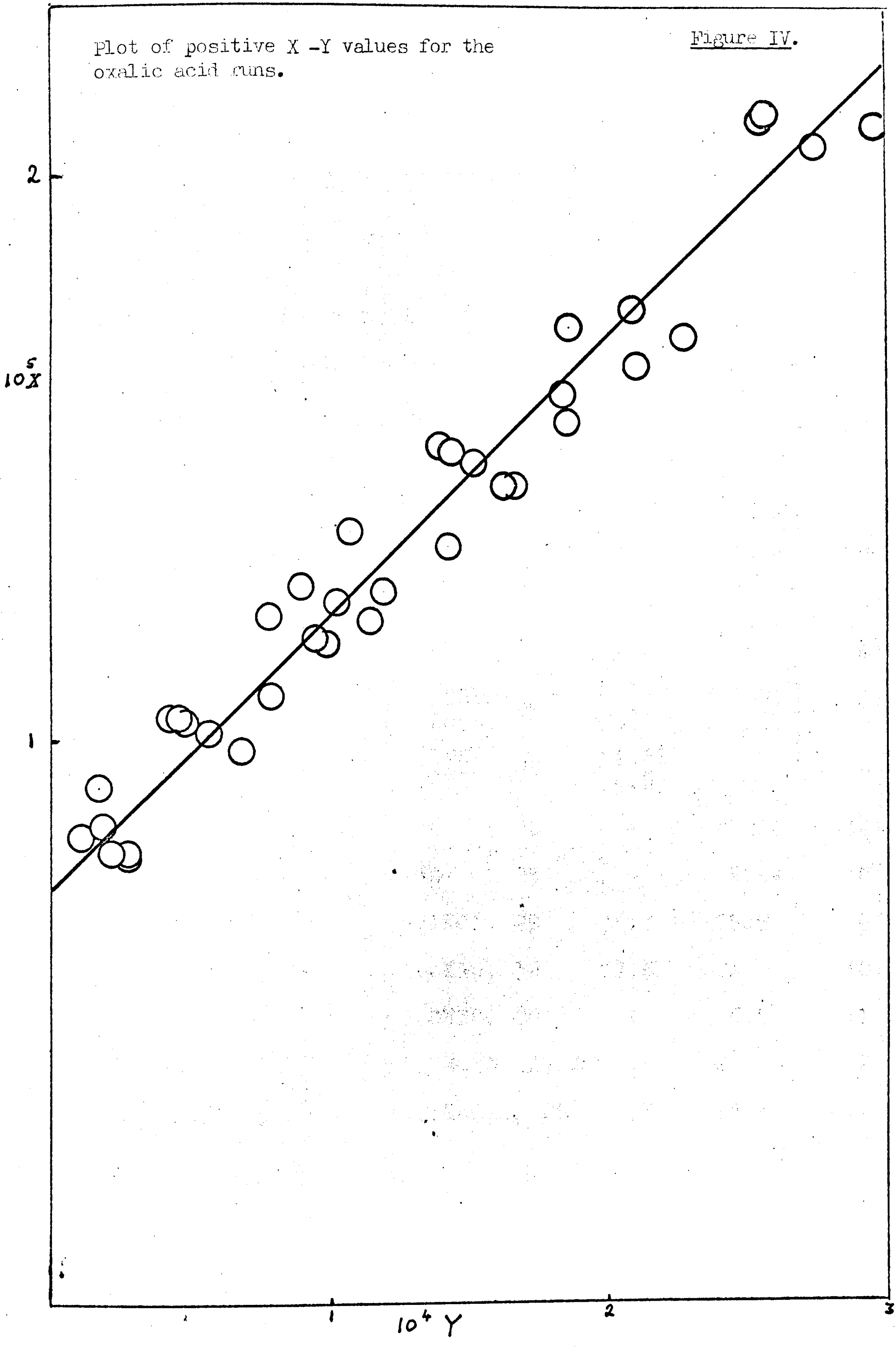
Plot of the electrode response for the glass electrode.

A tabulated summary of some earlier work on the dissociation constants of oxalic acid is given below. The table is chronological, with the more recent values at the foot. Work at 0.1 molar is asterisked, and abbreviations are those used in Stability Constants [118]. Good agreement with the work of ref. (22) is seen; this work was also performed in 0.1 molar sodium perchlorate. The values obtained in the present work, therefore, seem to be reasonable, and they have been used in the subsequent calculations.

A plot of the positive X and Y values is shown in figure IV.

Plot of positive X -Y values for the oxalic acid runs.

Figure IV.



Summary of previous work on the Dissociation Constants of Oxalic Acid

Method	I	T	$10^2 k_1$	$10^5 k_2$	Ref.
emf, f.pt., cond.	->0	18°C	5.7	6.9	26
kinetics(sugar inv.)	0.001	100	-	1.6	27,28
partition, cond.	0.001	25	3.8	4.9,4.1	29
kinetics*	0.1	25	7.3	11	30
emf	0.01 0.004 0.00125	25	6.2 6.05 5.94	8.45 7.30 6.74	31
kinetics(ester hyd.)	0.01	20	4	-	32
pH	0.2KCl	25	7.25	14	33
-	-	18	1.0	13	34
Q*	0.1283 0.0855	25	-	3.95 4.27	35
H*	0.1249 0.0851	25	4.61 4.57	- -	36
H	->0	25	-	5.18	37
H	->0	25	-	5.44	38
pH*	0.1KCl	20	6.3	15.9	39
-	1.0KNO_3	32	7.6	21	40
-	1.0HNO_3	20	11	6.5	41
pH	2.5$NaNO_3$	27.4	2.4	22	42
pH*	0.1$NaClO_4$	25	4.3	15.6	15

The Determination of some Complex Stability Constants by the Ion Exchange Method

The Ion-Exchange Method of Complex Stability Constant Determination

Historical Introduction

The first worker to employ ion-exchangers in a study of complexing was Guenther-Schulze(43,44) who in 1922 used inorganic zeolites to study the complexes formed between chloride ions and divalent metal cations. He assumed, however, that the presence of chloride ions in the exchanger was a result of the uptake by the exchanger of species like MCl^+. Later, Samuelson(45) examined the complex ions of chromium using synthetic organic cation exchangers which had recently been developed by Adams and Holmes.(55) Using synthetic anion exchangers, Samuelson(56-58) elucidated the structure of Graham's salt and used a cation exchanger to determine the composition and stability of the ferrimetaphosphate complex.

Schubert(59-66) was the first to investigate systems where the concentration of metal relative to the ligand concentration and the capacity of the cation exchanger was negligible, and he studied the complexes formed between the alkaline earth cations and various organic acids in a quantitative manner. Fronaeus(67,68,69) examined the method in a thoroughly rigorous analysis for systems more general than those considered by Schubert, and the equations employed by Schubert follow from the deductions of Fronaeus when the appropriate simplifications are made. A number of workers(60,67,68) have compared the results obtained by the ion-exchange method with those obtained under similar conditions by different methods and have demonstrated that, in general, good agreement is obtained.

Theory

If one considers a given mass of a cation-exchange resin in contact with an aqueous solution containing a given concentration of some polyvalent cation, then, because of the exchange characteristics of the resin, an equilibrium will be established, the cation distributing itself between the resin phase and the aqueous phase to an extent dependent on a number of variable factors such as the mass of resin, the volume of the solution, the temperature, the hydrated cationic radius and the nature of the cation exchange resin itself. The extent of the distribution will be described by a constant which is termed the distribution constant or the distribution coefficient. The latter term will be used throughout these analyses. If to the above system a ligand is now added some of the cations will be bound by the ligand, and the concentration of the free cations will thus be diminished. The free cations, however, will still be distributed according to the original distribution coefficient and if it has a positive charge the complex species which has been formed will also distribute itself between the aqueous and the resin phases according to a second distribution coefficient. Consequently, when there is a finite ligand concentration present in the aqueous phase, the total cationic concentration in each phase is found to have altered.

The ion-exchange method of stability constant determination makes use of the quantitative relationship between the stability constants of the complexes formed between the cation and the ligand, and the change in the concentration of cation in the aqueous phase. The argument will be developed first for a system involving a divalent cation and a monovalent ligand ion. The simplifications which are possible when a divalent ligand ion is used will then be considered.

Analyses which are of more general application than those developed below exist(70) but these are not necessary for the purpose of the present investigation.

In the following analyses, the divalent cation will be denoted by M, and the monovalent ligand anion by HA. The reason for the latter is that the only monovalent anion that will be considered in subsequent experiments is the hydrogen-oxalate species, a protonated ion. Charge signs will be omitted where possible for the sake of clarity. The resin is assumed to be in the sodium form. If the species which result from this mixture of ions are M, MHA and $M(HA)_2$ then the following equilibria may be considered to occur.

$$M + 2NaR \rightleftharpoons MR_2 + 2Na,$$

$$MHA + NaR \rightleftharpoons MHAR + Na.$$

Here the expressions NaR, MR_2 and MHAR refer to species which have been adsorbed by the resin phase.

The Law of Mass Action results in

$$k_0 = \frac{[MR_2][Na]^2}{[M][NaR]^2}$$

$$\therefore \quad \frac{[MR_2]}{[M]} = k_0 \frac{[NaR]^2}{[Na]^2} \quad ;$$

$$k_1 = \frac{[MHAR][Na]}{[NaR][MHA]}$$

$$\therefore \quad \frac{[MHAR]}{[MHA]} = k_1 \frac{[NaR]}{[Na]} \quad .$$

Let $$l_0 = k_0 \frac{[NaR]^2}{[Na]^2} = \frac{[MR_2]}{[M]}$$

and $$l_1 = k_1 \frac{[NaR]}{[Na]} = \frac{[MHAR]}{[MHA]} \quad .$$

It may readily be seen that the physical significance of the terms l_0 and l_1 is that they are respectively the distribution coefficients for the species M and MHA between the resin phase and the aqueous phase. If the total concentration of M is low, compared with the ionic strength which is maintained at a constant value with sodium ions then [Na] is almost constant in all the solutions. If the exchange capacity of the resin is denoted by α (which only with weak acid exchangers is a function of the pH) then

$$[NaR] = \alpha - 2[MR_2]-[MHAR] \ .$$

If the total metal concentration in the resin is given by C_{MR} and the average number of ligands per metal ion in the resin is $\bar{n}_R$ then since

$$C_{MR} = [MHAR] + [MR_2] ,$$

$$[NaR] = \alpha - 2C_{MR} + [MHAR]$$

and $$\frac{[MHAR]}{C_{MR}} = \bar{n}_R$$

so that $$[MHAR] = C_{MR}.\bar{n}_R ,$$

then $$[NaR] = \alpha - C_{MR}(2-\bar{n}_R).$$

Since l_0 and l_1 are the distribution coefficients for M and MHA respectively, between the resin and the aqueous phases it is obvious that

C_{MR} (i.e., total metal in the resin phase) =

$$l_0 [M] + l_1 [MHA] .$$

At this stage two new functions must be introduced, an overall distribution coefficient,

$$\phi = C_{MR}/C_M$$

and $$X = 1 + \sum_{j=1}^{N} \beta_j [HA]^j .$$

(In general, $X_n = \sum_{j=n}^{N} \beta_j [HA]^{j-n}, \ \beta_0 = 1$) .

Since $$X = \sum_{j=1}^{N} \beta_j [HA]^j$$

$$= 1 + \beta_1 [HA] + \beta_2 [HA]^2 + \ldots\ldots ,$$

then $$[M]X = [M] + [MHA] + [M(HA)_2] + \ldots\ldots$$

$$= C_M .$$

Since $$C_{MR} = l_0[M] + l_1[MHA]$$

then $$\phi = \frac{C_{MR}}{C_M} = \frac{l_0[M] + l_1[MHA]}{X[M]}$$

$$= \frac{l_0 + l_1[MHA]/[M]}{X} .$$

Because $$\beta_1 = \frac{[MHA]}{[M][HA]}$$

$$\phi = \frac{l_0 + l_1\beta_1[HA]}{X} ,$$

where $$l = l_1\beta_1 l_0^{-1} .$$

Now, if α is constant and C_{MR} is low the term

$$(2 - \bar{n}_R)C_{MR}$$

may be neglected. [NaR] is then approximately equal to α, that is, a constant. Consequently, at constant ionic strength l_0, l_1 and l are constant. It is therefore seen that C_{MR} should be kept as low as possible and constant and that the ionic strength in the aqueous phase should also be constant, in order that l should be a constant for a given [HA].

To obtain values for C_{MR} use is made of the relationship

$$m.C_{MR} = v.C'_M - v.\delta.C_M$$

where m is the mass of the ion exchanger expressed in grams, v is the volume of the aqueous phase expressed in litres, C'_M is the concentration of the divalent cation in the aqueous phase before the ligand, HA, has been added, and C_M is the concentration of the cation in the aqueous phase after the ligand has been added. δ is the swelling factor resulting from the fact that in the presence of the resin, some of the solution is adsorbed, so that the total volume is reduced. Instead of using v alone, therefore, $v.\delta$ is used. In all cases, δ is less than unity. To a good approximation it has been found that

$$\delta \simeq 1 - \frac{m}{v} \quad \text{where v is expressed in ml.}$$

Since

$$\phi = \frac{C_{MR}}{C_M}$$

it is possible to rearrange the equation involving $m.C_{MR}$ to give

$$\phi = \frac{v}{m}\left(\frac{C'_M}{C_M} - \delta\right)$$

so that if the experiment is arranged with m and v numerically equal and if the swelling factor is taken as unity

$$\phi = \frac{C'_M}{C_M} - 1 \ .$$

$\bar{n}$ is the average number of bound ligands per metal ion in the aqueous phase, the mean ligand number.

$$\bar{n} = \frac{\text{Number of bound ligand ions}}{\text{Number of metal ions}}$$

$$= \frac{[MHA] + 2[M(HA)_2] + \ldots}{[M] + [MHA] + [M(HA)_2] + \ldots}$$

$$= \frac{1 \times \frac{[MHA][HA]}{[M][HA]} + \frac{2[M(HA)_2][HA]^2}{[M][HA]^2} + \ldots}{\frac{[M]}{[M]} + \frac{[MHA][HA]}{[M][HA]} + \frac{[M(HA)_2][HA]^2}{[M][HA]^2} + \ldots}$$

$$= \frac{\sum_{j=1}^{N} j\beta_j[HA]^j}{1 + \sum_{j=1}^{N} \beta_n[HA]^j}$$

$$= \frac{\sum_{j=1}^{N} j\beta_j[HA]^j}{X} \quad \ldots\ldots \quad (A)$$

Because $\phi = 1_o \frac{1 + 1[HA]}{X}$

and if 1 is set to zero, the approximation $\phi = 1_o/X$ is obtained. If now the numerator and the denominator of equation (A) are multiplied by X, the following expression is obtained.

$$\bar{n} = \frac{1_o}{\phi X^2} \sum_{j=1}^{N} j\beta_j[HA]^j \quad .$$

If now it is assumed that C_{HA} approximates to [HA], an assumption which is reasonable when $C'_M << C'_{HA}$, it is possible to write

$$\bar{n} = \frac{C_{HA} 1_o}{\phi[HA]X^2} \sum_{j=1}^{N} j\beta_j[HA]^j \quad .$$

Since $\phi \simeq 1_o/X$, on differentiation

$$\left(\frac{\partial\phi}{\partial C_{HA}}\right)_{C_{MR}} = 1_o\left(\frac{\partial X^{-1}}{\partial C_{HA}}\right)_{C_{MR}} = 1_o\left(\frac{\partial X^{-1}}{\partial X} \cdot \frac{\partial X}{\partial C_{HA}}\right)_{C_{MR}}$$

$$= 1_o \frac{-1}{X^2} \sum_{j=1}^{N} j\beta_j[HA]^{j-1}$$

$$= l_o \frac{-1}{[HA]X^2} \sum_{j=1}^{N} j\beta_j[HA]^j \quad ,$$

so that $$\bar{n} = -\frac{C_{HA}}{\phi} \frac{\partial\phi}{\partial C_{HA}}\bigg|_{C_{MR}} \quad .$$

This value of $\bar{n}$ allows the calculation of [HA] from the relationship

$$[HA] = C_{HA} - \bar{n}C_M \quad .$$

To obtain the stability constants, β_j, it is necessary to differentiate ϕX twice with respect to [HA].

Since $$\phi X = l_o(1 + l[HA])$$

$$(\phi X)' = l$$

and $$(\phi X)'' = 0.$$

Since $$(uv)'' = uv'' + 2u'v' + u''v, \text{ then}$$

$$\phi''X + 2\phi'X' + \phi X'' = 0 \quad .$$

Since

$$X = 1 + \sum_{j=1}^{N} \beta_j[HA]^j$$

$$X' = \sum_{j=1}^{N} j\beta_j[HA]^{j-1}$$

and $$X'' = \sum_{j=1}^{N} j(j-1)\beta_j[HA]^{j-2} \quad ,$$

$$\phi'' + \phi'' \sum_{j=1}^{N} \beta_j[\mathrm{HA}]^j + 2\phi' \sum_{j=1}^{N} j\beta_j[\mathrm{HA}]^{j-1}$$

$$+ \phi \sum_{j=1}^{N} j(j-1)\beta_j[\mathrm{HA}]^{j-2}$$

$$= \quad \phi'' + \sum_{j=1}^{N} \beta_j\{\phi''[\mathrm{HA}]^j + 2\phi' j[\mathrm{HA}]^{j-1} + \phi j(j-1)[\mathrm{HA}]^{j-2}\}$$

$$= \quad 0 \; .$$

For convenience this may be abbreviated as

$$\phi'' + \sum_{j=1}^{N} \alpha_j\beta_j = 0 \; ,$$

where $\alpha_j = \phi''[\mathrm{HA}]^j + 2\phi'[\mathrm{HA}]^{j-1} + \phi j(j-1)[\mathrm{HA}]^{j-2}$.

Values of ϕ' may be obtained from a plot of ϕ versus [HA], and values of ϕ'' from a plot of ϕ' versus [HA]. It is thus possible to determine the values of the coefficients α_j at N different values of [HA] and so to obtain N equations from which β_1 to β_N may be calculated. In practice it is much more convenient to obtain these values by calculation involving a curve-fitting procedure. The equation of the curve of ϕ versus [HA] is obtained by calculation and the expressions for the first and second derivatives are thence found. To facilitate these calculations a computer program was written, and this is included in Appendix II.

In general it is found that of the stability constants, only the first may be found by the method to any acceptable degree of accuracy.(67) Accordingly, the remaining constants must be found by a different approach. It may easily be shown that, because

$$\phi = l_0 \frac{1 + l[HA]}{X}$$

$$\lim_{[HA] \to 0} \phi^{-1} = l_0^{-1} \,.$$

The limiting value of a plot of ϕ^{-1} versus [HA] is therefore l_0^{-1} and so l_0 is obtained.

It is now necessary to define a new function,

$$\phi_1 = \left(\frac{1}{\phi} - \frac{1}{l_0}\right)\frac{1}{[HA]}$$

$$= \frac{X}{l_0[HA](1+l[HA])} - \frac{1}{l_0[HA]}$$

$$= \frac{1 + \sum_{j=1}^{N} \beta_j[HA]^j - 1 - l[HA]}{l_0[HA](1 + l[HA])}$$

$$= \frac{[HA](\beta_1 - l) + \sum_{j=2}^{N} \beta_j[HA]^j}{l_0[HA](1 + l[HA])}$$

$$= \frac{\beta_1 - l}{l_0(1 + l[HA])} + \frac{\sum_{j=2}^{N} \beta_j[HA]^j}{l_0[HA](1+l[HA])} \,.$$

$$\therefore \quad \lim_{[HA]\to 0} \phi_1 = \frac{\beta_1 - 1}{l_0} \ .$$

The values of X may therefore be calculated from the corresponding ϕ values since $\phi = l_0 \frac{1+l[HA]}{X}$ and β_1 and l_0, and consequently l, have been calculated. Earlier in the analysis the definition was made of

$$X_n = \sum_{j=n}^{N} \beta_j [HA]^{j-n} \ .$$

$$\therefore \quad X_0 = \beta_0[HA]^0 + \beta_1[HA]^1 + \beta_2[HA]^2 + \ldots\ldots$$

$$= 1 + \beta_1[HA] + \beta_2[HA]^2 + \ldots\ldots ,$$

$$X_1 = \beta_1[HA]^0 + \beta_2[HA] + \beta_3[HA]^2 + \ldots\ldots$$

$$= \beta_1 + \beta_2[HA] + \beta_3[HA]^2 + \ldots\ldots$$

and

$$X_2 = \beta_2[HA]^0 + \beta_3[HA] + \beta_4[HA]^2$$

$$= \beta_2 + \beta_3[HA] + \beta_4[HA]^2 \ .$$

A plot of X_1 versus [HA] therefore gives β_1 at [HA] -> 0, a plot of X_2 versus [HA] gives β_2 at [HA] -> 0 and so on.

A summary of the foregoing argument is perhaps relevant at this stage. The experimental data yield values for C_M', C_M and C_{HA}. If the swelling factor is taken as unity, values for ϕ may be calculated. Plots of ϕ versus C_{HA} and of C_{MR} versus C_{HA}, each plot at given values of C_M', may then be made. A series of plots of ϕ versus C_{MR} at different values of C_{HA}

is made. A convenient, low value is C_{MR} is then selected and from the graph ϕ values corresponding to a series of definite arbitrary C_{HA} values are taken. From the values of ϕ and C_{MR} the values of C_M corrected to a constant low C_{MR} are found. The corresponding [HA] are then calculated from the expression which was derived. ϕ^{-1} is plotted versus [HA] so that l_0 may be found. ϕ_1 is calculated and its limiting value is found. β_1 is obtained from the solution of the series of simultaneous equations, and so the value of l is found. X, X_1, X_2, etc., may be calculated, and from their limiting values at zero ligand concentration the overall stability constants are obtained. The first and second derivatives of the plot of ϕ versus [HA] may be found either by graphical methods or, as was done in the present studies, by computer curve-fitting.

If, instead of a monovalent ligand anion, a divalent ligand is used, a number of significant simplications may be made.

Since $[MHAR] = 0,$

because the complex is uncharged,

$$k_1 \frac{[NaR]}{[Na]} = l_1 = 0 \; .$$

Consequently $C_{MR} = l_0[M]$

so $\phi = l_0/X$

$$\therefore \qquad l_0/\phi = 1 + \beta_1[HA] + \beta_2[HA]^2 + \ldots\ldots$$

$$\therefore \qquad \frac{l_0}{\phi} - 1 = \beta_1[HA] + \beta_2[HA]^2 + \ldots\ldots$$

$$\therefore \qquad \frac{\left(\frac{l_0}{\phi} - 1\right)}{[HA]} = \beta_1 + \beta_2[HA] + \ldots\ldots$$

In this case $\left(\frac{l_0}{\phi} - 1\right)\frac{1}{[HA]}$ is X_1, and by the evaluation of X_2, etc., it is possible to calculate β_2, etc.

It is possible to obviate the necessity for the determination of ϕ values at constant C_{MR} if the polyvalent cation is used at trace concentration. α, the exchanger capacity and [NaR] may then be regarded as constant and identical and the approximations which depend on this assumption become more acceptable. Furthermore, if the cation is used at trace concentration, C_{HA} and [HA] become virtually identical because only a relatively small proportion of the ligand is involved in complex formation. The cation may be used at tracer level if suitable radioactive isotopes are employed, and such an expedient also makes the determination of the cation, and hence of the distribution coefficients, simpler.

The constancy of α and [NaR] is of the greatest importance. If the cation is not used in trace quantities, and an interpolation is made to a constant value of C_{MR} the latter itself comprises two contributions, l_0[M] and l_1[MHA] so that although C_{MR} is constant in different experiments, with different values of C_{HA} there will be different concentrations of M and of MHA within the resin phase. Since these two species possess different charges, the former being divalent and the latter being monovalent, the ionic strength inside the resin might be expected to vary from experiment to experiment. It is accordingly theoretically more desirable to use cation at trace concentration. The interpolation method is presumably most acceptable when the cation and the anion have equal charges, so that there is only one charge type within the resin.

The graphical interpolation method has however been used many times to examine systems which have also been studied by other techniques(67,68) and the results have indicated satisfactory agreement, so that it is presumably sufficiently accurate for most purposes. Further refinement of the method in terms of the ionic strength within the resin phase might prove difficult at present, as there is little really quantitative data extant on the topic.

The Ion-Exchange Method of Stability Constant Determination in the Presence of a Second Complexing Anion

It is sometimes necessary to perform the experiments in the presence of a buffer which may complex with the cation. This is the case when a weak acid exchanger is used, because the capacity is pH dependent. When this is done a correction for this additional retention by the buffer anions of the cation in the aqueous phase must be included in the analysis. The buffer anion is denoted by B.

To take a simple case,

$$\phi = \frac{[MR_2]}{[M] + [MB] + [MA] \ldots\ldots}$$

Here M is a divalent cation and A is a divalent anion. Under these conditions

$$l_o = \frac{[MR_2]}{[M] + [MB]} \quad ,$$

$$\beta_1 = \frac{[MA]}{[M][A]}$$

and

$$\beta_B = \frac{[MB]}{[M][B]}$$

so that

$$l_o = \frac{[MR_2]}{[M] + \beta_B[M][B]}$$

and

$$\phi = \frac{[MR_2]}{[M] + \beta_B[M][B] + [MA] + [MA_2] + \ldots} \quad .$$

It may readily be shown that

$$\frac{l_o}{\phi} = \frac{[M] + \beta_B[M][B]}{[M] + \beta_B[M][B]} + \frac{[MA]}{[M] + \beta_B[M][B]} + \frac{[MA_2]}{[M] + \beta_B[M][B]}$$

$$\therefore \quad \frac{\left(\frac{l_o}{\phi} - 1\right)}{[A]} = \frac{\beta_1}{1 + \beta_B[B]} + \frac{\beta_2[A]}{1 + \beta_B[B]} + \ldots\ldots \quad .$$

Since C_M is very much smaller than B and β_B is a constant, then, even if the buffer complexes with the metal ion, the correction is very simple to apply and requires only the concentration of the buffer anion and the stability constant of any complex formed between the cation and the buffer anion. This stability constant may be determined by the ion-exchange method. In the present work, some of the preliminary experiments in which calcium oxalate complexes were studied were performed in the presence of buffer. This was strictly unnecessary, because the purpose of holding the pH at a rigorously constant value is to avoid exchanger capacity changes with pH. The resin used for all the experiments however was CG-120, a sulphonated polystyrene resin, which, because it is a strong acid resin, has a capacity independent of pH. None of the other systems was studied in the presence of buffer. The calcium-oxalate system, however, illustrates the additional precautions which must be observed when the experiments are performed in the presence of an additional anion.

Experimental

Preparation of Materials

Conditioning of the Ion-Exchange Resin

The resin which was used was Amberlite CG 120, the chromatographic grade of Amberlite IR 120. This is a cation exchanger of which the fixed sites are sulphonic acid groups and in consequence the resin capacity is independent of pH because the fixed sites are strong acid groups. The bead size was 200 mesh. The resin was conditioned as follows. 300 ml of the resin (dry volume) were soaked for twelve hours in distilled water to allow the resin to expand fully. Fine particles were removed by decantation. More water was added, and the mixture was agitated, after which the water was decanted as before to remove more of the fine particles. This procedure was repeated until no fine particles remained. The resin was then converted completely to the hydrogen form in a column by the passage through the resin of 0.1 molar hydrochloric acid. 0.1 molar sodium chloride was then passed through the column to convert the resin to the sodium form, and so on until four complete cycles had been completed. The resin was finally converted to the sodium form by the passage of 0.1 molar sodium chloride solution in excess. When the resin was fully converted it was transferred to a Buchner funnel and was rapidly washed with distilled water until no chloride ions were detected in the washings. The wet resin was then spread out on a glazed earthenware dish and dried at 25°C, after which it was transferred to a desiccator which contained no drying agent, and stored at 25°C.

Conditioning of the Ion-Exchange Resin to the Hydrogen Form

About 100 ml of dry CG 120 in the hydrogen form were soaked in distilled water for about 24 hours. Fine particles were decanted from time to time, and more distilled water was added. When the resin was considered to be fully expanded, and when all the fine particles had been removed the resin was transferred to a suitable column and approximately 0.1 molar perchloric acid was passed through. After about two litres of perchloric acid had been passed through the resin, the resin was poured out into a Hirsch funnel, and rapidly washed until no hydrogen ions were detected in the washings. The resin was then transferred to a glass crystallising basin and dried in an oven at 40°C.

Preparation of pure Sodium Oxalate

Excess AnalaR sodium oxalate was added to about 350 ml of distilled water in a one litre conical flask. The temperature of the flask and its contents was raised to about 80°C and the solution was filtered through preheated Millipore apparatus. The solution was then boiled down to about half its volume and was allowed to cool. The resulting yield of crystals was filtered off with a sintered glass filter funnel and was dried in an oven at 50°C. Sodium oxalate is anhydrous, so that there was no complication involving hydration state.

Solutions of sodium oxalate were made by adding the correct weight of the salt to a grade A graduated flask, and by adding distilled water up to the mark.

Sodium Malonate

B.D.H. sodium malonate was used without further purification. Solutions were made by adding distilled water to the correct weight of the salt in a grade A graduated flask.

Preparation of pure Sodium Succinate

Sodium succinate was recrystallised by dissolving B.D.H. material in distilled water according to the solubilities quoted in the literature.(71) The hot solution was filtered by means of Millipore apparatus and the filtrate was cooled in a refrigerator. Since no crystals appeared, a small crystal of sodium succinate was added in order to seed the solution. The crystals which appeared were separated by means of a sintered glass filter funnel, and dried in an oven for several days at 50°C. It was necessary to estimate the composition of the material because the degree of hydration was doubtful after this process. This was done by an ion-exchange method. Known weights of sodium succinate were dissolved in a little water and these solutions were passed through an ion exchange column containing Amberlite IR 120 in the hydrogen form. The eluent was collected and was titrated against standard sodium hydroxide solution. It was found that after drying, the recrystallisation process had yielded anhydrous sodium succinate.

Preparation of pure Sodium Tartrate and Sodium Diethylbarbiturate

AnalaR grade sodium tartrate was dissolved in hot distilled water and the resultant solution was filtered by means of Millipore apparatus. The filtered solution was then concentrated by boiling off solvent until on cooling a reasonable yield of material was obtained. This was removed by means of a sintered glass filter funnel.

Sodium diethylbarbiturate was prepared in the same way.

Preparation of standard Perchloric Acid Solutions

These solutions were prepared from AnalaR perchloric acid of specific gravity 1.54. An approximate volume of concentrated acid (MW = 100.46) necessary for two litres of 0.1 molar acid was measured into a standard flask and made up to the mark with distilled water. Samples of this solution were titrated against sodium hydroxide solution which had been previously standardised with potassium hydrogen phthalate prepared as described in an earlier section. The indicator used was phenolphthalein. The necessary dilution of the approximately 0.1 molar acid was then calculated and the correct volume of distilled water added. This solution was used in all the experiments on the protonated ligand complexes.

Preparation of Oxalic Acid Solutions

Oxalic acid was recrystallised as described in an earlier section, and solutions made by adding to the calculated weight of acid distilled water up to the mark of a grade A flask.

Characterisation of the Resin

Water Content

The water content of the resin was found as follows. Known weights of the resin were dried in an oven at 110°C for two hours. The samples were then allowed to cool over silica-gel for thirty minutes and were reweighed. This procedure was repeated until the weight of the dried resin was constant when it was found that the water content was about 15%.

Resin Exchange Capacity

The exchange capacity of the resin was found by converting known weights of the air-dried resin to the hydrogen form by the passage of an excess of 0.1 molar hydrochloric acid, followed by distilled water until no chloride ions were detected in the washings. 0.1 molar sodium chloride solution was then passed through the columns until all the hydrogen ions had been eluted. The eluent was titrated with standard sodium hydroxide solution, and phenolphthalein was used as an indicator.

It was found that the capacity of the resin was about 4 milli-equivalents per gram of dry resin. This figure was obtained for the sodium form of the resin, and it is reasonable to assume that the capacity of the resin in the hydrogen form is of the same order of magnitude.

Radioactive Calcium

Calcium 45 was obtained as a high activity solution of the chloride from the Radiochemical Centre at Amersham. The specific activity of the calcium was 8.5 curies per gram, and the calcium content was 176 micrograms per ml so that the radioactive concentration was about 1.49 millicuries per ml. The pH was 6.6 and the scandium 46 content was 0.02%.

Calcium 45 is a weak beta emitter and decays according to the following scheme:

$$^{45}\mathrm{Ca} \xrightarrow{\beta^-} {}^{45}\mathrm{Sc} \quad .$$

The maximum energy of the beta emission is 250 kilo-electron volts; scandium 45 is stable, and is the naturally occurring isotope of the element.

The calcium was added to the equilibration mixtures in such amounts that the concentration in the solutions was of the order of 10^{-8} molar, so that the ionic product of the ions under consideration was always less than their solubility product. There was therefore no possibility of precipitation. In some of the experiments on the calcium oxalate system, the calcium was added in a buffer solution.

Radioactive Strontium

Strontium 90 was obtained from the Radiochemical Centre at Amersham as a solution of strontium nitrate in molar nitric acid. The radiochemical concentration was about 5 millicuries per ml. The decay scheme is as follows:

$$\underset{25\text{yr}}{{}^{90}\text{Sr}} \xrightarrow[0.6\text{ MeV}]{\beta^-} \underset{60\text{hr}}{{}^{90}\text{Y}} \xrightarrow[2.2\text{ MeV}]{\beta^-} \underset{\text{stable}}{{}^{90}\text{Zr}}$$

Since strontium 90 exists in equilibrium with yttrium 90, the experiments, which involve the distribution of the ions between the resin and the solution phases according to their ionic charges and the stability constants of the complexes formed, will result in a departure of the system from radiochemical equilibrium. It is therefore necessary, in the case of experiments involving strontium 90, firstly to allow the establishment of the chemical equilibrium, then, after the samples of the aqueous phase have been taken, to allow the re-attainment of the radioactive equilibrium between strontium and yttrium 90. Work(72) which has been done on the complexes of yttrium with oxalate indicates that at 0.8 molar, the stability constant for the first oxalate complex of yttrium is of the order of 5×10^4. It therefore appears that in those experiments where there is oxalate present, an excess of yttrium will be retained in the aqueous phase, although in the absence of oxalate the resin might be expected to adsorb yttrium in preference to strontium because of its higher charge. The samples were left for a period of about four weeks before they were counted, after which they were left for a further week and re-counted. The data thus obtained were used only if there was no systematic change in the radioactivity recorded.

In the experiments on the calcium systems and on the strontium systems, the isotope was added in quantities of about 0.8 microcurie per experiment. No cold carrier was added, although there was possibly a small amount of calcium as an impurity in certain of the salts used.

Counting of Calcium 45

The counting method for the calcium which was finally used was liquid scintillation spectrometry. In this system the counting sample consists of three components, the radioactive material, an organic solvent mixture and one or more organic phosphors. Radiation emitted by the sample material is absorbed in the solvent, and its energy is thus transferred to the solvent. From the solvent the energy is transferred to the phosphor which emits a scintillation of light photons. These are absorbed by the photocathode of a photomultiplier tube which converts them into an electronic pulse, which, after suitable amplification, is registered as a count corresponding to the emission of the radiation. In this method detection of the radiation is very efficient and may approach 100%.

