ION ASSOCIATION IN AQUEOUS SOLUTIONS OF SOME BI-BIVALENT METAL SALTS.

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

by

Robert Hefin Jones.

August 1957.
Abstract.

The work of Davies and his co-workers provides ample evidence of ion-association in aqueous solutions of bi-bivalent metal salts. In the work described in this Thesis, this association has been investigated in aqueous solutions of bivalent metal salts of the acids COOH·(CH₂)ₓ·COOH. The methods available for determining the dissociation constants of these salts are reviewed, and three of them are discussed in detail.

Section 1. Stock and Davies showed that for a solution containing a standard concentration of a sulphone-phthalein indicator, equality of indicator colour denotes equality of the function \( f_2(H^+) \). This fact has been utilised in the determination of the dissociation constants of a number of salts. A method is also suggested for the simultaneous determination of the dissociation constants of a dibasic acid.

Section 2. The solubility of copper malonate in water, and in aqueous solutions of malonic acid, sodium malonate and copper sulphate is reported. The enhanced solubility is attributed to the formation of the complex ions \( \text{CuMal}_2^- \) and \( \text{Cu}_2\text{Mal}^{++} \). Approximate values are given for the dissociation constants of these two ions.
Section 3. An attempt has been made to determine the dissociation constants of the copper salts of oxalic, malonic, succinic and glutaric acids by a spectrophotometric method. The method is critically discussed and it is shown that in these solutions ion-association is too extensive for any quantitative treatment of the available data to be possible. An alternative method is suggested.
Contents.

General Introduction .............................................. (1)

Section 1. Colorimetric Determination of
Dissociation Constants ............................... (10)

Section 2. Solubility Study of Copper
Malonate .......................................................... (95)

Section 3. Spectrophotometric Study of some
Copper Salts .................................................... (141)

Appendix ............................................................ (177)

References .......................................................... (182)
Debye and Hückel (1), assuming complete dissociation of strong electrolytes in aqueous solution, were able to provide a relatively satisfactory interpretation of the thermodynamic properties of many electrolyte solutions. Their theory is adequate to explain the behaviour of 1-1, 1-2, and 2-1 valent electrolytes. In the case of the bivalent electrolytes however, marked deviations from the Debye-Hückel theory appear even at high dilutions. Various attempts have been made to modify the theory, and to remove the approximations inherent in it.

Bjerrum (2) developed a theory that took into account the interactions of the ions at short range, and introduced the concept of ion-pairs. When two ions of opposite charge are close together the energy of their mutual electrical attraction may be considerably greater than their thermal energy. This results in the formation of a virtually new entity in the solution, which is sufficiently stable to withstand a number of collisions with the solvent molecules. Such entities will have no net charge in the case of symmetrical electrolytes, but should have a dipole moment. As they have no charge they therefore make no contribution to the electrical conductivity. With unsymmetrical electrolytes...
the position is more complicated as it involves the appearance of a new ionic species of a charge type not previously present. This new species may further associate to give neutral molecules.

Bjerrum treated this problem mathematically on the basis that all oppositely charged ions within a certain distance of one another are associated into ion-pairs. This picture is not really correct as it neglects the possibility that a fast-moving ion might come within this critical distance of another ion and move away without forming an ion-pair. The ions are regarded as rigid unpolarisable spheres, contained in a medium of fixed macroscopic dielectric constant. Non-polar bonds between the ions, as well as ion-solvent interaction are excluded. The potential energy $E(r)$ of the ion-pair is given as a function of the inter-ionic distance $r$. According to Coulomb's Law

$$E(r) = -\frac{z_1 z_2 e^2}{Dr}$$

where $D$ is the macroscopic dielectric constant. By applying the Maxwell-Boltzmann distribution law Bjerrum calculated that for two ions of opposite sign the probability of ionic association can be shown to be a minimum at a distance

$$r_{min} = a = \frac{e^2 z_1 z_2}{2DKT}$$

where $k$ is the Boltzmann constant. Bjerrum assumed that two
ions at a distance of \( r \approx q \) apart were associated. On this theory the degree of association will be given by

\[
(1 - \alpha) = \frac{4\pi Nc}{1000} \left[ \frac{z_1 z_2 e^2}{DkT} \right]^3 Q(b)
\]

where \( Q(b) = \frac{b}{2} \int e^{-Y} Y^{-4} dY \)

\[
Y = \frac{z_1 z_2 e^2}{rDkT}, \quad b = \frac{z_1 z_2 e^2}{aDkT}
\]

where \( a \) is the distance between the centers of the two ions forming the ion-pair, at their distance of closest approach.

The equilibrium constant for the formation of an ion-pair is given by

\[
K^{-1} = \frac{f_+ (1 - \alpha)}{f_+ f_- \alpha^2 c}
\]

At low concentrations, the activity coefficient ratio and \( \alpha^2 \) approach unity, and therefore

\[
(1 - \alpha) = K^{-1} c
\]

and

\[
K^{-1} = \frac{4\pi N}{1000} \left[ \frac{z_1 z_2 e^2}{DkT} \right]^3 Q(b)
\]

Substituting numerical values for the constants at 25°C in the above equations

\[
-\log K = 5.9308 - 3 \log D + \log Q(b)
\]

\[
-\log b = 4.6496 + \log D + \log a
\]
Values of $Q(b)$ and $b$ have been tabulated by Bjerrum (2) and by Fuoss and Kraus (3). For a 1-1 electrolyte in water at 25°C $q$ is 3.57 Å, whilst for a 2-2 electrolyte the value is 14.28 Å. Stock and Davies (4) using their values for the dissociation constants of bivalent metal malonates, calculated the 'a' values from the above equations. A comparison of these values with the cationic radii showed a rough parallelism, but indicated that the assumptions of Bjerrum's theory were inadequate.

A review of the work of Davies and his co-workers in this field shows that ion-association is extensive in aqueous solutions of bi-bivalent salts. These salts are very weak compared with the majority of the 1-1, 1-2, and 2-1 valent salts (5-8). The dissociation constant of zinc sulphate for example is of the same order as that of o-nitro benzoic acid ($6.4 \times 10^{-4}$). The salts of the monocarboxylic acids are generally much stronger than those of the dicarboxylic acids. A variety of experimental techniques have been employed to study the extent of ion-association in aqueous solution. Some of these methods are discussed briefly below.

In dicarboxylic acid buffer solutions the ionic concentrations are governed by the following equilibria:

\[
\begin{align*}
H_2A & \rightleftharpoons H^+ + HA' \\
HA' & \rightleftharpoons H^+ + A''
\end{align*}
\]
Addition of a bivalent metal ion $M^{++}$ causes the displacement of these equilibria and a change in the hydrogen ion concentration of the solution occurs due mainly to the reaction:

$$M^{++} + HA' \rightleftharpoons MA + H^+$$

This change in pH has been utilised to measure the dissociation constant of $MA$. Using an electrometric method Peacock and James (9) determined the $K$ values for the copper, lanthanum, and hexamine cobalti salts of malonic, succinic, glutaric, adipic, phthalic, maleic and fumaric acids. Canaan and Kilbrick (10) using a similar method obtained values for the dissociation constants of the calcium, strontium, barium, magnesium and zinc salts of oxalic, malonic, succinic, glutaric, maleic and r-tartaric acids. Gelles and Nancollas have studied the dissociation of rare earth oxaloacetates (11) and malonates by a potentiometric method at 25°C over a range of concentration and pH. A colorimetric method of determining the hydrogen ion concentration and hence the dissociation constant of metal dicarboxylates, was suggested by Stock and Davies (4). $K$ values in good agreement with previously published ones, were obtained for a series of metal malonates. This method is further discussed in Section 1.

The measurement of the conductivity of an electrolyte solution provides one of the most convenient methods for the study of ionic interaction. Ives and Riley (13) carried out
extensive conductivity measurements on aqueous solutions of copper and zinc malonates and alkyl malonates. Peacock and James (9) repeated these measurements on copper malonate solutions, and calculated a value of $1.59 \times 10^{-6}$ for its dissociation constant. Both these experiments involved the straightforward determination of the conductivity of a dilute aqueous solution of the salt. A modified conductivity method was used by Topp and Davies (14) to determine the extent of dissociation of calcium and barium salts of dicarboxylic acids. This method involved the determination of the mobility of the anion of the acid by carrying out a conductimetric titration of the pure acid with ammonia. This was then followed by the titration of the acid with calcium and barium hydroxide solutions. The dissociation constants evaluated for barium succinate and adipate are in agreement with the results of similar experiments by Peacock and James (9).

The increased solubility of a sparingly soluble salt in solutions of other salts has been used for studying ion-association. Topp (15) applied this method to some metal oxalates, but in some cases found difficulty in interpreting the data. Stock (16) repeated some of his work and extended it to some other metal oxalates. Another method suggested by Davies (17), involving the determination of the solubility of the metal iodate, has been used by Monk et alia (18,19) to study salts of monocarboxylic acids.
Cation exchange resins have been used for the determination of the dissociation constants of metal complexes. By making measurements in the absence of the complexing agent and in the presence of two or more concentrations of the complexing material, the dissociation constant can be determined. A number of methods may be used for determining the ratio of free to associated metal ions, but the usual practice is to use radioactive tracers. Schubert and Richter (20) employed this method for the determination of the stability constant of strontium citrate and tartarate. The main advantages of the ion exchange method are that:

(i) it can be used with very low concentrations of the metal, and over a wide range of temperature and pH.
(ii) it is very rapid.

In general complex formation produces a negative shift of the reduction potential of a metal at a dropping mercury electrode. This shift may be used to determine the dissociation constant of the complex. In cases where several complexes are formed by successive association of the ions, the polarographic method is particularly suitable. It provides the most direct evidence of the number of ligands held by the reducible ion. Nancollas and Gelles (21) studied the formation of copper malonate complexes by this method. Peacock and James (9) failed to observe any displacement of the polarographic half wave potential for the cupric ion in copper malonate solutions.
Nancollas and Gelies attribute this to insufficient resolution of the potential scale. They found that the association was sufficiently strong to produce appreciable shifts in the half-wave potential which enabled them to calculate successive association constants. Their value of pK for copper malonate (5.7) is in fair agreement with the values obtained potentiometrically (5.9) and conductimetrically (5.8).

A spectrophotometric determination of the dissociation constants of complexes usually requires a knowledge of the formula of the complex. This can generally be deduced by applying the method of continuous variation (21). The optical density of the solution is used to determine the relative concentration of the complex. A number of assumptions are made e.g. that the absorption is due mainly to one component, and that Beer's law is applicable to the solution under examination. This method has been used to study ion association in solutions of copper salts, and is discussed fully in Section 3 of this thesis. It differs from all other methods in one respect, in that it is the actual concentration of the complex that is measured and not the activity.

Kinetic studies of certain reactions have been utilised to evaluate stability constants of some complexes. Taube (22) investigated the association between Mn ions and oxalate ions by studying the catalytic oxidation of the oxalate by
chlorine and bromine, and the rate of disappearance of 
managanic ions in the reaction between oxalate and permanganate 
ions.

Brown and Prue (23) carried out a number of high precision 
measurements of the freezing point depressions of a series 
of aqueous solutions of bivalent metal sulphates. Their values 
for the dissociation constants were generally in close 
agreement with the conductivity values.

The work described in this thesis was undertaken to 
provide a systematic study of ion-association in aqueous 
solutions of bivalent metal salts of the acids COOH\cdot(CH_2)_n\cdotCOOH. 
The choice of methods for this study was limited by a number 
of factors, mainly the difficulty of preparing the pure salt, 
and the very low solubility of most of them. Three of the 
methods discussed above have been employed.