This method was chosen as a result of the apparent unsuitability of other counting methods for the systems involved. Planchette counting was unsuitable because of the high dependence of the counting efficiency upon the geometry of the sample. Since the experiments were performed at 0.1 molar, there would have been a large amount of solid material in the planchette. An added complication was the fact that the supporting electrolyte, sodium perchlorate, was deliquescent. Because of the low beta particle energy, conventional liquid counting was inapplicable.

For the calcium 45 a scintillant mixture described by Bray(73) was used. It comprised

80 g naphthalene,
4 g PPO (2,5 diphenyloxazole),
0.2 g POPOP (1,4 bis(2-(4 methyl-phenyloxazolyl))benzene),
10 ml ethylene glycol,
100 ml methanol,
dioxan to one litre.

To 10 ml of this mixture it was possible to add 1 ml of aqueous phase 0.1 molar in sodium perchlorate, without excessive heterogeneity resulting. Medium density polyethylene counting vials were used. These have lower background count rates than glass vials,(119) although background counts from high energy cosmic radiation and random thermal emission of electrons from the photocathode of the photomultiplier tube still remain; this latter source of background is much reduced by the operation of the instrument at low temperature.

In liquid scintillation counting it is necessary to determine the amount, if any, of <u>quenching</u> occurring with the particular sample being counted. Quenching is the decrease in counting efficiency produced by processes which interfere with the production of light in the liquid scintillant and its transmission to the photomultiplier tube of the counter. It may take two forms, <u>chemical quenching</u> and <u>colour quenching</u>. In the former case, compounds in solution in the liquid scintillant interfere with the transfer of energy from the emitted radiation to the organic phosphor, and the energy is dissipated by processes which do not result in light emission. In the latter case coloured materials in the liquid scintillant absorb light emitted by the organic phosphor and prevent it being detected by the photomultiplier tube. In the experiments performed to study quenching in the systems examined in the present work, only chemical quenching occurred because there were no coloured reagents. In all the experiments performed on the calcium and strontium systems, a series of standards was set up in order to examine the quenching which occurred, if any. When quenching was found to occur, a correction factor, called in this work the relative efficiency factor (r.e.f.) was calculated for each mixture used, and the counts from that experiment multiplied by this factor.

Counting of Radioactive Strontium

Because of the high energy, 2.2 MeV, of the beta emission from yttrium-90, the daughter isotope of strontium-90, it was decided to make use of Cerenkov counting(74) for the determination of this isotope. Water is used as the medium in this aspect of liquid scintillation counting. Cerenkov radiation is produced when a charged particle passes through a transparent medium at a velocity greater than the speed of light in the same medium. The photons thus produced have a continuous spectral distribution and a defined geometrical configuration. The photon emission has been described(75) as the particle electro-magnetic shock wave analogous to the sonic boom created by hypersonic aircraft. The wavelength of the emitted light is reported(75) to be between 3000 and 7000 ångstroms, and in water, a solvent of refractive index 1.33, the threshhold for stimulation of Cerenkov radiation can be calculated as 260 keV, but, because of the broad energy distribution exhibited by the radiation from a given beta emitter, the maximum energy of the radiation from a given emitter has to exceed this value substantially, before a reasonable efficiency can be attained.

As in the case of calcium, quenching experiments were performed in conjunction with the systems under study. Sample volumes of 20 ml were used in the strontium experiments.

The Method

Initially, the experiments were performed in the following manner. Resin was weighed into glass sample tubes, and these samples were added to 250 ml Pyrex glass conical flasks to which were subsequently added via calibrated pipettes the various solutions required for the system under study. These flasks with their contents were then agitated for about six hours to ensure that equilibrium had been attained. The solutions were sampled by means of one ml pipettes of which a random sample had been calibrated to ensure that no serious deviations from formal delivery occurred. The samples of solution were added to glass counting vials containing 10 ml of Bray's (loc.cit.) scintillant and counted on a Packard Tricarb liquid scintillation counter.

When the first results were obtained it was apparent that something was seriously wrong with the method as reproducibility was very poor. (cf.(120)) It was thought possible that since calcium was present in tracer concentration it could be adsorbed to an appreciable extent on to the surface of the glassware used, thus depleting the solution. An experiment was set up, therefore, in which identical mixtures containing the same amount of isotope were placed in flasks which had been coated with a P.T.F.E. film applied from an aerosol, and in uncoated flasks. Although the reproducibility was poor, it was found that in every case the concentration of radioactive calcium in the aqueous phase in the untreated flasks was lower than in the treated flasks. This implied that adsorption occurred to an appreciable extent. The film, however, was found to be somewhat impermanent, and could not be relied upon to remain intact for the duration of an experiment.

The next expedient employed was the use of polyethylene bottles for the equilibrations. These proved reasonably satisfactory and have been used in all the experiments quoted in this work. There is, however, probably a slight adsorption of nuclide on the polythene surface. This is proved by the fact that polyethylene bottles, which had been used to store solutions containing strontium at the concentrations used in the experiments, after having been rinsed several times with water, still retained a detectable degree of activity. The same adsorption presumably occurs also with calcium, but the decay energy is insufficient for its ready detection.

With a view to minimising the errors due to adsorption, the pipettes used were pretreated by exposure to prolonged contact with the solutions which they were intended to dispense. The pipette used for delivery of the nuclide was filled with the solution and left for about an hour, the solution being renewed from time to time. Ten aliquots were taken and rejected from the pipettes which were to be used for sampling, before the final sample was taken and added to the counting vial.

In order to optimise the method the use of glass counting vials was eventually discontinued and polythene vials used instead, because, apart from considerations of nuclide adsorption, they exhibit lower background activity and allow a higher counting efficiency.

The foregoing sections describe the method which was used for the preliminary measurements on the calcium-oxalate system. It was found that as a result of the precautions observed acceptably reproducible data could be obtained and this is reflected in the good linearity displayed by the relevant plots.

For all subsequent experiments, Hamilton syringes with the Chaney adaption were used for addition of the concentrated nuclide and withdrawal of the samples. This allowed a more rapid procedure to be adopted but it was still necessary to pretreat the syringe with the reagent solutions. This necessity is illustrated by the following experiment. From a clean dry syringe ten deliveries were made one after the other to a clean dry weighing bottle. The results are as shown.

No.	Wt. of delivery
1	0.3992 g
2	0.3992
3	0.3994
4	0.3996
5	0.3996
6	0.3994
7	0.3996
8	0.3994
9	0.3996
10	0.3994

Ten deliveries of a solution containing strontium 90 in trace amounts were made in the same manner to ten polythene counting vials which were then counted. The counts are as follows.

1	83866 c.p.m.
2	88166
3	99479
4	89933
5	91203
6	93751
7	94312
8	98258
9	91777
10	92200

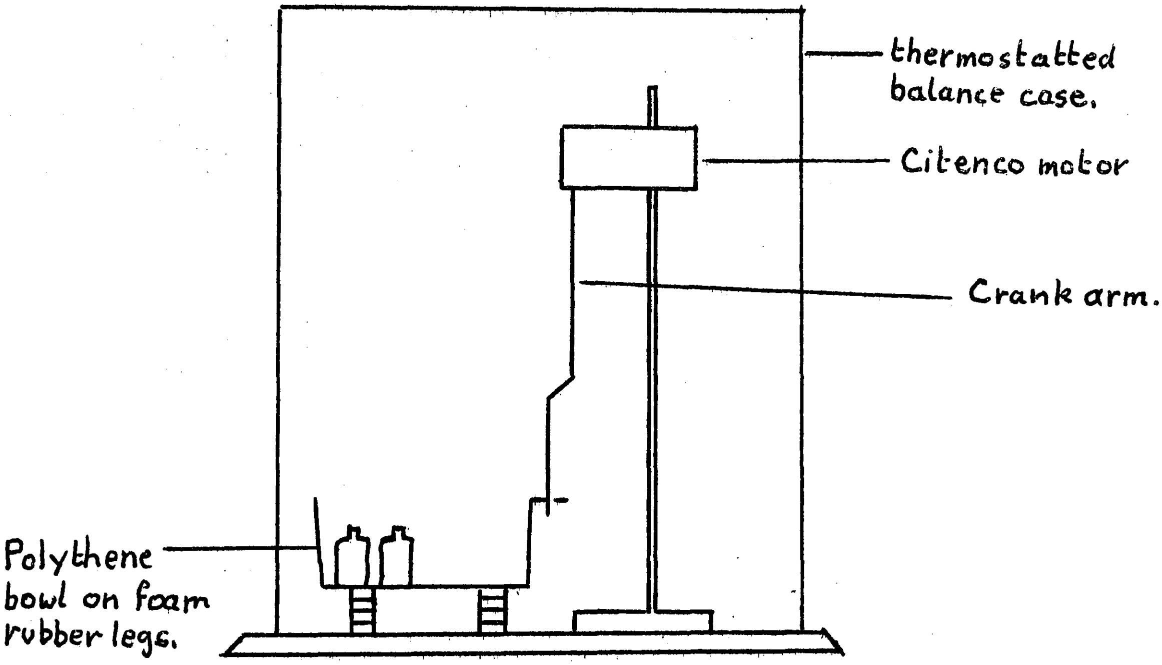
It is thus shown that when the nuclide is present in trace quantity the delivery is far from reproducible. It was observed that the steel needle of the syringe became far more radioactive in terms of monitor response than did the glass section of the instrument, which implies that much of the adsorption occurred on to the inner surface of the needle. This seems reasonable in view of the fact that because of the narrow bore of the needle, a far greater proportion of the solution would come into contact with the metal surface than would come into contact with the glass surface.

These experiments supported the practice of multiple fillings and rejections before nuclide addition and sample withdrawal.

The method of agitation was investigated as a possible source of irreproducibility. It was found undesirable to agitate the solutions by means of a magnetic stirrer because, owing to the friability of the resin, suspensions of very finely divided resin particles were produced, the presence of which resulted in large errors. The mode of agitation ultimately employed was the use of the shaking device illustrated in fig. (V) and set up in an air thermostat.

The experiments, with the exception of the preliminary ones on the calcium oxalate system, were performed in

Figure V



Equilibration Apparatus.

quadruplicate, and each equilibration bottle was sampled four times, the four samples from each bottle being added to two counting vials. In all, each ligand concentration was thus represented by eight figures. Reproducibility of counts was taken as the criterion for absence of significant nuclide adsorption.

Determination of Optimum Equilibration Period

In view of the fact that isotopic adsorption on to the polyethylene containers could be detected in the case of strontium 90 it was decided to ascertain how short a period of equilibration was compatible with the production of acceptably reproducible data. The following experiment was therefore performed. To a mixture of 100 ml of 0.1 molar sodium perchlorate solution and 100 mg of CG 120 in the sodium form was added approximately 2 ml of solution of calcium 45. The plastic container was agitated for an extended period, and samples were withdrawn from time to time, in triplicate, and added to polyethyl counting vials containing 10 ml of Bray s scintillant. The results were as shown.

Time (min.)	Total counts/sample/min.	$f = \frac{\text{counts at time t}}{\text{counts at equilibrium}}$
5	117500	2.66
22	51016	1.16
36	47116	1.07
49	45599	1.035
76	44888	1.015
108	44006	1.000
136	43345	0.982
216	44131	1.000
291	43416	0.980
380	44082	1.000

These figures are shown graphically in figs. VI and XXVI. Although the withdrawal of samples will disturb the final equilibrium position of the system before equilibrium has been attained, the withdrawal will have no effect once equilibrium has been established. It is seen from the graph that equilibrium is effectively established after about 50 minutes of agitation. It is also apparent that after equilibrium has been established, there is no rapid reduction of radioactive content of the solution as a result of surface adsorption so that no appreciable errors ought to arise if the addition of nuclide to the experiments, the agitation and the sampling are all performed within six hours.

All the experiments, with the exception of some of the experiments performed on the calcium oxalate system were agitated for periods of between three to three and a half hours. The earlier calcium oxalate experiments, the results of which are quoted, were agitated for about six hours.

Effect of Calcium as an Impurity in the System

Provided that the total amount of radioactive calcium is the same from experiment to experiment, that the total calcium concentration is very much lower than the resin exchange capacity, that the calcium concentration is very much lower than the ligand concentration and that the distribution coefficient is the same for active and inactive calcium, the accuracy of the method is independent of the total calcium concentration present.

Suppose that a certain number of atoms of radioactive calcium have been added to an aqueous phase in contact with a resin phase, and the distribution coefficient for the system is K_d. If there are m ions in the aqueous phase, there will be $K_d . m$ in the resin phase. Now if a certain number of inactive ions are added to the system, so that there are m' in the aqueous phase, there will be $K_d . m'$ in the resin phase. The total ions in the aqueous phase will be $(m + m')$ and the total in the resin phase will be $K_d(m + m')$ so that the ratio of active calcium in each phase will be the same as if there were no inactive calcium present. Similar considerations obtain if there is a ligand present. Provided that the calcium concentration is much less than the ligand concentration and since

$$\frac{[CaL]}{[Ca][L]} = k$$

it is possible to write

$$\frac{[CaL]}{[Ca]} = k[L]$$

$$= k'$$

Over a wide range of calcium concentration the ratio of complexed to uncomplex calcium, for a given ligand concentration should therefore be constant. If then there is a mixture of active and inactive calcium each state of the metal, i.e. resin or solution phase, complexed or free, will have the same proportion of active to inactive calcium, so that again the ratio of active calcium in the aqueous phase to that in the resin phase will not be altered. Accordingly the method may be used even when the contaminant, inactive calcium, is present in concentrations which vary and which are far larger than the active calcium. This assumes, of course, that the increase in the concentration of calcium does not cause the solubility product at that ionic strength to be exceeded.

Complexing between Calcium and Oxalate in the Presence of a Buffer

Some of the first measurements on the calcium-oxalate system in the present work were made in the presence of a buffer. The buffer used was one described by Michaelis(76) modified to have an ionic strength of 0.1 molar, and to result in a pH of about 7. In each 100 ml of liquid phase there were 3.7 ml of 0.123 molar hydrochloric acid and 5.6 ml of a solution which was 0.1 molar in sodium diethyl barbiturate and 0.0657 molar in sodium perchlorate. It was found that the pH in all the solutions used was 7.2. A preliminary study was made to find if the diethyl barbiturate ions complexed with the calcium ions; a study was also made of the quenching effect of oxalate ions on the radiation from the calcium.

Complexing between Calcium Ions and Diethylbarbiturate Ions

The following experiments were set up.

Expts.	0.1M $NaClO_4$	0.01M $NaClO_4$, 0.09M NaDi	Resin
1,2	0.050 litre	0.000 litre	0.000 g
3,4	0.050	0.000	0.100
5,6	0.000	0.050	0.000
7,8	0.000	0.050	0.100

[Di = diethylbarbiturate]

An aliquot of solution containing calcium 45 was added to each of these experiments in polythene bottles, and they were agitated for several hours. They were then sampled and counted. The results are as shown.

Experiments	Activity
1,2	23310, 23843
3,4	3692, 3823
5,6	20848, 22157
7,8	3321, 3268

Experiments 1,2 and 5,6 result in a quenching factor of 1.096. Application of the correction to experiments 7,8 give a count rate of 3611 as compared with 3758 when the buffer is not present. The small discrepancy is in the direction opposite to that which would have occurred if complex formation had taken place, and is the result of experimental error combined with counting statistical error. It is thus seen that no complexing between calcium and diethylbarbiturate occurs. It should be remembered that the comparison of the distribution of calcium between the aqueous and resin phases in the presence of 0.1 molar sodium perchlorate in one case, and a buffer at 0.1 molar in the other case is not strictly valid since the pH difference is probably about 2 units. CG 120 is a sulphonated resin and the distribution should therefore be pH independent. It is possible that there is, however, some slight difference in the ionic strengths of the solutions.

Subsequent experiments indicated that the value of l_0 obtained in a buffered medium (pH 7.2) agreed closely with that obtained in an unbuffered medium (pH 5.5). It was also seen that in general there was close agreement between the values of l_0 obtained directly in an unbuffered medium, and the extrapolated value, obtained from a series of measurements where there was ligand present. Both of these observations suggested that there was very little, if any, pH dependence of the distribution of the calcium, and so the practice of using a buffered medium for the experiments was discontinued.

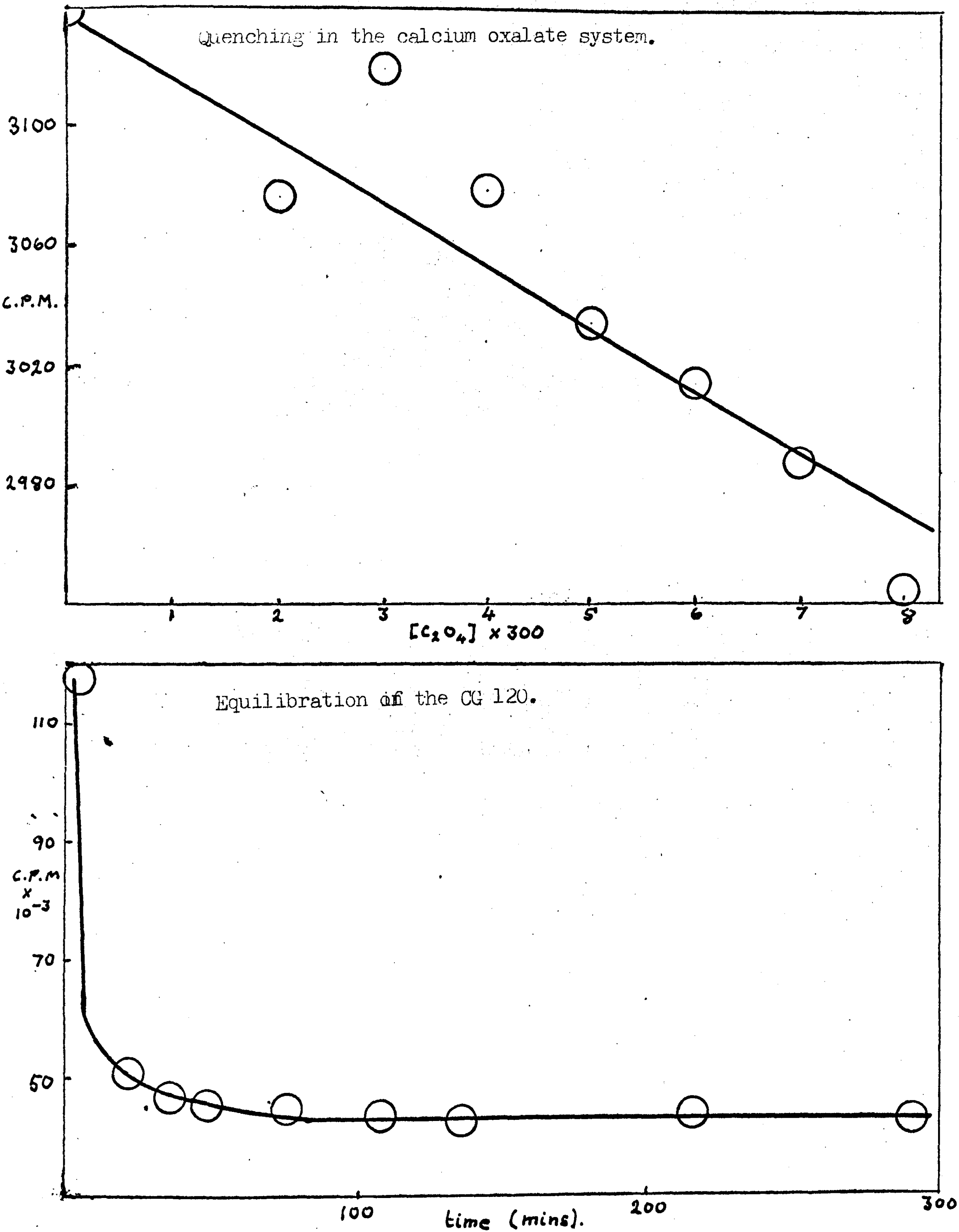
Quenching by the Oxalate Ion

The following experiments were set up, agitated and sampled. The results are shown in the last column of the following table.

Expts.	0.1M $NaClO_4$	0.0333M $Na_2C_2O_4$	Buffer, Ca^{45}	c.p.m.
1	0.090 litre	0.000	0.0093	3139
2	0.080	0.010	0.0093	3080
3	0.070	0.020	0.0093	3076
4	0.060	0.030	0.0093	3120
5	0.050	0.040	0.0093	3163
6	0.040	0.050	0.0093	3080
7	0.030	0.060	0.0093	3035
8	0.020	0.070	0.0093	3015
9	0.010	0.080	0.0093	2988
10	0.000	0.090	0.0093	2944

These figures are shown plotted in figure VI. Relative efficiency factors were calculated on a best straight line basis and are shown in the following table.

Figure VI.


Quenching in the calcium oxalate system.
3100
3060
C.P.M.
3020
2980
1
2
3
4
5
6
7
8
[C₂O₄] x 300
Equilibration of the CG 120.
110
90
C.P.M x 10⁻³
70
50
100
200
300
time (mins).

Oxalate Concentration (moles/litre)	Relative eff. factor
0.00000	1.000
0.00333	1.006
0.00667	1.013
0.00999	1.019
0.01332	1.026
0.01665	1.033
0.01998	1.040
0.02332	1.047
0.02665	1.054
0.02998	1.061

The measurements on the calcium-oxalate system were made by preparing, agitating and sampling, the mixtures described in the table below.

Expt	0.1M $NaClO_4$ (litre)	*0.0333M $Na_2C_2O_4$ (litre)	0.123M HCl (litre)	buffer ^{45}Ca (litre)	resin g.
1	0.090	0.000	0.0037	0.0056	0
2	0.090	0.000	0.0037	0.0056	0.100
3	0.080	0.010	0.0037	0.0056	0.100
4	0.070	0.020	0.0037	0.0056	0.100
5	0.060	0.030	0.0037	0.0056	0.100
6	0.050	0.040	0.0037	0.0056	0.100
7	0.040	0.050	0.0037	0.0056	0.100
8	0.030	0.060	0.0037	0.0056	0.100
9	0.020	0.070	0.0037	0.0056	0.100
10	0.010	0.080	0.0037	0.0056	0.100

*or 0.01M

Independently determined values for l_o

A number of independent determinations of the value of the distribution coefficient at infinitely low ligand concentration were made. The results of these were as follows.

Determination	l_o
1	2.959
2	3.021
3	2.985
4	2.924
5	3.003
6	3.067
7	3.049
8	3.096
9	3.106
10	3.175
11	3.175

The average value of l_o from these figures is 3.05, with a standard deviation of 0.08; this value has been employed in most of the systems involving calcium with CG 120.

Results

The results of the initial experiments are tabulated in appendix I, tables 3A-3D, and plotted in figures VII-X. The average value for the stability constant which was obtained is 175 ± 20.

Figure VII.

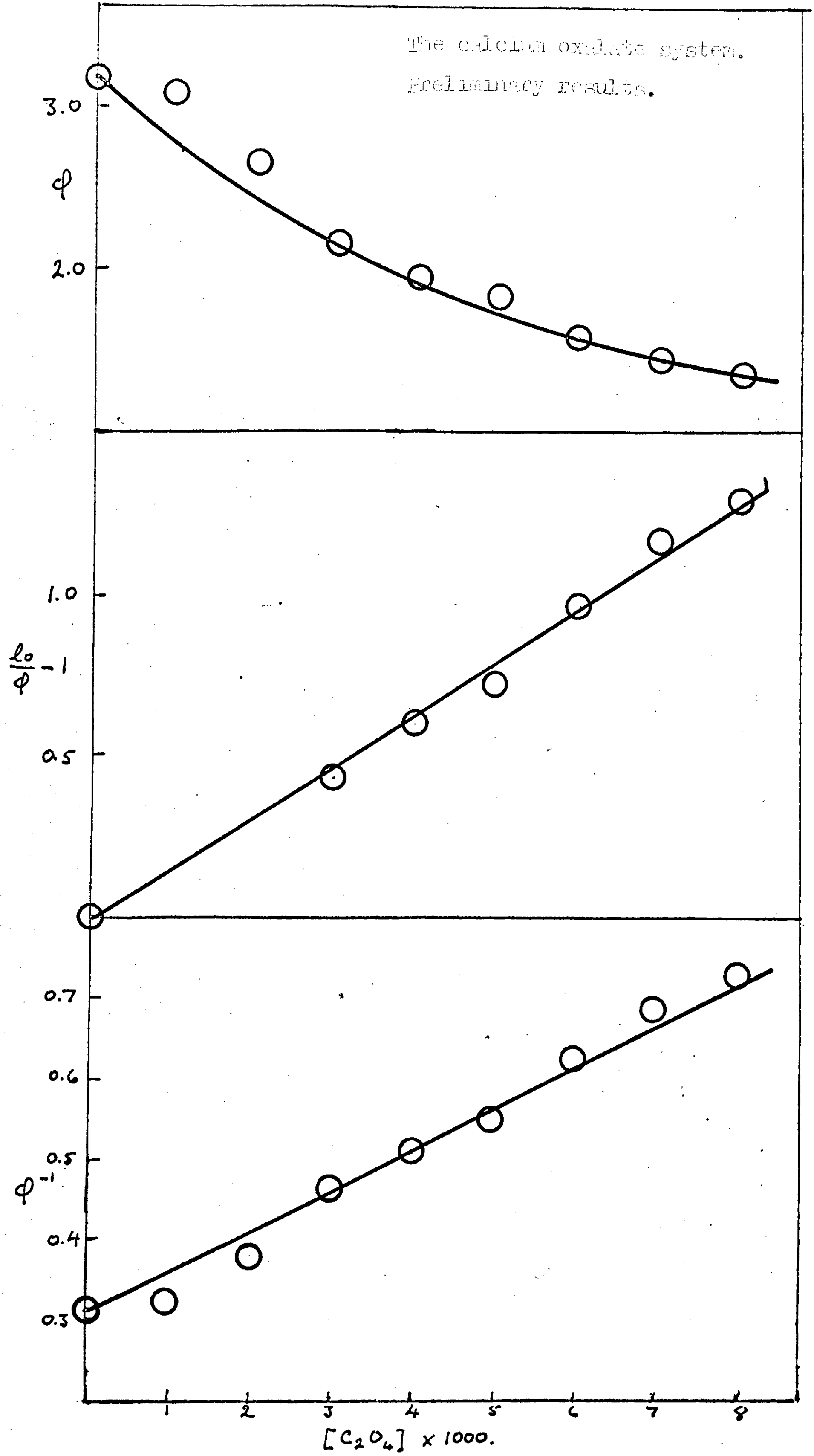

The calcium oxalate system.
Preliminary results.

Figure VIII.

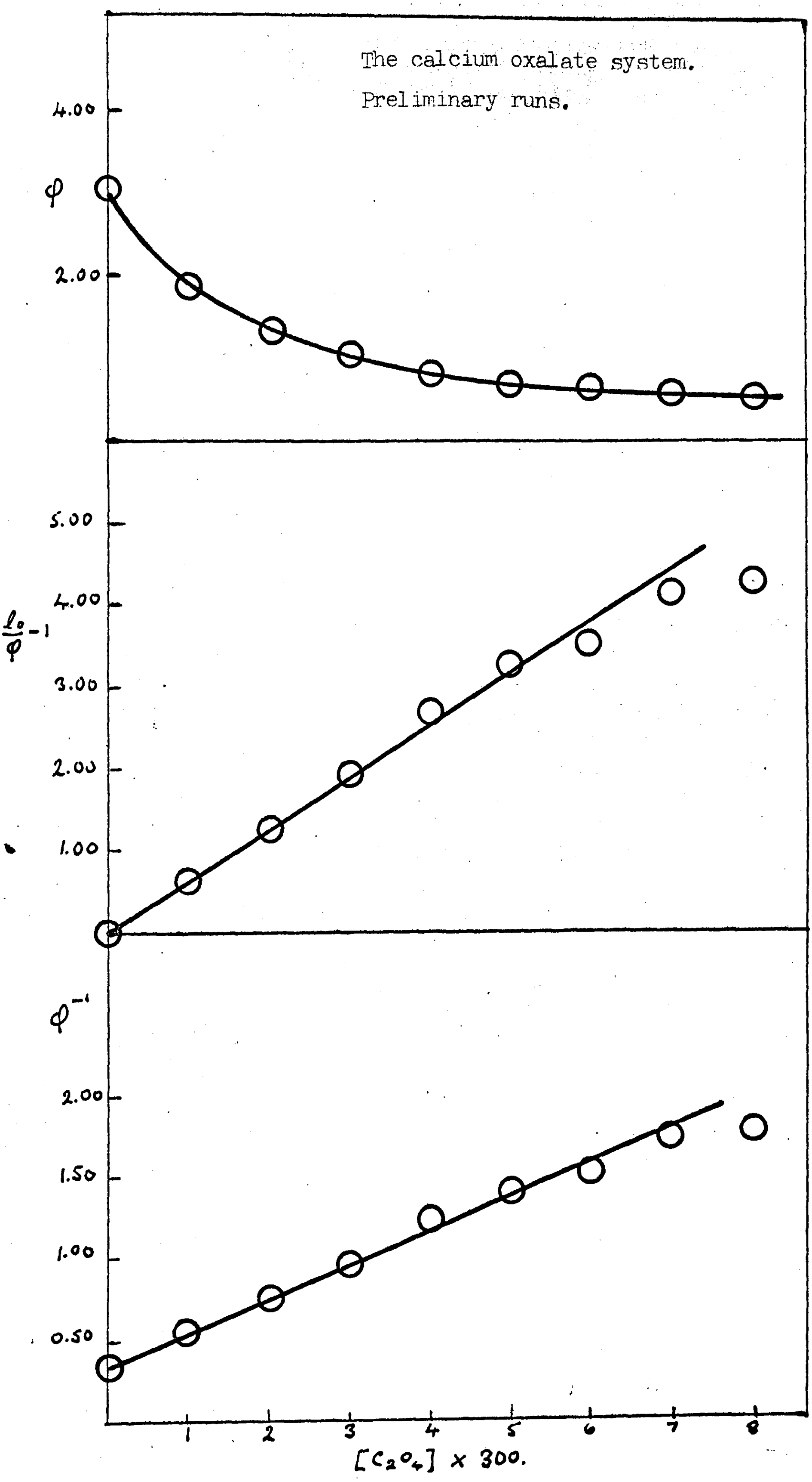
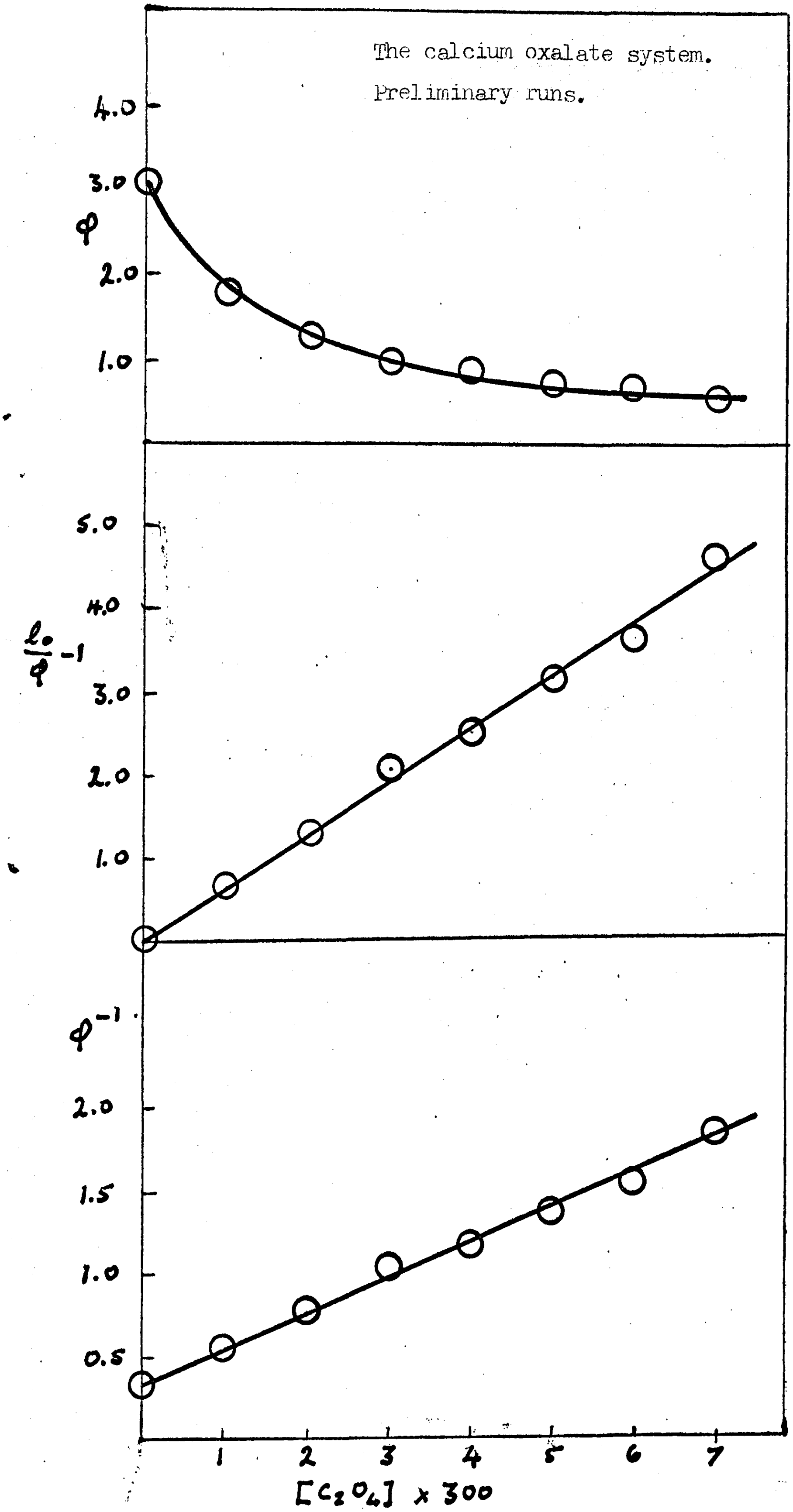
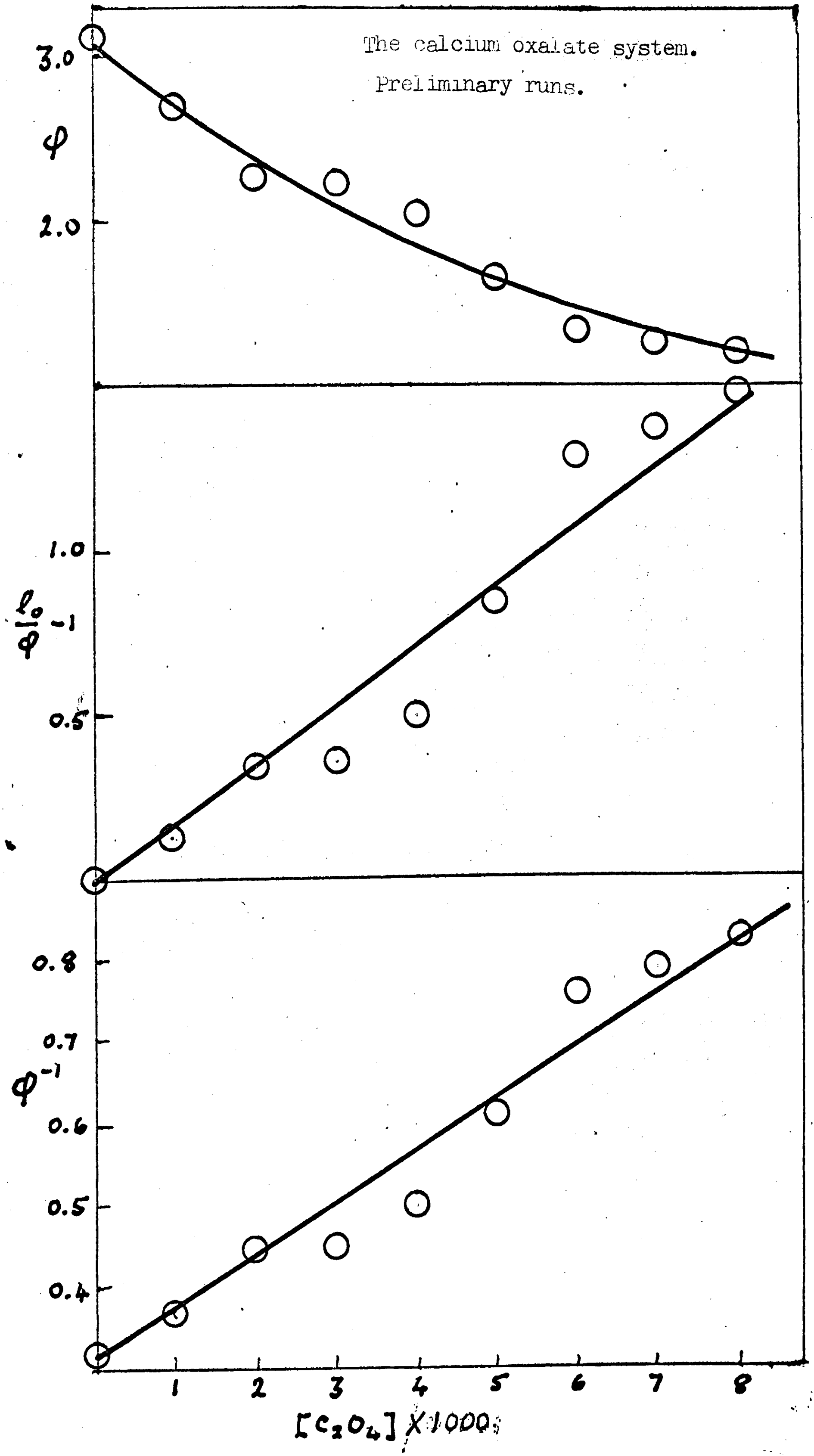

The calcium oxalate system.
Preliminary runs.
4.00
φ
2.00
5.00
4.00
$\frac{I_0}{\varphi}-1$
3.00
2.00
1.00
φ^{-1}
2.00
1.50
1.00
0.50
1
2
3
4
5
6
7
8
$[C_2O_4] \times 300.$

Figure IX.