The colorimetric method of Stock and Davies has been 
examined, and used to determine the dissociation constants 
of a number of bi-bivalent salts. A method is also given for 
the simultaneous determination of the primary and secondary 
dissociation constants of dibasic acids. Solubility data are 
reported for copper malonate in water, malonic acid, sodium 
malonate and copper sulphate solutions. A spectrophotometric 
study of a number of copper salts is also discussed.
Section 1.

Colorimetric Determination of Dissociation Constants.
Contents

(i) Introduction ........................................ (12)
(ii) The Ionisation of Dicarboxylic Acids ....... (18)
(iii) Buffer Solutions ................................. (30)
(iv) Experimental ................................. (35)
(v) Calculations ................................. (42)
(vi) Tables and Graphs ................... (55)
(vii) Discussion ................................. (87)
(i) Introduction

Davies (24) emphasised the significance of the weakness of bi-bivalent salts in connection with the determination of pH by a colorimetric method. When an acid salt of a weak dibasic acid dissolves in water, the dissociation is not simply as described in the equations:

\[ \text{NaHA} \rightarrow \text{Na}^+ + \text{HA}' \quad \text{(i)} \]

\[ \text{HA}' \rightleftharpoons \text{H}^+ + \text{A}'' \quad \text{(ii)} \]

A third process \( \text{HA}'+ \text{HA}' \rightleftharpoons \text{H}_2\text{A} + \text{A}'' \) is much more important than the one described in (ii). It can be shown by calculation that if the ratio of the first dissociation constant of the acid to the second is 4 (the minimum possible calculated by Bjerrum (25), 25% of the acid radical appears in the form of undissociated \( \text{H}_2\text{A} \), 25% as the doubly charged ion \( \text{A}'' \), and 50% as \( \text{HA}' \). In his paper Davies quotes the percentages of these species for six common acids. For example in malonic, succinic, and glutaric acids, the percentage of \( \text{H}_2\text{A} \) is 3.6, 14.2, and 18.4 respectively. "If the acid salt is that of a multivalent cation \( M^{n+} \), it is still more incorrect to regard the solute as existing substantially in the form of the ions, as extensive interaction will occur between \( M^{n+} \) and \( A'' \) to give the undissociated ion-pair \( \text{MA} \). This will reduce still further the proportion of the acid radical present as the intermediate ion".

Britton and Jarret (26) carried out extensive pH
measurements on copper hydrogen malonate. They found that it had a low pH and a high conductivity in aqueous solution. The authors attributed this to hydrolysis, but Davies (27) showed that the experimental results were fully explicable on the basis of the first and second dissociation constants of malonic acid, and the dissociation constant of copper malonate determined by Ives and Riley (13).

In a 0.000625 M solution of copper hydrogen malonate 73.2% of the malonate radical is present as HMal', 2.9% as Mal", 21.1% as CuMal and 2.8% as H₂Mal. The low pH is therefore shown to be due, not to hydrolysis, but to the weakness of copper malonate. The main reaction is:

\[ \text{Cu}^{++} + \text{HMal}' \rightarrow \text{CuMal} + \text{H}^+ \]

It is obvious therefore that when the pH of a buffer solution is determined colorimetrically the presence of multivalent cations will give quite anomalous results. This effect may be demonstrated (24) by adding 5 mls of 0.025 M zinc nitrate to 50 mls of 0.025 M sodium hydrogen malonate buffer coloured with bromophenol blue. The colour of the indicator changes mainly as the result of the reaction:

\[ \text{Zn}^{++} + \text{HMal}' \rightarrow \text{ZnMal} + \text{H}^+ \]

The pH of the solution is reduced from 4.26 to 3.72. The hydrogen ion concentration is more than trebled by the addition of the zinc nitrate. It can be shown by calculation that the zinc salt solution causes a greater alteration in the pH of
the buffer solution than does a strong acid of the same molar concentration. Stock and Davies (4) discuss a colorimetric determination of pH and its use in determining the dissociation constants of metal malonates.

In recent years the development of the glass electrode and its incorporation in pH meters has made the electrometric method the most common one of determining pH. This method has undoubtedly many advantages, e.g. it can be used with turbid and colloidal solutions. The advent of photoelectric colorimeters has however made the colorimetric method of pH measurement as accurate, if not more so, than the electrometric one. Whereas in the former results reproducible to a third place are possible, their interpretation is rendered difficult by the uncertainties in the magnitude of liquid junction potentials and activity corrections. Using a simple comparator indicators, under suitable conditions, readily give a reproducibility of 0.01 pH units.

The main colour change of the sulphone-phthalein indicators is known to be associated with the ionisation of a phenolic hydrogen in the singly charged yellow carboxylate ion (28). For bromo cresol green (the indicator used in most of the present work) the indicator equilibrium will be controlled by the equation:

$$\frac{f_{H^+}f_{B^+}(H^+)(B^+)}{f_{HB^+}(HB^+)} = K_I$$
and the colour by the ratio \((B'')/(HB')\). Therefore when two solutions of identical colour are compared the quantity

\[
\frac{f_{H^+}f_{B''}(H^+)}{f_{HB'}}
\]

is the same in each. At low ionic strengths, the ion activity coefficients may be evaluated by means of the Debye-Hückel limiting equation or some empirical extension. The equation which has been used in the present work is the one proposed by Davies (29):

\[
\log f_1 = -0.5 z_1^2 \left( \frac{J_1}{1 + J_1} \right) - 0.21
\]

At ionic strengths below 0.05 the departures (at 25°C) from this equation should be well within the accuracy of the experiment (see Appendix A).

Taking the activity of univalent ions as being equal, equality of indicator colour in two solutions will mean the identity of \(pf_2(H^+)\) in each, where \(pf_2(H^+) = -\log f_2(H^+)\) and \(f_2\) is the activity of the bivalent ion \(B''\). Substituting in the Davies equation

\[
pf_2(H^+) = -\log (H^+) + 2 \left( \frac{J_1}{1 + J_1} \right) - 0.21
\]

This conclusion was confirmed by Stock and Davies (4) by preparing two buffer solutions of known ionic composition but of widely different ionic strengths, which gave identical colours with a standard concentration of indicator.

A solution 0.004931 M with respect to sodium hydrogen
malonate and 0.033404 M with respect to KCl was calculated (using German and Vogel's values for the first and second dissociation constants of malonic acid (30)), to have a hydrogen ion concentration of $7.86 \times 10^{-5}$ g.ion/litre, an ionic strength of 0.03831 and $p_f^2(H^+)$ of 4.42. A second solution, giving identical colour with the former, was 0.00585 M with respect to sodium benzoate, and 0.004012 M with respect to benzoic acid. The hydrogen ion concentration was calculated to be $5.09 \times 10^{-5}$, the ionic strength 0.005850 and $p_f^2(H^+)$ 4.43. Agreement between the two values of $p_f^2(H^+)$ was good, although the hydrogen ion concentration of one solution was nearly twice that of the other. Utilizing the usual definition of pH viz: $-\log f_1(H^+)$, the pH values of the solutions are 4.18 and 4.33 respectively, a difference of 0.15 pH units. This illustrates the errors that may be involved in basing colorimetric measurements on electrometric standards.

Stock (16) extended this work to the determination of the composition of succinate buffers and again found that equality of indicator colour meant equality of $p_f^2(H^+)$. Values were obtained for the dissociation constants of bivalent metal malonates and succinates by determining the value of $p_f^2(H^+)$ in buffer solutions containing the metal ions and partially neutralised dicarboxylic acid. By comparing the colour of the solution with that of a standard benzoate buffer containing the same concentration of indicator, a value for $p_f^2(H^+)$ was obtained.
The method of calculation is illustrated in detail below. It will be noted that the ultimate value obtained for the dissociation constant of the metal dicarboxylate depends on the values used for the dissociation constants of the acid. The application of the colorimetric method to the determination of the primary and secondary thermodynamic dissociation constants of a dibasic acid is discussed in the following section. Using a modified form of the Stock and Davies method values have been obtained for the dissociation constants of a number of bi-bivalent salts.
(ii) The Ionisation of Dicarboxylic Acids.

Two main methods have been employed to determine the dissociation constants of dibasic acids. The conductimetric method has been extensively used by Vogel et alia (31, 32) to determine the primary thermodynamic dissociation constants of a series of dicarboxylic acids. $K_1$ can normally be determined by the ordinary conductivity method if $K_2$ is very much smaller than $K_1$. By choosing a suitable concentration range so that the dissociation $\text{HA}' \rightleftharpoons H^+ + A''$ is negligible the value of $K$ for $\text{H}_2\text{A} \rightleftharpoons H^+ + \text{HA}'$ can be found. For example, succinic acid in the range 0.001 M to 0.02 M behaves as an unibasic acid, and the second stage dissociation is not appreciable until the first stage has proceeded to an extent of about 50%. However, with the higher members of the homologous series COOH$\cdot$$(\text{CH}_2)_n\cdot$COOH $K_2$ is not very much smaller than $K_1$, and the ionisation steps overlap considerably. To determine $K_2$ it is usual to study the conductivity of an aqueous solution of the acid sodium salt NaHA. This ionises:

$$\text{NaHA} = \text{Na}^+ + \text{HA}'$$
$$\text{HA}' \rightleftharpoons H^+ + A''$$

If the first stage is assumed to be complete, and if the mobilities of the various ions, and the degree of dissociation are known, it is theoretically possible to calculate $K_2$. The main difficulty of the method is that the mobility of the intermediate ion HA' cannot be obtained directly. To overcome
this difficulty Chandler (32) suggested two methods.

(1) The mobility of HA' is assumed to be the same as that of the most closely related unibasic anion.

\[ \Lambda_{\text{COOH} \cdot \text{COO}'} = \Lambda_{\text{CH}_3 \cdot \text{COO}'} \]

(2) \[ \Lambda_{\text{HA}'} = 0.6 \Lambda_{\text{A}''} \]

Vogel and his co-workers have examined the conductivity method in great detail, and used it to study members of the series COOH·(CH₂)ₙ·COOH. Jeffrey and Vogel (33) discuss the difficulties encountered in determining the dissociation constants. In addition to the impossibility of measuring the mobility of the intermediate ion HA' directly, there is also the added complication of making a correction for the hydrolysis of the sodium salt. It was suggested that \( \Lambda_{\text{HA}'} \) should be taken as being equal to the mobility of the amic ion

\[ \Lambda_{\text{COOH} \cdot (\text{CH}_2) \cdot \text{COO}'} = \Lambda_{\text{NH}_2 \cdot \text{CO} \cdot (\text{CH}_2) \cdot \text{COO}'} \]

The correction for the hydrolysis involved the determination of a value for \( K_2 \) by a potentiometric method. This value was very approximate as it was found that the variation in \( K_1 \) with \( K_2 \) was very small. Accurate values for the primary thermodynamic dissociation constant were obtained for many organic acids, but it was found impossible to obtain satisfactory values of \( K_2 \).

Whilst the conductivity method has only yielded values for the primary thermodynamic dissociation constant, the potentiometric method has been used by a number of workers (34-41) for the simultaneous determination of \( K_1 \) and \( K_2 \).
In order to calculate the distance between the carboxyl groups in the acids COOH, \((\text{CH}_2)_n\).COOH and their alkyl derivatives, Gane and Ingold (35) determined \(K_1\) and \(K_2\) using a hydrogen electrode. The constants were calculated employing the mixed activity-concentration method of Auerbach and Smolczyk (39). These values can however only be regarded as approximate. The authors state "... in the absence of appropriate corrections, the measurements remain qualitative, and therefore ought to be used only for purposes of comparison".