The calcium oxalate system.
Preliminary runs.

Figure X.



The calcium oxalate system.
Preliminary runs.

The Effect of Ionic Strength on the Stability of the Calcium Oxalate Complex

Method. In each case the following scheme was employed.

Experiments	mass resin (g)	vol. $NaClO_4$ (litre)	vol. $Na_2C_2O_4$ (litre)
1	0.000	0.050	0.000
2	0.050	0.050	0.000
3	0.050	0.045	0.050
4	0.050	0.040	0.010
5	0.050	0.035	0.015
6	0.050	0.030	0.020
7	0.050	0.025	0.025
8	0.050	0.020	0.030
9	0.050	0.015	0.035
10	0.050	0.010	0.040

The resin was CG 120 in the sodium form; the concentrations of sodium perchlorate used were 0.02, 0.04, 0.06, 0.08, 0.10 and 0.20 molar, and the corresponding sodium oxalate concentrations used were 0.00666, 0.01333, 0.02000, 0.02666, 0.03333, and a solution of 0.03333 molar sodium oxalate made up to an ionic strength of 0.2 with sodium perchlorate. In each case, calcium-45 was added in a volume of 0.8 ml, so that in all the experiments, the ratio, v/m was 1.016. As before, quenching experiments were performed in conjunction with the partition measurements. These were identical in composition to the corresponding partition experiments, except that the resin was omitted. They were shaken for the same period, that is, three hours. The partition experiments were performed in quadruplicate, and doubly sampled; the quenching experiments were performed in duplicate, and doubly sampled. These systems were not buffered, since the pH change over the ligand range used was found to be slight. Experimental data are tabulated in Appendix I, tables IVA-X, and are plotted in figures XI-XV.

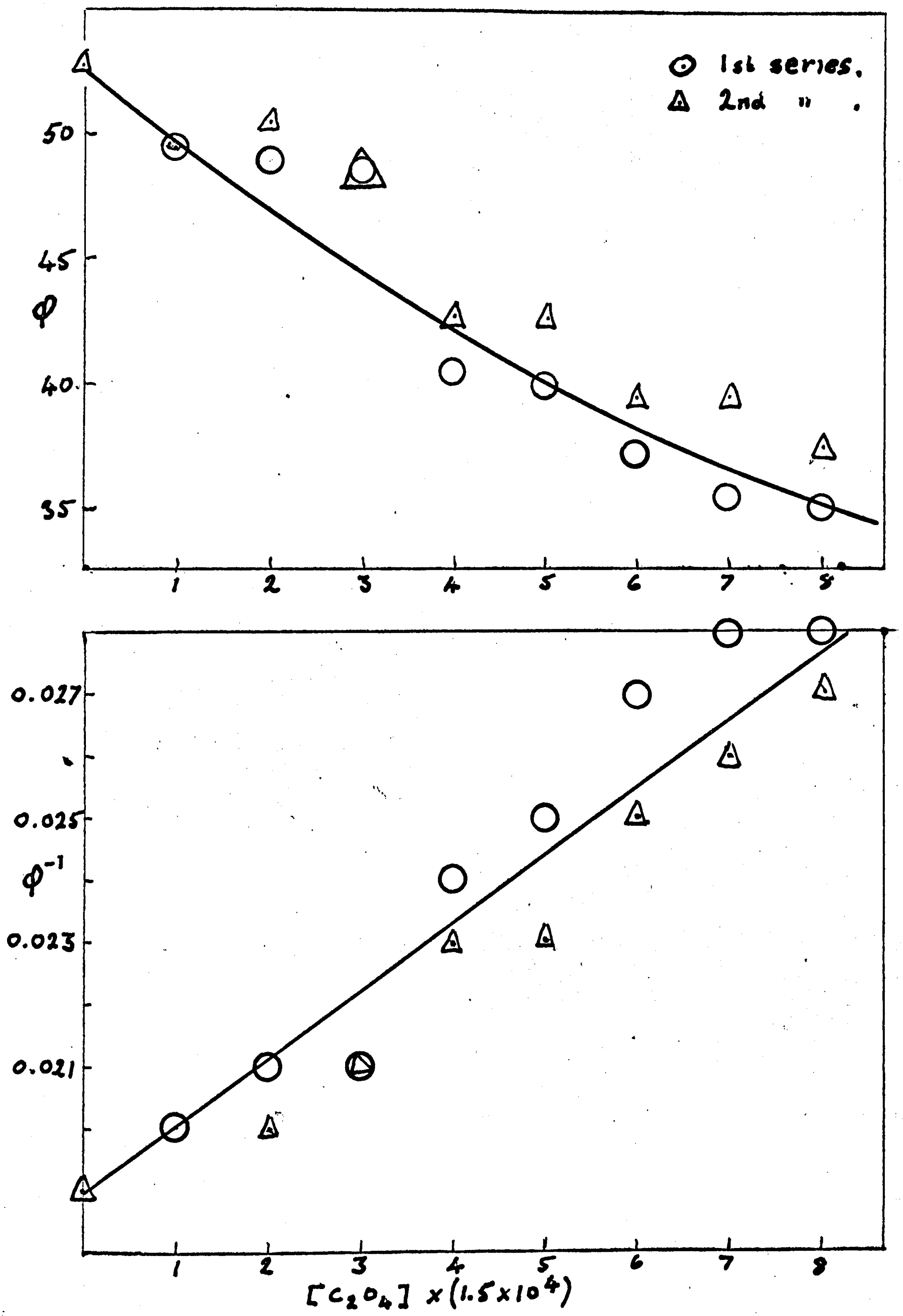
Results and Discussion

The experimental data are tabulated in Appendix I. The stability constants obtained are as follows.

I	l_o	β	β from Davies equation with β at $\mu \to 0$ taken as 1000
0.02	55	121	324
0.04	16	121	225
0.06	8	132	176
0.08	4.8	158	146
0.10	3.0	123	126
0.20	0.75	116	80

It was considered that the results at 0.02M and 0.04M might be in error because of the apparent low stability, and repeat experiments were made in duplicate for these systems. The results fully confirmed the first findings. Both series of runs are shown in Appendix I. In the 0.02M system the high distribution coefficient results in a low count rate in the aqueous phase. The resin took up activity corresponding to about 10,000 c.p.m. in the aqueous phase leaving about 300 c.p.m. in the aqueous phase. An error in the resin weight

The calcium oxalate system at 0.02 Molar.



The calcium oxalate system at 0.04 Molar.

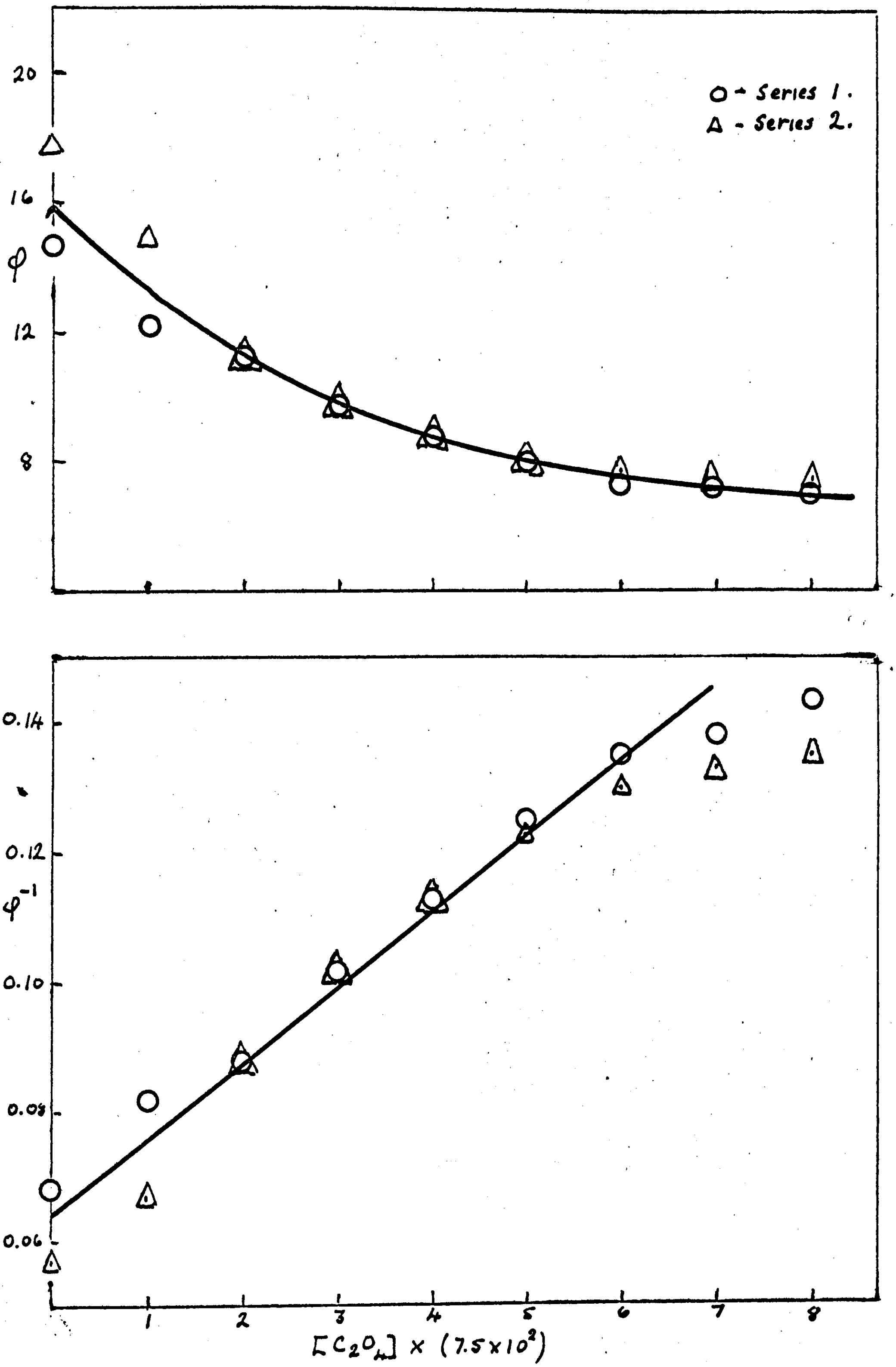


Figure XIII.

The calcium oxalate system at 0.06 Molar.

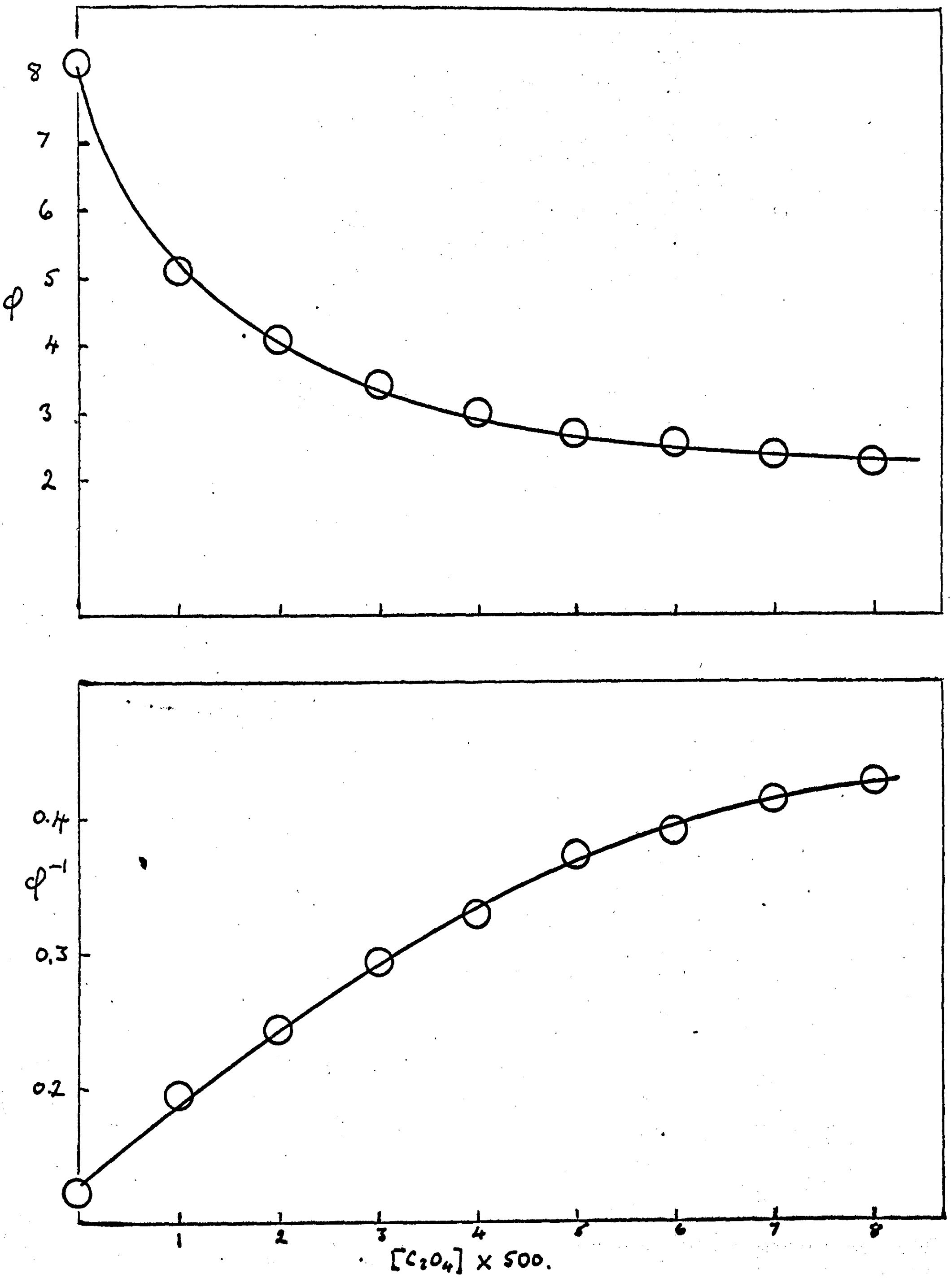


Figure XIV.

The calcium oxalate system at 0.08 Molar.

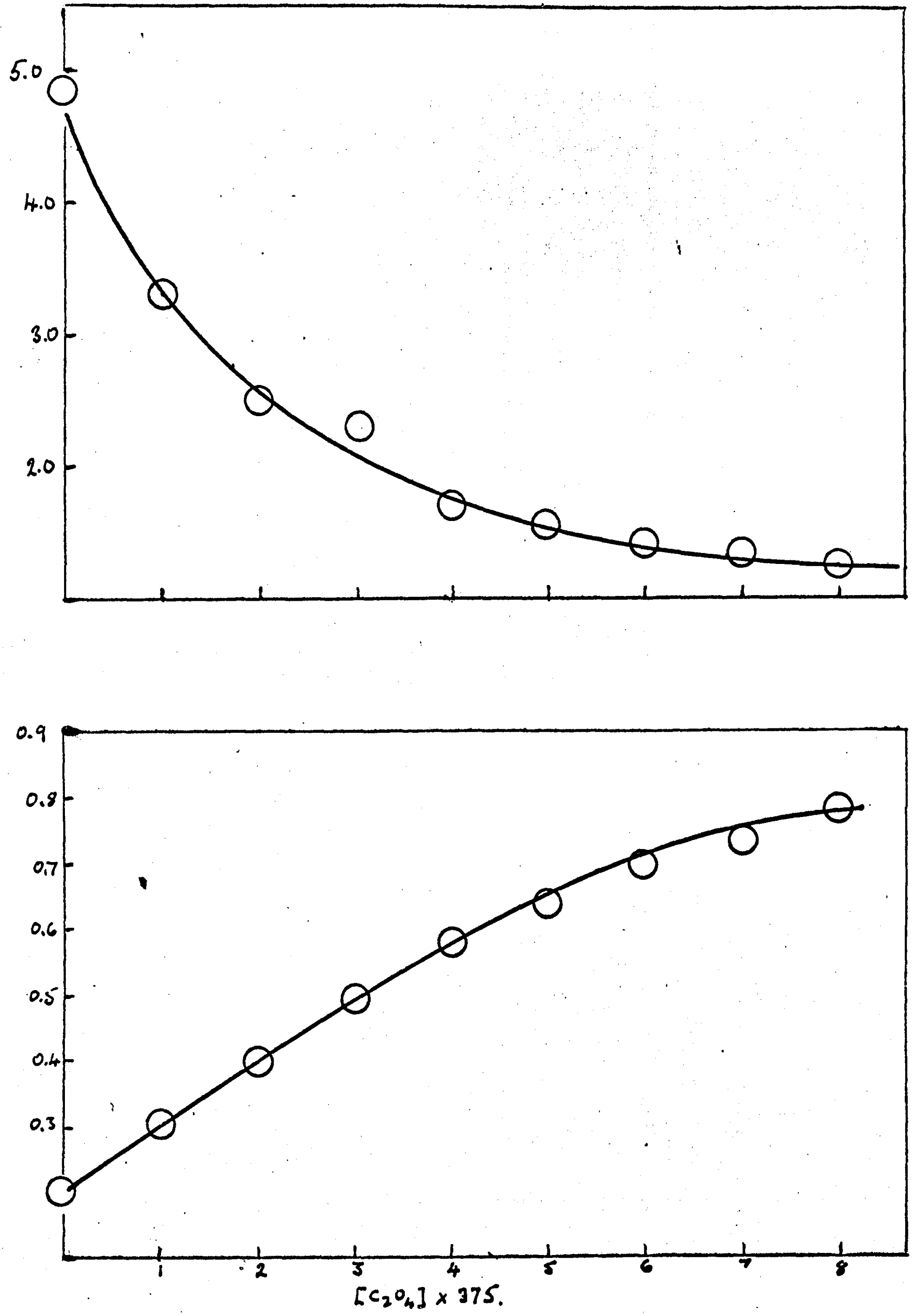
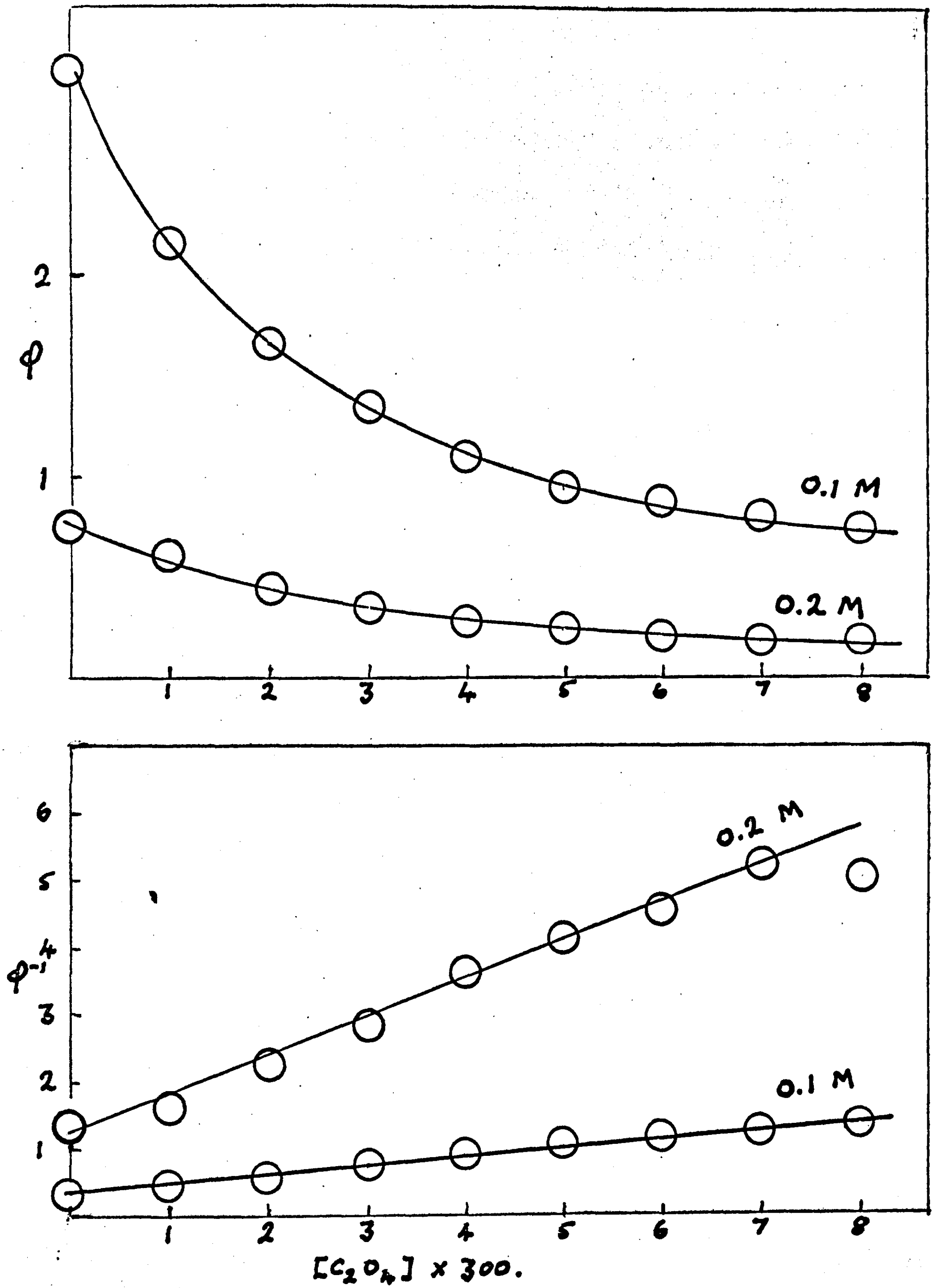


Figure XV.

The calcium oxalate system at 0.10 and 0.20 Molar.



used of 0.5% (0.050 g was used in the experiments) would introduce to the aqueous phase count an error of 50 c.p.m. which was an appreciable proportion of the total count rate. Counting statistical error would increase the overall error. The experiments were performed in quadruplicate and duplicate sampling was used. When these possible errors were taken into consideration the actual reproducibility was surprisingly good. The same considerations obtain to a less extent with the work at 0.04M. In the case of the data at 0.06M and 0.08M curvature appeared to develop in the plots of ϕ^{-1} versus oxalate concentration. In view of the fact that the data were highly reproducible it must be concluded that this is a real effect. The same comment may be made about the experiments involving different ion exchange resins of which the results will be presented below. Various methods of explaining or removing this curvature were examined. Calculations involving different values of C'_m altered the mean gradient of the ϕ^{-1} v oxalate concentration plot, but did not remove the curvature. Precipitation of calcium oxalate was ruled out, since the solubility of calcium oxalate$^{(78,\ 4\rightarrow 79,71)}$ was calculated to be ten times greater than the maximum concentration used in the experiments. Further, it would be expected that precipitation would lead to irreproducibility, but the results were highly reproducible. Calculations on the hydrolysis of the oxalate ion indicated that only a fraction of one percent of the ions were hydrolysed. The assumption of complex formation between sodium ions and oxalate ions was also found to be ineffective in accounting for the curvature. Since determinations of l_0 had been made with a variety of concentrations of Ca^{45} it seemed unlikely that a resin loading factor was the cause. Calculation showed that in a typical series of experiments about 5.6×10^{-5} of the available sites in the quantity of resin used in the experiments were taken up by calcium exchange; at this low fraction, a large loading effect would not be expected. In the repeat experiments on the 0.02M and 0.04M systems a resin loading five times greater than that used in the first experiments was used. No difference was found in the results. The effects of precipitation of calcium oxalate would also be expected to be sensitive to the concentration of calcium. Polynuclear species are very unlikely to be formed at trace metal levels especially when the ligand concentration is much greater than the metal concentration. Li et al.(9) have shown that a five-fold variation in the v/m ratio had no effect on the distribution coefficients. Sani(80) found that for the distribution of Y(III) between an aqueous phase and Zeo-Carb 225 a three-fold variation in v/m had no effect. In the experiments on different cation exchangers described below, it is seen that for sulphonated polystyrene-DVB resins, the v/m ratio has no apparent effect on the results. Raman spectroscopic studies(81) indicate no complexing between calcium and perchlorate; this finding is confirmed by other work(82) on vapour pressure studies on the $Ca^{2+} - ClO_4^- - H_2O$ system at 25°C. At infinite dilution, Bell and Prue(83) found, as a result of their work on the depolymerisation of diacetone alcohol, that the stability constant of the $CaOH^+$ complex was about 20. Since it is probably less at 0.1M and since in the present work the hydroxide concentration is of the order of 10^{-7}M formation of such a complex cannot be considered a source of error.

Schubert(11) has suggested that for the reaction

$$M^{2+} + 2NaR \longrightarrow MR_2 + 2Na^+ ,$$

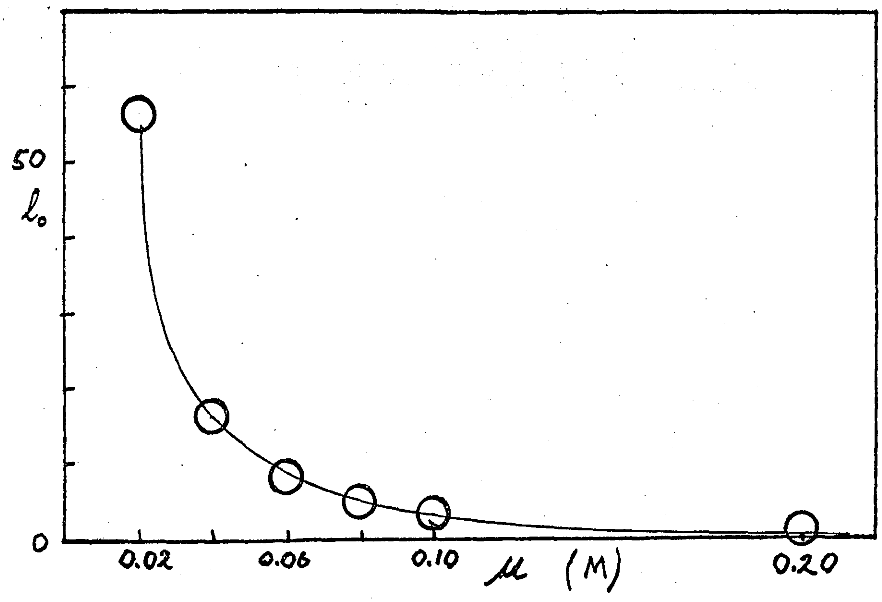
if $$[Na] \gg [MR_2]$$

and $$[NaR] \gg [MR_2]$$

then $$k = \frac{[MR_2][Na]^2}{[M][NaR]^2} = l_0 \frac{[Na]^2}{[NaR]^2}$$

and $[NaR]^2$ is virtually constant. If this is so, the law of Mass Action requires that $l_0[Na]^2$ should be constant. The values obtained in the present work are as shown below.

I	$l_0[Na]^2$	$l_0[Na]^2f_1^2$
0.02	0.0224	0.0169
0.04	0.0256	0.0178
0.06	0.0288	0.0188
0.08	0.0307	0.0192
0.10	0.0300	0.0181
0.20	0.0300	0.0162



Effect of ionic strength upon l_o for CG 120.

The function appears to be constant above 0.06M, but not below. This could be an indication of some error - introducing effect in this concentration range. The use of activities, however, in this relationship, makes the figures more constant. There is a fair amount of evidence to indicate(4,5,6) that at infinite dilution the stability of the calcium oxalate complex is about 1000. If this is so the present results suggest that there is a minimum in the region of about 0.02M. Behaviour of this sort has been observed by Mori et al.(84) in their studies of the formation of the tetramminoxalato cobalt(III) complex. A study of the stability of the calcium oxalate complex at ionic strengths below 0.02M would be very rewarding, since it would indicate whether or not the present observed effect is real. Unfortunately, it would be very difficult to apply the ion exchange method to this problem, because the distribution coefficient would presumably be much greater than 55, vide figure XVI, and this would increase the experimental error due to the causes outlined above.

The Calcium Malonate System

Recently Evans and Monk(85) have obtained a stability constant for the sodium malonate complex at infinite dilution. They have found a value of 6; application of the Davies equation gives a value of 2 at 0.1M. Since the supporting electrolyte in the present work is sodium perchlorate, complexing between the sodium ions and the ligand may be expected to occur and a correction must be applied. Since the calcium is present as a tracer, the correction may be made on the assumption that the only species engaging in complex formation are the sodium ions and the malonate ions.

Calculation of the Correction for Complexing between Sodium and Malonate

For the following equilibrium

$Na^+ + M^{2-} = NaM^-$, where M^{2-} = malonate,

let $\beta_1 = \frac{[NaM]}{[Na][M]}$

Let the initial total Na concentration be C_{Na};
let the initial total M concentration be C_M.
The final Na concentration may then be written $C_{Na} - [NaM]$ and the final M concentration may be written $C_M - [NaM]$ so that

$$\beta_1 = \frac{[NaM]}{\{C_{Na}-[NaM]\}\{C_M-[NaM]\}}$$

$$\therefore \quad \beta_1 = \frac{[NaM]}{C_{Na}.C_M - C_M[NaM] - C_{Na}[NaM] + [NaM]^2}$$

$$\therefore \quad \beta_1 C_{Na}C_M - \beta_1 C_M[NaM] - \beta_1 C_{Na}[NaM] + \beta_1[NaM]^2 - [NaM] = 0$$

$$\therefore \quad \beta_1[NaM]^2 - \{1+\beta_1 C_{Na}+\beta_1 C_M\}[NaM] + \beta_1 C_{Na}C_M = 0$$

This is a simple quadratic equation and may be solved by the standard formula, so that

$$[NaM] = \frac{\{1+\beta_1 C_{Na}+\beta_1 C_M\} \pm \{[-(1+\beta_1 C_{Na}+\beta_1 C_M)]^2 - 4\beta_1^2 C_{Na}C_M\}^{\frac{1}{2}}}{2\beta_1}$$

It is found that the use of the positive root of the equation gives [NaM] $>$ C_M so that the negative root is taken for the correction.

The results of the calculations on the concentrations of sodium malonate complex are as follows.

C_M	C_{Na}	[NaM]	[M]
0.00333	0.09666	0.0005	0.0028
0.00667	0.09332	0.0011	0.0056
0.00999	0.08998	0.0015	0.0085
0.01332	0.08664	0.0020	0.0113
0.01665	0.08330	0.0023	0.0143
0.01998	0.07998	0.0027	0.0173
0.02331	0.07662	0.0030	0.0203
0.02665	0.07330	0.0033	0.0233

Method

The experimental procedure used was the same as for the other experiments, the aqueous phase volume being 50 ml and the resin mass 0.050 g. A quenching experiment was first performed and it was found that the quenching effect more than cancelled out the count increase in the aqueous phase due to complex formation. Further, accurate quenching data could not be easily obtained for this system so that the stability constants which were obtained cannot be regarded as much better than an approximation. The quenching factors are as shown in the table below, and the experimental data are tabulated in Appendix I (Tables

XIA - XIC). The average stability constant which was obtained from the experiments was 20 ± 10.

Quenching in the Calcium Malonate System

Expt	0.1 MNaClO$_4$	0.0333M Na$_2$M	Ca^{45} soln.	r.e.f.
1	0.050 litre	0.000	0.0008	1.000
2	0.045	0.005	0.0008	1.231
3	0.040	0.010	0.0008	1.381
4	0.035	0.015	0.0008	1.708
5	0.030	0.020	0.0008	1.693
6	0.025	0.025	0.0008	1.979
7	0.020	0.030	0.0008	2.093
8	0.015	0.035	0.0008	2.039
9	0.010	0.040	0.0008	2.269

The Calcium Succinate System

The general procedure adopted was the same as for all the other systems examined. A quenching experiment was set up in the manner described earlier, and a relative efficiency factor was calculated for each mixture used. The results are shown in the following table. As in the case of the calcium malonate complex, it was found that the combination of the low stability constant of the calcium succinate complex and the quenching effect of the succinate ions in the scintillant mixture resulted in a zero increase in the measured radioactivity in the aqueous phase. The stability constants which were calculated, therefore, depend entirely on the application of a correction and so cannot be regarded as very accurate. The experimental results are tabulated in the Appendix I (Tables XIIA,B). The graphs are shown in figure XVII.