German and Vogel (33) reviewed previous determinations of \(K_1\) and \(K_2\). They suggested that the discrepancies in the values published by different authors could not be attributed solely to varying concentrations and temperatures. They noted the very large discrepancy between the values for succinic acid obtained by Gane and Ingold (36) with the hydrogen electrode and those obtained by Ashton and Partington (41) with the quinhydrone electrode. By titrating the acid against sodium hydroxide and measuring the potential with a quinhydrone electrode new values for the primary and secondary dissociation constants of malonic, succinic, and glutaric acids were obtained. The values of \(K_1\) agreed to within 2% with the conductivity value for malonic and glutaric acids, and to within 5% for the succinic acid. It was also calculated that an error of 1 mV would cause an error of approximately 5% in \(K_1\) and \(K_2\).
The exact determination of the thermodynamic dissociation constants of many weak dibasic acids is complicated by the 'overlapping' of the ionisation steps. In the case of most aliphatic dicarboxylic acids $K_1/K_2 \ll 500$, and the ionic and molecular concentrations cannot be established with sufficient accuracy by considering a single equilibrium. The two inflexions obtained in the potentiometric titration correspond to the two equivalence points. It can be shown that the two inflexions occur only if $K_1/K_2 > 16$. In practice this ratio has to be very much higher for the titration to be carried out accurately (42). The evaluation of the constants requires laborious arithmetical approximations (39). The potentiometric method has also the uncertainties attendant upon the presence of a liquid-liquid junction. All the authors mentioned above assumed that the liquid junction potential was negligible.

Cells without liquid junctions have been successfully employed in some cases (43). Jones and Soper (44) determined $K_1$ and $K_2$ for succinic, glutaric, $\beta$-methyl glutaric, and $\beta\beta'$-dimethyl glutaric acids using the cell:

$$H_2(Pt) \mid Acid + \text{NaOH} \quad 0.001 \text{M NaCl} \mid AgCl \cdot Ag$$

The dissociation constants were calculated by the method of Kolthoff and Bosch (40). This involved a preliminary calculation of $K_2$ using the mixed activity-concentration method of Auerbach and Smolczyk (39). This constant was then used to determine $K_1$, which was insensitive to small errors in $K_2$. An accurate
value of $K_2$ was then calculated from this $K_1$. Using a cell without liquid junction, Adell (45) obtained values for $K_1$ and $K_2$ of a number of acids of the series COOH.(CH$_2$)$_n$.COOH.

In addition to the uncertainty due to the presence of a liquid junction potential, potentiometric methods present two difficulties which have to be overcome, viz:

1. the standardisation of the pH scale
2. activity corrections

Although the potentiometric method gives strictly comparable values of the successive constants, for work of very high accuracy cells without liquid junction must be used. The method requires an elaborate series of experiments followed by an extrapolation to zero ionic strength. This extrapolation can be difficult with a dibasic acid, particularly if it is highly dissociated e.g. oxalic acid. Speakman (46) suggested a potentiometric titration method using a cell with a liquid junction which overcame the two difficulties of standardisation and activity correction. The cell used was:

$$\text{Ag} | \text{AgCl} \cdot \text{HCl (0.02M)} | \text{glass solution} | \text{sat. KCl HCl} | \text{AgCl} | \text{Ag}$$

The glass electrode was calibrated against the Hitchcock and Taylor buffers (47,48) By using solutions of low concentrations so that activity corrections could be made using the Debye-Hückel equation, he obtained values for the primary and secondary thermodynamic dissociation constants of oxalic, malonic, succinic, glutaric and adipic acids. The acids were
titrated against standard sodium hydroxide. $K_1$ and $K_2$ are related by the equation

$$X = K_1 Y + K_1 K_2$$

where $X$ and $Y$ are parameters involving the activity coefficients, the concentration of the sodium hydroxide added, and the hydrogen ion concentration. By calculating $X$ and $Y$ for each concentration of sodium hydroxide, and plotting a graph of $X$ against $Y$, a straight line of slope $K_1$, and of intercept $K_1 K_2$ on the $y$-axis, is obtained. Although not as accurate as the method using a cell without liquid junction, this method is far less laborious. The graphical solution also smooths out any experimental error. It is applicable to most of the acids $\text{COOH} \cdot (\text{CH}_2)_n \cdot \text{COOH}$ with the exception of oxalic acid, which in dilute solution behaves as an unibasic acid, making it impossible to obtain an accurate value of $K_2$.

Robinson and Kiang (49) have lately employed a spectro-photometric method for determining the dissociation constants of a dibasic acid. The method involved the measurement of the optical density of an aqueous solution of the acid at various pH's, ranging from the strongly acid to the strongly alkaline. None of the acids used in the present work has been examined by this method.

In his work on the dissociation of bivalent metal succinates Stock (16) found that by employing the $K_2$ value for
succinic acid given by German and Vogel (30) unreal values were obtained for the dissociation constants of some of the salts. He determined an arbitrary value of $K_2$ by a colorimetric method, assuming that the primary dissociation constant determined conductimetrically was accurate.

It is possible, by preparing a series of buffer solutions of the dicarboxylic acids containing a standard concentration of indicator for comparison purposes, to determine $K_1$ and $K_2$ by Speakman's method. Comparison with a standard buffer solution will give the value of $f_2(H^+)$ in each solution of the acid. This enables a plot of $X$ against $Y$ to be made, and hence $K_1$ and $K_2$ calculated.

In the present work this method has been used to determine the primary and secondary thermodynamic dissociation constants of all the acids used. The secondary dissociation constants of glutaric, adipic, $\beta$-methyl, and $\beta\beta'$-dimethyl glutaric acids have also been determined by Stock's method. These experiments are discussed in detail below.
The Determination of the Primary and Secondary Thermodynamic Dissociation Constants of Dibasic Acids.

The solutions were made up as follows:

25 mls. of 0.02 N dibasic acid
x mls of 0.02 N sodium hydroxide
5 mls of indicator (0.04% solution)
4 mls of 0.4 M KCl
(21 - x) mls of water.

By comparison with a series of standard benzoate buffers (mandelate buffers in the case of malonic acid) f_2(H^+) for each solution was determined (see specimen calculations)

The acid dissociates in two stages:

\[ H_2A \rightleftharpoons H^+ + HA' \] ..............(i)
\[ HA' \rightleftharpoons H^+ + A'' \] ..............(ii)

\[ K_1 = \frac{f_1^2 f_2 (H^+) (HA')}{(H_2A) f_0} \]
\[ K_2 = \frac{f_1 f_2^2 (H^+) (A'')}{f_1 (HA')} \]

where \( f_1, f_2 \) and \( f_0 \) are the activity coefficients of the univalent ion, the bivalent ion and the undissociated molecule respectively.

The total acid concentration 'a' is equal to:

\[ (H_2A) + (HA') + (A'') \]
From the condition of electroneutrality

\[(HA') + 2(A") + (OH') = b + (H^+)\]

where 'b' is the concentration of the added alkali.

\[b + (H^+) - (OH') = (HA') + 2(A") = L\]

\[a - b - (H^+) + (OH') = (H_2A) - (A") = M\]

\[2a - b - (H^+) + (OH') = 2(H_2A) + (HA') = N\]

At pH less than 7 \((OH')\) can safely be neglected. Combining the above equations we get that

\[\frac{(H^+)^2 \cdot f_1^2 \cdot f_2 \cdot L}{N \cdot f_0} = \frac{K_1 \cdot (H^+) \cdot f_2 \cdot M}{N} + K_1 K_2\]

or

\[X = \frac{Y K_1 + K_1 K_2}{f_0}\]

We can assume that in dilute solution \(f_0\) is unity. Using some suitable modification of the Debye-Hückel equation e.g. the Davies equation, \(X\) and \(Y\) can be calculated for each value of \('b'\). A plot of \(X\) against \(Y\) is a straight line of slope \(K_1\) and of intercept \(K_1 K_2\) on the 'y' axis. The slope and intercept can be calculated by the method of least squares (see Appendix B).

Approximate values of \(K_1\) and \(K_2\) were first obtained by giving \(L\) an approximate value which made it possible to calculate approximate values of \(f_1, f_2\) and hence \((H^+)\), \(X\), and \(Y\). These values of \(K_1\) and \(K_2\) were then used to obtain a new value for \(L\).
The calculations were then repeated until constant values of $K_1$ and $K_2$ were obtained. Usually three approximations were required to obtain constant $K$ values.

Speakman assumed that for most of his solutions $f_1$ was unity, and in the cases where allowance was made for the activity $f$ was calculated from the Debye-Hückel equation:

$$
\log f_1 = -0.5J_I \\
\log f_2 = -2.0J_I
$$

In the present work, in order that the ionic strengths in the test solutions and in the standard buffer solutions should be approximately the same, a fixed concentration of potassium chloride was added to each solution. This made the ionic strength in each case approximately 0.035, a value too high for the Debye-Hückel equation to be used. The Davies equation which has been found valid up to an ionic strength of 0.05 was used instead.

Data for the acids examined are given in Tables 4 - 9. Specimen graphs of $X = YK_1 + K_1K_2$ are given for glutaric and adipic acids in figures 5 and 6. The values of $pK_1$ and $pK_2$ for the various acids are collected in table 14, together with the potentiometric values reported by other authors.
The Determination of the Secondary Thermodynamic Dissociation Constants of a Dibasic Acid, assuming a value for \( K_1 \)

For the buffer solution, made up as described on p 25, the following equations are valid:

(a) \((\text{Na}^+) + (\text{H}^+) = (\text{HA}') + 2(\text{A}'')\) electroneutrality

(b) \((\text{A}'') + (\text{HA}') + (\text{H}_2\text{A}) = X\) total acid content

(c) \(K_1 = \frac{f_1^2 (\text{H}^+) (\text{HA}')}{(\text{H}_2\text{A})}\)

(d) \(K_2 = \frac{f_2 (\text{H}^+) (\text{A}'')}{(\text{HA}')}\)

(e) \(\log f_1 = -0.5 \left\{ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 \right\}\)

Multiply equation (b) by 2 and subtract (a)

(f) \((\text{HA}') + 2(\text{H}_2\text{A}) = 2X - (\text{Na}^+) - (\text{H}^+)\)

From (c) \((\text{H}_2\text{A}) = \frac{f_1^2 (\text{H}^+) (\text{HA}')}{K_1}\)

Substituting in (f) for \(\text{H}_2\text{A}\)

\((\text{HA}') + \frac{2f_1^2 (\text{H}^+) (\text{HA}')}{K_1} = 2X - (\text{Na}^+) - (\text{H}^+)\)

\((\text{HA}') \left\{ 1 + \frac{2f_1^2 (\text{H}^+)}{K_1} \right\} = 2X - (\text{Na}^+) - (\text{H}^+)\)

or \((\text{HA}') = \frac{2X - (\text{Na}^+) - (\text{H}^+)}{1 + \frac{2f_1^2 (\text{H}^+)}{K_1}}\)
By comparison with a benzoate buffer the value of $f_2(H^+)$ can be obtained, and by giving $I$ an approximate value, a value for $(H^+)$ can be calculated. The values for the concentrations of the other species present can then be obtained. These values provide a basis for further approximations. This is continued until constant values of $I$ are obtained. In order to obtain a series of values of $K_2$ the ionic strength was varied by adding potassium chloride.

The value of $K_2$ for four acids has been determined by this method. The data are given in tables 10 - 13.
(iii) **Buffer Solutions**

As subsequent calculations call for the determination of ionic strengths and hydrogen ion concentrations as accurately as possible, it was decided to use buffer solutions made up by partially neutralising solutions of monobasic acids of accurately known dissociation constants, with standard sodium carbonate solution. The requisite pH range was covered by using mandelate and bonzoate buffers. The dissociation constants of these acids were taken as $6.320 \times 10^{-5}$ for benzoic acid (50), and $3.88 \times 10^{-4}$ for mandelic acid (51).

To indicate the principles involved in the preparation of the buffers, details are now given for the preparation of a mandelate buffer of any required hydrogen ion concentration. 50 mls of each buffer solution is made up as follows:

- 25 mls. of 0.02 N mandelic acid
- "x" mls, of 0.02 N sodium carbonate
- $(25 - x)$ mls of water.

The total concentration of mandelate radical is thus 0.01 M. It has been shown (51) that solutions of sodium mandelate up to 0.1 M are completely dissociated, so that there is no need to correct for the species $\text{NaMand}^\text{-}$ (undissociated). The total concentration of $(\text{Na}^+)$ = "$x"/50 \times 0.02 = 0.0004x$. The mean activity coefficient of the buffer solution was calculated by means of the Davies extension of the Debye-Huckel limiting law.
The ions actually present in these solutions are:

\( \text{Na}^+, \ M'^+, \ H^+, \ \text{HCO}_3'^-, \ \text{CO}_3'^-, \ \text{OH}'^- \), of which the last three may be neglected as shown later.

The equilibria in any given buffer solution are governed by the following equations:

(a) \( (\text{Na}^+) = 0.0004x \)

(b) \( (H^+) + (\text{Na}^+) = (M') + (\text{HCO}_3') + (\text{CO}_3'^-) + (\text{OH}') \) 

(c) \( (HM) = 0.01 - (M') \) total mandelate concentration constant at 0.01

(d) \( \frac{x^2(H^+(M'))}{(HM)} = 3.88 \times 10^{-4} \)

If these equations are combined (neglecting \( \text{HCO}_3'^-, \ \text{CO}_3'^- \) and \( \text{OH}'^- \)) and \( (H^+) \), \( (\text{Na}^+) \) and \( (HM) \) substituted for in terms of \( (M') \) then

(e) \( \frac{x^2(M')(M')}{0.01 - (M')} = 3.88 \times 10^{-4} \)

The activity coefficient \( f_1 \) is obtained by substituting for

\[ I = \frac{1}{2} [ (\text{Na}^+) + (H^+) + (M') ] = \frac{1}{2} [2(M')] \] in the Davies equation.

Hence the ionic strength of any solution is numerically equal to the concentration of \( M' \).

A curve connecting "x" with \( (H^+) \) is most easily obtained by giving \( (M') \) various values in the range of neutralisation required (20 - 80%), and then solving for "x" in equation (e) in the form

\[ (M') - 0.0004x = \frac{3.88 \times 10^{-4} \times 0.01 - (M')}{f_1^2} \]
From equations (a) and (b) it is seen that the left hand side of this equation is equal to \( H^+ \).

For buffer solutions based on any other acid the theory and calculations are identical, with the substitution of the appropriate value for the dissociation constant. In the present work, the buffers used contained KCl in order to adjust the ionic strength to a comparable value with that of the buffers containing metal chloride. In this case the only difference is that the ionic strength now is equal to \( \mu' + (K^+) \).

Results for the mandelate and benzoate buffers without KCl are given in tables 1 and 2. Column 1 gives the ionic strength \( \mu \), columns 2 and 3 contain the activity coefficients of an univalent ion \( f_1 \) and of a bivalent ion \( f_2 \), column 5 gives the hydrogen ion concentration, and the last column the value of \( f_2(H^+) \).

The neglect of the ions \( HCO_3' \), \( CO_3'' \) and \( OH' \) previously mentioned is justified as follows.

\( OH' \) in buffers of pH approximately 4 - 5 is of the order of \( 10^{-10} \) to \( 10^{-9} \) g.ions/litre, and consequently negligible. The ions \( CO_3'' \) and \( HCO_3' \) are governed by the two dissociation constants of carbonic acid. Neglecting activity corrections we may write these in terms of concentrations.
\[
\frac{(H^+)(HCO_3^-)}{(H_2CO_3)} = 4.45 \times 10^{-7} \quad (52)
\]
\[
\frac{(H^+)(CO_3^{2-})}{(H_2CO_3)} = 5.7 \times 10^{-11} \quad (53)
\]

hence at a pH of 5 the concentration of $CO_3^{2-}$ is \[ \frac{5.7 \times 10^{-11}}{10^{-5}} \]
that is to say that at a pH of 5, $(CO_3^{2-})$ is 200,000 times smaller than $(HCO_3^-)$ and at lower pH's will be still more unimportant.

To obtain an estimate of the possible $(HCO_3^-)$ concentration the total $CO_2$ concentration may be given the approximate value of $1.5 \times 10^{-5}$ g.mols/litre, this being the concentration of $CO_2$ in equilibrium water (54). This is present almost entirely as either $H_2CO_3$ or $HCO_3^-$, $CO_3^{2-}$ having been shown to be negligible, so that the total $CO_2$ content is equal to $H_2CO_3 + (HCO_3^-)$.

The first dissociation constant of carbonic acid gives
\[
(H_2CO_3) = \frac{(H^+)(HCO_3^-)}{4.45 \times 10^{-7}}
\]

Therefore at pH 4,
\[
1.5 \times 10^{-5} = (HCO_3^-) \left\{ 1 + \left( \frac{10^{-4}}{4.45 \times 10^{-7}} \right) \right\}
\]
whence $(HCO_3^-) = 6.4 \times 10^{-3}$

and at pH 5, $(HCO_3^-) = 6.4 \times 10^{-7}$

so that in either case $(HCO_3^-)$ may be safely neglected. As a check on this, sets of two buffer solutions were made up, containing equal volumes of indicator, each identical except for the
substitution of an equivalent amount of sodium hydroxide for the sodium carbonate. In no case was any difference in colour detectable, whereas one further drop of carbonate solution caused a perceptible colour change.
(iv) **Experimental.**

(a) **Preparation of Solutions.**

The dicarboxylic acids were recrystallised several times from conductivity water, and dried in a vacuum desiccator over concentrated sulphuric acid. In the case of the glutaric acid (B.D.H. commercial grade) some decolorizing charcoal was used for the first recrystallisation. The monocarboxylic acids used for preparing the standard buffer solutions were: benzoic acid (thrice recrystallised from conductivity water), and mandelic acid previously purified for other work in this laboratory. The purity of each acid was checked by titration against standard alkali. The acid solutions were freshly prepared for each run, as they were found to be subject to bacterial degradation. In no case was a solution kept longer than three days.

The metal salts used were the B.D.H. AnalR chlorides, used without further purification. As some of the chlorides are deliquescent the procedure adopted was to weigh out the approximate weight of the chloride, and analyse the solution for either metal or the chloride. In the case of the magnesium cobalt and nickel solutions, an analysis was carried out for both. The metal was estimated volumetrically by complexing the metal ion with E.D.T.A. (the disodium salt of ethylenediamine-
tetra acetic acid), and backtitrating the E.D.T.A. against a standard zinc solution using Erichrome Black as indicator. The solutions used were 0.01 M at a pH of 11 (adjusted by addition of ammonium hydroxide) (55). The remaining solutions were analysed for chloride. The values obtained by the volumetric and gravimetric methods agreed to within 0.1%.

Preparation of Sodium Hydroxide solution.

1 gram of clean, dry, freshly cut sodium was placed in a platinum dish, in a vacuum desiccator over boiled out conductivity water until the reaction was complete. The resulting concentrated solution was quickly transferred to a pure nickel flask containing two litres of conductivity water. The flask was connected to a baryta burette and fitted with soda lime guard tubes. The resulting solution of sodium hydroxide (approximately 0.02 N) was standardised against hydrochloric acid, itself standardised against sodium carbonate.

Conductivity Water.

This was prepared by passing distilled water slowly through a column packed with about 150 gms of a mixture of anion- and cation exchange resins, supplied by The Permutit Co., Ltd., under the name of "Bio-Deminrolit".
Sodium Carbonate Solution.

This was prepared by dissolving pure AnalAr anhydrous sodium carbonate in conductivity water. A solution of strength 0.4 N was used in the present work.

Indicator Solutions.

The indicators required, bromocresol green, and bromophenol blue, were purchased as solids from Messrs. B.D.H. The solutions were prepared by the method of Clark and Lubs (56). 0.1 g. of the solid was accurately weighed out and ground in an agate mortar with the calculated quantity of N/50 sodium hydroxide solution. The resulting solution was transferred to a 250 ml. graduated flask and diluted to the correct volume with distilled water. The solution thus obtained was 0.04%. Fresh indicator solutions were prepared every week, and were always kept in the dark as they are liable to fade in direct sunlight.

Apparatus.

Stock and Davies's method in the original work was to make up a buffer solution to give the same colour with a standard amount of indicator as the solution under examination. The comparison was made using a direct vision prismatic comparator. This method of comparison has a number of disadvantages.
(1) The observer's sense of colour discrimination may not be accurate.
(2) The sensitivity is not great. At extreme concentrations the eye cannot detect small differences. At the optimum concentration the error may be \( \pm 5\% \).
(3) Interfering colours and differences of shade sometimes make matching impossible.
(4) It is very difficult to obtain standard illumination.

Consideration of these factors made it desirable to use some other method.

Preliminary experiments were performed using a photoelectric colorimeter. This consisted of two units: (i) a colorimeter incorporating a light source, filter and a photoelectric cell. (ii) a very sensitive galvanometer. The light source was a small lamp connected to a battery of "Nickel-irons", providing a steady e.m.f. of 6 volts over a long period of time. Suitable filters were chosen to give the maximum sensitivity with the indicator in use e.g. it was found that using bromocresol green, Ilford 609 gave the maximum sensitivity. This apparatus, whilst perhaps superior to the simple comparator in that it minimises the personal error, is however not really satisfactory. It was found that the addition of one drop of 0.02 N sodium carbonate solution did not affect the deflection of the galvanometer.
Erode (57) measured the absorption of a series of indicators over a wide wavelength range, and found that with a few exceptions (e.g. methyl violet) the height of the absorption peak varied with the pH of the solution, but its position remained unchanged. At the wavelength of maximum absorption the sensitivity of the indicator to pH change was also a maximum. These facts have been utilised for the determination of pH by a photoelectric method (58,59).

A series of solutions of dilute HCl containing equal concentrations of indicator solution and varying concentrations of sodium hydroxide was made up. The absorption curves of all these solutions were then obtained by measuring the percentage transmission on an Unicam S.P. 600 spectrophotometer using $\lambda$ cm. glass cells. The curves obtained are shown in figs. 1 and 2 (bromocresol green and bromophenol blue respectively). The concentration of the indicator was 5 mls. of the stock solution in 55 mls of buffer solution. Using the S.P. 600 the transmission can be measured to an accuracy of 0.2%.

The following method was then adopted for the determination of the hydrogen ion concentration of the test solutions:

A series of solutions of 0.02 N benzoic acid, containing varying amounts of 0.04 N sodium carbonate, was made up. The percentage transmission of each solution was measured, and a graph drawn of the percentage transmission at $\lambda_{\text{max}}$ against
the volume of sodium carbonate added. A standard concentration of indicator (5mls/55mls solution) was used in all measurements. From this graph the range over which the colour of the indicator varied linearly with the volume of alkali added was found.

In the subsequent experiments matters were arranged so that the transmission of the test solution was always in the range 25 - 60%.

The buffer solutions containing metal chloride were then prepared as follows:

25 mls of 0.02 N dibasic acid, 'x' mls of standard sodium hydroxide solution (where 'x' is the volume required to approximately half neutralise the acid), 10 mls of 0.06 M solution of the metal chloride, 5 mls of indicator solution, diluted with water to give a total volume of 55 mls.