Quenching by the Succinate Ion

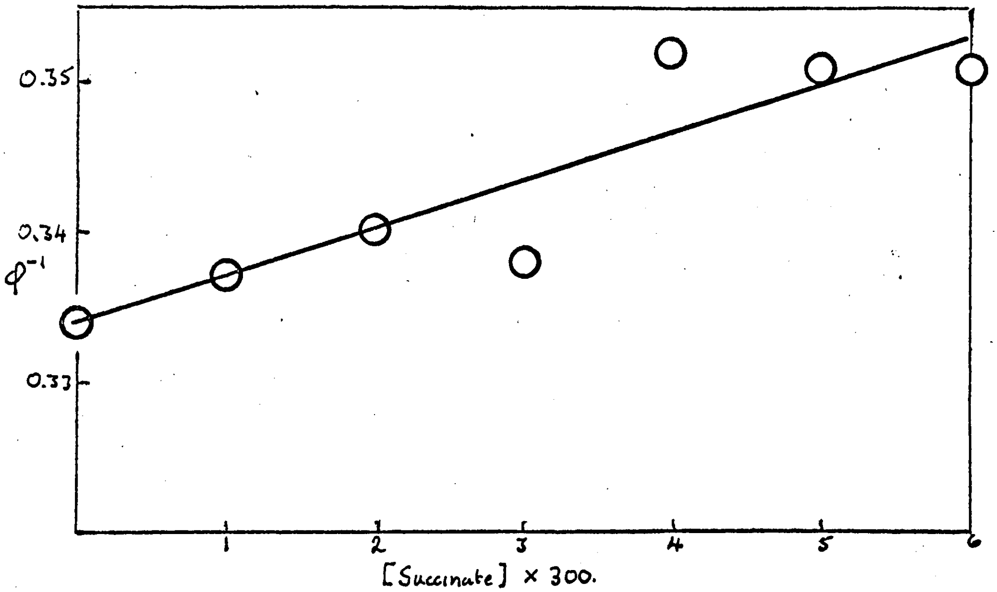
Expt	0.1M $NaClO_4$	0.033M $Na_2(CH_2COOH)_2$	c.p.m. per 0.8 ml.	r.e.f.
1	50.0 ml	0.0 ml	18910	1.000
2	45.0	5.0	16537	1.145
3	40.0	10.0	16378	1.152
4	35.0	15.0	16116	1.167
5	30.0	20.0	16527	1.181
6	25.0	25.0	16141	1.189
7	20.0	30.0	15862	1.204
8	15.0	35.0	15831	1.212
9	10.0	40.0	15478	1.227

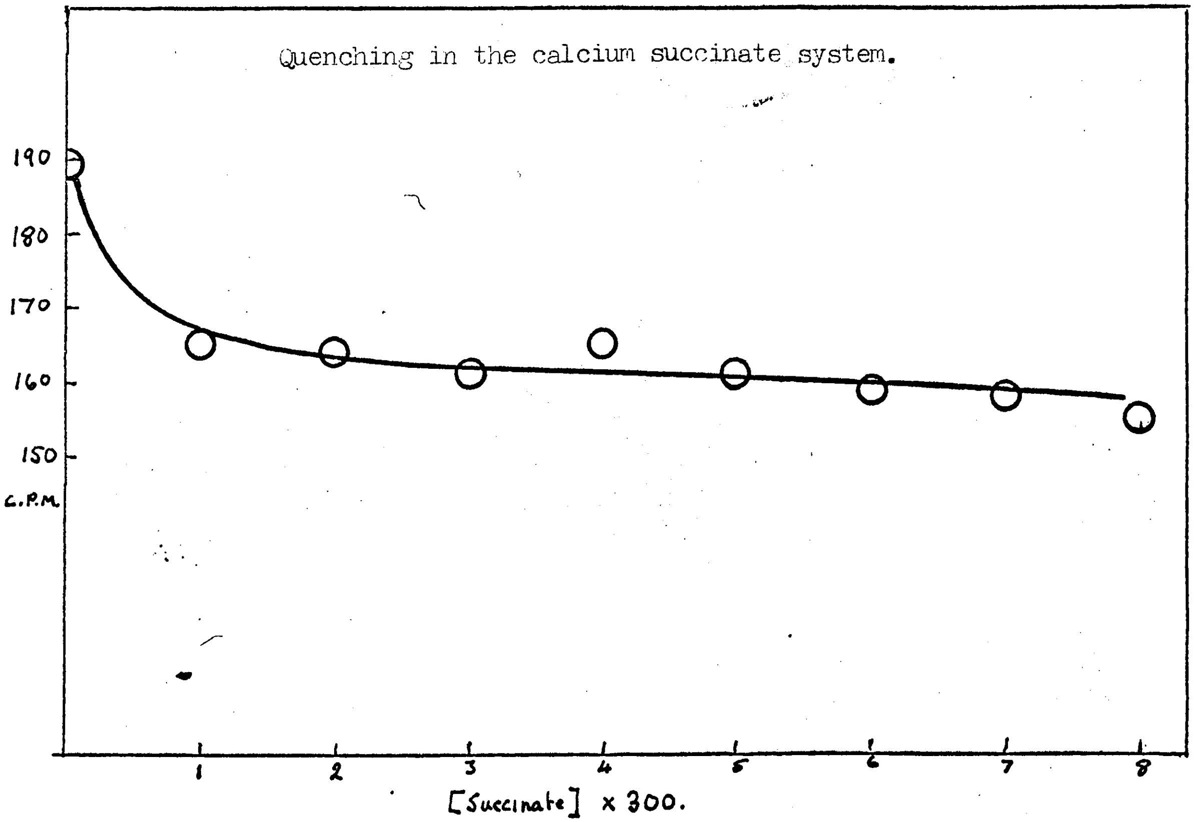
0.8 ml of a solution of calcium 45, of radioactive concentration about 1.0 microcurie per ml was added to each of these experiments, and 0.8 ml samples were withdrawn. Results are plotted in figure XVII.

For the stability constant of the calcium succinate complex a value of ~5 is obtained from the data. In view of the fact that the calculation of the constant results from the application of a correction to the original data this figure can be considered as representing an order of magnitude only. Despite the severe limitations involved, however, when the method is applied to a case such as this there appears to be reasonably good correspondence between

Figure XVII.

The calcium succinate system.




Quenching in the calcium succinate system.

the figure obtained and the figures found at comparable ionic strengths by other workers(87,95,97) in the literature.

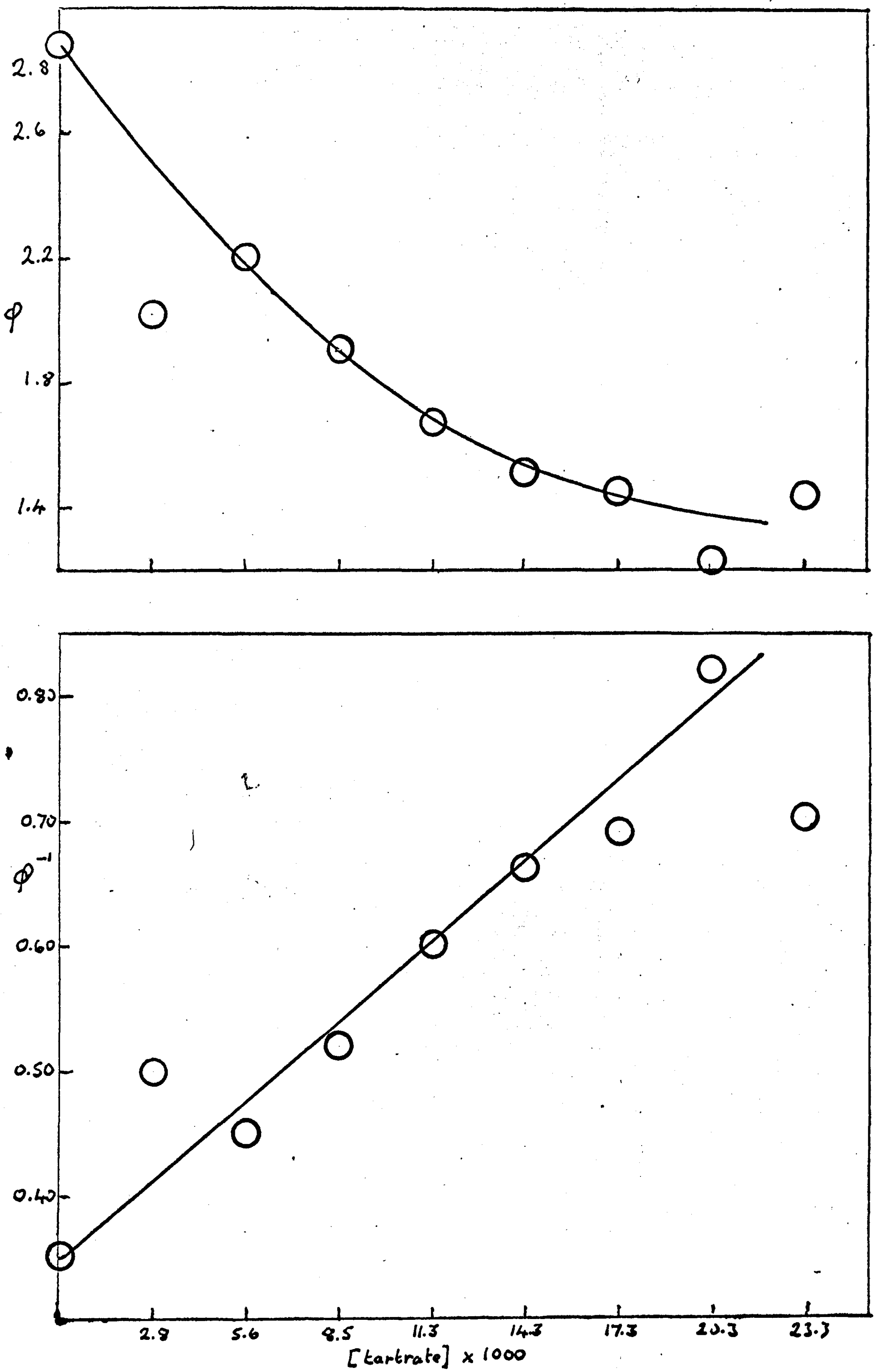
The Calcium Tartrate System

The method was the same as for all the other systems. Recent work(86), however, indicated that there is complex formation between sodium ions and tartrate ions and that, at 0.1M, the stability constant is 2. A calculation of the corrected tartrate concentrations is therefore necessary, and it is found that the concentrations obtained are the same as those which were found for the corrected malonate values. An investigation of quenching by the tartrate ion was made and relative efficiency factors were applied to the counts obtained from the experiments. These factors are tabulated below, and the experimental data are tabulated in Appendix I (Tables XIIIA - XIIIC). Plots of ϕ and ϕ^{-1} vs [tartrate] are shown in figure XVIII.

Expt	0.1M $NaClO_4$	0.0333M Na_2T	Ca^{45} soln	r.e.f.
1	0.050 litre	0.000	0.0008	1.000
2	0.045	0.005	0.0008	1.676
3	0.040	0.010	0.0008	1.107
4	0.035	0.015	0.0008	1.052
5	0.030	0.020	0.0008	1.079
6	0.025	0.025	0.0008	1.100
7	0.020	0.030	0.0008	1.111
8	0.015	0.035	0.0008	1.232
9	0.010	0.040	0.0008	1.132

The stability constant which was obtained from these experiments was 60 ± 10.

The calcium tartrate system.



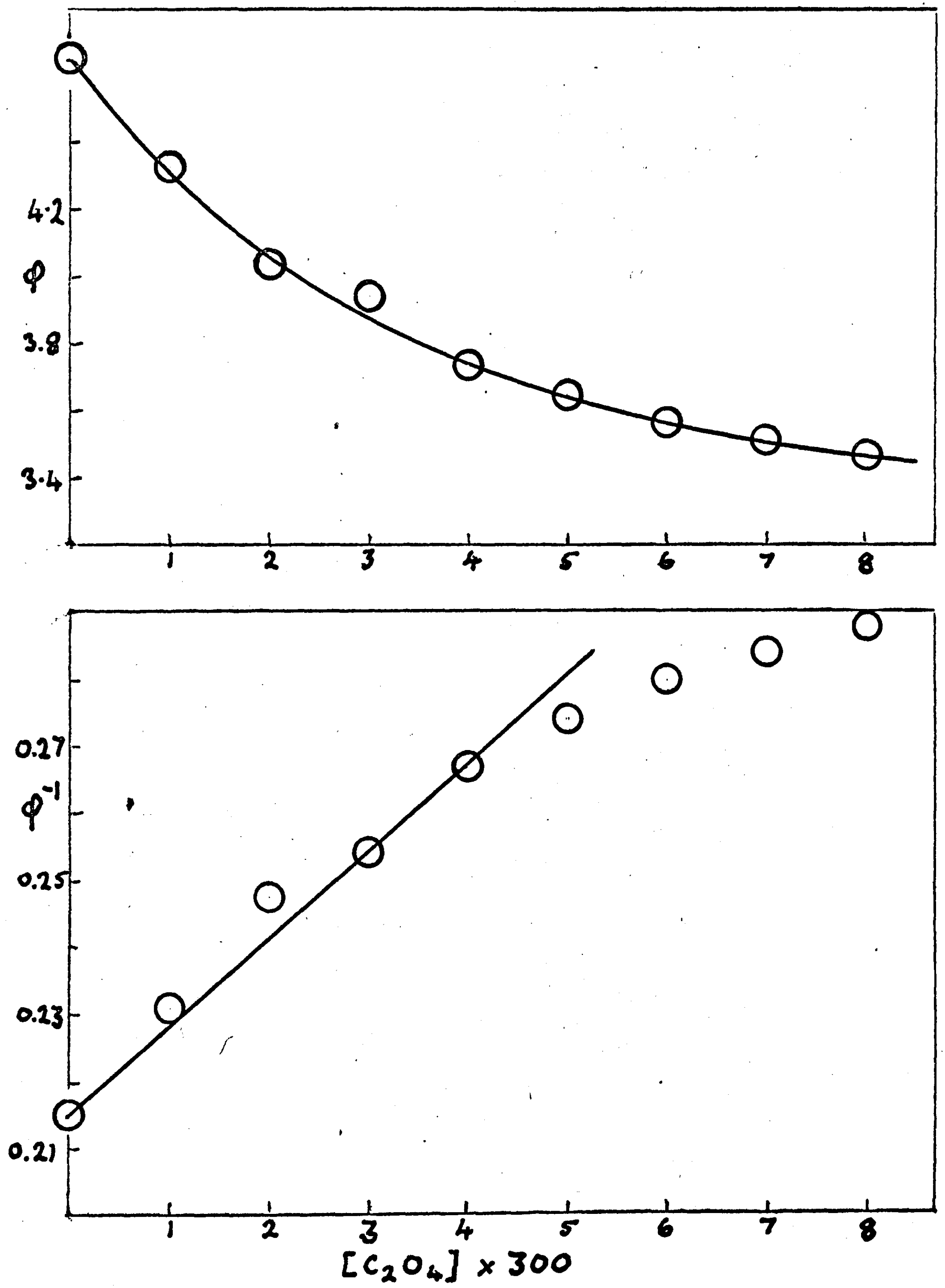
Studies on the Strontium Oxalate System

The general procedure was the same as for the other systems examined. After being sampled the batches were left for a period of about four weeks before being counted, then left for a further week and recounted. The results were used if there was no significant alteration in the counts. An examination was made of possible quenching in the system. The following mixtures were made up, an aliquot of solution containing strontium 90 was added to each and the mixtures were agitated and sampled. The results are included in the table.

Expt	0.1M $NaClO_4$	0.0333M Na_2 Ox	Sr^{90} soln	c.p.m.
1	0.050 litre	0.000 litre	0.0001 litre	638
2	0.045	0.005	0.0001	718
3	0.035	0.015	0.0001	727
4	0.030	0.020	0.0001	690
5	0.025	0.025	0.0001	681
6	0.020	0.030	0.0001	688
7	0.015	0.035	0.0001	698
8	0.010	0.040	0.0001	726
9	0.005	0.045	0.0001	698
10	0.000	0.050	0.0001	711

It is seen that there appears to be no progressive quenching effect so that no correction need be applied. The experimental results are tabulated in the Appendix (Tables XIVA,B). Plots of ϕ and ϕ^{-1} v [Oxalate] are shown in fig. XIX. A value of 18 ± 5 is obtained for the stability constant of the strontium oxalate complex.

The strontium oxalate system.



The Strontium Tartrate System

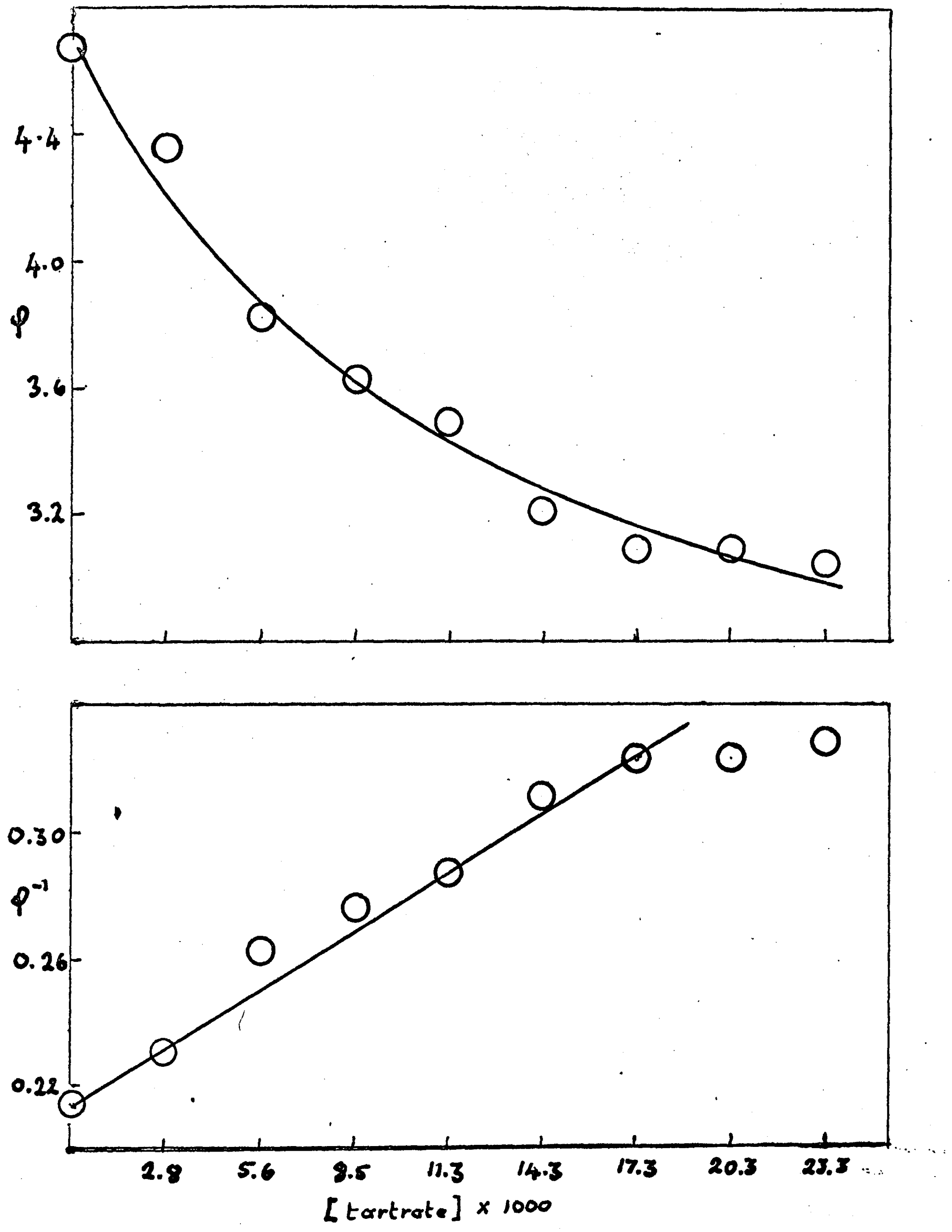
The method was the same as for most of the other systems examined. Tartrate concentrations corrected for sodium complex formation were used. A quenching experiment was performed before the measurements were made. The following experiments were set up, a quantity of radioactive strontium added, samples taken and counted. The results are as shown below.

Expt	0.1M $NaClO_4$	0.0333M NaT	Sr^{90} soln.	c.p.m.
1	0.000 litre	0.050	0.0004	3964
2	0.005	0.045	0.0004	3948
3	0.010	0.040	0.0004	3916
4	0.015	0.035	0.0004	3977
5	0.020	0.030	0.0004	3933
6	0.025	0.025	0.0004	3955
7	0.030	0.020	0.0004	3941
8	0.035	0.015	0.0004	3994
9	0.040	0.010	0.0004	3957
10	0.045	0.005	0.0004	3907

These results indicate that there is no progressive quenching effect. The results of the equilibration experiments are included in Appendix I (Tables XVA,B). Plots of ϕ and ϕ^{-1} vs [tartrate] are shown in figure XX. The average value obtained for the stability constant is 30 ± 5.

Figure XX.

Strontium tartrate system.



The Calcium-Hydrogen-Oxalate System

General Considerations

Because of the relatively high dissociation constant of the species hydrogen-oxalate at 0.1 molar it was undesirable to study this system at the high pH (about 7) which was used in the study of the other systems. A half-neutralised solution of 0.1 molar oxalic acid has a pH in the region of 4, which indicates that in such a solution there is an appreciable concentration of the oxalate ion. From purely electrostatic considerations this species is expected to complex more readily with calcium ions than will the hydrogen-oxalate species, so that the presence of the former anion must be excluded for reliable measurements to be made. It was therefore decided to employ a medium of much lower pH than had been used for the other systems so that the second ionisation of oxalic acid could be repressed. If the first dissociation constant of oxalic acid is taken to be about 10^{-2} and the second to be about 10^{-4} it is easily shown that at pH 1.0 the ratio of hydrogen-oxalate to oxalate concentrations is of the order of 1000:1 whilst at pH 2.0 the ratio is of the order of 100:1. From this it appears that the highest pH which can be employed is 2.0, above which value the proportion of oxalate is greater than 1%. Mixtures of perchloric acid and oxalic acid were used to provide the ligand at suitable concentrations in a medium of suitable ionic strength.

Theory. Calculation of the Concentrations of the Species present in Mixtures of a weak dibasic Acid and a strong Monobasic Acid

In the following analysis T_{Ox} is the total oxalic acid concentration. A subscripted letter C refers to the concentration of a species. To a first approximation

$$T_{ox} = C_{HOx} + C_{H_2Ox}$$

if the concentration of oxalate ion, which will be low in solutions of strong acid at low pH, is neglected.

Since $$K_1 = \frac{C_H . C_{HOx}}{C_{H_2Ox}}$$

and $$K_2 = \frac{C_H . C_{Ox}}{C_{HOx}}$$

then $$T_{Ox} = C_{HOx}(1 + \frac{C_H}{K_1}) .$$

To a first approximation

$$C_H = C_A + C_{HOx}$$

where C_A is the concentration of the perchlorate ion or other strong acid anion, so that

$$T_{Ox} = C_{HOx} \left\{ 1 + \frac{C_A + C_{HOx}}{K_1} \right\} ,$$

$$C_{HOx} = T_{Ox} / \left\{ 1 + \frac{C_A + C_{HOx}}{K_1} \right\}$$

and $$C^2_{HOx} + C_{HOx}(K_1 + C_A) - K_1 T_{Ox} = 0.$$

This is a quadratic equation so it may be solved by the usual formula giving

$$C_{HOx} = \{-(K_1+C_A) + ([K_1+C_A]^2 + 4K_1T_{Ox})^{\frac{1}{2}}\}/2 .$$

This procedure yields a first value of C_{HOx}. It is now possible to employ two explicit functions,

$$T_{Ox} = C_{H_2Ox} + C_{HOx} + C_{Ox}$$

and $$C_H = C_A + C_{HOx} + 2C_{Ox} .$$

$$\therefore \quad T_{Ox} = C_{HOx}\left\{1 + \frac{C_H}{K_1} + \frac{K_2}{C_H}\right\}$$

so that $$C_{HOx} = T_{Ox}\Big/\left\{1 + \frac{C_H}{K_1} + \frac{K_2}{C_H}\right\}$$

and $$C_H = C_A + C_{HOx} + 2K_2C_{HOx}/C_H$$

$$= C_A + C_{HOx}\left\{1 + \frac{2K_2}{C_H}\right\} .$$

$$\therefore \quad C_H = C_A + \frac{T_{Ox}\left\{1 + \frac{2K_2}{C_H}\right\}}{\left\{1 + \frac{C_H}{K_1} + \frac{K_2}{C_H}\right\}}$$

which may be rearranged to give

$$\frac{C_H^3}{K_1} + C_H^2\left\{1 - \frac{C_A}{K_1}\right\} + C_H(K_2-C_A-T_{Ox}) - (C_A+2T_{Ox})K_2 = 0$$

Since this expression is a cubic in C_H it may be solved by Newton's method using as the approximate value of the root of the equation the value

$$C_H = C_A + C_{HOx}$$

defined in the first part of the analysis. When the accurate value of the hydrogen ion concentration has been found an accurate value for C_{HOx} may be calculated by substitution into the equation

$$C_{HOx} = T_{Ox} \Big/ \left\{ 1 + \frac{C_H}{K_1} + \frac{K_2}{C_H} \right\} .$$

Results of the Calculations

Various systems were examined to calculate the concentrations of the species present in them, the most suitable of these being the following series.

Mixture	Molarity of oxalic acid	Volume of oxalic acid	Molarity of perchloric acid	Volume of perchloric acid
1	0.300	0.100 litre	0.100	0.000 litre
2		0.090		0.010
3		0.080		0.020
4		0.070		0.030
5		0.060		0.040
6		0.050		0.050
7		0.040		0.060
8		0.030		0.070
9		0.020		0.080
10		0.010		0.090

The calculations which yielded the following concentrations were performed by computer using a program written for the purpose. The program is included in Appendix II. In the table of concentrations [A] is the oxalate concentration, $[H_2A]$ the oxalic acid concentration, and [HA] the hydrogen oxalate concentration. No correction has been made for the

Mixture	[A]	[H_2A]	[HA]	T_{Ox}	I	pH	R
1	0.00015	0.20011	0.09975	0.30001	0.10020	0.9996	660
2	0.00014	0.18009	0.08978	0.27001	0.10018	0.9996	660
3	0.00012	0.16008	0.07980	0.24000	0.10017	0.9996	660
4	0.00011	0.14007	0.06983	0.21000	0.10015	0.9996	660
5	0.00009	0.12005	0.05968	0.18000	0.10013	0.9996	660
6	0.00008	0.10004	0.04988	0.15000	0.10011	0.9996	660
7	0.00006	0.08003	0.03991	0.12000	0.10009	0.9997	660
8	0.00005	0.06002	0.02993	0.09000	0.10007	0.9997	660
9	0.00003	0.04001	0.01996	0.06000	0.10005	0.9997	660
10	0.00002	0.02001	0.00998	0.03001	0.10002	0.9997	659

Concentrations of species present in mixtures of perchloric acid and oxalic acid activity coefficients in the calculation of pH. T_{Ox} is the total concentration as calculated by summing [A], [HA] and [H_2A], and agreement with the formal value is seen. R is the ratio of hydrogen oxalate to oxalate concentrations. The program was designed to use the dissociation constants of the acid at infinite dilution, to alter them according to ionic strength calculated, and recalculate the concentrations of the species present. Recycling was performed until successive calculations yielded the same results. Insertion of the appropriate concentrations gave values of K_1 and K_2 for oxalic acid very close to those at 0.1M. This gave a good check of the program's functioning.

It is apparent from the figures that a conveniently high concentration of the protonated species is obtained in the series of mixtures, and that the concentration of the oxalate ion is low in all cases; R, the ratio of the concentration of hydrogen oxalate to oxalate is virtually constant throughout the series. The ionic strength is seen to be sufficiently constant to be considered as being at a constant value. The pH however is rather low, although almost constant, so that it is undesirable to use the resin in the sodium form because sodium ions would be replaced to some extent by hydrogen ions, leaving the resin containing appreciable proportions of both species. This situation was avoided by using the resin in the hydrogen form so that there will be only one predominating cationic species in the resin phase.

Experimental Details

The general procedure was the same as for most of the other systems. Although only three runs were performed on the system, and one sample only was taken from each experiment, excellent agreement was obtained from run to run.

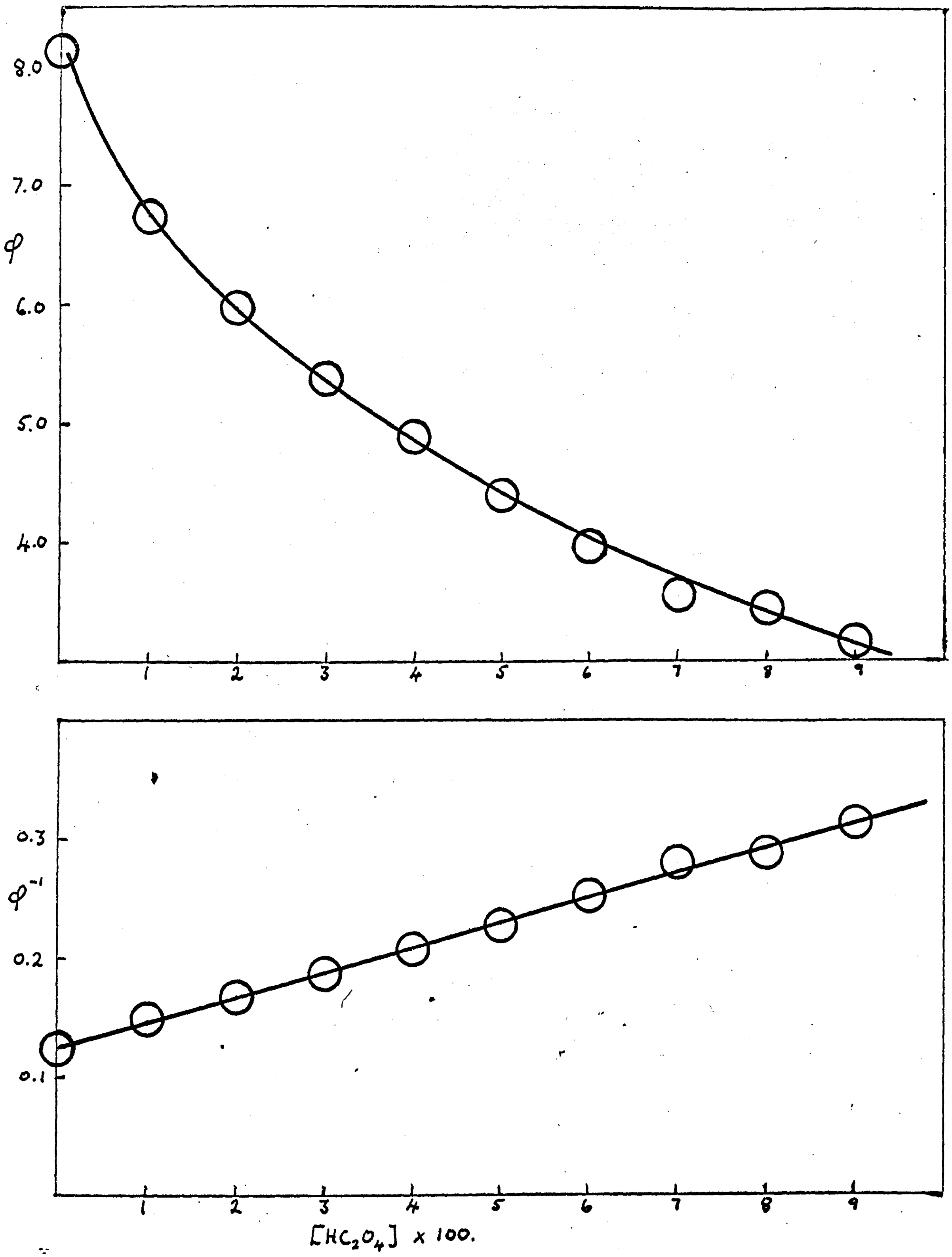
Quenching by the Hydrogen Oxalate Ion

In view of the fact that Bray$^{(\text{loc.cit.})}$ states that acids in general have a pronounced quenching effect it was considered especially desirable to examine the system for quenching in this case. Experiments were set up as follows, and the results are included in the last column.

Expt.	0.3M $H_2C_2O_4$	0.1M $HClO_4$	HO_2O_4	Ca-45 soln	c.p.m.
1	0.010 l.	0.090 l.	0.00998	0.0005 l.	252
2	0.020	0.080	0.01996	0.0005	250
3	0.030	0.070	0.02993	0.0005	240
4	0.040	0.060	0.03991	0.0005	254
5	0.050	0.050	0.04998	0.0005	249
6	0.060	0.040	0.05986	0.0005	247
7	0.070	0.030	0.06983	0.0005	257
8	0.080	0.020	0.07980	0.0005	254
9	0.090	0.010	0.08978	0.0005	248

It is seen that there is no progressive quenching effect, so that no correction need be included. Plots of ϕ and ϕ^{-1} vs. [hydrogen oxalate] are shown in figure XXI.

The calcium hydrogen oxalate system.



Treatment of Results

A least-squares curve-fitting program, which is included in Appendix II, was written in order to study the variation of the distribution coefficient as a function of hydrogen-oxalate concentration. Although higher orders of fit gave smaller deviations in the calculated value of the coefficient as compared with the experimental value it was decided to use a cubic function in order to simplify the mathematics involved and to obviate the possibility of a spurious fit. The fit used was

$$\phi = 8.0185 - 124.67[HC_2O_4] + 1319.1[HC_2O_4]^2 - 5955.7[HC_2O_4]^3 .$$

The first derivative of this function, therefore, is

$$\phi' = -124.67 + 2638.2[HC_2O_4] - 17867.1[HC_2O_4]^2$$

and the second derivative is

$$\phi'' = 2638.2 - 35734.2[HC_2O_4] .$$

These expressions give the following

$[HC_2O_4]$	$[HC_2O_4]^2$	ϕ (calc.)	ϕ'	ϕ''
0.000	0.0000	8.0185	-124.67	2638.2
0.010	0.0001	6.8977	-100.08	2280.9
0.020	0.0004	6.0050	- 79.06	1923.6
0.030	0.0009	5.3047	- 61.60	1566.3
0.040	0.0016	4.7610	- 47.73	1209.0
0.050	0.0025	4.3381	- 37.43	851.7
0.060	0.0036	4.0004	- 30.70	494.4
0.070	0.0049	3.7121	- 27.55	137.1
0.080	0.0064	3.4375	- 27.96	-220.2
0.090	0.0081	3.1409	- 31.95	-577.5

ϕ' and ϕ'' are plotted vs. [hydrogen oxalate] in fig. XXII.

Stability constants may be calculated from the relationship

$$\phi'' + \sum_{j=1}^{N}\left\{[HC_2O_4]^j\phi'' + 2j[HC_2O_4]^{j-1}\phi' + j(j-1)[HC_2O_4]^{j-2}\phi\right\}\beta_j = 0 \,.$$

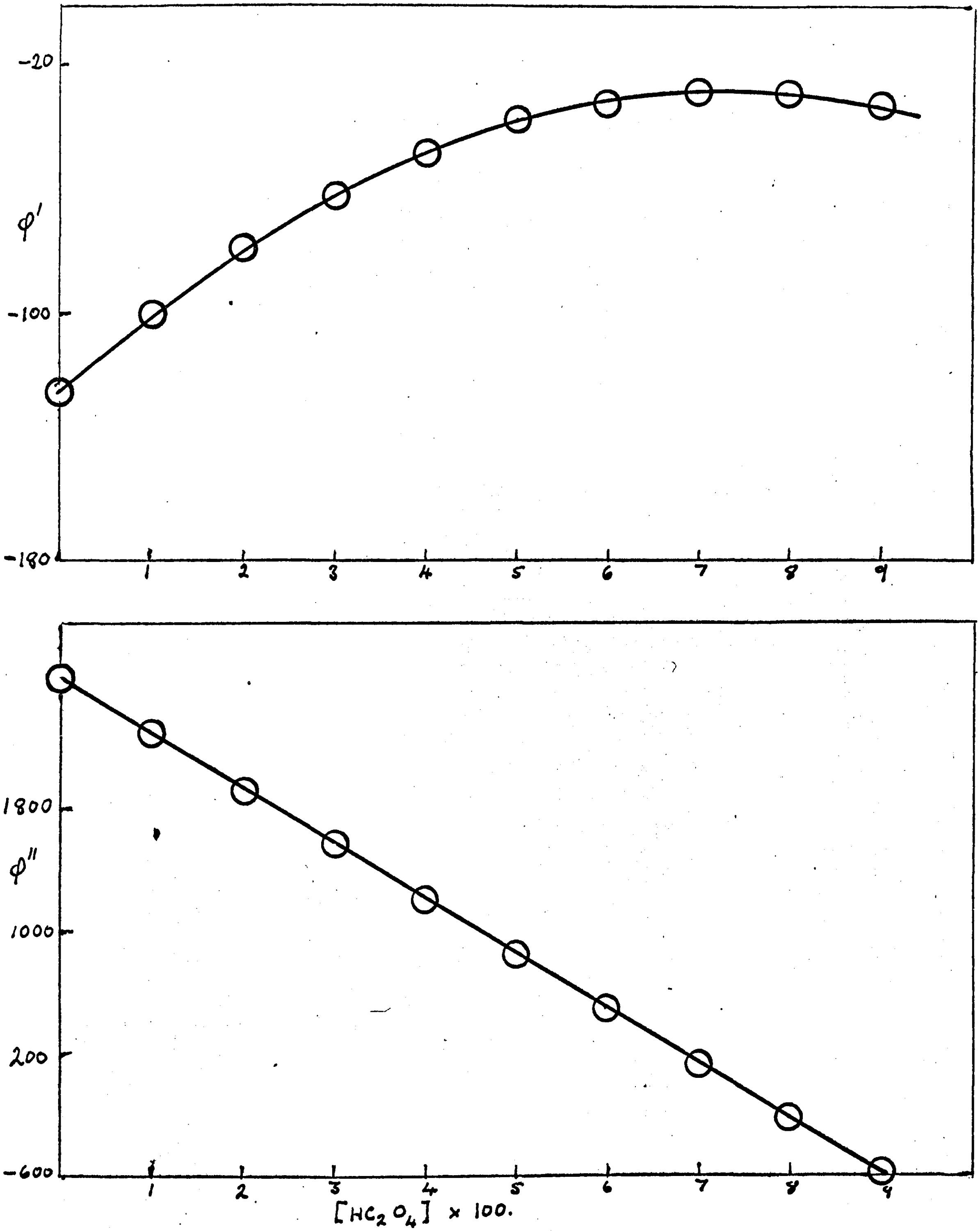
If the data at $[HC_2O_4] = 0.020M$, $0.030M$ and $0.040M$ are examined the following set of equations is obtained.

$$119.65\ \beta_1 - 6.46\ \beta_2 - 0.53\ \beta_3 = 1923.6\ ;$$
$$76.21\ \beta_1 - 4.63\ \beta_2 - 0.62\ \beta_3 = 1566.3\ ;$$
$$47.10\ \beta_1 - 3.81\ \beta_2 - 0.68\ \beta_3 = 1209.0\ .$$

Solutions of these equations results in a value for β_1 of 24.1, but little reliance may be placed on any other than the first stability constant obtained by this mathematical procedure.(67) If data points at higher concentrations are treated by this procedure it is found that the equations yield negative stability constants. This is associated with the change of sign of the second derivative of the distribution coefficient possibly reflecting experimental inaccuracy in this region.

The problem may be approached by another route. It may be assumed that only one complex is formed in the lower ligand concentration region, and the equations solved on this basis. Such an approach gives

The calcium hydrogen oxalate system.



$[HC_2O_4]$	β_1
0.020	16
0.030	21
0.040	26
0.050	26
0.060	16

The assumption that only one complex is formed is likely to be least erroneous in the region of lower ligand concentration so that it seems likely that the first stability constant is in the region of 20; this confirms the finding from the solution of the equations constructed on the basis of three complexes, that $\beta_1 = 24$.

Alternatively, it may be assumed that the species $CaC_2O_4H^+$ is not taken up at all by the resin phase. It is then possible to calculate stability constants according to the method regularly used for systems of the type $M^{n+} - A^{n-}$. This gives the following.

$[HC_2O_4]$	ϕ	l_0/ϕ	$(l_0/\phi)-1$	$\{(l_0/\phi)-\}/[HC_2O_4]$
0.000	8.136	-	-	-
0.010	6.708	1.217	0.217	21.7
0.020	5.959	1.370	0.370	18.5
0.030	5.352	1.525	0.525	17.5
0.040	4.882	1.672	0.672	16.8
0.050	4.398	1.856	0.856	17.1
0.060	3.970	2.056	1.056	17.6
0.070	3.573	2.285	1.285	18.4
0.080	3.461	2.359	1.359	17.0
0.090	3.177	2.569	1.569	17.4

Apart from the first value which appears to agree badly with the rest, an average figure taken by this approximation shows good agreement with the values of β_1 obtained by the other methods. $\beta_1 = 24.1$ is therefore a reasonable value to use in the subsequent calculations.

It is next necessary to calculate the value of the function

$$\phi_1 = \frac{\{\phi^{-1} - l_0^{-1}\}}{[HC_2O_4]}$$

of which the limiting value, when the ligand concentration tends to zero is $(\beta_1 - 1)/l_0$. This gives the following figures.

$[HC_2O_4]$	ϕ^{-1}	$\phi^{-1} - l_0^{-1}$	ϕ_1
0.000	-	-	-
0.010	0.149	0.026	2.60
0.020	0.168	0.045	2.25
0.030	0.187	0.064	2.13
0.040	0.205	0.082	2.05
0.050	0.227	0.104	2.08
0.060	0.252	0.129	2.15
0.070	0.280	0.157	2.24
0.080	0.289	0.166	2.08
0.090	0.315	0.192	2.13

The values of the calculated function, with the exception of the first value, are virtually constant, so that instead of extrapolating to zero ligand concentration it is permissible to use the average value of all the figures except the first. The mean value thus obtained, and consequently the limiting value, is 2.14. This results in a value for l of 6.63, when $\beta_1 = 24.1$.

Because

$$\phi = l_0 \frac{1 + l[HC_2O_4]}{X}$$

giving $$X = l_0\phi^{-1}\{1 + l[HC_2O_4]\}$$

it is possible to calculate values for X. Further, since

$$X_j = \frac{\{X_{j-1} - \beta_{j-1}\}}{[HC_2O_4]}$$

$$(X_0 = X; \quad \beta_0 = 1)$$

values for X_1 and X_2 may be calculated, and hence, from their limiting values, estimates of β_1 and β_2.

Calculation of these functions gives

$[HC_2O_4]$	X	X_1	X_2
0.010	1.30	30.0	-
0.020	1.55	27.5	-
0.030	1.83	27.7	-
0.040	2.11	27.8	-
0.050	2.47	29.4	-
0.060	2.87	31.2	70
0.070	3.35	33.6	94
0.080	3.61	32.6	70
0.090	4.11	34.6	84

From the table it is seen that the limiting value of X_1 is about 27 which agrees well with the values of β_1 obtained by other methods. The limiting value of X_2 is shown to be about 70 if the values obtained when the function X_1 is almost identical to β_1, when large errors in the function $X_1-\beta_1$ are to be expected, are neglected. For the system calcium-hydrogen-oxalate at 0.1 molar the following are hence the stability constants.

$$\beta_1 = 24 \pm 5 ;$$

$$\beta_2 \simeq 70 .$$

The Strontium-Hydrogen-Oxalate System

The general procedure was the same as for the other systems examined. The mass of resin used was 0.050 g, and the total volume of the solutions was about 0.050 litres. A quenching experiment was performed to determine if the Cerenkov radiation from the strontium 90 was quenched in the presence of the mixtures used.

Quenching in the Strontium-Hydrogen-Oxalate System

The following experiments were set up, and to each of them an aliquot of solution containing strontium 90 was added. After the experiments were shaken, samples were withdrawn and counted. The results are included in the table.

Expt.	0.1M $HClO_4$	0.3M $H_2C_2O_4$	c.p.m.
1	0.045 litre	0.005 litre	313
2	0.040	0.010	317
3	0.035	0.015	312
4	0.030	0.020	305
5	0.025	0.025	300
6	0.020	0.030	334
7	0.015	0.035	330
8	0.010	0.040	384
9	0.005	0.045	491
10	0.000	0.050	739

It is seen that in the presence of low perchloric acid concentrations the Cerenkov radiation is counted at a higher efficiency than at greater concentrations. These figures are shown plotted in fig. XXV and it is seen that there is little quenching in the region of interest. The experimental data are included in Appendix I, table XVII.

Treatment of Results

Expts.	c.p.m.	b.g.	ϕ	ϕ^{-1}
1	7695	7670	-	-
2	593	568	12.072	0.0828
3	656	631	10.816	0.0925
4	721	696	9.750	0.1026
5	810	785	8.568	0.1167
6	888	863	7.726	0.1294
7	963	938	7.047	0.1419
8	1011	986	6.664	0.1501
9	1085	1060	6.141	0.1628
10	1180	1155	5.565	0.1797

A least-squares analysis on the variation of the reciprocal of the distribution coefficient as a function of $[HC_2O_4]$ indicates a good linear relation of which the extrapolation to zero concentration gives $l_0^{-1} = 0.08081$. A least-squares curve-fit was performed on the variation of the distribution coefficient as a function of $[HC_2O_4]$. As with the calcium hydrogen oxalate case a cubic fit was taken to avoid mathematical complication and spurious fitting. The fit used was

$$\phi = 12.127 - 146.52[HC_2O_4] + 1124.1[HC_2O_4]^2 - 3843.4[HC_2O_4]^3$$

so that

$$\phi' = -146.52 + 2248.2[HC_2O_4] - 11530.2[HC_2O_4]^2$$

and

$$\phi'' = 2248.2 - 23060.4[HC_2O_4].$$

These relationships yield the following results:

$[HC_2O_4]$	$[HC_2O_4]^2$	ϕ (calc.)	ϕ'	ϕ''
0.000	0.0000	12.127	-146.52	2248.2
0.010	0.0001	10.771	-125.19	2017.6
0.020	0.0004	9.616	-106.17	1787.0
0.030	0.0009	8.640	- 89.45	1556.4
0.040	0.0016	7.819	- 75.04	1325.8
0.050	0.0025	7.131	- 62.94	1095.2
0.060	0.0036	6.553	- 53.14	864.6
0.070	0.0049	6.061	- 45.65	634.0
0.080	0.0064	5.632	- 40.45	403.4

The variation of ϕ and ϕ^{-1} with $[HC_2O_4]$ is shown in fig. XXIII, ϕ', ϕ'' in fig. XXIV. Stability constants are

Figure XXIII.

The strontium hydrogen oxalate system.

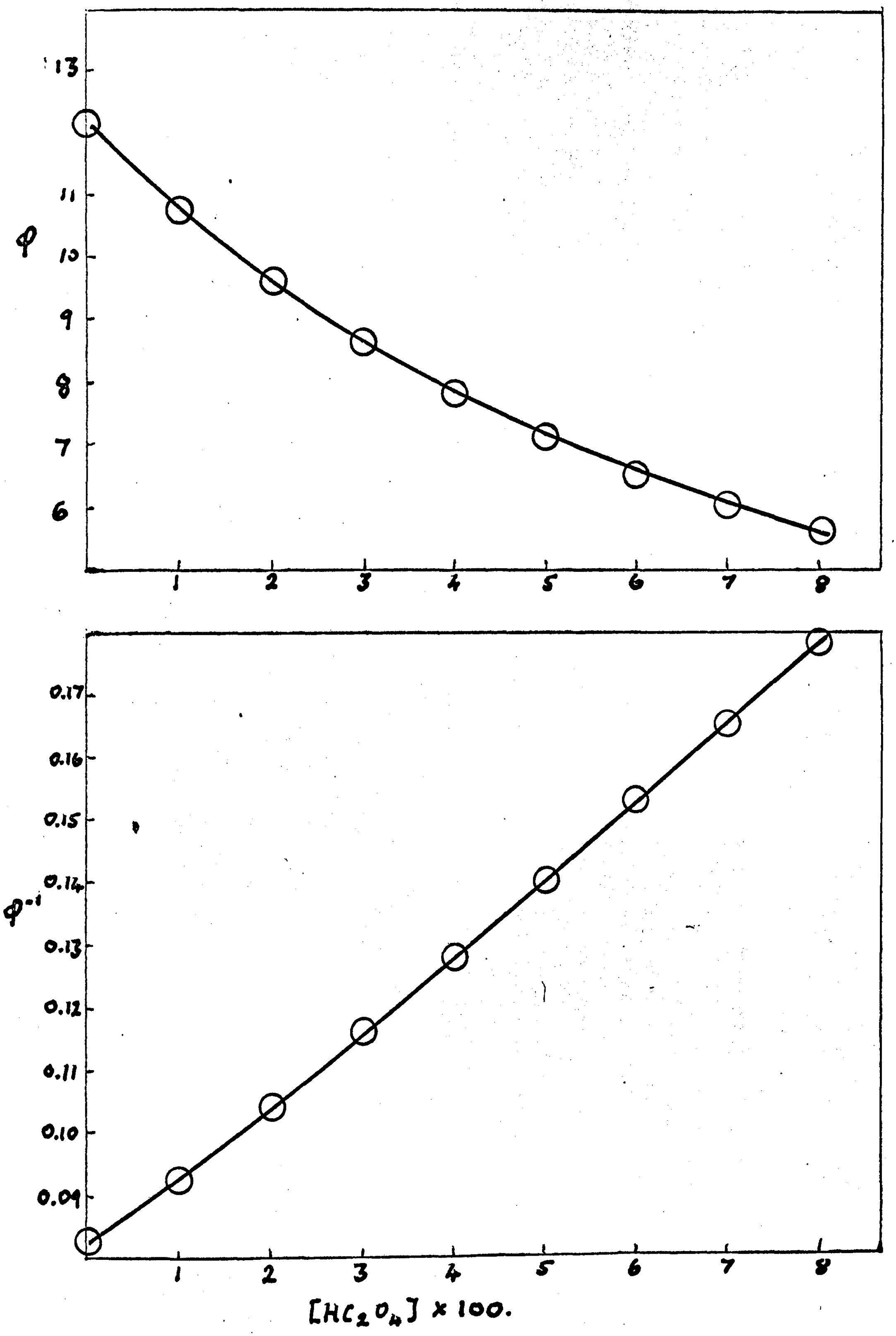
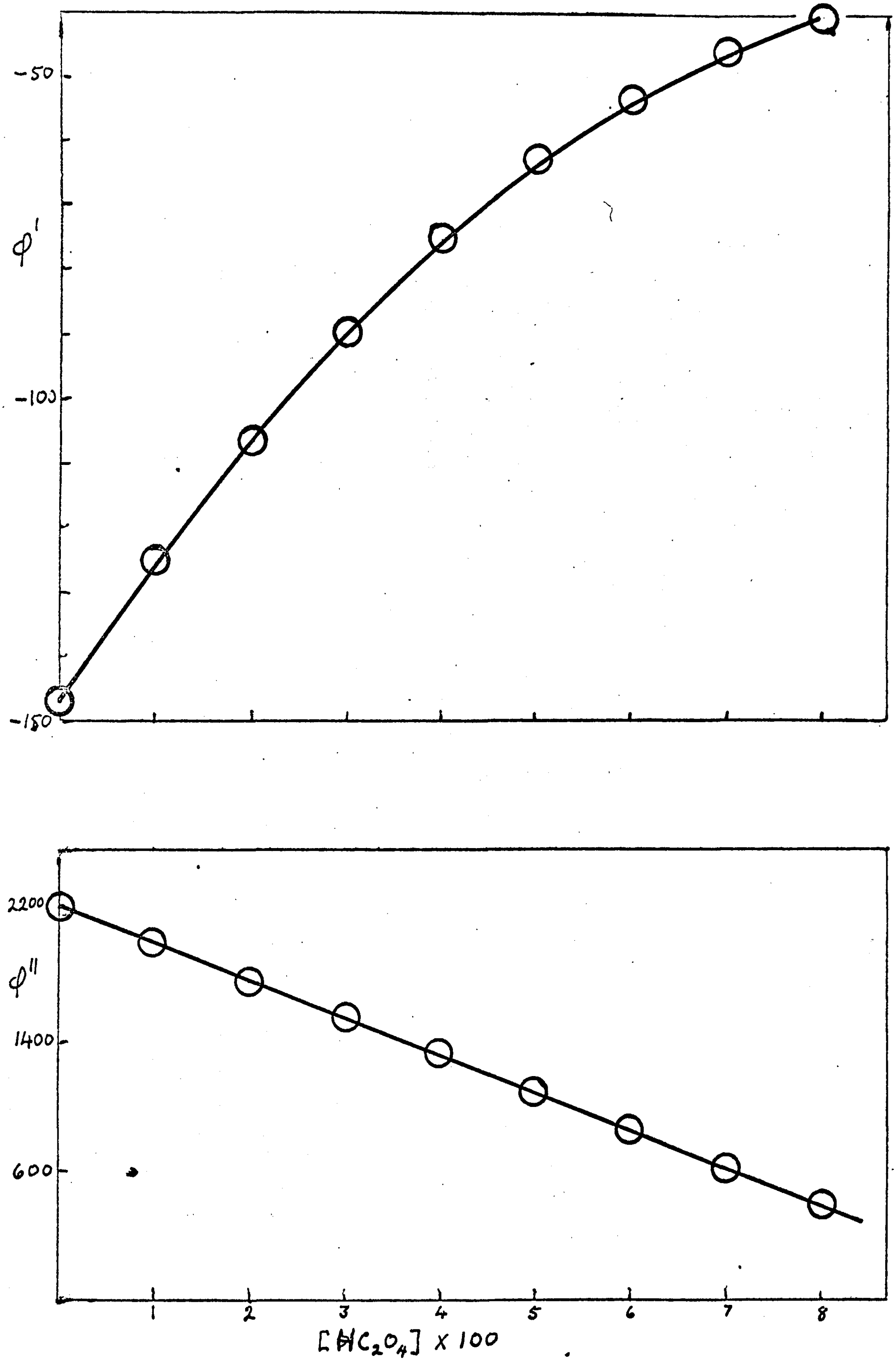


Figure XXIV.

The strontium hydrogen oxalate system.



calculated from the relationship

$$\phi'' + \sum_{j=1}^{N} \left\{ [HC_2O_4]^j \phi'' + 2j[HC_2O_4]^{j-1}\phi' + j(j-1)[HC_2O_4]^{j-2}\phi \right\} \beta_j = 0 \,.$$

The following equations are obtained.

$$176.60\ \beta_1 - 11.45\ \beta_2 - 0.90\ \beta_3 = 1787.0\ ;$$

$$132.21\ \beta_1 - 7.95\ \beta_2 - 1.08\ \beta_3 = 1556.4\ ;$$

$$97.05\ \beta_1 - 5.75\ \beta_2 - 1.16\ \beta_3 = 1325.8\ .$$

Solution of these equations on the basis of formation of one complex only results in a value for the stability constant of about 13. Solution on the basis of two complexes gives $\beta_1 = 32.8$ and $\beta_2 = 349.7$. On the basis of formation of three complexes the results are $\beta_1 = 9.57$, $\beta_2 = 30.3$, with a negative value for β_3.

It is possible as in the case of calcium to make the assumption that little or none of the unipositive complex is taken up by the resin. This seems reasonable because the ion has one charge only, and must be moderately large. It is then possible to use the $M^{n+} - A^{n-}$ method of calculation to obtain a good approximation to the stability constant. The following are obtained.

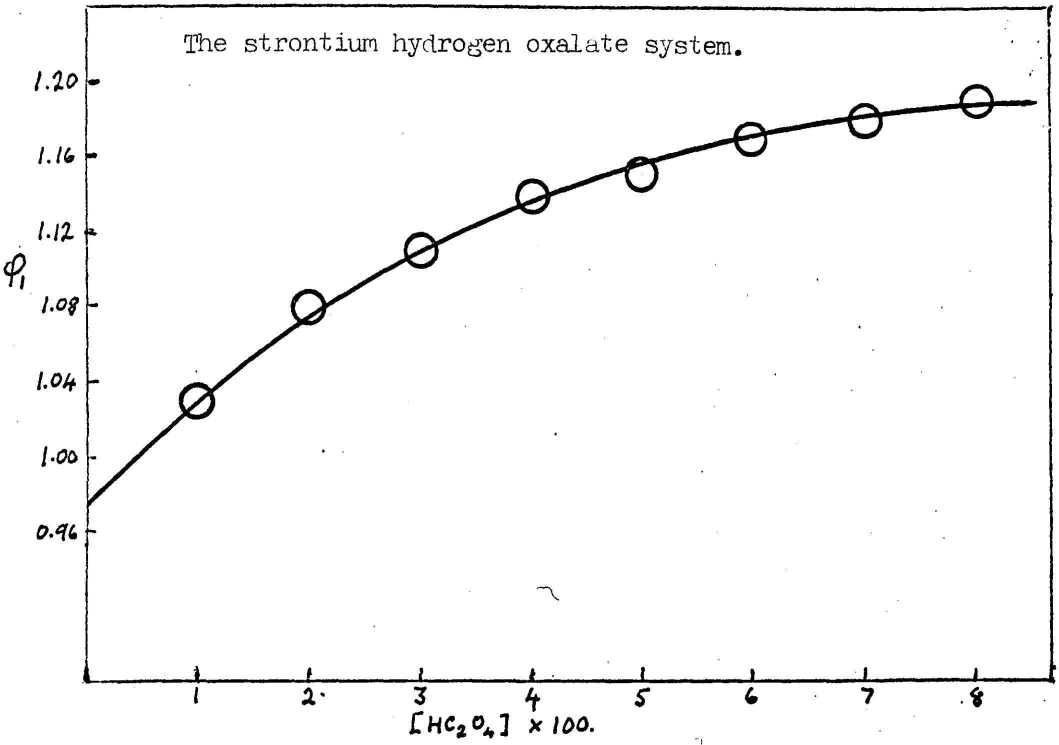
$[HC_2O_4]$	ϕ (calc.)	l_0/ϕ	$(l_0/\phi)-1$	$\{(l_0/\phi)-1\}/[HC_2O_4]$
0.000	12.127	-	-	-
0.010	10.771	1.126	0.126	12.60
0.020	9.616	1.261	0.261	13.05
0.030	8.640	1.404	0.404	13.47
0.040	7.819	1.551	0.551	13.78
0.050	7.131	1.701	0.701	14.02
0.060	6.553	1.851	0.851	14.18
0.070	6.061	2.001	1.001	14.30
0.080	5.632	2.153	1.153	14.41

These figures confirm that the value of β_1 may be taken as about 13 which is obtained by the solution of the systems of simultaneous equations on the basis of the assumption that either only one, or else three complexes are formed.

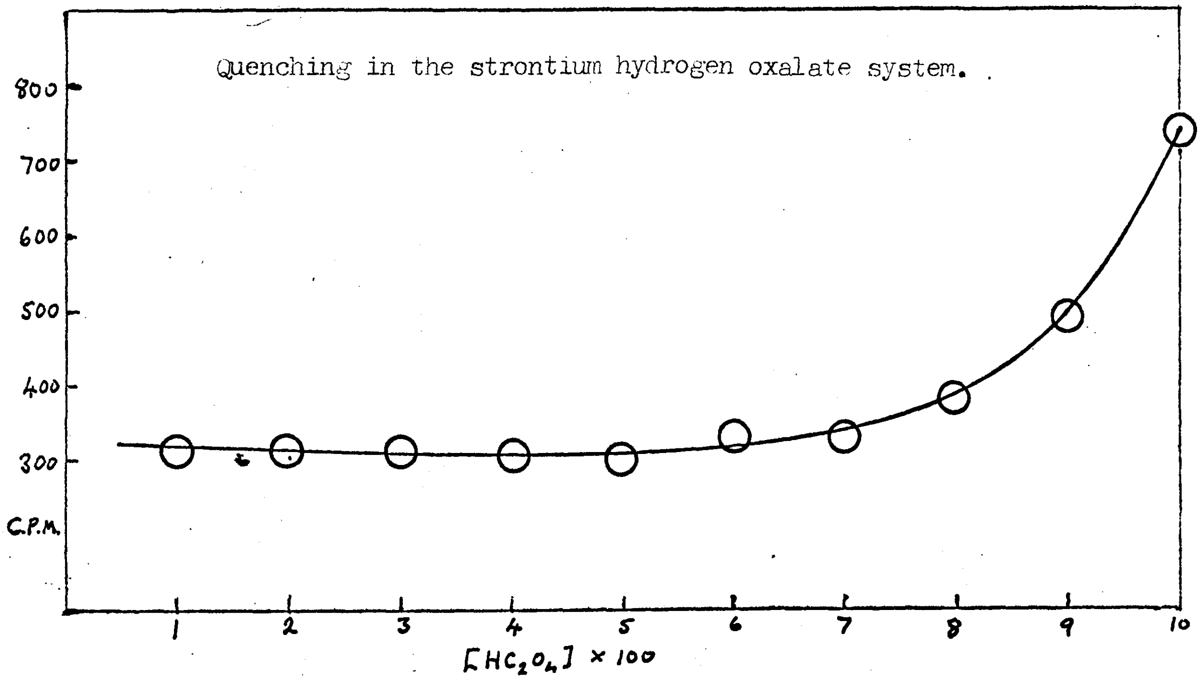
It is now necessary to calculate the value of the function ϕ_1 as defined earlier. The limiting value of this function as the ligand concentration tends towards zero is $(\beta_1-1)/l_0$ so that a figure for l may be found. The values of the function at each concentration are calculated below.

$[HC_2O_4]$	ϕ^{-1}	$\phi^{-1}-l_0^{-1}$	ϕ_1
0.000	0.0825	-	-
0.010	0.0928	0.0103	1.03
0.020	0.1040	0.0215	1.08
0.030	0.1157	0.0332	1.11
0.040	0.1279	0.0454	1.14
0.050	0.1402	0.0577	1.15
0.060	0.1526	0.0701	1.17
0.070	0.1650	0.0825	1.18
0.080	0.1776	0.0951	1.19

Figure XXV.



The strontium hydrogen oxalate system.



Quenching in the strontium hydrogen oxalate system.

In order to find the limiting value of this function it is necessary to plot it against ligand concentration and extrapolate to zero. This limiting value together with a value for l_0 and a value for β_1 allow the calculation of a value for l which is a function of the distribution coefficient for the unipositive complex and always positive, although it may be very small. If, however, the value of 9.6 is taken it is found that l becomes negative, so that it is desirable to use the value of 13 which was obtained in the calculations. The functions X, X_1 and X_2 previously defined are now calculated, and values for the stability constants are found.

$[HC_2O_4]$	X	X_1	$X_1-\beta_1$	X_2
0.010	1.140	14.00	0.06	60
0.020	1.292	14.60	1.20	60
0.030	1.456	15.20	1.80	60
0.040	1.628	15.70	2.30	58
0.050	1.806	16.12	2.72	54
0.060	1.989	16.48	3.08	51
0.070	2.175	16.79	3.39	48
0.080	2.367	17.09	3.69	46

The limiting value of X_1 as the ligand concentration tends to zero is found to be 13.4. X_2 is calculated on the basis of this figure. In the estimation of the value of β_1 the points where X_1 and β_1 are of the same order of magnitude are ignored because of the large errors involved in their subtraction. A value of about 50 may therefore be taken as the stability constant of the second complex so that the results of the calculations are

$$\beta_1 \simeq 13 ;$$

$$\beta_2 \simeq 50 .$$

General Discussion

The results of the present work are summarised in the table below which includes the results obtained in some earlier investigations on these systems.

System	ref	T	I	$\log\beta_1$	$\log\beta_2$
Ca-Ox	4	18	0	3.00	-
	5	25	0	3.10	-
	6	25	0	3.07	-
	3	25	1M $NaClO_4$	1.66	2.69
	p.w.	25	0.1M $NaClO_4$	2.08	-
Ca-Mal	93	25	0	2.49	-
	94	25	0	2.50	-
	95	25	0.16 NaCl	1.36	-
	87	25	0.2 KCl	1.46	HMal 0.46
	p.w.	25	0.1 $NaClO_4$	1.32	-
Ca-Succ	96	25	0	2.00	-
	97	25	0.15	1.15	-
	95	25	0.16 NaCl	1.00	-
	87	25	0.2 KCl	1.20	-
	p.w.	25	0.1 $NaClO_4$	0.70	-
Ca-T	98	25	0	2.98	6.03
	99		0	2.64	-
	96	25	0	2.80	-
	95	25	0.16 NaCl	1.78	-
	87	25	0.2 KCl	1.80	-
	p.w.	25	0.1 $NaClO_4$	1.78	-
Sr-Ox	4	18	0	2.54	-
	3	25	1M $NaClO_4$	1.26	1.90
	p.w.	25	0.1M $NaClO_4$	1.26	-

Sr-T	99		0	2.55	-
	97	25	0.15	1.94	-
	95	25	0.16 NaCl	1.59	-
	p.w.	25	0.1 $NaClO_4$	1.46	-

Fairly good agreement is seen where the earlier work has been performed under comparable conditions. If the present work is corrected by means of the Davies equation to a value approximating to that at infinite dilution good agreement is again seen, where such data at infinite dilution exist. The only exception appears to be the strontium oxalate system. For this system, additional experiments were performed and the results fully corroborated the results of the previous experiments. The results for the calcium malonate and the calcium succinate systems agree surprisingly closely with work done under fairly similar conditions when the fact that the quenching effect of the anion in these cases more than cancelled out the count increase due to complex formation is considered. All the results, therefore, can be considered to be reasonably accurate, with the possible exception of the result for the strontium oxalate complex, which may have a spuriously low stability.

It should be mentioned that stability constants for complexes of different charge types cannot be compared with each other at any ionic strength except zero in view of the fact that the different activity effects have different effects on the magnitude of the stability constants of the different complex types. The following relationships obtain.

$$2{:}1\ \beta_1^0 = 2{:}1\ \beta_1^{\mu}/f_2$$

$$2{:}1\ \beta_2^0 = 2{:}1\ \beta_2^{\mu}/f_2 f_1^2$$

$$2{:}2\ \beta_1^0 = 2{:}2\ \beta_1^{\mu}/f_2^2$$

$$2{:}2\ \beta_2^0 = 2{:}2\ \beta_2^{\mu}$$

The correction increments have the following values.

	2:1	2:2	2:1:1
μ		to log β^{μ} add	
0.1	0.46	0.91	0.68
0.16	0.52	1.04	0.77

Relatively little work has been performed on the stabilities of the metal dicarboxylic acid complexes in conjunction with the stabilities of the corresponding protonated complexes. Cannan and Kibrick(87) made such a study of some alkaline earth malonate, succinate and tartrate complexes, but omitted oxalates, because of the low solubility of their complexes. Their results are summarised in the table below.

Acid	logβ					
	Ca		Sr		Ba	
	A	HA	A	HA	A	HA
Malonic	1.46	0.47	1.25	0.41	1.23	0.44
Succinic	1.20	0.52	1.06	0.48	1.03	0.45
Tartaric	1.80	1.11	1.65	0.91	1.62	0.88

From their results they deduced that in general the stability of a protonated complex of an unsubstituted dicarboxylic acid was close to that of the corresponding unsubstituted monocarboxylic acid so that it appeared that an unionised carboxyl group had little effect on complexing at a neighbouring carboxylate group. The stability of the protonated complex was found in all cases to be lower than that of the dicarboxylate complex but no simple relationship was found to obtain. A study of the protonated complexes of the trivalent lanthanide malonates and succinates was made by Li et al.(88) who deduced from a comparison of plots of logβ versus 1/r* with the corresponding plots for acetate and glycollate complexes of the same metals that the hydrogen malonate ion behaves as a bidentate ligand and that the hydrogen succinate ion behaves as a monodentate ligand. This is explained in terms of the instability of the seven-membered ring which would result if the hydrogen succinate ion were to behave as a bidentate ligand. One of the implications of this interpretation is that the undissociated carboxyl group is capable of acting as a point of coordination. A number of studies have been made of the uranyl-oxalate system. L.J. Heidt(89) found that results of experiments on quantum yield, adsorption spectroscopy and pH could be interpreted in terms of the species $UO_2H_2C_2O_4{}^{2+}$, $UO_2C_2O_4{}^{0}$ and $UO_2(C_2O_4)_2{}^{2-}$. Rollefson(7) has referred to the work of McGinnis(8) in which it is deduced that the species

* r = ionic radius.