The solutions were allowed to equilibrate overnight in a thermostat maintained at 25°C ± .01. The transmission was measured, at \( \lambda_{\text{max}} \) for the indicator used, on the spectrophotometer in a room maintained at 25°C. The solutions were then allowed to equilibrate for a further twelve hours; no change was detected in the transmittance. In the case of the chloride solutions containing a coloured cation, buffer solutions were prepared as described above omitting the indicator solution. These were then placed in the reference cell, so that the intrinsic colour of the cation was compensated.
A plot of $f_2(H^+)$ against percentage transmission is shown in figure 3. By interpolating on this curve it is possible to determine directly the value of $f_2(H^+)$ in the dicarboxylate buffer. In figure 4 is shown a graph of percentage transmission against volume of sodium carbonate added, for a benzoate buffer. Knowing the % transmission for a test solution, from this graph the volume of sodium carbonate required to prepare a benzoate buffer of identical colour can be determined. This enables the value of $f_2(H^+)$ to be calculated as shown below. Since equality of colour is taken to mean equality of $f_2(H^+)$, this function is then known for the test solution. The calculations are explained in detail below.
(v) Calculations.

(a) Analysis of Benzoate Buffer.

The buffer was made up as follows:

25 mls of 0.02 N benzoic acid

'x' mls of 0.04 N sodium carbonate

4.2 mls of 0.4 M KCl

water to make the total volume 55 mls

The equations on which the calculations are based are:

(a) \((Na^+) = 0.007273x\)

(b) \((H^+) + 0.007273x = (Benz')\) electroneutrality

(c) \(\frac{f_1^2(H^+)(Benz')}{(HBenz)} = 6.320 \times 10^{-5}\)  

(d) \((HBenz) = 0.009091 - (Benz')\) total benzoate

(e) \(\log f_1 = -0.5 \left\{ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 I \right\}\)

(f) Ionic strength = \((Benz') + (K^+)\)

A simple method of obtaining values for the species present which satisfy the above equations is to give a likely value to I = \((Benz') + (K^+)\). A likely value for \((Benz')\) can be obtained from table 1. Equation(e) then gives the first approximation for \(f_1\), and equation (b) leads to a value for 'x'. This value is then compared with the experimental figure, and further approximations made for I. The process is repeated until the value of 'x' calculated agrees with the experimental value.
To make the method clear an example is worked out.

A buffer was made up with the above concentrations of acid and KCl, and containing 8.06 mls of sodium carbonate. From table 1 a value of .005904 was ascribed to (Benz'). This gave a value for I = .036449. From this a value for $f_1$ of .83847 was obtained using equation (e), and a value of $4.83526 \times 10^{-5}$ for (H$^+$) from equation (d). (HBenz) was then found to be .003187, which gave a value for 'x' of 8.05. This is slightly smaller than the experimental value, so the initial value of I was too small. A second approximation was made using $I = .036455$, this gave the following values:

- $(Benz') = .005910$
- $(HBenz) = .003181$
- $(H^+) = 4.839 \times 10^{-5}$
- $f_1 = .83847$
- 'x' = 8.06

This value agrees with the experimental value and therefore no further approximations are necessary.

Table 3 shows the composition of a series of benzoate buffers.
(b) The Calculation of the Second Dissociation Constant of a Dibasic Acid.

The calculation is based on the following equations:

(a) \((\text{Na}^+) + (\text{H}^+) = (\text{HA'}) + 2(\text{A}^2)\) electroneutrality
(b) \((\text{A}^2) + (\text{HA'}) + (\text{H}_2\text{A}) = X\) total acid content

c) \(K_1 = \frac{f_1^2 \cdot (\text{H}^+) \cdot (\text{HA'})}{(\text{H}_2\text{A})}\)

d) \(K_2 = \frac{f_2 \cdot (\text{H}^+) \cdot (\text{A}^2)}{(\text{HA'})}\)

e) \(\log f_1 = -0.5 \left\{ \frac{J}{1 + J} - 0.2 \right\}\)

Multiply equation (b) by 2 and subtract (a)

(f) \((\text{HA'}) + 2(\text{H}_2\text{A}) = 2X - (\text{Na}^+) - (\text{H}^+)\)

From (c) \((\text{H}_2\text{A}) = \frac{f_1^2 \cdot (\text{H}^+) \cdot (\text{HA'})}{K_1}\)

Substituting in (f) for \((\text{H}_2\text{A})\)

\((\text{HA'}) + \frac{2f_1^2 \cdot (\text{H}^+) \cdot (\text{HA'})}{K_1} = 2X - (\text{Na}^+) - (\text{H}^+)\)

\((\text{HA'}) \left\{ 1 + \frac{2f_1^2 \cdot (\text{H}^+)}{K_1} \right\} = 2X - (\text{Na}^+) - (\text{H}^+)\)

or \((\text{HA'}) = \frac{2X - (\text{Na}^+) - (\text{H}^+)}{1 + \frac{2f_1^2 \cdot (\text{H}^+)}{K_1}}\)
By comparison with a benzoate buffer the value of $f_2(H^+)$ can be obtained, and by giving $I$ an approximate value, a value for $(H^+)$ can be obtained. The values for the concentrations of the other species present can then be calculated. These values provide a basis for further approximations. This is continued until constant values are attained. An example is worked out below to illustrate the method.

A partially neutralised solution of glutaric acid, containing KCl was found by comparison with a benzoate buffer to have an $f_2(H^+)$ value of $0.7011 \times 10^{-5}$. The concentrations were:

$$(Na^+) = .004902$$

Total glutarate = .004548

KCl = .008364

The German and Vogel value for the primary dissociation constant was used. $4.46 \times 10^{-5}$ (30).

Let $I = .014247$

Equation (e) then gives $f_1 = .88738$, and $f_2 = .62007$

Substituting the appropriate values in equation (g) we get

$(HA') = .002989$ and from (f) $(H_2A) = .005968$. Using these values for the ionic concentrations a new value of $I$ is obtained, and a further series of approximations made. The values obtained using $I = .014239$ are:

$(A^-) = .0009619 \quad f_1 = .88740$
Using these values $I = \cdot014239$, therefore no further approximation is necessary.

$K_2$ can then be calculated from equation (d).

The concentration of KCl was varied, so that a set of values of $K_2$ was obtained at different ionic strengths.
(c) The Calculation of the Dissociation Constant of Copper Glutarate.

The calculation is based on the following equations:

\[ \frac{f_1 \cdot (H^+)(HA')}{{\text{H}_2\text{A}}} = 4.46 \times 10^{-5} \]  
(50)

\[ \frac{f_2 \cdot (H^+)(A''_1)}{{\text{HA}'}} = 2.51 \times 10^{-6} \text{ (recalculated value)} \]

\[ (H^+) + (Na^+) + 2(Cu^{++}) = (Cl') + (HA') + 2(A'') \text{ (condition for electroneutrality)} \]

\[ (A'') + (HA') + (H_2A) + (CuA) = \text{total glutarate.} \]

\[ (Cu^{++}) + (CuA) = \text{total copper content.} \]

The composition of the solution was as follows:

\[ (Na^+) = .0043476 \]

\[ \text{total glutarate} = .004580 \]

\[ \text{total copper} = .01088 \]

\[ \text{total chloride} = .02176 \]

Multiplying equation (e) by 2 and subtracting (c)

\[ 2(CuA) = (H^+) + (Na^+) - (HA') - 2(A'') \]

Substituting for \((Na^+)\)

\[ 2(CuA) = .004348 + (H^+) - (HA') - 2(A'') \]  
......(f)

Multiplying (d) by 2

\[ 2(A'') + 2(HA') + 2(H_2A) + 2(CuA) = 0.009160 \]  
...(g)

Substituting for \(2(CuA)\) from \(f\) in equation \(g\) we get
(HA') + 2(H_2A) = 0.004812 - (H^+) ...........(h)

and from equation (a)

\[
\frac{(HA')}{\frac{f_1^2(H^+)}{x^2}} = \frac{4.46 \times 10^{-5} \times (H_2A)}{3.1464 \times 10^{-5}}
\]

\[
(HA') = 1.4175(H_2A)
\]

Equation (h) then gives

\[
3.4175(H_2A) = 0.004768
\]

\[
(H_2A) = 0.001395
\]

and

\[
(HA') = 0.001978
\]

Equation (d) then gives

\[
(A^+) = 0.000222
\]

Equation (d) then gives

\[
(CuA) = 0.0009851
\]

and from (e) \( (Cu^{++}) = 0.009893 \)

Using the above values for the concentrations of the ionic species present in the solution, a new value for I is calculated.
This value 0.034293 provides the starting point for the recalculation of the above values. The new values are:

- \((A'') = 0.0002217\)
- \((HA') = 0.001975\)
- \((H_2A) = 0.001397\)
- \((Cu^{++}) = 0.009891\)
- \((CuA) = 0.000987\)
- \(f_1 = 0.34200\)
- \(f_2 = 0.50262\)

These new values make it possible to calculate yet another value for the ionic strength 0.034287. Recalculation gives the same values for the concentrations of the various species. No further approximation is therefore needed, and \(K\) for copper glutarate can now be calculated.

\[
K_{CuGlut.} = \frac{f_2^2 \cdot (Cu^{++})(Glut'\prime)}{(CuGlut')} = \frac{0.2526 \times 2.217 \times 9.891 \times 10^{-7}}{9.870 \times 10^{-4}} = 5.61 \times 10^{-4}
\]

Calculation of the other dissociation constants is made in exactly the same way. It has been assumed that any association between the metal ions and the indicator is negligible at the low concentration of indicator used. The effect of errors in the various measured quantities on the value of \(K\) is illustrated in the following calculations.
(d) In calculating the dissociation constants of the various salts no correction has been made for the possible formation in the solution of the species MOH⁺. The concentration of this species in the copper glutarate solutions has been calculated using Davies's value for $K_{CuOH⁺}$ (60).

The concentrations were as follows:

- Total copper = 0.010878
- Total chloride = 0.0217560
- Total glutarate = 0.0045806
- Total sodium = 0.0043476

\[
f_2(H⁺) = 2.2360 \times 10^{-5}, \quad K_1 = 4.45 \times 10^{-5}
\]

\[
K_2 = 3.95 \times 10^{-6}
\]

\[
K_{CuOH⁺} = 3.4 \times 10^{-7}
\]

\[
f_1(H⁺)(OH⁺) = 10^{-14}
\]

Let $I_1 = 0.034786$, $f_1 = 0.84115$, $f_2 = 0.50063$

The concentration of OH⁺ is therefore $3.16 \times 10^{-10}$

Let $(Cu^{++}) = \text{total copper} - (CuGlut) = 0.010153$

\[
(CuOH⁺) = \frac{f_2 \times 1.0153 \times 3.6 \times 10^{-12}}{3.4 \times 10^{-7}}
\]

\[
= f_2 \times 1.06 \times 10^{-5}
\]

\[
= 0.000005
\]

The $(CuOH⁺)$ will therefore not make any appreciable difference in the value of $K$. As there are no values reported in the literature for $K_{MOH⁺}$ for most of the other metals used (with the exception of Mg, and Ca), it was not possible to estimate the concentration of MOH⁺. It is likely however that this would be less than in the case of the copper salts.
(e) Calculation of $K$ for copper succinate using different equations for the Activity Coefficient.

\[
\begin{align*}
(Cu^{2+}) &= 0.0109164 \\
(Cl^-) &= 0.0218328 \\
(Acid) &= 0.0045868 \\
(Na^+) &= 0.0042548 \\
\end{align*}
\]

\[
f_2(H^+) = 2.8720 \times 10^{-5}
\]

\[
K_1 = 5.99 \times 10^{-5}, \quad K_2 = 2.0 \times 10^{-6}
\]

<table>
<thead>
<tr>
<th></th>
<th>Davies</th>
<th>Debye-Hückel</th>
<th>Güntelberg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I$</td>
<td>0.034266</td>
<td>0.034086</td>
<td>0.034238</td>
</tr>
<tr>
<td>$f_1$</td>
<td>0.84203</td>
<td>0.80851</td>
<td>0.83547</td>
</tr>
<tr>
<td>$f_2$</td>
<td>0.50271</td>
<td>0.42733</td>
<td>0.48833</td>
</tr>
<tr>
<td>$(H^+)10^5$</td>
<td>5.7130</td>
<td>6.7208</td>
<td>5.8312</td>
</tr>
<tr>
<td>$(HA')$</td>
<td>0.0020666</td>
<td>0.0019667</td>
<td>0.0020500</td>
</tr>
<tr>
<td>$(A')$</td>
<td>0.0001439</td>
<td>0.0001369</td>
<td>0.0001428</td>
</tr>
<tr>
<td>$(H_2A)$</td>
<td>0.0013975</td>
<td>0.0014425</td>
<td>0.0014050</td>
</tr>
<tr>
<td>$(M^{++})$</td>
<td>0.0099374</td>
<td>0.0098757</td>
<td>0.0099274</td>
</tr>
<tr>
<td>$(MA)$</td>
<td>0.0009791</td>
<td>0.0010407</td>
<td>0.0009890</td>
</tr>
<tr>
<td>$K_{MA}10^4$</td>
<td>3.70</td>
<td>2.37</td>
<td>3.42</td>
</tr>
</tbody>
</table>
(f) **Error in weighing the acid.**

An error of 0.0002 gm in the weight of the acid makes little difference in the value of $K$.

*E.g.* Copper Succinate.

$$(\text{Cu}) = 0.0109164, \quad (\text{Cl}^-) = 0.0218328$$

$$(\text{Na}^+) = 0.0042548, \quad f_2(H^+) = 2.8720 \times 10^{-5}$$

$$(\text{Acid}) = 0.0045868 \quad (\text{Acid}) = 0.0045840$$

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$I$</td>
<td>0.034266</td>
<td>0.034266</td>
</tr>
<tr>
<td>$f_1$</td>
<td>0.84203</td>
<td>0.84203</td>
</tr>
<tr>
<td>$f_2$</td>
<td>0.50271</td>
<td>0.50271</td>
</tr>
<tr>
<td>$(H^+)^{10^5}$</td>
<td>5.7130</td>
<td>5.7130</td>
</tr>
<tr>
<td>$(HA')$</td>
<td>0.0020666</td>
<td>0.0020643</td>
</tr>
<tr>
<td>$(A'')$</td>
<td>0.001439</td>
<td>0.001438</td>
</tr>
<tr>
<td>$(H_2A)$</td>
<td>0.0013975</td>
<td>0.0013959</td>
</tr>
<tr>
<td>$(M^{++})$</td>
<td>0.0099374</td>
<td>0.0099364</td>
</tr>
<tr>
<td>$(MA)$</td>
<td>0.0009790</td>
<td>0.0009800</td>
</tr>
<tr>
<td>$K_{MA} \times 10^4$</td>
<td>3.70</td>
<td>3.69</td>
</tr>
</tbody>
</table>

Similar calculations showed that small errors in measuring the volume of the metal chloride solution, and the alkali added had little effect on the value of $K$ e.g. when an error of .02 mls is made in measuring the cupric chloride solution in the above example $K = 3.69 \times 10^{-4}$.
(g) Error of 5% in $K_1$ for the acid.

\[
\begin{align*}
(Cu^+) &= .0109164 \\
(Cl^-) &= .0218328 \\
(\text{Acid}) &= .0045868 \\
(Na^+) &= .0042548
\end{align*}
\]

\[f_2(H^+) = 2.3720 \times 10^{-5}, \quad K_2 = 2.0 \times 10^{-6}\]

\[
\begin{align*}
K_1 &= 5.99 \times 10^{-5} & K_1 &= 5.69 \times 10^{-5} \\
I &= .034266 & I &= .034161 \\
f_1 &= .34203 & f_1 &= .84220 \\
f_2 &= .50271 & f_2 &= .50313 \\
(H^+)10^5 &= 5.7130 & (H^+)10^5 &= 5.7082 \\
(HA^-) &= .0020666 & (HA^-) &= .0020063 \\
(A^-) &= .0001439 & (A^-) &= .0001397 \\
(H_2A) &= .0013975 & (H_2A) &= .0014277 \\
(M^{++}) &= .0099374 & (M^{++}) &= .0099033 \\
(MA) &= .000979 & (MA) &= .0010131 \\
K_{MA}10^4 &= 3.70 & K_{MA}10^4 &= 3.46
\end{align*}
\]

Another series of calculations introducing an error of 5% in $K_2$ gave a value of $K = 3.49 \times 10^{-4}$. As the salt becomes stronger the effect of errors in $K_1$ and $K_2$ on its dissociation constant becomes greater. For example, in the case of cadmium glutarate an error of 5% in $K_2$ gives rise to an error of nearly 20% in $K$. A similar error is introduced when an error of 5% is made in $K_1$.  
(h) **Error of 5% in \( f_2(H^+) \)**

The effect of this error is illustrated for copper succinate.

\[
\begin{align*}
(\Theta_1) &= 0.0109164 & (\text{Cl}^-) &= 0.0218328 \\
(\text{Acid}) &= 0.0045868 & (\text{Na}^+) &= 0.0042548 \\
K_1 &= 5.99 \times 10^{-5} & K_2 &= 2.0 \times 10^{-6}
\end{align*}
\]

<table>
<thead>
<tr>
<th>(10^5 f_2(H^+))</th>
<th>2.872</th>
<th>2.730</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>0.034266</td>
<td>0.034409</td>
</tr>
<tr>
<td>(f_1)</td>
<td>0.84203</td>
<td>0.84177</td>
</tr>
<tr>
<td>(f_2)</td>
<td>0.50271</td>
<td>0.50211</td>
</tr>
<tr>
<td>((H^+)10^5)</td>
<td>5.7130</td>
<td>5.4371</td>
</tr>
<tr>
<td>((HA^-))</td>
<td>0.0020666</td>
<td>0.0021276</td>
</tr>
<tr>
<td>((A^-))</td>
<td>0.001439</td>
<td>0.001558</td>
</tr>
<tr>
<td>((H_2A)^-)</td>
<td>0.0013975</td>
<td>0.0013684</td>
</tr>
<tr>
<td>((M^{++}))</td>
<td>0.0099374</td>
<td>0.0099214</td>
</tr>
<tr>
<td>((MA))</td>
<td>0.009979</td>
<td>0.009350</td>
</tr>
<tr>
<td>(K_{MA}\cdot10^4)</td>
<td>3.70</td>
<td>4.19</td>
</tr>
</tbody>
</table>
(vi) Tables and Graphs

All concentrations are expressed in g.mols / litre.
Table (1)

Composition of standard benzoate buffer.

<table>
<thead>
<tr>
<th>l</th>
<th>$f_1$</th>
<th>$f_2$</th>
<th>$'x'$</th>
<th>$(H^+).10^5$</th>
<th>$(H^+).10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0015</td>
<td>0.9582</td>
<td>0.8433</td>
<td>2.775</td>
<td>38.995</td>
<td>32.890</td>
</tr>
<tr>
<td>0.0017</td>
<td>0.9558</td>
<td>0.8345</td>
<td>3.408</td>
<td>33.698</td>
<td>28.125</td>
</tr>
<tr>
<td>0.0020</td>
<td>0.9524</td>
<td>0.8225</td>
<td>4.303</td>
<td>27.872</td>
<td>22.928</td>
</tr>
<tr>
<td>0.0025</td>
<td>0.9472</td>
<td>0.8050</td>
<td>5.722</td>
<td>21.133</td>
<td>17.010</td>
</tr>
<tr>
<td>0.0030</td>
<td>0.9424</td>
<td>0.7893</td>
<td>7.085</td>
<td>16.598</td>
<td>13.103</td>
</tr>
<tr>
<td>0.0035</td>
<td>0.9334</td>
<td>0.7757</td>
<td>8.417</td>
<td>13.327</td>
<td>10.336</td>
</tr>
<tr>
<td>0.0040</td>
<td>0.9348</td>
<td>0.7631</td>
<td>9.729</td>
<td>10.852</td>
<td>8.282</td>
</tr>
<tr>
<td>0.0045</td>
<td>0.9312</td>
<td>0.7517</td>
<td>11.027</td>
<td>8.909</td>
<td>6.697</td>
</tr>
<tr>
<td>0.0050</td>
<td>0.9280</td>
<td>0.7410</td>
<td>12.316</td>
<td>7.341</td>
<td>5.441</td>
</tr>
<tr>
<td>0.0055</td>
<td>0.9246</td>
<td>0.7313</td>
<td>13.599</td>
<td>6.047</td>
<td>4.422</td>
</tr>
<tr>
<td>0.0060</td>
<td>0.9220</td>
<td>0.7221</td>
<td>14.876</td>
<td>4.958</td>
<td>3.580</td>
</tr>
<tr>
<td>0.0065</td>
<td>0.9192</td>
<td>0.7135</td>
<td>16.149</td>
<td>4.029</td>
<td>2.875</td>
</tr>
<tr>
<td>0.0070</td>
<td>0.9164</td>
<td>0.7053</td>
<td>17.419</td>
<td>3.225</td>
<td>2.275</td>
</tr>
<tr>
<td>0.0075</td>
<td>0.9140</td>
<td>0.6976</td>
<td>18.667</td>
<td>2.522</td>
<td>1.760</td>
</tr>
<tr>
<td>0.0080</td>
<td>0.9116</td>
<td>0.6903</td>
<td>19.952</td>
<td>1.902</td>
<td>1.313</td>
</tr>
<tr>
<td>0.0085</td>
<td>0.9092</td>
<td>0.6833</td>
<td>21.216</td>
<td>1.349</td>
<td>0.923</td>
</tr>
<tr>
<td>0.0090</td>
<td>0.9070</td>
<td>0.6766</td>
<td>22.479</td>
<td>0.854</td>
<td>0.578</td>
</tr>
<tr>
<td>0.0095</td>
<td>0.9050</td>
<td>0.6701</td>
<td>23.740</td>
<td>0.406</td>
<td>0.272</td>
</tr>
</tbody>
</table>
ABSORPTION CURVES
BROMOCRESOL GREEN

\[ \lambda_{\text{max}} = 614 \]

\% Trans.

Wavelength \( \text{m} \mu \)

FIG. 1

| 70 |
| 60 |
| 50 |
| 40 |
| 30 |
| 20 |
| 10 |
Table (2)

Composition of standard mandelate buffer.