$UO_2HC_2O_4^+$ occurs. E.C. Pitzer, N.E. Gordon and D.A. Wilson(90) have stated that only divalent oxalate ions can behave as ligands. Li et al.(9) performed an ion-exchange study on the oxalate complexes of the uranyl ion and based their interpretation of the results on the complexes $UO_2HC_2O_4^+$ and $UO_2(HC_2O_4)_2$. They state that the species $UO_2H_2C_2O_4^{2+}$ is not formed since as a result of its positive charge it should be taken up by the exchanger and be detectable. No oxalate was found in the exchanger. A.I. Moskvin and F.A. Zakharova(91) examined the uranyl-oxalate system by the solubility method and interpreted their results in terms of the species $UO_2C_2O_4$ and $UO_2(C_2O_4)_2^{2-}$. They did not rule out the possibility of formation of the species $UO_2HC_2O_4^+$ but pointed out that if the results of Li et al.(loc.cit.) were analysed in terms of the oxalate complexes as opposed to the hydrogen oxalate complexes agreement with their results, and also with the results of Heidt(loc.cit.) was obtained. J.M. White, P. Tang and N.C. Li(10) have studied the hydrogen oxalate complexes of In(III) by liquid ion-exchange at 0.3M, and also the Co(II) hydrogen-oxalate system. J. Schubert, E.L. Lind, W.M. Westfall, R. Pfleger and N.C. Li(11) used the ion-exchange method at 25° and 0.16M to examine the Co(II) and Zn(II) hydrogen oxalate systems and have found that two hydrogen oxalate ions can coordinate to each of the metal ions. A.I. Moskvin, G.V. Khalturin and

A.D. Gel'man(12) studied oxalate and hydrogen oxalate complexes of Am(III) and found the species $Am(C_2O_4)_2^{2-}$ and $Am(HC_2O_4)_4^-$ to be formed in the pH range which they examined. They stated that the species $Am(HC_2O_4)_3^0$ was also formed and suggested that Pu(III) probably behaved in the same way. V.L. Zolotavin and N.N. Kalugina(13) have studied oxalate complex of the vanadyl ion and have identified the species $VO(HC_2O_4)_2$ and probably the species $VO(HC_2O_4)^+$. In their anion exchange studies of the Cu(II)-oxalate system L.D. Cockerell and P.H. Woods(14) suggested that the complex ion $Cu(HC_2O_4)_6^{4-}$ was formed in and stabilised by the ion exchanger in the oxalate form because of the high density of positive charges. A. McAuley and G.H. Nancollas(15) studied Cu(II) oxalate complexes by a potentiometric method and showed that the species present were CuC_2O_4, $Cu(C_2O_4)_2^{2-}$ and $CuHC_2O_4^+$. Yu. A. Zolatov, I.N. Marov and A.I. Moskvin(16) made an ion exchange study of complex formation between the neptunyl ion and the oxalate and hydrogen oxalate ions, finding the species $NpO_2HC_2O_4$, $NpO_2C_2O_4^-$ and $NpO_2(C_2O_4)_2^{3-}$. V.V. Subbama, G.S. Rao and A.K. Bhattacharaya(92) have made a spectrophotometric and conductivity investigation of Ti(III) oxalate complexes and report the existence of a species which is formulated $H(TiO)C_2O_4$.

From the foregoing it is seen that the existence of the hydrogen oxalate complexes of metal ions is fairly well substantiated and a summary of the stability constants where these have been published follows below.

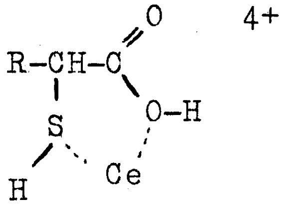
Ref.	Cation	Ligand	T	I	Stability	
89	UO_2	Ox	25	0	$\log\beta_1$	5.82
					$\log\beta_2$	10.57
		HOx			$\log\beta_1$	2.57
90	UO_2	Ox	F.Pt.	dil.	log	4.92
9	UO_2	HOx	25	0.16	$\log\beta_1$	3.4
					$\log\beta_2$	5.96
				1.0	$\log\beta_1$	2.83
				2.0	$\log\beta_1$	2.89
91	UO_2	Ox	20		$\log\beta_1$	6.77
					$\log\beta_2$	12.00
11	Co	Ox	25	0.16	$\log\beta_1$	3.72
					$\log\beta_2$	6.03
		HOx			$\log\beta_1$	1.66
					$\log\beta_2$	2.90
10		HOx	25	0.1	$\log\beta_1$	1.61
					$\log\beta_2$	2.89
11	Zn	Ox	25	0.16	$\log\beta_1$	3.88
					$\log\beta_2$	6.23
		HOx			$\log\beta_1$	1.72
					$\log\beta_2$	3.11
10	In	HOx	25	0.3	$\log\beta_1$	3.08
12	Am	Ox	?	1.0	$\log\beta_2$	10.00
		HOx			$\log\beta_3$	9.64
					$\log\beta_4$	11.0
16	NpO_2	Ox	20	0	$\log\beta_1$	4.39
					$\log\beta_2$	7.36
		HOx			$\log\beta_1$	2.70
15	Cu	Ox	25	0.1	$\log\beta_1$	4.85
					$\log\beta_2$	9.21
		HOx			$\log\beta_1$	2.48
p.w.	Ca	Ox	25	0.1	$\log\beta_1$	2.08
		HOx			$\log\beta_1$	1.38
					$\log\beta_2$	1.85
p.w.	Sr	Ox	25	0.1	$\log\beta_1$	1.26
		HOx			$\log\beta_1$	1.11
					$\log\beta_2$	1.70

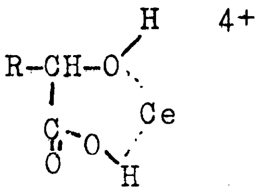
Denticity of the Hydrogen Oxalate Ion

The quantitative data in the literature on the hydrogen oxalate and acetate complexes are so sparse that it is difficult to make definite assertions as to the relative stability of corresponding acetate and hydrogen oxalate complexes. The following have been corrected to zero ionic strength in each case.

Cation	$\log\beta_{Ac}$	ref	$\log\beta_{HOx}$	ref
UO_2^{2+}	(2.38)	100	(3.92)	9
Co^{2+}	1.36	101	2.18	11
Zn^{2+}	1.59	101	2.24	11
In^{3+}	3.50(2M)	102	3.08(0.3M)	10
Cu^{2+}	2.24	103	2.94	15
Ca^{2+}	0.77	104	1.84	p.w.
Sr^{2+}	0.44	104	1.57	p.w.

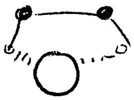
With such data as there are it appears that in most cases the stability of the hydrogen oxalate complex is greater than that of the corresponding acetate complex. This is not in accord with the general observation of Cannan and Kibrick(loc.cit.) who suggested that the stability of a protonated complex of an unsubstituted dicarboxylic acid was close to that of the corresponding unsubstituted monocarboxylic acid. It appears that this is the case, however, with the hydrogen malonate and hydrogen succinate complexes. This comparatively high stability could be rationalised if the undissociated carboxyl group were capable of coordinating to the metal ion in the manner of a dissociated carboxyl group. Li(loc.cit.) has suggested that the hydrogen malonate ion can act as a bidentate ligand coordinating through the dissociated and also the undissociated carboxyl groups. On the other hand, if the carboxyl group were able to act as a ligand it might be expected that undissociated dicarboxylic acids would exhibit some tendency toward complex formation with cations, and there seems to be little or no evidence for this occurrence. Ion-exchange experiments on ligand uptake by the ion exchanger have indicated(123) that no ligand appears to be adsorbed by the resin. If cationic species of the type MH_2A^{n+} were formed, they would probably be taken up by the resin, and ligand would be detected in the resin phase. The cationic species so formed would be quite large, and it could be argued that they would be excluded on this account. The present work indicates finite l_1 values for the uptake by the resin of the species $CaHC_2O_4^+$ and $SrHC_2O_4^+$ which would be of a size comparable with these metal-acid complexes, but have a lower charge. It seems certain, therefore, that such species, if they were formed, would be taken up by the resin, and would have been detected. The only species of this type which appears in the literature is the species $UO_2H_2C_2O_4^{2+}$ suggested by Heidt(loc.cit.). There has been no verification of the existence of this species by any of the other workers who have examined the uranyl-oxalate system. Support for the concept of metal-unionised carboxyl interactions appears in McAuley's review article105) on the role of complexes in metal ion oxidation reactions, in which species such as those shown below are postulated as intermediates to describe the reactions which occur.

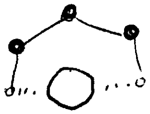


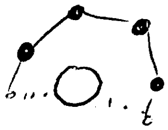


In all the cases where the hydrogen oxalate complexes have been examined as well as the oxalate complexes it is seen that the oxalate complex is more stable than the hydrogen oxalate complex. This is as expected. In the case of calcium, the cation is doubly charged, and has a fairly large Pauling ionic radius (0.99Å) so that there is only a moderate electrostatic field round the calcium ion. Since the calcium ion has no d-orbitals of sufficiently low energy to accept electrons from the ligand there can be no ligand field stabilisation of its complexes, so that the complexes of calcium and strontium, which has a larger ionic radius, tend to be fairly weak, and a result of the electrostatic interactions between the cations and the anionic ligands. Williams(106) has listed evidence which supports this view. On this basis it would be expected that the calcium oxalate complex would be stronger than the calcium hydrogen oxalate complex. In the case of the calcium oxalate, malonate and succinate complexes it is reasonable to assume that some enhanced measure of stability is added to the complex by the formation of a chelate. The enhanced stability of a chelate has been interpreted as an entropy effect. Schwartzenbach(107) has described the chelation effect in terms of a comparison of the stability of a chelate with that of the second complex of a related or similar unidentate ligand. When a 2:2 chelate is formed the entropy change involved results from a number of contributions. There is a removal of particles from solution due to complex formation and there is a release of coordinated water molecules as a result of the removal or reduction of charge from the complex species formed in the association. This removal (or reduction) of the hydration sheaths of the ions sets free more particles than are removed from the solution by the formation of the complex so that there is a net increase in the number of particles in the system. The additional entropy increase that occurs in the case of chelate formation may be regarded as a result of the removal of <u>one</u> particle from solution upon complex formation in conjunction with the release, from the inner coordination sphere, of water molecules in numbers corresponding to the attachment of <u>two</u> ligands. The entropy of the system is further increased by the newly acquired translational, vibrational and rotational contributions to the entropy of the released water molecules, and reduced by the restriction of these entropy contributions to the entropy of the newly bound ligand. Schwartzenbach has assumed that when a bidentate ligand is replaced by two monodentate ligands there is no enthalpy change, and that the free energy difference is a consequence of the entropy only. Irving et al.(108) have suggested that this is untrue, but is an adequate approximation when both particles engaging in the association are charged. They have also suggested that in the formation of a chelate the enthalpy change is more favourable, because of a reduction in interactions between neighbouring ligands, as compared with a complex formed from separate unidentate ligands.

In the present work it is seen that there is a marked decrease in the stability of the series of complexes: calcium oxalate, calcium malonate, calcium succinate. This trend has been observed frequently(95,108). Schubert(95) has explained this in terms of entropy. If it is assumed that in the first instance the ligand has one point of attachment to the central ion for the series oxalate, malonate and succinate, a progressively greater restriction has to be placed on the other end of the anion in order to attach it to the cation. This means that there is a greater loss of entropy from the system as oxalate is replaced by malonate and malonate by succinate. On the assumption that the enthalpy change is unaltered the free energy change is modified by this entropy contribution and becomes less favourable. Explanation of the decreasing stability of the complexes in terms of entropy only is an over-simplification. It is tacitly assumed that oxalate, malonate and succinate bind to the cation in an identical manner, and this is clearly impossible, as the following schematic illustrations indicate.


Oxalate


Malonate


Succinate

It may reasonably be expected that interactions between the ends of the ligands, the ends of the ligand and the inner sphere water molecules, and the body of the ligand and the more distant orientated water molecules will be altered. In consequence, there will be repulsion terms of various types which will alter the enthalpy of the association, and also other entropy contributions. It should be noticed that this fall in stability occurs despite the fact that the acid dissociation constants would appear to favour the formation of stronger complexes from oxalate to succinate. Schwartzenbach has related the magnitude of the chelation effect to the volume swept out by one end of a bidentate ligand, the other end being attached to the central ion.

The tartrate complexes which were examined in the present work were observed to possess an enhanced stability. This may be accounted for by the assumption that the tartrate ion is able to act as a quadridentate ligand as a result of the hydroxyl groups on the molecule, since tartrate complexes are invariably stronger than succinate complexes. Williams has postulated(loc.cit.) a "crowding effect": the points of attachment of a polydentate ligand require a greater degree of restriction in order to "focus" them on to a central ion, the smaller the central ion is. This is reflected in the apparently anomalously low stabilities observed with some magnesium chelates, but it appears that this effect is absent in the case of calcium and strontium tartrates because of their greater sizes.

Dissociation of Protonated Complexes according to the Scheme

$$\underline{MHA \rightleftharpoons MA + H^+}$$

V.N. Kumok and V.V. Serenbrennikov(109) have examined the above behaviour. The following equilibria are involved.

$$M + L \rightleftharpoons ML \qquad \beta_1 ,$$

$$M + HL \rightleftharpoons MHL \qquad \beta_2 ,$$

$$H + L \rightleftharpoons HL \qquad \beta_A ,$$

$$MHL \rightleftharpoons ML + H \qquad K .$$

These equilibria are interconnected by the relationship

$$\beta_1/\beta_2 = K\beta_A$$

In the case of the ith and jth cations

$$\beta_{1i}/\beta_{2i} = K_i\beta_A$$

$$\beta_{1j}/\beta_{2j} = K_j\beta_A \ .$$

These workers have also shown(110-112) that the following empirical relationship obtains.

$$\log\beta_i = a_{ij}\log\beta_j + b_{ij} \ .$$

a_{ij} and b_{ij} are the empirical correlational parameters. j refers to the cation of reference, and i is the cation which is being compared with the reference cation. These workers show that a_{ij} is equal to the ratio ϕ_i/ϕ_j of the ionic potentials of the cations. The ionic potential is Z_i/r_i where Z_i is the charge of the ith cation and r_i is its radius. It is possible to write

$$\log\beta_{1i}-\log\beta_{2i} = \log K_i + \log\beta_A$$

$$\therefore \quad a_{ij}\log\beta_{1j} + b_{ij}-a_{ij}\log\beta_{2j}-b_{ij} = \log K_i + \log\beta_A$$

$$\therefore \quad a_{ij}\log\beta_{1j}/\beta_{2j} = \log K_i\beta_A$$

$$\therefore \quad a_{ij}\log K_j\beta_A = \log K_i\beta_A$$

$$\therefore \quad \log K_i = a_{ij}\log K_j\beta_A-\log\beta_A + \log K_j-\log K_j$$

$$= \log K_j + a_{ij}\log K_j\beta_A-\log K_j\beta_A$$

$$\therefore \quad \log K_i = \log K_j + \log K_j\beta_A(a_{ij}-1) \ .$$

The relationship between log K_i and log K_j depends therefore on the signs of $a_{ij} - 1$ and of log $K_j\beta_A$. Since log $K_j\beta_A$ is equal to log β_{1j}/β_{2j} it is greater than zero, because $\beta_{1j} > \beta_{2j}$; this is a result of the protonated ligand having a lower charge and possibly a lower denticity. This means that

$$\log K_i > \log K_j \Leftrightarrow \alpha_{ij} > 1$$

$$\therefore \quad \log K_i > \log K_j \Leftrightarrow \phi_i > \phi_j$$

For calcium we have $Z_{Ca} = 2$, $r_{Ca} = 1.08$ Å and for strontium $Z_{Sr} = 2$ and $r_{Sr} = 1.29$ Å. We then have

$$\phi_{Ca} = 1.85 \qquad \phi_{Sr} = 1.55$$

$$K_i = \beta_{1i}/\beta_{2i}\beta_A = \beta_{1i}k_2/\beta_{2i}$$

From the present data on calcium hydrogen oxalate and strontium hydrogen oxalate it is found that

$$K_{Ca} = \beta_{CaOx} \cdot 1.56 \times 10^{-4}/\beta_{CaHOx}$$

$$K_{Sr} = \beta_{SrOx} \cdot 1.56 \times 10^{-4}/\beta_{SrHOx}$$

$$\therefore \quad K_{Ca} = \frac{[CaOx][H]}{[CaHOx]} = 8 \times 10^{-4}$$

$$K_{Sr} = \frac{[SrOx][H]}{[SrHOx]} = 2 \times 10^{-4}$$

It is seen that in the case of the calcium and strontium complexes the inequality arrived at in the above analysis obtains, the calcium hydrogen oxalate species dissociating more readily into the oxalate complex and the hydrated proton than the corresponding strontium complex.

In conclusion it may be said that where comparison is possible the results of the present work are in agreement with hitherto published work. The existence of hydrogen oxalate complexes is supported by a fair number of workers who have characterized them and obtained stability constants for them. A critical comparison of data relating to hydrogen oxalate complexes and acetate complexes suggests that there is some reason to believe that the hydrogen oxalate species is able to act as a bidentate ligand but this is not proved conclusively. The hydrogen oxalate complexes are invariably weaker than the corresponding oxalate complexes, while the order of complex stability for a given cation decreases in the order oxalate - malonate - succinate. Tartrate complexes are stronger than the corresponding succinate complexes, because of their higher denticity. An examination of the dissociation of the protonated complexes to an unprotonated complex and a (hydrated) proton suggests that the relationship derived by Kumok and Serebrennikov(109) is obeyed in the case of the hydrogen oxalate complexes of calcium and strontium.

The Effect of the Degree of Cross Linking of the Resin on the Stability Constants obtained by the Ion Exchange Method.

The Effect of the Degree of Cross Linking of the Resin on the Stability Constants obtained by the Ion Exchange Method

Introduction

The mathematical analysis of the ion exchange method for determination of complex stability constants does not include terms which take account of the degree of cross linking of the resin, and it has been assumed that the method is independent of this variable. Support for this assumption comes from the fact that agreement between constants obtained by the method, and by other methods, is generally fairly good,(60,67,68) as is the agreement when the same system is studied by two different exchangers(10,11). It was, however, considered desirable to study the effect of the cross linking of the resin, to see if any definite conclusions could be reached. Sani(80) made an examination of this effect but nothing definite emerged. His work is discussed below.

Experimental

Conditioning of the Ion-Exchange Resins

Commercial Amberlite IR 120 was used; samples of IR 122 and IR 124 were kindly supplied by Messrs. Lennig Chemical Ltd. The resins were conditioned as follows. A quantity of the resin was placed in a beaker and distilled water was added in order to allow the resin to expand fully. The water was decanted off from time to time to remove fine particles. It was noticed that, in the case of the Amberlite IR 122, the supernatant became appreciably discoloured presumably as a result of the diffusion of uncrosslinked polyelectrolyte from the beads. A comparatively slight discolouration was observed in the case of the Amberlite IR 120 and 124. The resin was next soaked for an hour in methanol to remove any residual uncrosslinked polyelectrolyte. This was followed by several rinsings in distilled water, an hour-long soaking in 1.0 molar sodium hydroxide solution, more rinsings in distilled water and an hour-long soaking in 1.0 molar hydrochloric acid. The resin was then placed in a glass column and 5 litre cycles of 0.1 molar NaCl, HCl, NaCl and HCl passed through at a slow drop rate. Finally the resin was converted to the sodium form by the passage of 10 litres of 0.1 molar sodium chloride solution, after which the pH of the outflow was about 6.0. The resin was then transferred to a Buchner funnel and washed with distilled water until no chloride ions were detected in the rinsings ($AgNO_3$). The ion exchangers were placed in large crystallising dishes which were partially covered and dried in the laboratory at 25°C for 24 hours. Each resin was sieved to 16-30 mesh, i.e. to a particle diameter range of 1000μ - 500μ (0.04 - 0.02").

Water Content

In order to provide a reference state for the experiments it was necessary to know the proportion of water in the resin as prepared by this method. This was found by placing six samples of known weight (2 of each resin) in a desiccator containing phosphorus pentoxide, and evacuating. The desiccator was placed in an oven at 45°C. The samples were dried to constant weight. The results are as follows.

	IR120		IR122		IR124	
Sample	I	II	I	II	I	II
% H_2O	23.1	23.0	24.9	25.0	26.0	26.0

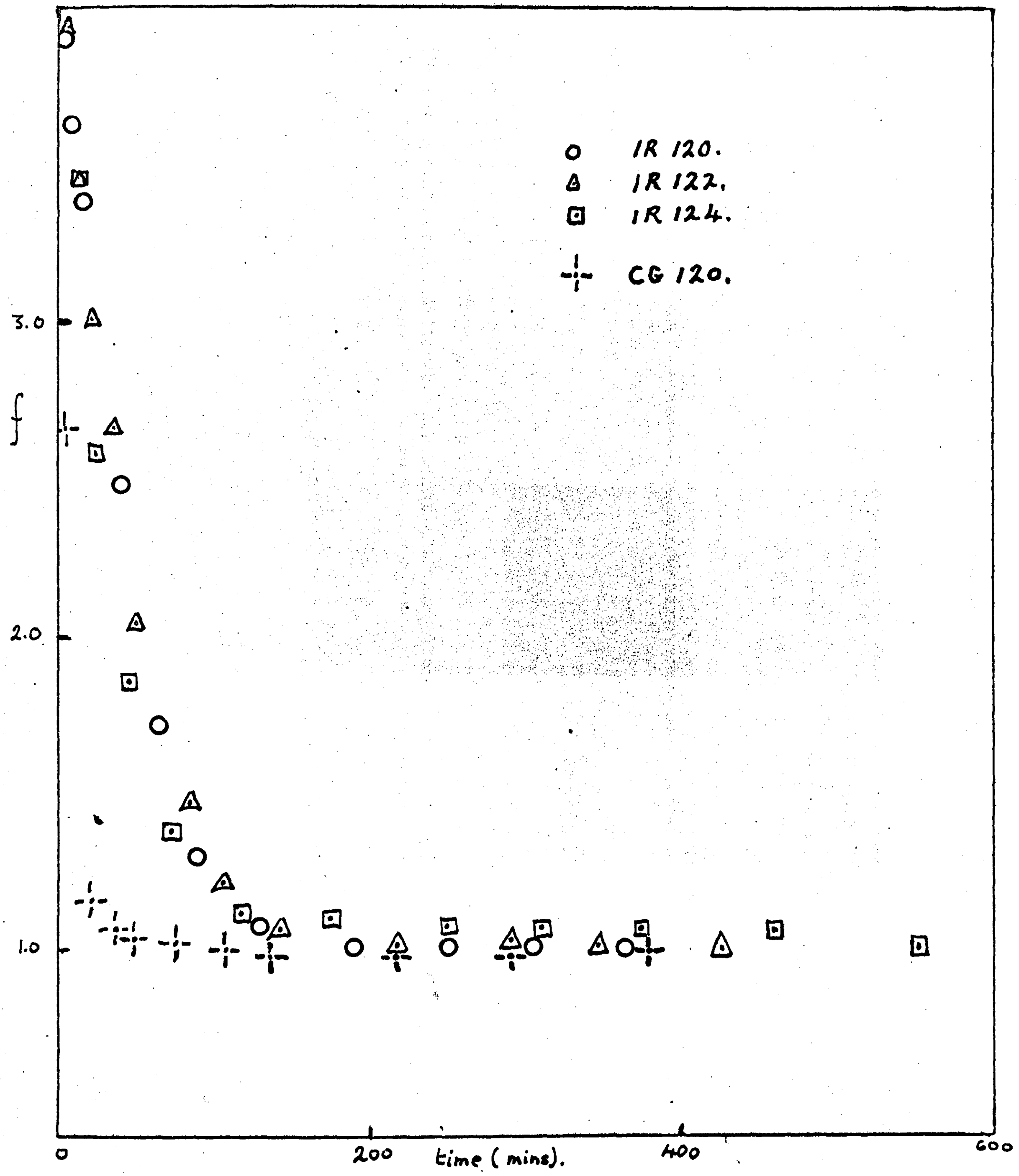
Although, as supplied, more highly cross-linked resins tend to have lower water contents, these results are quite reasonable as it would be expected that resins with lower degrees of cross-linking will dry more readily than those with a higher degree of cross-linking, because of their less tightly bound structure. For the same amount of drying, therefore, the more highly cross-linked resins will retain water for the longest time. It is desirable that the resin should retain a moderate amount of moisture as dry resins are reported to be erratic and hygroscopic in behaviour.(116) It was observed in the present work that dry resins tended to disintegrate when added to solutions. In view of the similarity between the water contents, no correction factor was introduced.

Determination of Optimum Equilibration Period

The time taken for equilibrium in the distribution of a cation between a cation-exchange resin and an aqueous phase depends on a number of factors.(117) The variables which are of relevance to the present work are particle size, the capacity of the ion-exchanger, and the degree of cross-linking. The speed of attainment of equilibrium is inversely proportional to the particle size, and the capacity of the ion-exchanger. The higher the degree of cross-linking, the more slowly is the equilibrium attained. These factors indicate that the equilibrium will be attained more slowly than in the case of the CG 120. It was considered desirable, therefore, to perform independent experiments on the resins, to find the shortest period of agitation compatible with the establishment of equilibrium. The method was identical to that which was used for the study of the CG 120. 100 mg of resin was used in each case, and 100 ml of 0.1M $NaClO_4$ solution. The experimental results are tabulated in Appendix I. A plot of the function f=(counts at time t)/(counts at equilibrium) versus time is plotted in fig. XXVI. This function should of course equal unity at equilibrium.

Experiments on Calcium Oxalate

In principle, the method was identical to that employed in the other experiments. The larger particle size, however, precluded the convenient weighing of 0.050 g quantities, so that different resin masses were used from experiment to experiment, and the quantity $(C_m'/C_m) - 1$ was multiplied by an appropriate v/m factor. The equilibration time used was 4 hours in the case of IR 120, and 10 hours in


○ IR 120.
△ IR 122.
⊡ IR 124.
-¦- CG 120.
f
3.0
2.0
1.0
0
200
400
600
time (mins).

the case of IR 122 and IR 124. There was no need to perform additional quenching experiments, since the earlier results were applicable to the present systems also.

Tables of the experimental results, with v/m ratios and distribution coefficients are included in Appendix I.

Results and Discussion

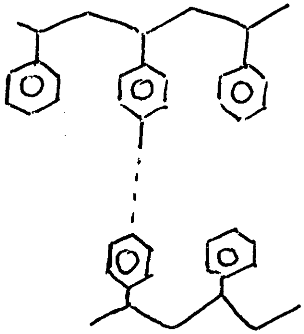
Mean values for the stability of the calcium oxalate complexes as obtained by the ion-exchange method with resins of different degrees of cross-linking are as follows.

Resin	%DVB	β	σ
IR 120	8	104	6
IR 122	10	104	7
IR 124	12	98	8

It is seen that within the limits of error as specified by the standard deviation, if the error is taken to be random rather than systematic, there is no significant difference between the results.

IR 120, IR 122 and IR 124 are styrene-divinylbenzene copolymers with 8, 10 and 12% of divinylbenzene respectively. In principle, the process of their manufacture is as follows. Polymerisation of styrene yields linear polystyrene.

If divinylbenzene is added to the monomer, a cross-linked matrix is obtained. The polymerisation may be catalysed by the addition of benzoyl peroxide.



Treatment of the matrix with concentrated sulphuric acid or chlorosulphonic acid sulphonates the benzene rings, introducing $-SO_3^-H^+$ groups. The degree of cross-linking may be adjusted by the variation of the divinylbenzene content of the monomer mixture. As a result of the deactivating effect of the sulphonate group, each benzene ring is sulphonated once only, and the sulphonation extends right to the centre of the bead because while the sulphonation is proceeding the bead swells, and permits the reagent to penetrate the bead. Beads with a higher degree of cross-linking possess a higher molarity of fixed groups, taken with respect to the water content of the bead. They have therefore a higher capacity per unit volume, and they swell to a smaller extent when they are placed in water. A higher degree of cross-linking means that the swelling pressure of the resin is higher, and larger solvated counter ions will result in a proportionately larger swelling pressure than would occur in the case of a resin with a lower degree of cross-linking. Because of the tendency of the resin to contract, there will be a greater tendency, in the case of the resin with the higher degree of cross-linking, to exchange a large solvated ion for a smaller solvated ion. This has been discussed by Gregor(115). It would therefore be expected that there would be an increase in selectivity exhibited by the resin, the higher the degree of cross-linking. This is seen in the l_o values which were obtained in the present work.

Resin	%DVB	$l_o^{Ca^{2+}-Na^{+}}$
IR 120	8	2.42
IR 122	10	3.01
IR 124	12	3.21

The higher the degree of cross-linking of the resin, the greater is the tortuosity of the porous structure of the bead, and in turn, the longer is any pathway through the bead to a given site. Assuming that the diffusion of the ion under consideration occurs at a constant rate, it will take longer for a given ion to reach a given site. In consequence, the higher the degree of cross-linking of the resin, the longer it will take that resin to attain equilibrium with a surrounding ionic solution. Examination of the graph of the data obtained in the present work confirms this qualitative prediction. As would be expected, the effect of particle size is to increase the speed of attainment of equilibrium, when the particle size is reduced. This may be explained in terms of the increased surface area of the beads, taken overall, combined with the shorter average path to any given site for any given ion. The effect of particle size is strikingly illustrated in the present work.

In the studies on the effect of different degrees of cross-linking on the apparent stability constants plots of the functions ϕ^{-1} and $(l_0\phi^{-1} - 1)$ versus $[C_2O_4^{2-}]$ were drawn. (Fig XXVII) Assuming that the same result for the stability constant were to be obtained for each degree of cross-linking, it would be expected that the plots of ϕ^{-1} versus $[C_2O_4^{2-}]$ would be non-parallel, and the larger the value of l_0, the lower would be the gradient of the plot. The reason is as follows.

$$l_0\phi^{-1} - 1 = \beta[C_2O_4]$$

$$\therefore \quad l_0\phi^{-1} = 1 + \beta[C_2O_4]$$

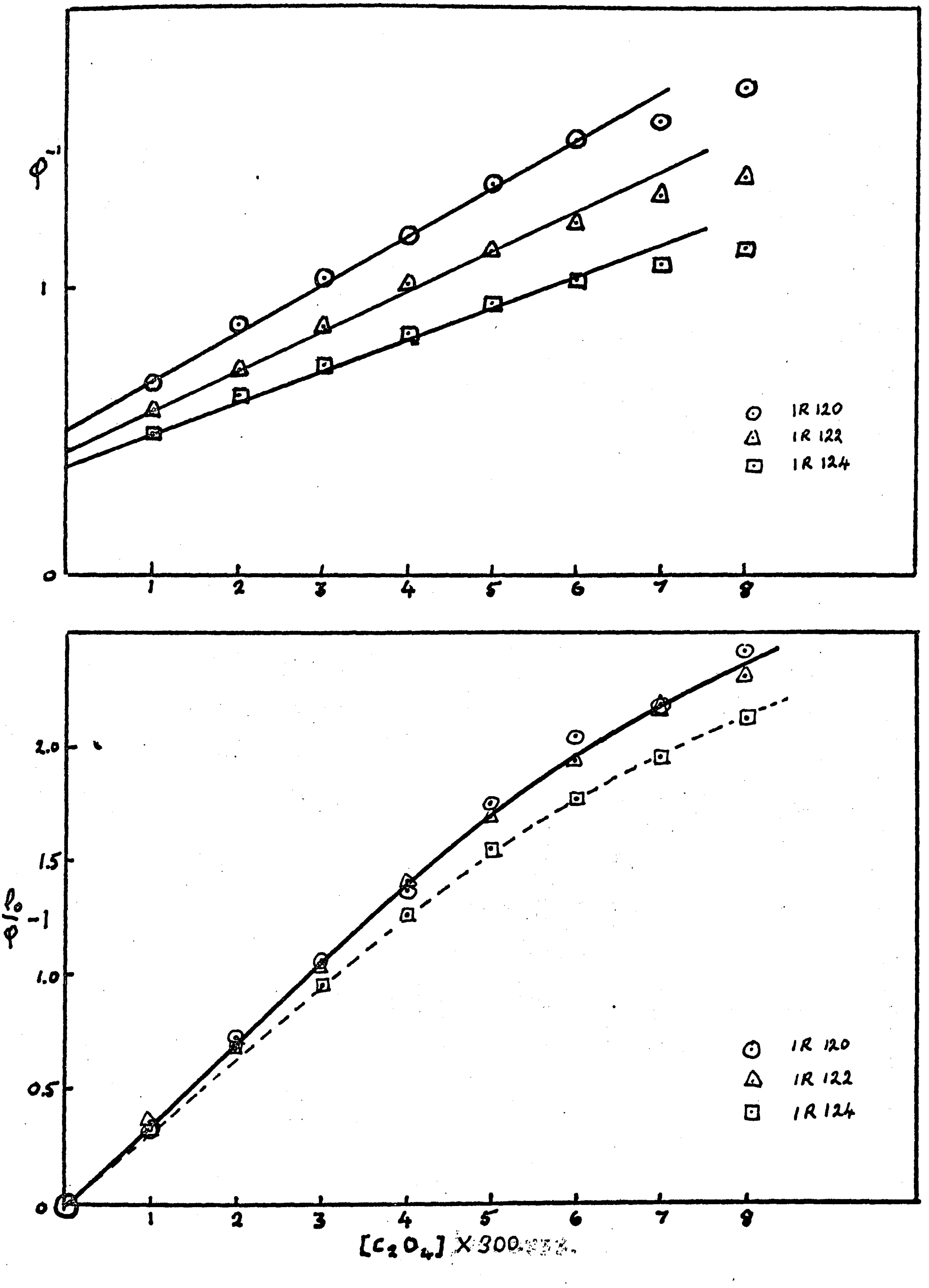
$$\therefore \quad \phi^{-1} = l_0^{-1} + l_0^{-1}\beta[C_2O_4]$$

Plots of ϕ^{-1} versus $[C_2O_4^{2-}]$ should therefore have intercepts of l_0^{-1} and gradients βl_0^{-1}. This effect is seen in the present work. For the same stability constant to be obtained for each cross-linking it is to be expected that plots of the function $(l_0\phi^{-1} - 1)$ versus $[C_2O_4^{2-}]$ will be coincident. In the present work it is seen that the plots for 8% DVB and 10% DVB are virtually coincident; on the other hand the position of the 12% DVB is not so clear. If standard deviations are taken, there is no significant difference, but to use such an approach implies that the errors are random, whereas there would seem to be a gradually increasing divergence of the 12% plot. Further, the curvature which has been discussed earlier appears to develop in this case also, at higher ligand concentrations. It is therefore unwise to place any great degree of significance on this apparent effect. On the other hand, Sani(80) investigated the distribution of Y^{III} between cation exchangers with different degrees of cross-linking and an aqueous phase which contained glycollate ions. Plots of the function $(l_0\phi^{-1} - 1)$ versus ligand concentration coincided when the DVB was present to the extent of 2%, 4/5% and 8%, but there appeared to be a departure from coincidence in the case of 20% DVB.

A fact which appears to emerge from these experiments is that in the case of ion-exchange resins of this type there is no loading effect for such small resin loadings. In these experiments the resin particles were too large to allow of a predecided mass to be used in each experiment. Each experiment, therefore, employed a different resin weight, and the calculated distribution coefficient was multiplied by the factor v/m. It was seen that alteration of this ratio had no effect on the distribution coefficients obtained. An alteration in the v/m ratio is equivalent to an alteration in the resin loading, so that this may also be eliminated as a possible source of error. Further, the fact that the different resin masses resulted in the same distribution coefficients is an indication that the system had reached equilibrium when the samples were taken.

Figure XXVII.

The calcium oxalate system at 0.10 Molar.



Sani(80) tentatively attributed the deviation which occurred in the case of the 20% DVB resin to a selectivity reversal due to possible polyfunctionality of the resin. This has been discussed by Reichenberg et al.(113). The concentration of metal in the resin phase examined by these workers, however, ran from a mole fraction of zero to one of unity, while in the type of work performed by Sani(loc.cit.) and in the present work, the mole fraction of the metal under consideration is so small, being at tracer level, that it may be regarded as constant. Reichenberg later(114) ascribed the selectivity reversal to the presence in the resin bead of regions of different degrees of cross-linking, and abandoned the use of polyfunctionality to explain the observed effects. It is assumed in the ion exchange method of stability constant determination that the selectivity is constant when the cation is present in trace amounts, and this was observed to be the case in the present work, when different isotope concentrations led always to the same values of l_0. Further, in the present work on the effect of ionic strength on the stability of the calcium oxalate complex, a selectivity reversal does occur, the l_0 value for the calcium-sodium equilibrium falling below unity, but there appears to be no anomalous result for the stability of the complex. One possibility which was considered to explain the apparent difference in the results for the 12% DVB resin was the uptake of ligand by the resin phase. Examination of the relevant plot (fig. XXVII) however, indicates that the differences in ligand concentration, which would have to be invoked, are far too large to be accounted for by this approach, when the very high v/m ratio is considered. The mass of resin is so low that any ligand concentration differences would be expected to be very small.