<table>
<thead>
<tr>
<th>I</th>
<th>$f_1$</th>
<th>$f_2$</th>
<th>'x'</th>
<th>$(H^+)*10^5$</th>
<th>$f_2(H^+)*10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0020</td>
<td>.9524</td>
<td>.8225</td>
<td>0.722</td>
<td>17.112</td>
<td>14.077</td>
</tr>
<tr>
<td>0.0025</td>
<td>.9472</td>
<td>.8050</td>
<td>3.007</td>
<td>12.974</td>
<td>10.442</td>
</tr>
<tr>
<td>0.0030</td>
<td>.9424</td>
<td>.7893</td>
<td>4.955</td>
<td>10.189</td>
<td>8.044</td>
</tr>
<tr>
<td>0.0035</td>
<td>.9384</td>
<td>.7757</td>
<td>6.705</td>
<td>8.182</td>
<td>6.346</td>
</tr>
<tr>
<td>0.0040</td>
<td>.9348</td>
<td>.7631</td>
<td>8.334</td>
<td>6.662</td>
<td>5.084</td>
</tr>
<tr>
<td>0.0045</td>
<td>.9311</td>
<td>.7517</td>
<td>9.883</td>
<td>5.470</td>
<td>4.112</td>
</tr>
<tr>
<td>0.0050</td>
<td>.9280</td>
<td>.7410</td>
<td>11.373</td>
<td>4.507</td>
<td>3.340</td>
</tr>
<tr>
<td>0.0055</td>
<td>.9246</td>
<td>.7313</td>
<td>12.822</td>
<td>3.712</td>
<td>2.715</td>
</tr>
<tr>
<td>0.0060</td>
<td>.9220</td>
<td>.7221</td>
<td>14.239</td>
<td>3.044</td>
<td>2.193</td>
</tr>
<tr>
<td>0.0065</td>
<td>.9192</td>
<td>.7135</td>
<td>15.632</td>
<td>2.473</td>
<td>1.765</td>
</tr>
<tr>
<td>0.0070</td>
<td>.9164</td>
<td>.7053</td>
<td>17.005</td>
<td>1.980</td>
<td>1.396</td>
</tr>
<tr>
<td>0.0075</td>
<td>.9140</td>
<td>.6976</td>
<td>18.363</td>
<td>1.549</td>
<td>1.080</td>
</tr>
<tr>
<td>0.0080</td>
<td>.9116</td>
<td>.6903</td>
<td>19.708</td>
<td>1.168</td>
<td>0.806</td>
</tr>
<tr>
<td>0.0085</td>
<td>.9092</td>
<td>.6833</td>
<td>21.043</td>
<td>0.828</td>
<td>0.566</td>
</tr>
<tr>
<td>0.0090</td>
<td>.9070</td>
<td>.6766</td>
<td>22.369</td>
<td>0.524</td>
<td>0.355</td>
</tr>
<tr>
<td>0.0095</td>
<td>.9050</td>
<td>.6701</td>
<td>23.688</td>
<td>0.249</td>
<td>0.167</td>
</tr>
</tbody>
</table>
Table (3)
Analysis of Benzolate Buffers.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>f_1</th>
<th>f_2</th>
<th>(H^+) *10^5</th>
<th>(Benz^-)</th>
<th>(H benz)</th>
<th>f_2 (H^+) *10^5</th>
<th>t' mls.</th>
<th>% Trans.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.035119</td>
<td>.84061</td>
<td>.49935</td>
<td>8.3325</td>
<td>.004574</td>
<td>.004517</td>
<td>4.4105</td>
<td>6.17</td>
<td>61.7</td>
</tr>
<tr>
<td></td>
<td>.035855</td>
<td>.83944</td>
<td>.49655</td>
<td>6.3863</td>
<td>.005310</td>
<td>.003781</td>
<td>3.1711</td>
<td>7.21</td>
<td>54.1</td>
</tr>
<tr>
<td></td>
<td>.036491</td>
<td>.83840</td>
<td>.49429</td>
<td>4.7557</td>
<td>.005946</td>
<td>.003145</td>
<td>2.3507</td>
<td>8.11</td>
<td>46.8</td>
</tr>
<tr>
<td></td>
<td>.037174</td>
<td>.83733</td>
<td>.49159</td>
<td>3.3478</td>
<td>.006629</td>
<td>.002462</td>
<td>1.6457</td>
<td>9.07</td>
<td>38.7</td>
</tr>
<tr>
<td></td>
<td>.037927</td>
<td>.83615</td>
<td>.48883</td>
<td>2.0928</td>
<td>.007382</td>
<td>.001709</td>
<td>1.0230</td>
<td>10.13</td>
<td>30.3</td>
</tr>
</tbody>
</table>
FIG. 3

BROMOCRESOL GREEN

% Transmission

$10^5$
BROMOCRESOL GREEN

% Transmission

FIG. 4

mls. Sodium Carbonate

7.0 8.0 9.0 10.0 11.0
Table (4)

Malonic Acid

<table>
<thead>
<tr>
<th>(Na⁺⁺) x 10³</th>
<th>f₂H⁺ x 10⁴</th>
<th>(H⁺) x 10⁶</th>
<th>x x 10⁸</th>
<th>y x 10⁴</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1957</td>
<td>4.886</td>
<td>9.5691</td>
<td>17.699</td>
<td>1.1485</td>
<td>0.032285</td>
</tr>
<tr>
<td>2.3491</td>
<td>4.401</td>
<td>8.6171</td>
<td>14.120</td>
<td>1.0540</td>
<td>0.032310</td>
</tr>
<tr>
<td>2.7105</td>
<td>3.456</td>
<td>6.9533</td>
<td>10.046</td>
<td>0.7610</td>
<td>0.032515</td>
</tr>
<tr>
<td>2.9276</td>
<td>2.957</td>
<td>5.8057</td>
<td>7.684</td>
<td>0.5514</td>
<td>0.032633</td>
</tr>
<tr>
<td>3.0719</td>
<td>2.818</td>
<td>5.5348</td>
<td>7.017</td>
<td>0.5202</td>
<td>0.032718</td>
</tr>
<tr>
<td>3.2936</td>
<td>2.260</td>
<td>4.4427</td>
<td>4.990</td>
<td>0.3427</td>
<td>0.032785</td>
</tr>
<tr>
<td>3.4333</td>
<td>2.130</td>
<td>4.1920</td>
<td>4.441</td>
<td>0.3219</td>
<td>0.032931</td>
</tr>
</tbody>
</table>

Total Malonate = 0.0045514

K₁ = 1.36 x 10⁻³ ; K₂ = 2.0 x 10⁻⁶
Table (5)

Succinic Acid

<table>
<thead>
<tr>
<th>(Na(^{++})) (10^3)</th>
<th>(f_2 H^+ 10^5)</th>
<th>(H(^+)) (10^5)</th>
<th>X (10^{10})</th>
<th>Y (10^5)</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9615</td>
<td>5.8192</td>
<td>11.2902</td>
<td>13.467</td>
<td>2.0788</td>
<td>.031222</td>
</tr>
<tr>
<td>2.3567</td>
<td>4.4832</td>
<td>8.7327</td>
<td>9.941</td>
<td>1.4472</td>
<td>.031639</td>
</tr>
<tr>
<td>2.9642</td>
<td>2.8434</td>
<td>5.5647</td>
<td>5.404</td>
<td>0.7424</td>
<td>.032261</td>
</tr>
<tr>
<td>3.3448</td>
<td>2.2503</td>
<td>4.4210</td>
<td>4.042</td>
<td>0.4844</td>
<td>.032718</td>
</tr>
<tr>
<td>3.9742</td>
<td>1.5732</td>
<td>3.1116</td>
<td>2.613</td>
<td>0.1960</td>
<td>.033561</td>
</tr>
</tbody>
</table>

Total succinate = .0046700

\[ K_1 = 5.99 \times 10^{-5}; \quad K_2 = 2.0 \times 10^{-6} \]
Table (6)

Glutaric Acid.

<table>
<thead>
<tr>
<th>((\text{Na}^{++}) \times 10^3)</th>
<th>(f_2(\text{H}^+) \times 10^5)</th>
<th>(X \times 10^{10})</th>
<th>(Y \times 10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3761</td>
<td>6.7541</td>
<td>13.0686</td>
<td>2.6857</td>
</tr>
<tr>
<td>1.6601</td>
<td>5.6951</td>
<td>11.3272</td>
<td>2.1374</td>
</tr>
<tr>
<td>2.0969</td>
<td>4.1635</td>
<td>7.9112</td>
<td>1.3833</td>
</tr>
<tr>
<td>2.5484</td>
<td>3.2145</td>
<td>6.0612</td>
<td>0.9673</td>
</tr>
<tr>
<td>2.9306</td>
<td>2.5953</td>
<td>5.8939</td>
<td>0.6412</td>
</tr>
<tr>
<td>3.2947</td>
<td>2.1064</td>
<td>5.5394</td>
<td>0.4188</td>
</tr>
</tbody>
</table>

Total glutarate = .004438

\[ K_1 = 4.45 \times 10^{-5} ; \quad K_2 = 3.95 \times 10^{-6} \]
FIG. 5

GLUTARIC ACID

X \times 10^{10}

Y \times 10^5

1.0

2.0

1.0

2.0

10.0

10.0

12.0

12.0
Table (7)

<table>
<thead>
<tr>
<th>(Na(^{+})) (\times 10^3)</th>
<th>(f_2(H^+)) (\times 10^5)</th>
<th>(X \times 10^{10})</th>
<th>(Y \times 10^5)</th>
<th>(I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5165</td>
<td>5.2424</td>
<td>8.3518</td>
<td>2.0519</td>
<td>0.032313</td>
</tr>
<tr>
<td>2.2748</td>
<td>3.3077</td>
<td>5.3224</td>
<td>1.0792</td>
<td>0.033080</td>
</tr>
<tr>
<td>2.9893</td>
<td>2.1293</td>
<td>3.2033</td>
<td>0.5306</td>
<td>0.033920</td>
</tr>
<tr>
<td>3.6455</td>
<td>1.4727</td>
<td>2.0915</td>
<td>0.2352</td>
<td>0.034757</td>
</tr>
<tr>
<td>4.4426</td>
<td>1.0303</td>
<td>1.4476</td>
<td>0.0203</td>
<td>0.035643</td>
</tr>
<tr>
<td>5.1110</td>
<td>0.7293</td>
<td>0.9823</td>
<td>-0.1087</td>
<td>0.036012</td>
</tr>
</tbody>
</table>

Total adipate = 0.004537

\[ K_1 = 3.85 \times 10^{-5}; \quad K_2 = 3.05 \times 10^{-6} \]
ADIPIC ACID

FIG. 6
Table (8)

α-Methyl Glutaric Acid.

<table>
<thead>
<tr>
<th>(Na(^{++})) (10^3)</th>
<th>(f_2H^+) (10^5)</th>
<th>((H^+)) (10^5)</th>
<th>(X) (10^{-10})</th>
<th>(Y) (10^5)</th>
<th>(I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9071</td>
<td>7.0336</td>
<td>13.7231</td>
<td>18.436</td>
<td>2.5787</td>
<td>.031934</td>
</tr>
<tr>
<td>1.9377</td>
<td>4.7161</td>
<td>9.2187</td>
<td>9.043</td>
<td>1.6723</td>
<td>.032114</td>
</tr>
<tr>
<td>2.1684</td>
<td>4.3129</td>
<td>8.4490</td>
<td>8.404</td>
<td>1.4603</td>
<td>.032369</td>
</tr>
<tr>
<td>2.3491</td>
<td>3.8268</td>
<td>7.5121</td>
<td>7.307</td>
<td>1.2320</td>
<td>.032621</td>
</tr>
<tr>
<td>2.5298</td>
<td>3.3962</td>
<td>6.6803</td>
<td>6.331</td>
<td>1.0336</td>
<td>.032873</td>
</tr>
<tr>
<td>2.7105</td>
<td>3.0638</td>
<td>6.0392</td>
<td>5.652</td>
<td>0.8749</td>
<td>.033129</td>
</tr>
</tbody>
</table>

Total \(\alpha\)-methyl glutarate = \(0.004616\)

\[ K_1 = 4.37 \times 10^{-5}; \quad K_2 = 4.25 \times 10^{-6} \]
Table (9).