APPENDIX I

EXPERIMENTAL DATA

DISSOCIATION CONSTANTS OF OXALIC ACID

TABLE I

Point No.	Total Acid x 10^3	Total Base x 10^2	pH
1	9.1648	0.4292	2.360
2	9.1248	0.4748	2.401
3	9.0853	0.5198	2.445
4	9.0461	0.5644	2.494
5	9.0073	0.6086	2.548
6	8.9689	0.6524	2.608
7	8.9308	0.6958	2.667
8	8.8926	0.7392	2.732
9	8.8551	0.7819	2.808
10	8.8182	0.8240	2.889
11	8.7813	0.8660	2.977
12	8.7451	0.9074	3.071
13	8.7088	0.9487	3.163
14	8.6725	0.9900	3.257
15	8.6369	1.0306	3.347
16	8.6014	1.0710	3.432
17	8.5664	1.1109	3.517
18	8.5320	1.1501	3.560
19	8.4975	1.1894	3.681
20	8.4631	1.2285	3.762
21	8.4292	1.2672	3.847
22	8.3954	1.3057	3.932
23	9.2050	0.3834	2.314
24	9.1248	0.4748	2.394
25	9.0853	0.5198	2.436
26	9.0461	0.5644	2.485
27	9.0073	0.6086	2.539
28	8.9689	0.6524	2.599
29	8.9308	0.6958	2.660
30	8.8926	0.7392	2.726

Point No.	Total Acid x 10^3	Total Base x 10^2	pH
31	8.8551	0.7819	2.803
32	8.8182	0.8240	2.883
33	8.7813	0.8660	2.970
34	8.7451	0.9074	3.062
35	8.7088	0.9487	3.157
36	8.6725	0.9900	3.250
37	8.6369	1.0306	3.339
38	8.6014	1.0710	3.427
39	8.5664	1.1109	3.510
40	8.5320	1.1501	3.592
41	8.4975	1.1894	3.673
42	8.4631	1.2285	3.758
43	8.4292	1.2672	3.841
44	8.3954	1.3057	3.925
45	8.3619	1.3438	4.016
46	9.4549	0.0099	2.130
47	9.2459	0.3368	2.281
48	9.2050	0.3834	2.318
49	9.1648	0.4292	2.355
50	9.1248	0.4748	2.396
51	9.0853	0.5198	2.441
52	9.0461	0.5644	2.489
53	9.0073	0.6086	2.545
54	8.9689	0.6524	2.605
55	8.9308	0.6958	2.666
56	8.8926	0.7392	2.733
57	8.8551	0.7819	2.807
58	8.8182	0.8240	2.887
59	8.7813	0.8660	2.976
60	8.7451	0.9074	3.072
61	8.7088	0.9487	3.167
62	8.6369	1.0306	3.348
63	8.6014	1.0710	3.435
64	8.5664	1.1109	3.520

Point No.	Total Acid x 10^3	Total Base x 10^2	pH
65	8.5320	1.1501	3.600
66	8.4975	1.1894	3.683
67	8.4631	1.2285	3.762
68	8.4292	1.2672	3.850
69	8.3954	1.3057	3.934
70	8.3619	1.3438	4.024
71	16.924	0.3537	1.966
72	16.789	0.4378	1.996
73	16.656	0.5205	2.029
74	16.525	0.6019	2.064
75	16.394	0.6829	2.100
76	16.267	0.7618	2.144
77	16.142	0.8399	2.185
78	15.429	1.2826	2.568
79	15.317	1.3525	2.656
80	15.097	1.4889	2.860
81	14.990	1.5553	2.973
82	14.884	1.6214	3.088
83	14.779	1.6870	3.197
84	14.675	1.7511	3.300
85	14.573	1.8145	3.395
86	14.473	1.8769	3.484
87	14.375	1.9377	3.572
88	14.277	1.9984	3.658
89	14.181	2.0585	3.737
90	14.086	2.1176	3.827
91	13.991	2.1761	3.916
92	13.899	2.2336	4.008
93	9.3628	0.1955	2.184
94	9.2473	0.3272	2.272
95	9.1969	0.3847	2.315
96	9.0697	0.5297	2.447
97	9.0384	0.5654	2.488
98	9.0074	0.6007	2.531

Point No.	Total Acid x 10^3	Total Base x 10^2	pH
99	8.9612	0.6534	2.601
100	8.9307	0.6881	2.648
101	8.8846	0.7407	2.730
102	8.8546	0.7749	2.793
103	8.8100	0.8258	2.887
104	8.7658	0.8761	2.996
105	8.7362	0.9099	3.071
106	8.6928	0.9594	3.186
107	8.6214	1.0408	3.367
108	8.6641	0.9922	3.258
109	8.5930	1.0732	3.438
110	8.5649	1.1052	3.504
111	8.5371	1.1370	3.569
112	8.4956	1.1843	3.669
113	8.4546	1.2309	3.769
114	8.4140	1.2773	3.871
115	8.3737	1.3232	3.973
116	8.3338	1.3687	4.076
117	8.3069	1.3994	4.145
118	13.451	0.1875	2.017
119	13.224	0.3673	2.101
120	13.114	0.4550	2.143
121	13.006	0.5411	2.195
122	12.899	0.6257	2.250
123	12.794	0.7092	2.312
124	12.691	0.7909	2.377
125	12.590	0.8711	2.451
126	12.490	0.9507	2.544
127	12.391	1.0289	2.644
128	12.295	1.1052	2.756
129	12.200	1.1810	2.882
130	12.106	1.2556	3.021
131	12.013	1.3296	3.161
132	11.922	1.4020	3.300
133	11.877	1.4377	3.359
134	11.832	1.4734	3.422

Point No.	Total Acid x 10^3	Total Base x 10^2	pH
135	11.787	1.5085	3.480
136	11.742	1.5446	3.536
137	11.655	1.6136	3.651
138	11.612	1.6477	3.708
139	11.570	1.6815	3.764
140	11.527	1.7151	3.820
141	11.485	1.7486	3.876
142	9.1568	0.4393	2.361
143	9.1248	0.4759	2.394
144	9.1010	0.5030	2.419
145	9.0774	0.5300	2.447
146	9.0461	0.5658	2.485
147	9.0228	0.5924	2.516
148	8.9996	0.6189	2.550
149	8.9689	0.6539	2.598
150	8.6014	1.0735	3.430
151	8.5664	1.1136	3.513
152	8.5320	1.1529	3.595
153	8.5112	1.1765	3.644
154	8.4906	1.2001	3.693
155	8.4631	1.2314	3.758
156	8.4427	1.2548	3.808
157	8.4224	1.2780	3.858
158	8.3954	1.3089	3.925
159	9.1568	0.4393	2.368
160	9.1409	0.4575	2.383
161	9.1248	0.4759	2.401
162	9.1089	0.4940	2.419
163	9.0931	0.5120	2.436
164	9.0774	0.5300	2.454
165	9.0618	0.5479	2.473
166	8.4631	1.2314	3.774
167	8.4495	1.2470	3.804
168	8.4360	1.2625	3.840
169	8.4224	1.2780	3.873

Point No.	Total Acid x 10^3	Total Base x 10^2	pH
170	8.4089	1.2934	3.906
171	8.3954	1.3089	3.942
172	8.3820	1.3242	3.978
173	8.3686	1.3394	4.012
174	8.3553	1.3546	4.043
175	8.3420	1.3698	4.078

TABLE II

Summary of the positive X and Y values

Point No.	X	Y
1	1.710×10^{-5}	2.277×10^{-4}
2	1.447×10^{-5}	1.675×10^{-4}
3	1.207×10^{-5}	1.140×10^{-4}
4	9.839×10^{-6}	6.809×10^{-5}
5	7.856×10^{-6}	2.802×10^{-5}
23	2.108×10^{-5}	2.575×10^{-4}
24	1.514×10^{-5}	1.444×10^{-4}
25	1.275×10^{-5}	8.929×10^{-5}
26	1.040×10^{-5}	4.641×10^{-5}
27	8.281×10^{-6}	1.050×10^{-5}
46	4.385×10^{-5}	7.462×10^{-4}
47	2.389×10^{-5}	3.380×10^{-4}
48	2.051×10^{-5}	2.753×10^{-4}
49	1.765×10^{-5}	2.098×10^{-4}
50	1.492×10^{-5}	1.520×10^{-4}
51	1.239×10^{-5}	1.024×10^{-4}
52	1.014×10^{-5}	5.654×10^{-5}
53	8.007×10^{-6}	2.184×10^{-5}
71	8.639×10^{-5}	1.423×10^{-3}
72	7.703×10^{-5}	1.226×10^{-3}
73	6.797×10^{-5}	1.045×10^{-3}
74	5.933×10^{-5}	8.791×10^{-4}
75	5.163×10^{-5}	7.170×10^{-4}
76	4.299×10^{-5}	5.953×10^{-4}
77	3.661×10^{-5}	4.575×10^{-4}
93	5.576×10^{-5}	5.480×10^{-4}
94	2.503×10^{-5}	3.378×10^{-4}
95	2.095×10^{-5}	2.546×10^{-4}
96	1.220×10^{-5}	7.747×10^{-5}
97	1.026×10^{-5}	4.752×10^{-5}
98	8.541×10^{-6}	1.898×10^{-5}

Point No.	X	Y
118	6.873×10^{-5}	1.227×10^{-3}
119	4.924×10^{-5}	8.644×10^{-4}
120	4.187×10^{-5}	6.821×10^{-4}
121	3.273×10^{-5}	5.453×10^{-4}
122	2.698×10^{-5}	4.121×10^{-4}
123	2.090×10^{-5}	2.956×10^{-4}
124	1.609×10^{-5}	1.844×10^{-4}
125	1.185×10^{-5}	9.365×10^{-5}
126	8.021×10^{-6}	2.778×10^{-5}
142	1.732×10^{-5}	1.870×10^{-4}
143	1.516×10^{-5}	1.403×10^{-4}
144	1.367×10^{-5}	1.074×10^{-4}
145	1.223×10^{-5}	7.779×10^{-5}
146	1.042×10^{-5}	4.213×10^{-5}
147	9.191×10^{-5}	1.686×10^{-5}
159	1.660×10^{-5}	2.110×10^{-4}
160	1.557×10^{-5}	1.857×10^{-4}
161	1.451×10^{-5}	1.629×10^{-4}
162	1.345×10^{-5}	1.443×10^{-4}
163	1.257×10^{-5}	1.195×10^{-4}
164	1.165×10^{-5}	9.920×10^{-5}
165	1.080×10^{-5}	7.870×10^{-5}

All the X values greater than 2.3×10^{-5} when Y is greater than 5.3×10^{-4} are shown plotted in figure (IV).

TABLE IIIA

Preliminary experiments on the calcium oxalate system
Series A

$[C_2O_4]$	c.p.m.	−b.g.*	ϕ	ϕ^{-1}
0.000	2066	2045	-	-
0.000	508	487	3.177	0.315
0.001	518	497	3.093	0.323
0.002	579	558	2.646	0.378
0.003	664	643	2.165	0.462
0.004	711	690	1.950	0.513
0.005	744	723	1.816	0.551
0.006	805	784	1.597	0.626
0.007	853	832	1.448	0.691
0.008	881	860	1.368	0.731

Plots of the functions ϕ, ϕ^{-1} and $\{(I_0/\phi)^{-1}\}$ against $[C_2O_4]$ are shown in fig. (VII). * background.

TABLE IIIB

Preliminary experiments on the calcium oxalate system
Series B

$[C_2O_4]$	c.p.m.	−b.g.	×r.e.f.	ϕ	ϕ^{-1}
0.00000	1918	1897	1897	-	-
0.00000	492	471	471	3.006	0.333
0.00333	678	657	661	1.857	0.539
0.00666	820	799	809	1.335	0.749
0.00999	935	914	931	1.030	0.971
0.01332	1038	1017	1043	0.813	1.230
0.01666	1091	1070	1105	0.712	1.404
0.01999	1115	1094	1138	0.662	1.511
0.02333	1163	1141	1195	0.583	1.715
0.02666	1167	1146	1208	0.566	1.768

Plots of the functions ϕ, ϕ^{-1} and $\{(I_0/\phi)^{-1}\}$ against $[C_2O_4]$ are shown in fig. (VIII).

TABLE IIIC

Preliminary experiments on the calcium oxalate system
Series C

$[C_2O_4]$	c.p.m.	− b.g.	× r.e.f.	ϕ	ϕ^{-1}
0.00000	3063	3018	3018	-	-
0.00000	792	747	747	3.019	0.331
0.00333	1117	1072	1080	1.782	0.561
0.00666	1356	1311	1328	1.264	0.791
0.00999	1534	1489	1517	0.983	1.017
0.01333	1631	1586	1627	0.849	1.178
0.01666	1735	1690	1745	0.724	1.381
0.01999	1799	1754	1824	0.650	1.538
0.02332	1915	1870	1958	0.538	1.859
0.02665	1828	1783			

Plots of the functions ϕ, ϕ^{-1} and $\{(l_0/\phi)^{-1}\}$ against $[C_2O_4]$ are shown in fig. (IX).

TABLE IIID

Preliminary experiments on the calcium oxalate system
Series D

$[C_2O_4]$	c.p.m.	− b.g.	ϕ	ϕ^{-1}
0.000	1952	1932	-	-
0.000	489	469	3.098	0.323
0.001	543	523	2.675	0.374
0.002	613	593	2.242	0.446
0.003	618	598	2.215	0.451
0.004	660	640	2.005	0.499
0.005	750	730	1.635	0.612
0.006	853	833	1.310	0.763
0.007	869	849	1.267	0.789
0.008	894	874	1.202	0.832

Plots of the functions ϕ, ϕ^{-1} and $\{(l_0/\phi)^{-1}\}$ against $[C_2O_4]$ are shown in fig. (X).

TABLE IVA

Studies on the Calcium Oxalate System at 0.02 Molar

Experimental Results

Expts	Counts per vial per minute		Expts	Counts per vial per minute	
1	10504	10812	6	(339)	264
	11086	10929		(333)	271
	10395	11236		279	245
	11161	10989		286	266
2	330	353	7	281	287
	296	350		287	288
	245	325		265	276
	236	278			
3	168	209	8	293	325
	169	197		283	331
	177	271		295	295
	182	267		293	317
4	209	225	9	300	306
	217	228		303	317
	204	234		300	336
	202	213		290	315
5	236	240	10	315	319
	228	243		304	316
	224	237		304	319
	228	228		311	318

TABLE IVB

The calcium oxalate system at 0.02 molar

Supplementary measurements - Experimental Results

Expts	Counts per vial per minute	Expts	Counts per vial per minute
1	69911	6	1542
	74074		1552
	70922		2623*
	71942		1591
2	1473	7	1586
	1403		1622
	1329		1625
	1244		1632
3	964	8	1733
	1076		1750
	1951*		1792
	1078		1730
4	1188	9	1719
	1247		1724
	1184		1901
	1213		1756
5	1386	10	1760
	1397		1742
	1461		1947
	1362		1787

TABLE IVC

Quenching in the Calcium Oxalate System at 0.02 Molar

Expts	c.p.m.	Total	Expts	c.p.m.	Total
1	14859	58256	6	13369	55584
	14577			13661	
	14514			14430	
	14306			14124	
2	11628	47702	7	13755	55639
	11947			14085	
	12180			14025	
	11947			13774	
3	12300	49335	8	13850	55367
	12019			13831	
	12500			13680	
	12516			14006	
4	12771	52352	9	13699	54996
	12771			13908	
	13477			13966	
	13333			13423	
5	13423	54402			
	13298				
	13831				
	13850				

TABLE IVD

The Calcium Oxalate System at 0.02 Molar

Expts	c.p.m.	- b.g.	x r.e.f.	ϕ
1	87112	86912	86912	-
2	2413	2213	2213	38.885
3	1640	1440	1758	49.213
4	1732	1532	1809	47.797
5	1864	1664	1852	46.664
6	2148	1948	2086	41.315
7	2245*	2045	2143	40.189
8	2432	2232	2337	36.769
9	2467	2267	2385	36.008
10	2506	2306	2442	35.143

Expts	ϕ^{-1}	$(1^{\circ}/\phi)-1$	$\{(1^{\circ}/\phi)-1\}/[C_2O_4]$
2	0.026	-	-
3	0.020	0.111	166
4	0.021	0.167	125
5	0.021	0.167	84
6	0.024	0.333	125
7	0.025	0.389	117
8	0.027	0.500	125
9	0.028	0.556	119
10	0.028	0.556	104
			(mean 121)

*scaled

TABLE IVE

Distribution coefficients for the supplementary experiments

Expts	Total c.p.m.	- b.g.	x r.e.f.	ϕ	ϕ^{-1}
1	286849	286749	286749	-	-
2	5449	5349	5349	53.450	0.019
3	4157	4057	4954	57.792	0.017
4	4832	4732	5588	51.120	0.020
5	5606	5506	6128	46.526	0.021
6	6247	6147	6583	43.240	0.023
7	6465	6365	6671	42.656	0.023
8	7005	6905	7230	39.280	0.025
9	7100	7000	7364	38.546	0.026
10	7236	7136	7557	37.536	0.027

TABLE VA

Studies on the Calcium Oxalate System at 0.04 Molar Experimental Results

Expts	Counts per vial per minute	
1	11050	11364
	10309	11429
	11561	11429
	11765	11429
2	844	788
	810	732
	781	671
	773	642
3	702	778
	700	753
	825	866
	736	851
4	905	910
	904	895
	870	911
	884	897
5	1032	1052
	1024	1041
	1040	1058
	1043	1029
6	1168	1166
	1188	1130
	1129	1195
7	1276	1257
	1263	1260
	1261	1257
8	1369	1327
	1356	1308
	1387	1340
	1392	1321
9	1411	1396
	1394	1366
	1396	1364
	1388	1386
10	1458	1450
	1473	1409
	1480	1435

TABLE VB

The calcium oxalate system at 0.04 Molar

Supplementary measurements - Experimental Results

Expts	Counts per vial per minute	Expts	Counts per vial per minute
1	74074	6	7505
	73529		7368
	74074		7460
	73529		7360
2	4242	7	7838
	4179		7922
	4049		8200
	3845		8094
3	3982	8	8440
	4023		8439
	4117		8489
	4285		8347
4	5800	9	8559
	5698		8659
	6501*		?
	5561		8818
5	6717	10	8854
	6400		8910
	6732		8946
	6758		8834

TABLE VC

Quenching in the Calcium Oxalate System at 0.04 Molar

Expts	c.p.m.	Total	Expts	c.p.m.	Total
1	14347	57234	6	14085	55830
	14556			13889	
	14025			13928	
	14306			13928	
2	11628	49626	7	13831	55928
	12270			14144	
	12500			13928	
	13228			14025	
3	13477	53843	8	14144	56440
	13717			14065	
	13280			13986	
	13369			14245	
4	13736	54723	9	14409	56823
	13495			14205	
	13680			14124	
	13812			14085	
5	13774	56048			
	14144				
	14065				
	14065				

TABLE VD

The Calcium Oxalate System at 0.04 Molar

Expts	c.p.m.	- b.g.	x r.e.f.	ϕ
1	90336	90136	90136	-
2	6041	5841	5841	14.663
3	6211	6011	6931	12.197
4	7176	6976	7415	11.334
5	8319	8119	8492	9.768
6	9301*	9101	9292	8.839
7	10099*	9899	10146	8.011
8	10800	10600	10844	7.429
9	11101	10901	11054	7.268
10	11607*	11407	11487	6.957

Expts	ϕ^{-1}	$(1_0/\phi)-1$	$\{(1_0/\phi)-1\}/[C_2O_4]$
2	0.0682	-	-
3	0.0820	0.2022	152
4	0.0882	0.2937	110
5	0.1024	0.5011	125
6	0.1131	0.6589	124
7	0.1248	0.8304	125
8	0.1346	0.9378	117
9	0.1376	1.0175	109
10	0.1437	1.1077	104
			(mean 121)

*scaled

TABLE VE

Distribution coefficients for the supplementary experiments

Expts	Total c.p.m.	- b.g.	x r.e.f.	ϕ	ϕ^{-1}
1	295206	295106	295106	-	-
2	16315	16215	16215	17.475	0.057
3	16407	16307	18802	14.930	0.067
4	22745	22645	24072	11.439	0.087
5	26607	26507	27726	9.798	0.102
6	29693	29593	30214	8.907	0.112
7	32054	31954	32753	8.138	0.123
8	33715	33615	34388	7.703	0.130
9	34715	34615	35100	7.527	0.133
10	35544	35444	35692	7.384	0.135

TABLE VIA

Studies on the Calcium Oxalate System at 0.06 Molar

Experimental Results

Expts	Counts per vial per minute	
1	10050	9569
	10101	9615
	9852	9662
	9901	9569
2	1138	1096
	1118	1112
	1083	1061
3	1400	1435
	1404	1437
	1427	1462
4	1794	1840
	1810	1813
	1762	1823
	1775	1800
5	2070	2141
	2103	2088
	2079	2132
	2073	2103
6	2291	2350
	2301	2307
	2361	2315
	2361	2286
7	2545	2554
	2516	2554
	2528	2567
	2528	2528
8	2628	2601
	2646	2542
	2717	2732
	2717	2717
9	2789	2751
	2782	2813
	2821	2793
	2793	2751
10	2894	2915
	2920	2886
	2829	2903
	2837	2821

TABLE VIB

Quenching in the Calcium Oxalate System at 0.06 Molar

Expts	c.p.m.	Total	Expts	c.p.m.	Total
1	14559	58545	6	13812	55117
	14684			13831	
	14556			13624	
	14706			13850	
2	12903	50690	7	13774	55773
	12516			13889	
	12771			14104	
	12500			14006	
3	13459	53674	8	14124	56141
	13351			14006	
	13369			14025	
	13495			13986	
4	13423	54411	9	13986	56566
	13459			13947	
	13812			14347	
	13717			14286	
5	14065	54958			
	13514				
	13755				
	13624				

TABLE VIC

The Calcium Oxalate System at 0.06 Molar

Expts	c.p.m.	- b.g.	x r.e.f.	ϕ
1	78319	78119	78119	-
2	8810*	8610	8610	8.202
3	11420	11220	12959	5.108
4	14417	14217	15511	4.101
5	16789	16589	17850	3.430
6	18572	18372	19566	3.041
7	20320	20120	21367	2.698
8	21410	21210	22271	2.548
9	22293	22093	23043	2.428
10	23005	22805	23603	2.347

Expts	ϕ^{-1}	$(1_0/\phi)-1$	$\{(1_0/\phi)-1\}/[C_2O_4]$
2	0.1219	-	-
3	0.1958	0.2633	132
4	0.2438	0.5730	143
5	0.2915	0.8808	147
6	0.3288	1.1214	140
7	0.3706	1.3911	139
8	0.3925	1.5324	128
9	0.4119	1.6576	118
10	0.4261	1.7492	109
			(mean 132)

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*scaled

TABLE VIIA

Studies on the Calcium Oxalate System at 0.08 Molar

Experimental Results

Expts	Counts per vial per minute		Expts	Counts per vial per minute	
1	10695	10526	6	3690	3623
	10638	10638		3503	3534
	10753	10753		3831	3781
	10526	10695		3521	3540
2	1857	1934	7	3906	3929
	1866	1910		3861	3774
	1791	1910		3984	3891
	1808	1848		3817	3883
3	2250	2107	8	4115	4149
	2301	2172		4141	4124
	2171	2002		4090	4193
	2179	2121		4073	4149
4	2845	2667	9	4211	4454
	2869	2674		4115	4329
	2972	2611		4376	4338
	2825	2656		4329	4264
5	3344	3135	10	4425	4494
	3356	3160		4415	4386
	3350	3115		4454	4484
	3344	3145		4405	4454

TABLE VII B

Quenching in the Calcium Oxalate System at 0.08 Molar

Expts	c.p.m.	Total	Expts	c.p.m.	Total
1	15106	60608	6	13928	56087
	15129			13947	
	15221			14265	
	15152			13947	
2	12987	57866	7	14104	56578
	12853			14265	
	12920			14025	
	13106			14184	
3	13624	54128	8	14620	57255
	13550			14164	
	13459			14347	
	13495			14124	
4	13624	55003	9	14327	56921
	13812			14164	
	13736			14205	
	13831			14225	
5	14085	55485			
	13850				
	13870				
	13680				

TABLE VII C

The Calcium Oxalate System at 0.08 Molar

Expts	c.p.m.	- b.g.	x r.e.f.	ϕ
1	85224	85024	85024	-
2	14924	14724	14724	4.851
3	17303	17103	19993	3.305
4	22119	21919	24549	2.502
5	25949	25749	28375	2.028
6	29023	28823	31475	1.728
7	31045	30845	33343	1.575
8	33034	32834	35165	1.441
9	34416	34216	36235	1.368
10	35517	35317	37613	1.280

Expts	ϕ^{-1}	$(1_0/\phi)-1$	$\{(1_0/\phi)-1\}/[C_2O_4]$
2	0.2061	-	-
3	0.3026	0.4679	175
4	0.3997	0.9389	176
5	0.4931	1.3920	174
6	0.5787	1.8073	169
7	0.6349	2.0799	156
8	0.6940	2.3666	148
9	0.7310	2.5461	136
10	0.7813	2.7901	131
			(mean 158)

TABLE VIII A

Studies on the Calcium Oxalate System at 0.10 Molar.

Experimental Results

Expts	Counts per vial per minute		Expts	Counts per vial per minute	
1	10684		6	4980	5092
	10776			5010	5010
	10799			4878	5005
	10707			4831	5040
2	2693		7	5274	5447
	2713			5342	5501
	2740			5353	5543
	2747			5274	5285
3	3141	3300	8	5507	5727
	3053	3279		5417	5587
	3038	3285		5543	5562
	3053	3298		5537	5574
4	3831	4032	9	5747	5862
	3820	4075		5826	5938
	3828	4149		5701	5834
	3834	4072		5695	5663
5	4266	4625	10	5988	5848
	4167	4529		5938	5959
	4413	4717		5959	5967
	4219	4744		5945	5952

TABLE VIII B

Quenching in the Calcium Oxalate System at 0.10 Molar

Expts	c.p.m.	Total	Expts	c.p.m.	Total
1	14493	56557	6	13661	54686
	14286			13514	
	13850			13812	
	13928			13699	
2	13369	52087	7	13550	53837
	13369			13441	
	12723			13477	
	12626			13369	
3	13774	55249	8	13661	54243
	13850			13736	
	13889			13405	
	13736			13441	
4	13850	54541	9	13850	54686
	13441			13550	
	13736			13587	
	13514			13699	
5	13661	54277			
	13405				
	13624				
	13587				

TABLE VIII C

The Calcium Oxalate System at 0.10 Molar

Expts	c.p.m.	- b.g.	x r.e.f.	ϕ
1	85932*	85732	85732	-
2	21786*	21586	21586	3.0191
3	25447	25247	27418	2.1609
4	31641	31441	32626	1.6537
5	35680	35480	36828	1.3491
6	39846	39646	41153	1.1006
7	43019	42819	44446	0.9438
8	44454	44254	45936	0.8802
9	46266	46066	47817	0.8056
10	47556	47356	49156	0.7560

Expts	ϕ^{-1}	$1.\phi^{-1}-1$	$(1.\phi^{-1}-1)/[C_2O_4]$
2	0.3312	-	-
3	0.4628	0.3972	119
4	0.6047	0.8256	124
5	0.7412	1.2378	124
6	0.9086	1.7432	131
7	1.0595	2.1987	132
8	1.1361	2.4300	122
9	1.2413	2.7476	118
10	1.3228	2.9937	112
			(mean 123)

*scaled

TABLE IX A

Studies on the Calcium Oxalate System at 0.2 Molar. Experimental Results

Expts	Counts per vial per minute		Expts	Counts per vial per minute	
1	10661		6	7610	7825
	10846			7680	7788
	10684			7849	7862
	10776			7862	7764
2	6188		7	7874	7886
	6258			8157	8130
	6173			8000	8157
	6180			7886	7874
3	6203	6281	8	8389	8170
	6211	6196		8013	8091
	6166	5787		8104	8292
	6211	6031		7800	8157
4	7042	6702	9	8347	8361
	6983	6840		8375	8306
	6974	6748		8170	8460
	6964	6748		8264	8306
5	7645	7353	10	8418	8306
	7474	7267		8389	8170
	7342	7342		8251	8636
	7102	7143		8052	8361

TABLE IX B

Quenching in the Calcium Oxalate System at 0.2 Molar

Expts	c.p.m.	Total	Expts	c.p.m.	Total
1	14205	56738	6	13298	52532
	14164			13055	
	14205			13158	
	14164			13021	
2	12658	51460	7	13021	52848
	13123			13123	
	12658			13441	
	13021			13263	
3	12788	51284	8	13158	52848
	12853			12987	
	12920			13405	
	12723			13298	
4	12821	51322	9	13228	53193
	12658			13369	
	12788			13298	
	13055			13298	
5	13089	52324			
	12953				
	13193				
	13089				

TABLE IX C

The Calcium Oxalate System at 0.20 Molar

Expts	c.p.m.	- b.g.	x r.e.f.	ϕ
1	85934*	85734	85734	-
2	49598*	49398	49398	0.7474
3	49086	48886	53090	0.6247
4	55001	54801	59514	0.4476
5	58668	58468	63496	0.3558
6	62240	62040	67375	0.2769
7	63964	63764	69248	0.2419
8	65016	64816	70390	0.2215
9	66589	66389	72098	0.1921
10	66583	66383	72092	0.1992

Expts	ϕ^{-1}	$(1^{o}/\phi)-1$	$\{(1_0/\phi)-1\}/[C_2O_4]$
2	1.3380	-	-
3	1.6008	0.1964	59
4	2.2341	0.6698	101
5	2.8106	1.1006	110
6	3.6114	1.6992	127
7	4.1339	2.0897	125
8	4.5147	2.3743	119
9	5.2056	2.8907	124
10	5.0201	2.7520	103
			(mean 116)

*scaled

TABLE X

Summary of quenching data for the oxalate ion on calcium-45

I = 0.02M

$[C_2O_4]$	r.e.f.
0.00000	1.000
0.00067	1.221
0.00135	1.181
0.00200	1.113
0.00267	1.071
0.00333	1.048
0.00400	1.047
0.00467	1.052
0.00533	1.059

I = 0.04M

$[C_2O_4]$	r.e.f.
0.00000	1.000
0.00133	1.153
0.00267	1.063
0.00400	1.046
0.00533	1.021
0.00667	1.025
0.00800	1.023
0.00933	1.014
0.01067	1.007

I = 0.06M

$[C_2O_4]$	r.e.f.
0.00000	1.000
0.00200	1.155
0.00400	1.091
0.00600	1.076
0.00800	1.065
0.01000	1.062
0.01200	1.050
0.01400	1.043
0.01600	1.035

I = 0.08M

$[C_2O_4]$	r.e.f.
0.00000	1.000
0.00267	1.169
0.00533	1.120
0.00800	1.102
0.01067	1.092
0.01333	1.081
0.01600	1.071
0.01867	1.059
0.02133	1.065

I = 0.10M

$[C_2O_4]$	r.e.f.
0.00000	1.000
0.00333	1.086
0.00667	1.024
0.00999	1.037
0.01333	1.042
0.01667	1.034
0.01999	1.051
0.02333	1.043
0.02666	1.034

I = 0.20M

$[C_2O_4]$	r.e.f.
0.00000	1.000
0.00333	1.103
0.00667	1.106
0.00999	1.106
0.01333	1.084
0.01667	1.080
0.01999	1.074
0.02333	1.074
0.02666	1.067

TABLE XI A

Studies on the Calcium Malonate System:

Experimental Results

Expts	Counts per vial per minute		Expts	Counts per vial per minute	
1	172251	170452	6	25946	26240
	168347	171437		26436	26398
	167485	169933		26320	26228
	170701	166480		26604	26135
2	43172	44362	7	26163	26323
	43616	43758		26175	26697
	44152	44653		26868	27074
	43979	44027		26801	27040
3	36626	38420	8	25064	25533
	36846	36539		25736	24877
	37441	39082		25713	22878
	36466	35104		26058	23155
4	38275	38247	9	25528	23793
	37347	39275		25660	23846
	37613	37039		26199	24162
	37578	39575		25618	24691
5	28407	27130	10	25911	24413
	28328	27725		25866	25351
	29437	26518		25812	22915
	28611	26560			

TABLE XI B

Quenching in the Calcium Malonate System

Expts	c.p.m.
1	169041, 172853
2	136345, 141416
3	122467, 125071
4	99590, 100574
5	100108, 101794
6	85876, 86895
7	82442, 80944
8	84901, 82808
9	75336, 93248

TABLE XI C

The Calcium Malonate System

Expts	av. c.p.m.	- b.g.	x r.e.f.	ϕ
1	169636	169616	169616	-
2	43965	43945	43945	2.906
3	37066	37046	45604	2.763
4	38119	38099	52615	2.260
5	27840	27820	47517	2.611
6	26288	26268	44472	2.859
7	26630	26610	52661	2.257
8	24877	24857	52026	2.296
9	24937	24917	50806	2.376
10	25045	25025	56782	2.019

Expts	ϕ^{-1}	$1.\phi^{-1}-1$	$\{(1.\phi)^{-1}-1\}/[\text{Malonate}]$
2	0.34	-	-
3	0.36	0.05	17
4	0.44	0.29	47
5	0.38	0.11	12
6	0.35	0.02	(1)
7	0.44	0.29	19
8	0.44	0.27	15
9	0.42	0.22	11
10	0.50	0.44	18
			average 20 ± 10

TABLE XII A

Calcium-succinate experimental results

Expts	Counts/vial/10 mins	
1	203267	204892
	201765	203705
	200212	205547
	199239	194276
2	50735	51938
	50498	53653
	52369	52096
3	43729	43436
	44570	47331
	43660	46223
	44591	46559
4	45936	45010
	44904	43340
	45623	44037
	47666	44186
5	46050	46119
	46175	42042
	46679	39552
	44260	43525
6	45755	44635
	42490	45005
	47757	42291
	47933	45314
7	45859	43532
	42018	46916
	39491	46228
	46578	47029
8	43618	44335
	43531	44555
	44232	44839
	44192	44226
9	42062	42609
	42728	43495
	39053	44766
	41664	42203
10	40152	44017
	37834	42654
	41049	43215
	37370	43176

TABLE XII B

Calcium succinate. Calculation of Stability Constants.

Expts	Mean c.p.m.	x r.e.f.	- b.g.	ϕ	ϕ^{-1}
1	20161	20161	20141	-	-
2	5118	5118	5098	2.998	0.334
3	4501	5154	5134	2.970	0.337
4	4509	5194	5174	2.939	0.340
5	4430	5170	5150	2.958	0.338
6	4515	5332	5312	2.837	0.352
7	4471	5316	5296	2.848	0.351
8	4419	5320	5300	2.846	0.351
9	4232	5129	5109	2.989	0.335
10	4118	5053	5033	3.050	0.328

Experiments Nos. 9 and 10 give badly outlying values of the distribution coefficient, and have not been used in the calculation of the constants. The following are obtained:

Expts	$(1.0/\phi)-1$	$\{(1.0/\phi)-1\}/[\text{succinate}]$
3	0.028	8
4	0.037	6
5	0.031	3
6	0.074	6
7	0.071	4
8	0.071	4

TABLE XIII A

Studies on the Calcium Tartrate System.

Experimental Results

Expts	Counts per vial per minute		Expts	Counts per vial per minute	
1	163669	162079	6	56749	57331
	160698	166485		56736	56958
	165905	162289		57359	58674
	168781	164472		57995	59119
2	43018	41900	7	59873	59476
	42878	43218		59646	59528
	41756	44346		59994	59371
	41748	44482		60004	61090
3	32751	34637	8	60895	58948
	32820	33922		61315	59342
	32618	32087		61589	62377
	32191	31889		61235	61055
4	47668	47049	9	60144	58651
	46057	46852		60514	58789
	47523	46693		61775	60122
	46207	46837		62700	60938
5	54281	55940	10	59326	60681
	55254	53861		60097	60199
	53583	54241		60596	59984
	53364	53552		60758	59564

TABLE XIII B

Quenching in the Calcium Tartrate System at 0.1 Molar

Expts	c.p.m.	Total	Expts	c.p.m.	Total
1	14620	58395	6	13441	53093
	14663			13405	
	14535			13089	
	14577			13158	
2	8489	34833	7	13158	52567
	9042			13298	
	8681			12953	
	8621			13158	
3	13477	52759	8	11933	47405
	13774			10504	
	12315			12920	
	13193			12048	
4	14124	55524	9	13123	51590
	13850			12788	
	13889			13021	
	13661			12658	
5	13550	54129			
	13661				
	13441				
	13477				

TABLE XIII C

The Calcium Tartrate System at 0.10 Molar

Expts	c.p.m.	-b.g.	x r.e.f.	ϕ
1	1314378	1314178	1314178	-
2	343346	343146	343146	2.8751
3	262915	262715	440310	2.0165
4	374886	374686	414777	2.2031
5	434076	433876	456438	1.9093
6	460921	460721	497118	1.6699
7	478982	487882	526660	1.5192
8	486756	486556	540564	1.4540
9	483633	483433	595589	1.2258
10	481205	481005	544498	1.4362

Expts	ϕ^{-1}	$(1°/\phi)-1$	$\{(1.0/\phi)-1\}/[\text{Tartrate}]$
2	0.3478	-	-
3	0.4959	0.4258	(152)
4	0.4539	0.3050	54
5	0.5238	0.5060	60
6	0.5988	0.7216	64
7	0.6582	0.8924	62
8	0.6878	0.9775	57
9	0.8158	1.3455	66
10	0.6963	1.0019	(43)
			(mean 61)

TABLE XIV A

Studies on the Strontium-Oxalate System: Experimental Results

Expts	Counts per vial per minute	
1	26501	15752
	27706	27457
	26911	26392
	27041	27869
2	4616	4902
	4699	4933
	4839	4964
	4911	4951
3	4989	5144
	4819	5537
	5144	5203
4	5606	5315
	5335	5365
	5556	5418
5	5522	5491
	5562	5485
	5630	
6	5864	5801
	5623	5835
	5721	5722
	5820	
7	5846	5949
	5829	5805
	5905	5894
	5949	
8	5842	6137
	6060	5869
	5778	6096
	6008	6079
9	6096	6091
	6025	6063
	6023	6022
10	6054	6168
	6096	6159
	6080	6134

TABLE XIV B

The Strontium Oxalate System: Calculation of Results

From the experimental data the following distribution coefficients are calculated:

Expts	c.p.m.	- b.g.	ϕ	ϕ^{-1}
1	26954	26934	-	-
2	4852	4832	4.647	0.215
3	5139	5119	4.330	0.231
4	5433	5413	4.040	0.248
5	5538	5518	3.943	0.254
6	5769	5749	3.744	0.267
7	5882	5962	3.653	0.274
8	5984	5964	3.572	0.280
9	6053	6033	3.519	0.284
10	6115	6095	3.474	0.288

From these figures the stability constant is found.

Expts	$[C_2O_4]$	$(1^{o}/\phi)-1$	$\{(1_0/\phi)-1\}/[\text{oxalate}]$
3	0.00333	0.073	22
4	0.00667	0.152	23
5	0.00999	0.180	18
6	0.01332	0.241	18
7	0.01665	0.273	16
8	0.01998	0.301	15
9	0.02332	0.320	14
10	0.02665	0.338	13

TABLE XV A

Strontium Tartrate System: Experimental Results

Expts	Counts/vial/10 mins		Expts	Counts/vial/10 mins	
1	89442	92663	6	20886	20713
	89629	91615		21064	20869
	89852	93386		20477	20114
	89163	92478			
			7	21788	21535
2	15901	16545		21860	21698
	16206	16323		23481	21591
	16495	16548		22648	21616
	16565	16856			
			8	21587	22820
3	16351	18212		21446	22784
	15921	18028		22467	23993
	17156	18082		22107	24071
	17291	18203			
			9	21838	22721
4	18802	19142		22434	22806
	18578	19542		23364	22671
	20020	19281		22630	22698
	20080	18939			
			10	23147	22895
5	19999	20386		23093	22919
	19665	20479		22871	23011
	19728	20625		22396	22707
	19789	20260			

TABLE XV B

Calculations on the experimental data yield the following distribution coefficients:

Expts	av. c.p.m.	- b.g.	ϕ	ϕ^{-1}
1	9103	9083	-	-
2	1643	1623	4.670	0.214
3	1741	1721	4.346	0.230
4	1930	1910	3.815	0.262
5	2012	1992	3.617	0.276
6	2069	2049	3.488	0.287
7	2203	2183	3.212	0.311
8	2266	2246	3.093	0.323
9	2265	2245	3.093	0.323
10	2288	2268	3.053	0.328

These figures yield a value of l_0 of 4.670 and this value has been employed in the subsequent calculations.

The following are obtained:

Expts	$(l_0/\phi)-1$	[tartrate]	$\{(l_0/\phi)-1\}/[\text{tartrate}]$
1	-	0.0000	-
2	-	0.0000	-
3	0.074	0.0028	26
4	0.224	0.0056	40
5	0.289	0.0085	34
6	0.340	0.0113	30
7	0.432	0.0143	32
8	0.508	0.0173	29
9	0.508	0.0203	25
10	0.532	0.0233	23

The average figure obtained from these values is 30.

TABLE XVI

The Calcium-Hydrogen-Oxalate System: Results

Expt	$HClO_4$	$H_2C_2O_4$	CG 120	c.p.m. I	II	III
1	0.050 litre	0.000 litre	0.000 g	1738	1754	1748
2	0.050	0.000	0.100	124,122	121	123
3	0.045	0.005	0.100	-	145	140
4	0.040	0.010	0.100	-	160	153
5	0.035	0.015	0.100	173	171	170
6	0.030	0.020	0.100	183	188	182
7	0.025	0.025	0.100	196	205	198
8	0.020	0.030	0.100	220	217	215
9	0.015	0.035	0.100	235	240	232
10	0.010	0.040	0.100	247	242	237
11	0.005	0.045	0.100	259	-	-

Expt	Total	average - b.g.		ϕ	ϕ^{-1}
1	5240	1747	1725	-	-
2	490	123	101	8.136	0.123
3	285	143	121	6.708	0.149
4	313	157	135	5.959	0.168
5	514	171	149	5.352	0.187
6	553	184	162	4.882	0.205
7	599	200	178	4.398	0.227
8	652	217	195	3.970	0.252
9	707	236	214	3.573	0.280
10	726	242	220	3.461	0.289
11	259	259	237	3.177	0.315

TABLE XVII

The Strontium-Hydrogen-Oxalate System: Results

Expts	Counts/vial/20 mins	
1	152319	154427
	149052	158278
	146964	159089
	160205	150821
2	12131	12049
	12391	11246
	11859	11504
	12134	11621
3	13113	13218
	13196	13060
	12142	13338
	13192	13688
4	15252	13942
	14789	14821
	14389	13835
	14223	14081
5	16797	15808
	16868	15712
	16126	15857

Expts	Counts/vial/20 mins	
6	18088	17151
	18475	16951
	18020	17829
7	19844	19350
	19858	18318
	19523	18727
	18897	19528
8	21221	19599
	20108	20546
	19786	19796
	20784	19992
9	22179	21442
	21418	21362
	21986	17433*
	21836	16989*
10	24213	17972*
	23895	18107*
	18255*	18223*
	22688	18223*

*indicates that the vial used was of a type different from those used in the majority of the experiments, and therefore counted with a different efficiency. A scaling factor was used to bring these into line with the others when the calculations were performed.

TABLE XVIII

Equilibration of IR-120 at 0.1 Molar and 25°C

Time	Sample c.p.m.	Total
6 mins	7333 7328	14661
11	6794 6868	13662
17	6368 6335	12703
42	4687 4653	9340
66	3272 3257	6529
90	2424 2459	4883
130	2016 2062	4078
190	1925 1885	3810
250	1905 1898	3803
305	1903 1880	3783
365	1887 1874	3761

TABLE XIX

Equilibration of IR-122 at 0.1 Molar and 25°C

Time	Sample c.p.m.	Total
6 mins	6693 6468	13161
13	5924 5618	11542
21	5241 5086	10327
35	4404 4471	8875
50	3369 3436	6805
84	2443 2474	4917
106	2042 2006	4048
142	1813 1776	3589
218	1708 1690	3398
291	1674 1751	3425
348	1670 1683	3353
426	1687 1655	3342

TABLE XX

Equilibration of IR-124 at 0.1 Molar and 25°C

Time	Sample c.p.m.	Total
11 mins	5663 5624	11287
25	4178 4309	8487
45	3004 3082	6086
75	2221 2291	4512
118	1850 1808	3658
175	1855 1752	3607
249	1792 1764	3556
311	1760 1760	3520
376	1794 1711	3505
460	1732 1731	3463
552	1677 1637	3314
659	1649 1630	3279

TABLE XXI

Studies on the Calcium Oxalate System at 0.1 Molar with IR-120 cation exchanger

Expts	c.p.m.	v/m	Expts	c.p.m.	v/m
1/1	35714, 35088	-	-	-	-
2/1	37037, 37037	-	-	-	-
1/2	4963, 4878	0.3565	3/2	4773, 4785	0.3843
2/2	4587, 4619	0.3355	4/2	4285, 4237	0.3369
1/3	7092, 7547	0.4051	3/3	6623, 6667	0.3785
2/3	6849, 6897	0.3860	4/3	6097, 6061	0.3419
1/4	8299, 8197	0.3540	3/4	7547, 7519	0.3203
2/4	8658, 8547	0.3741	4/4	7843, 7843	0.3358
1/5	10695, 10811	0.4379	3/5	9615, 9302	0.3560
2/5	9709, 9901	0.3769	4/5	10638, 10870	0.4342
1/6	11050, 11111	0.3890	3/6	11050, 10929	0.3932
2/6	11299, 11236	0.3966	4/6	10152, 10050	0.3470
1/7	11299, 11236	0.3428	3/7	12422, 12270	0.4041
2/7	11765, 11905	0.3689	4/7	11299, 11429	0.3530
1/8	13793, 13605	0.4191	3/8	11494, 11364	0.3261
2/8	11236, 11173	0.3062	4/8	12121, 11905	0.3477
1/9	13986, 14085	0.4205	3/9	11429, 11236	0.3013
2/9	12422, 12500	0.3489	4/9	12422, 12739	0.3552
1/10	14599, 14599	0.4117	3/10	13889, 13605	0.3860
2/10	14085, 14184	0.3984	4/10	12658, 12195	0.3242

TABLE XXII

The Calcium Oxalate System at 0.1 Molar Distribution Coefficients (IR-120).

Expts	total c.p.m.	- b.g.	x r.e.f.	$(C'_m/C_m)-1$
1/1		$C'_m = 72388$		
2/1				
1/2	9841	9791	9791	6.3933
2/2	9206	9156	9156	6.9061
1/3	14639	14589	15844	3.5688
2/3	13746	13696	14874	3.4155
1/4	16496	16446	17071	3.2404
2/4	17205	17155	17807	3.0651
1/5	21506	21456	22271	2.2503
2/5	19610	19560	20303	2.5654
1/6	22161	22111	22951	2.1540
2/6	22535	22485	23339	2.1016
1/7	22535	22485	23339	2.1016
2/7	23670	23620	24518	1.9524
1/8	27398	27348	28387	1.5444
2/8	22409	22359	23209	2.1190
1/9	28071	28021	29086	1.4888
2/9	24922	24872	25817	1.8039
1/10	29198	29148	30256	1.3925
2/10	28269	28219	29291	1.4713
3/1		$C'_m = 72388$		
4/1				
3/2	9558	9508	9508	6.6134
4/2	8522	8472	8472	7.5464
3/3	13290	13240	14379	4.0343
4/3	12158	12108	13149	4.5132
3/4	15066	15016	15587	3.6441
4/4	15686	15636	16230	3.4601
3/5	18917	18867	19584	2.6963
4/5	21508	21458	22273	2.2500
3/6	21979	21929	22762	2.1802
4/6	20202	20152	20918	2.4606
3/7	24692	24642	25578	1.8301
4/7	22728	22678	23540	2.0751
3/8	22858	22808	23675	2.0576
4/8	24026	23976	24887	1.9087
3/9	22665	22615	23474	2.0838
4/9	25161	25111	26065	1.6708
3/10	27494	27444	28487	1.5411
4/10	24853	24803	25746	1.8116

TABLE XXIII

Studies on the Calcium Oxalate System at 0.1 Molar
Distribution Coefficients (IR-120)

Expts	ϕ	Expts	ϕ	Average
1/2	2.2792	3/2	2.5415	
2/2	2.3170	4/2	2.5424	2.4200
1/3	1.4457	3/3	1.5270	
2/3	1.4925	4/3	1.5431	1.5021
1/4	1.1471	3/4	1.1672	
2/4	1.1467	4/4	1.1619	1.1557
1/5	0.9854	3/5	0.9599	
2/5	0.9669	4/5	0.9770	0.9723
1/6	0.8379	3/6	0.8573	
2/6	0.8335	4/6	0.8538	0.8456
1/7	0.7204	3/7	0.7395	
2/7	0.7202	4/7	0.7325	0.7282
1/8	0.6496	3/8	0.6710	
2/8	0.6488	4/8	0.6637	0.6583
1/9	0.6260	3/9	0.6278	
2/9	0.6294	4/9	0.6313	0.6286
1/10	0.5735	3/10	0.5949	
2/10	0.5862	4/10	0.5873	0.5854

TABLE XXIV

Studies on the Calcium Oxalate System at 0.1 Molar with IR-122 cation exchanger

Expts	c.p.m.	v/m	Expts	c.p.m.	v/m
1/1	37037, 38461	-	3/1	37736, 37037	-
2/1	38462, 37736	-	4/1	37037, 37736	-
1/2	4202, 4132	0.3425	3/2	4525, 4494	0.3760
2/2	3221, 3322	0.3068	4/2	3717, 3711	0.3535
1/3	5495, 5291	0.3248	3/3	5634, 5405	0.3344
2/3	5464, 5376	0.3181	4/3	6079, 6006	0.3644
1/4	6579, 6711	0.3191	3/4	6472, 6410	0.3031
2/4	6623, 6452	0.3159	4/4	7380, 7299	0.3520
1/5	8403, 8475	0.3446	3/5	8197, 8163	0.3405
2/5	8230, 8264	0.3398	4/5	9009, 8850	0.3805
1/6	9479, 9132	0.3396	3/6	9804, 9950	0.3705
2/6	8969, 9346	0.3384	4/6	8772, 8658	0.3069
1/7	10638, 10811	0.3687	3/7	9662, 9524	0.3149
2/7	10101, 10101	0.3511	4/7	11050, 11111	0.3811
1/8	10256, 10309	0.3199	3/8	9950, 9615	0.2974
2/8	9901, 9901	0.3062	4/8	15038, 11111	0.3585
1/9	10929, 10870	0.3227	3/9	12121, 11976	0.3769
2/9	12500, 12270	0.3766	4/9	12270, 12048	0.3802
1/10	11834, 11976	0.3491	3/10	11905, 11905	0.3503
2/10	11111, 11364	0.3234	4/10	11429, 11299	0.3294

TABLE XXV

The Calcium Oxalate System at 0.1 Molar.

Distribution Coefficients (IR-122)

Expts	Total c.p.m.	- b.g.	x r.e.f.	$(C'_m/C_m)-1$
1/1 2/1	C'_m =	75261		
1/2	8334	8284	8284	8.0851
2/2	6543	6493	6493	10.5911
1/3	10786	10736	11659	5.4552
2/3	10840	10790	11718	5.4227
1/4	13290	13240	13743	4.4763
2/4	13075	13025	13520	4.5666
1/5	16878	16828	17467	3.3088
2/5	16494	16444	17069	3.4092
1/6	18611	18561	19266	2.9064
2/6	18315	18265	18959	2.9697
1/7	21449	21399	22212	2.3883
2/7	20202	20152	20918	2.5979
1/8	20565	20515	21295	2.5342
2/8	19802	19752	20503	2.6707
1/9	21799	21749	22575	2.3338
2/9	24770	24720	25659	1.9331
1/10	23810	23760	24663	2.0516
2/10	22475	22425	23277	2.2333
3/1 4/1	C'_m =	75261		
3/2	9019	8969	8969	7.3912
4/2	7428	7378	7378	9.2007
3/3	11039	10989	11934	5.3064
4/3	12085	12035	13070	4.7583
3/4	12882	12832	13320	4.6502
4/4	14679	14629	15185	3.9563
3/5	16360	16310	16930	3.4454
4/5	17859	17809	18486	3.0712
3/6	19754	19704	20453	2.6797
4/6	17430	17380	18040	3.1719
3/7	19186	19136	19863	2.7890
4/7	22161	22111	22959	2.2792
3/8	19565	19515	20257	2.7153
4/8	22222	22172	23015	2.2701
3/9	24097	24047	24961	2.0151
4/9	24318	24268	25190	1.9897
3/10	23810	23760	24663	2.0516
4/10	22728	22678	23540	2.1972

TABLE XXVI

Studies on the Calcium Oxalate System at 0.1 Molar

Distribution Coefficients (IR-122)

Expts	ϕ	Expts	ϕ	Average
1/2	2.7691	3/2	2.7791	
2/2	3.2493	4/2	3.2524	3.0125
1/3	1.7718	3/3	1.7745	
2/3	1.7250	4/3	1.7339	1.7513
1/4	1.4284	3/4	1.4095	
2/4	1.4426	4/4	1.3926	1.4183
1/5	1.1402	3/5	1.1732	
2/5	1.1584	4/5	1.1686	1.1601
1/6	0.9870	3/6	0.9928	
2/6	1.0049	4/6	0.9735	0.9896
1/7	0.8806	3/7	0.8783	
2/7	0.9121	4/7	0.8686	0.8848
1/8	0.8107	3/8	0.8075	
2/8	0.8178	4/8	0.8138	0.8125
1/9	0.7531	3/9	0.7595	
2/9	0.7280	4/9	0.7557	0.7491
1/10	0.7162	3/10	0.7187	
2/10	0.7222	4/10	0.7238	0.7202

TABLE XXVII

Studies on the Calcium Oxalate System at 0.1 Molar with IR 124 Cation Exchanger

Expts	c.p.m.	v/m	Expts	c.p.m.	v/m
1/1	32787,34483	-	3/1	34483,35714	-
2/1	34483,33333	-	4/1	36364,35088	-
1/2	3899,3839	0.4150	3/2	4484,4474	0.4528
2/2	3484,3515	0.3808	4/2	3515,3571	0.3460
1/3	5208,5038	0.3837	3/3	5305,5391	0.4144
2/3	4831,5305	0.3687	4/3	5102,4988	0.3884
1/4	7380,7407	0.4379	3/4	7299,7117	0.4572
2/4	6452,6452	0.3695	4/4	5970,5917	0.3605
1/5	7968,8032	0.4265	3/5	7937,7782	0.4291
2/5	7299,7299	0.3763	4/5	7692,7576	0.4178
1/6	9091,8929	0.4417	3/6	8264,8264	0.3929
2/6	8299,8230	0.3890	4/6	8511,8368	0.4058
1/7	9901,10000	0.4425	3/7	9950,9901	0.4560
2/7	8511,8264	0.3508	4/7	8439,8299	0.3530
1/8	9217,9050	0.3585	3/8	9615,9434	0.3875
2/8	8658,8889	0.3516	4/8	9852,10000	0.4202
1/9	10204,10050	0.3981	3/9	9524,9479	0.3719
2/9	10471,10582	0.4140	4/9	10363,10204	0.4058
1/10	10417,10582	0.3963	3/10	10638,10417	0.4025
2/10	11429,11364	0.4452	4/10	10000,9950	0.3708

TABLE XXVIII

The Calcium Oxalate System at 0.1 Molar.
Distribution Coefficients (IR-124)

Expts	Total c.p.m.	- b.g.	x r.e.f.	$(C'_m/C_m)-1$
1/1		C'_m = 69134		
2/1				
1/2	7738	7688	7688	7.9925
2/2	6999	6949	6949	8.9488
1/3	10246	10196	11073	5.2435
2/3	10136	10086	10953	5.3119
1/4	14787	14737	15297	3.5194
2/4	12904	12854	13342	4.1817
1/5	16000	15950	16556	3.1758
2/5	14598	14548	15101	3.5781
1/6	18020	17970	18653	2.7063
2/6	16529	16479	17105	3.0417
1/7	19901	19851	20605	2.3552
2/7	16775	16725	17361	2.9821
1/8	18267	18217	18909	2.6561
2/8	17547	17497	18162	2.8065
1/9	20254	20204	20972	2.2965
2/9	21053	21003	21801	2.1711
1/10	20999	20949	21745	2.1793
2/10	22793	27743	23607	1.9285
3/1		C'_m = 69134		
4/1				
3/2	8958	8908	8908	6.7609
4/2	7086	7036	7036	8.8258
3/3	10696	10646	11562	4.9794
4/3	10090	10040	10903	5.3408
3/4	14416	14366	14912	3.6361
4/4	11887	11837	12287	4.6266
3/5	15719	15669	16264	3.2507
4/5	15268	15218	15796	3.3767
3/6	16528	16478	17104	3.0420
4/6	16879	16829	17469	2.9575
3/7	19851	19801	20553	2.3637
4/7	16738	16688	17322	2.9911
3/8	19049	18999	19721	2.5056
4/8	19852	19802	20554	2.3635
3/9	19003	18953	19673	2.5142
4/9	20567	20517	21297	2.2462
3/10	21055	21005	21803	2.1708
4/10	19950	19900	20656	2.3469

TABLE XXIX

Studies on the Calcium Oxalate System at 0.1 Molar.

Distribution Coefficients (IR-124)

Expts	ϕ	Expts	ϕ	Average
1/2	3.3169	3/2	3.0613	
2/2	3.4077	4/2	3.0537	3.2099
1/3	2.0119	3/3	2.0635	
2/3	1.9585	4/3	2.0744	2.0271
1/4	1.5411	3/4	1.6624	
2/4	1.5451	4/4	1.6679	1.6041
1/5	1.3545	3/5	1.3949	
2/5	1.3464	4/5	1.4108	1.3767
1/6	1.1954	3/6	1.1952	
2/6	1.1832	4/6	1.2002	1.1935
1/7	1.0422	3/7	1.0778	
2/7	1.0461	4/7	1.0559	1.0555
1/8	0.9522	3/8	0.9709	
2/8	0.9868	4/8	0.9931	0.9758
1/9	0.9142	3/9	0.9350	
2/9	0.8988	4/9	0.9115	0.9149
1/10	0.8637	3/10	0.8737	
2/10	0.8586	4/10	0.8702	0.8666

TABLE XXX

Stability of the Calcium Oxalate complex at 0.1 Molar (IR-120)

$[C_2O_4]$	ϕ^{-1}	$l_{0}\phi^{-1}-1$	β
0.00333	0.6657	0.3314	100
0.00666	0.8653	0.7306	110
0.00999	1.0285	1.0570	106
0.01333	1.1826	1.3652	102
0.01666	1.3732	1.7464	105
0.01999	1.5191	2.0382	102
0.02332	1.5908	2.1816	94
0.02665	1.7082	2.4164	91

TABLE XXXI

Stability of the Calcium Oxalate complex at 0.1 Molar (IR-122)

$[C_2O_4]$	ϕ^{-1}	$l_{0}\phi^{-1}-1$	β
0.00333	0.5710	0.3596	108
0.00666	0.7051	0.6788	102
0.00999	0.8620	1.0524	105
0.01333	1.0105	1.4060	105
0.01666	1.1302	1.6910	102
0.01999	1.2308	1.9305	97
0.02332	1.3349	2.1784	93
0.02665	1.3885	2.3060	86

TABLE XXXII

Stability of the Calcium Oxalate Complex at 0.1 Molar (IR-124)

$[C_2O_4]$	ϕ^{-1}	$l_0\phi^{-1}-1$	β
0.00333	0.4933	0.3332	100
0.00666	0.6234	0.6849	103
0.00999	0.7264	0.9632	96
0.01333	0.8379	1.2646	95
0.01666	0.9474	1.5605	94
0.01999	1.0248	1.7697	89
0.02332	1.0930	1.9541	84
0.02665	1.1539	2.1186	79

APPENDIX II

COMPUTER PROGRAMS WRITTEN FOR THE WORK

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begin comment This program calculates the concentration of ionic
 species present in mixtures of a weak dibasic acid and a strong
monobasic acid, theDavies equation being applied to calculate
 activity coefficients to refine the acid dissociation constants
  and Newtons method being used to calculate the hydrogen ion
 concentration;
real   K1, K2, y, m, SK1, SK2, NK1, NK2, T, D, AO, BE, DHA, DHB,
 f1, f2, e;
integer   i, k, DV, Q1, Q2, Q3, Q4, Q5;
boolean   BO1, BO2;
Q1 := format ([ 7sd.ddddd]);
Q2 := format ([ 8sd.ddddd]);
Q3 := format ([ 7sd.dddd]);
Q4 := format ([ 5sd.ddddd]);
Q5 := format ([ 9sdddd]);
open ( 20 );
DV := read (20 ); comment output device;
open ( DV );
again: begin real procedure    ACTCO ( z,I );
value  I, z;
real  I;
integer  z;
```

```
begin  ACTCO := exp(-e × DHA × z↑2 ×(sqrt(I)/(1 + DHB × AO × sqrt(I
                              - BE × I))
end  ACTCO;
T := read (20);
D := read (20);
AO := read (20);
BE := read (20);
DHA := 1.8249₁₀6/sqrt (( D × T ) ↑ 3 );
DHB := 5.0293₁₀1/sqrt( D × T);
e := ln (10.0);
 copy text ( 20, DV, [;;]);
k := read (20); comment number of points;
K1 := read (20);
K2 := read (20); comment values at infinite dilution;
begin array TH2A, CH2A, CA, CHA, CH, CB, VH2A, MH2A, VB , MB ,
                           VS, PH, TV, I, R [ 1:k];
for i := 1 step 1 until k do begin
SK1 := K1;
SK2 := K2;
VH2A [i]  := read (20);
MH2A [i]  := read (20);
VB [i] := read (20);
MB [i] := read (20);
VS[i] := if in basic symbol (20) = 152 then 0.0 else read (20);
```

```
comment if solvent added insert asterisk and follow by typing
 volume of solvent;
TV [i] := VH2A [i] + VB [i] + VS[i];
TH2A [i] := VH2A [i] × MH2A [i] / TV [i];
CB [i] := VB [i] × MB [i] / TV [i];
Krefinement :   CHA [i] := (-(SK1 + CB [i]) + sqrt (( SK1 +
 CB [i])↑2 + 4.0 × SK1 × TH2A [i])) / 2.0;
CH [i] := CB [i] + CHA [i]; comment CH is now an approximation
 to the hydrogen ion nolarity;
begin array  a [1:4];
a [1] := 1.0 / SK1;
a [2] := 1.0 - CB [i] / SK1;
a [3] := SK2 - CB [i] - TH2A [i];
a [4] := - SK2 × CB [i] - SK2 × 2.0 × TH2A [i];
CHrefinement :  y := a[1] × CH [i]↑ 3 + a [2] × CH [i] ↑ 2
 + a [3] × CH [i] + a [4];
m := 3 × a [1] × CH [i]↑ 2 + 2 × a [2] × CH [i] + a [3];
CH[i] := CH [i] - y/m;
if abs ( y - a [1] × CH [i]↑ 3 - a[2] × CH [i]↑ 2 - a [3] ×
 CH [i] - a [4]) > 1.0₁₀-8
then goto CHrefinement; comment Newtons method for determination
 of a root of a cubic equation is used here;
CHA [i] := TH2A [i] / ( 1.0 + CH [i] / SK1 + SK2 /CH [i]);
CA [i] := CHA [i] × SK2 / CH [i];
I [i] := 0.5 × ( CB [i] + CHA [i] + 4 × CA [i] + CH [i]);
```

```
f1 := ACTCO ( 1, I [i]);
f2 := ACTCO ( 2, I [i]);
NK1 := K1 × f1 ↑ 2;
NK2 := K2 × f2;
B01 := if abs ( NK1 - SK1 ) > 1.0₁₀-6 then true else false;
B02 := if abs ( NK2 - SK2 ) > 1.0₁₀-6 then true else false;
if B01 or B02 then begin
SK1 := NK1;
SK2 := NK2;
goto Krefinement; end;
CH2A[i]:= CH [i]↑ 2 × CA [i] / (NK1 × NK2);
PH[i]:= - 0.4342 × ln (CH [i]);
R[i]:= CHA [i] / CA [i];
end; end;
write text ( DV, [[ 2c10s] A [ 12s ] H2A [12s] PH [12s]
 I [12s] HA [12s] R [ 2c ]]);
for i := 1 step 1 until k do begin
write ( DV, Q1,CA [i]);
write ( DV, Q2,CH2A [i]);
write ( DV, Q3,PH [i]);
write ( DV, Q2,I [i]);
write ( DV, Q4,CHA [i]);
write ( DV, Q5,R [i]);
```

```
new line ( DV, 2);
end; end; end;
if in basic symbol ( 20 ) = 142 then goto again;
close (20);
close (DV);
end→
```

```
begin comment This is a curve fitting program which
will fit given coordinates to any order of curve;
real SIGMA, e, ans, bans, b, in, q, a;
integer DV, Q1, Q2, Q3, i, j, k, l, m, n, o, p, ap, am,
 ma, mc, ka, mb;
open (20);
DV := read (20);
open (DV);
e := ln (10.0);
Q1 := format ([ ndd ]);
Q2 := format ([ s+d.dddd₁₀+nd ]);
Q3 := format ([ 5s+d.dddd₁₀+nd ]);
again:   copy text (20, DV, [;;]);
ap := read (20);
o := read (20);
begin real array A, O [1:o];
for i := 1 step 1 until o do begin
A [i] := read (20);
O [i] := read (20);        end;
for p := 1 step 1 until ap do begin
m := p + 1;
ma := p;
mc := m + 1;
```

```
begin real array OC, D [ 1: o ],c, d [1:m,1:m], t, x [1:m], d
detr [1:mc];
for i := 1 step 1 until m do begin
SIGMA := 0.0;
for k := 1 step 1 until o do
SIGMA := SIGMA + ( if i = 1 then O[k] else A [k]↑(i-1)×O[k]);
t[i] := SIGMA;
for j := 1 step 1 until m do begin
SIGMA := 0.0;
for k := 1 step 1 until o do
SIGMA := SIGMA + (if i = 1 and j = 1 and A[k] = 0.0 then 1.0 else
                     if  A[k] = 0.0 then 0.0 else A[k]↑(i+j-2));
c[i,j] := SIGMA;
end; end;
ans:= 0.0;
for i:=1  step 1 until m do ans :=ans+(ifc[i,i]>0.0 then
 ln(c[i,i])/e else if c[i,i] =0.0 then 0.0 else ln(abs(c[i,i]))/e);
am:=m;
ans:=ans/am;
bans:= 10.0↑ ans;
for i:=1 step 1 until m do
begin
t[i]:=t[i]/bans;
for j:=1 step 1 until m do
c[i,j]:= c[i,j]/bans;
end;
```

```
for j:=1 step 1 until  mc do
begin
for i:=1 step 1 until m do
for k:= 1 step 1 until m do
d[k,i]:=c[k,i];
b:=1.0;
mb:=j-1;
if mb≠0 then for k:=1 step 1 until m do  d[k,mb]:=t[k];
for k:=1 step 1 until ma do
begin
ka:=k+1;
if d[k,k]=0.0 then goto P86;
P80: b:=d[k,k]×b;
q:=d[k,k];
for l:=k step 1 until m do  d[k,l]:=d[k,l]/q;
for l:=ka step 1 until m do
begin
a:=d[l,k];
for n:=k step 1 until m do d[l,n]:= d[l,n]-d[k,n]×a;
end;
for l:=ka step 1 until m do d[k,l]:=0.0;
goto out;
P86: for i:=ka step 1 until m do if d[k,i]≠0.0 then
begin
b:= -b;
for l:=k step 1 until m do
begin
```

```
in:= d[1,k];
d[1,k]:=d[1,i];
d[1,i] := in;
end;
goto P80;
end;
detr[j]:=0.0;
goto fin;
out: end;
detr[j]:=d[m,m]×b;
fin: end;
for j:=2 step 1 until mc do x[j-1]:=detr[j]/detr[1];
write text ( DV, [[ 2c5s] ORDER*OF*FIT*=*]);
write ( DV, Q1, p);
for i := 1 step 1 until m do begin
write text ( DV, [[2c5s] COEFFICIENT*NUMBER*]);
write (DV, Q1, i);
write text ( DV, [ *=* ]);
write ( DV, Q2, x[i]);   end;
for i := 1 step 1 until o do begin
OC [i] := 0.0;
for j := 1 step 1 until m do
OC [i] := OC [i] + (if A[i] = 0.0 and j = 1 then x[j] else
                             x[j]×A[i]↑(j-1));
D[i] := OC[i] - O[i];   end;
```

```
write text ( DV, [[ 2c6s]ABSCISSA[11s] ORDINATE[11s]
                CALC*ORDINATE[11s] DEVIATION [2c]]);
for i := 1 step 1 until o do begin
write (DV,Q3,A[i]);
write text (DV,[[3s]]);
write (DV,Q3,O[i]);
write text (DV,[[3s]]);
write (DV,Q3,OC[i]);
write text (DV,[[8s]]);
write (DV,Q3,D[i]);
new line (DV,1);
end;
end of calculated arrays;
new line (DV,10);
 end of principal loop;
end of data arrays;
if in basic symbol (20) = 142 then goto again;
close (20);
close (DV);
end→
```

APPENDIX III

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BIBLIOGRAPHY

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