**ββ'-dimethyl Glutaric Acid.**

<table>
<thead>
<tr>
<th>(Ne) 10^3</th>
<th>f_pH 10^5</th>
<th>(H^+) 10^5</th>
<th>X 10^10</th>
<th>Y 10^5</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.730</td>
<td>8.0900</td>
<td>15.7758</td>
<td>40.910</td>
<td>2.2337</td>
<td>0.031984</td>
</tr>
<tr>
<td>2.9128</td>
<td>6.8433</td>
<td>13.3315</td>
<td>31.687</td>
<td>1.7660</td>
<td>0.03152</td>
</tr>
<tr>
<td>3.2769</td>
<td>5.0813</td>
<td>9.9610</td>
<td>20.458</td>
<td>1.1023</td>
<td>0.032456</td>
</tr>
<tr>
<td>3.4590</td>
<td>3.9161</td>
<td>7.6908</td>
<td>13.086</td>
<td>0.7653</td>
<td>0.032673</td>
</tr>
<tr>
<td>3.6410</td>
<td>3.5031</td>
<td>6.8854</td>
<td>11.331</td>
<td>0.5976</td>
<td>0.032778</td>
</tr>
<tr>
<td>3.8230</td>
<td>2.7730</td>
<td>5.4579</td>
<td>7.654</td>
<td>0.4023</td>
<td>0.032949</td>
</tr>
</tbody>
</table>

Total ββ'-dimethyl glutarate = .004671

K_1 = 1.85 \times 10^{-4}; \quad K_2 = 1.93 \times 10^{-7}
Table (10).

$K_2$ for Glutaric Acid assuming $K_1 = 4.46 \times 10^{-5}$ (61)

<table>
<thead>
<tr>
<th>I</th>
<th>$0.005882'$</th>
<th>$0.014239$</th>
<th>$0.021568$</th>
<th>$0.029146$</th>
<th>$0.039798$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_1$</td>
<td>$0.92250$</td>
<td>$0.88740$</td>
<td>$0.86720$</td>
<td>$0.85113$</td>
<td>$0.83333$</td>
</tr>
<tr>
<td>$f_2$</td>
<td>$0.72423$</td>
<td>$0.62013$</td>
<td>$0.56556$</td>
<td>$0.52431$</td>
<td>$0.48226$</td>
</tr>
<tr>
<td>$(H^+)^{10^5}$</td>
<td>$1.0631$</td>
<td>$1.1206$</td>
<td>$1.3251$</td>
<td>$1.4279$</td>
<td>$1.5373$</td>
</tr>
<tr>
<td>$(A')$</td>
<td>$0.000972$</td>
<td>$0.00962$</td>
<td>$0.01013$</td>
<td>$0.01030$</td>
<td>$0.01061$</td>
</tr>
<tr>
<td>$(HA^+)$</td>
<td>$0.002972$</td>
<td>$0.002989$</td>
<td>$0.002889$</td>
<td>$0.002855$</td>
<td>$0.002796$</td>
</tr>
<tr>
<td>$(H_2A)$</td>
<td>$0.000606$</td>
<td>$0.000597$</td>
<td>$0.000646$</td>
<td>$0.000662$</td>
<td>$0.000691$</td>
</tr>
<tr>
<td>$(HA^2)$</td>
<td>$0$</td>
<td>$0.003564$</td>
<td>$0.015637$</td>
<td>$0.023201$</td>
<td>$0.033819$</td>
</tr>
<tr>
<td>$K_2.10^6$</td>
<td>$2.53$</td>
<td>$2.26$</td>
<td>$2.15$</td>
<td>$2.30$</td>
<td>$2.90$</td>
</tr>
</tbody>
</table>
Table (11).

\( K_2 \) for Adipic Acid assuming \( K_1 = 3.72 \times 10^{-5} \) \hfill (61)

<table>
<thead>
<tr>
<th></th>
<th>( f_1 )</th>
<th>( f_2 )</th>
<th>((H^+)_{10^5})</th>
<th>((A'))</th>
<th>((HA'))</th>
<th>((M_A'))</th>
<th>((K\cdot10^5))</th>
<th>( K_2 \cdot 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>.020313</td>
<td>.036917</td>
<td>.049737</td>
<td>.064295</td>
<td>.079030</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.87028</td>
<td>.83773</td>
<td>.31997</td>
<td>.30405</td>
<td>.79099</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.57364</td>
<td>.49253</td>
<td>.45208</td>
<td>.41799</td>
<td>.39145</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.3311</td>
<td>.94114</td>
<td>1.0253</td>
<td>1.0900</td>
<td>1.1842</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.000741</td>
<td>.000762</td>
<td>.000781</td>
<td>.000792</td>
<td>.000814</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.003254</td>
<td>.003212</td>
<td>.003175</td>
<td>.003156</td>
<td>.003111</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.0000551</td>
<td>.0000571</td>
<td>.0000589</td>
<td>.0000598</td>
<td>.0000620</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.014837</td>
<td>.031419</td>
<td>.044220</td>
<td>.053766</td>
<td>.073530</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table (12).

$K_2$ for β-methyl Glutaric Acid assuming $K_1 = 5.7 \times 10^{-5}$ \(^{(31)}\)

<table>
<thead>
<tr>
<th></th>
<th>(I)</th>
<th>(f_1)</th>
<th>(f_2)</th>
<th>((H^+)^{10^5})</th>
<th>((A^{\prime\prime}))</th>
<th>((HA'))</th>
<th>((H_2A))</th>
<th>((KCl))</th>
<th>(K_2\cdot10^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.003594</td>
<td>0.010973</td>
<td>0.018147</td>
<td>0.025994</td>
<td>0.032842</td>
<td>0.93774</td>
<td>0.89884</td>
<td>0.87592</td>
<td>0.85740</td>
</tr>
<tr>
<td></td>
<td>0.93774</td>
<td>0.89334</td>
<td>0.87592</td>
<td>0.85740</td>
<td>0.84447</td>
<td>0.77325</td>
<td>0.65271</td>
<td>0.53863</td>
<td>0.54040</td>
</tr>
<tr>
<td></td>
<td>0.77325</td>
<td>0.65271</td>
<td>0.53863</td>
<td>0.54040</td>
<td>0.50358</td>
<td>0.29979</td>
<td>3.4187</td>
<td>3.7903</td>
<td>4.0650</td>
</tr>
<tr>
<td></td>
<td>0.29979</td>
<td>3.4187</td>
<td>3.7903</td>
<td>4.0650</td>
<td>4.2163</td>
<td>0.000386</td>
<td>0.000444</td>
<td>0.000460</td>
<td>0.000480</td>
</tr>
<tr>
<td></td>
<td>0.000386</td>
<td>0.000444</td>
<td>0.000460</td>
<td>0.000480</td>
<td>0.000435</td>
<td>0.002818</td>
<td>0.002739</td>
<td>0.002683</td>
<td>0.002645</td>
</tr>
<tr>
<td></td>
<td>0.002818</td>
<td>0.002739</td>
<td>0.002683</td>
<td>0.002645</td>
<td>0.002636</td>
<td>0.001278</td>
<td>0.001301</td>
<td>0.001342</td>
<td>0.001360</td>
</tr>
<tr>
<td></td>
<td>0.001278</td>
<td>0.001301</td>
<td>0.001342</td>
<td>0.001360</td>
<td>0.001363</td>
<td>0.0007346</td>
<td>0.014546</td>
<td>0.022401</td>
<td>0.029237</td>
</tr>
<tr>
<td></td>
<td>0.0007346</td>
<td>0.014546</td>
<td>0.022401</td>
<td>0.029237</td>
<td></td>
<td>3.2</td>
<td>3.6</td>
<td>3.8</td>
<td>3.9</td>
</tr>
</tbody>
</table>
Table (13).

$K_2$ for $\beta\beta'$-dimethyl Glutaric Acid assuming $K_1 = 1.90 \times 10^{-4}$

<table>
<thead>
<tr>
<th></th>
<th>$f_1$</th>
<th>$f_2$</th>
<th>$(H^+)^{10^5}$</th>
<th>$(A')$</th>
<th>$(HA')$</th>
<th>$(H_2A)$</th>
<th>$(KCl)$</th>
<th>$K_2 \cdot 10^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.93222</td>
<td>.75523</td>
<td>2.0240</td>
<td>.000119</td>
<td>.004095</td>
<td>.000373</td>
<td>0</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>.89538</td>
<td>.64274</td>
<td>2.2434</td>
<td>.000124</td>
<td>.004037</td>
<td>.000337</td>
<td>.007564</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>.85530</td>
<td>.53516</td>
<td>2.5159</td>
<td>.000139</td>
<td>.004061</td>
<td>.000393</td>
<td>.022692</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>.83981</td>
<td>.49746</td>
<td>2.6020</td>
<td>.000139</td>
<td>.004062</td>
<td>.000392</td>
<td>.031274</td>
<td>4.4</td>
</tr>
</tbody>
</table>

(31)
Table (14).

$pK_1$ and $pK_2$ values for some dicarboxylic acids.

<table>
<thead>
<tr>
<th>Acid</th>
<th>A</th>
<th></th>
<th></th>
<th>A</th>
<th></th>
<th></th>
<th>A</th>
<th></th>
<th></th>
<th>A</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td></td>
<td>a</td>
<td>b</td>
<td></td>
<td>a</td>
<td>b</td>
<td></td>
<td>a</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>Malonic</td>
<td>2.37</td>
<td>5.70</td>
<td></td>
<td>2.35</td>
<td>5.66</td>
<td></td>
<td>2.33</td>
<td>5.69</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Succinic</td>
<td>4.22</td>
<td>5.70</td>
<td></td>
<td>4.20</td>
<td>5.60</td>
<td></td>
<td>4.19</td>
<td>5.48</td>
<td></td>
<td>4.22</td>
<td>5.67</td>
<td></td>
</tr>
<tr>
<td>Glutaric</td>
<td>4.35</td>
<td>5.40</td>
<td></td>
<td>4.35</td>
<td>5.42</td>
<td></td>
<td>4.34</td>
<td>5.42</td>
<td></td>
<td>4.39</td>
<td>5.50</td>
<td></td>
</tr>
<tr>
<td>α-methyl Glutaric</td>
<td>4.36</td>
<td>5.37</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>β-methyl Glutaric</td>
<td>4.27</td>
<td>5.37</td>
<td></td>
<td>4.24</td>
<td>-</td>
<td></td>
<td>4.25</td>
<td>6.22</td>
<td></td>
<td>4.25</td>
<td>4.41</td>
<td></td>
</tr>
<tr>
<td>ββ'-dimethyl Glutaric</td>
<td>3.74</td>
<td>6.71</td>
<td></td>
<td>3.72</td>
<td>-</td>
<td></td>
<td>3.70</td>
<td>6.33</td>
<td></td>
<td>3.70</td>
<td>6.34</td>
<td></td>
</tr>
<tr>
<td>Adipic</td>
<td>4.44</td>
<td>5.42</td>
<td></td>
<td>4.43</td>
<td>-</td>
<td></td>
<td>4.42</td>
<td>5.41</td>
<td></td>
<td>4.43</td>
<td>5.42</td>
<td></td>
</tr>
</tbody>
</table>

$pK_1$ values are given in column 'a' and the $pK_2$ values in column 'b'.

A - present work; B - Vogel et alia (30,31,61)
C - Gane and Ingold (35,36); D - Jones and Soper (44)
Table (15).

Analysis of Malonate Buffers.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cu$^{++}$</th>
<th>Ni$^{++}$</th>
<th>Co$^{++}$</th>
<th>Mn$^{++}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.030743</td>
<td>0.032944</td>
<td>0.032983</td>
<td>0.028664</td>
</tr>
<tr>
<td>$f_1$</td>
<td>84.615</td>
<td>84.425</td>
<td>84.420</td>
<td>85.205</td>
</tr>
<tr>
<td>$f_2$</td>
<td>51.751</td>
<td>50.807</td>
<td>50.792</td>
<td>52.703</td>
</tr>
<tr>
<td>$(H^+)^{10^5}$</td>
<td>164.35</td>
<td>12.230</td>
<td>10.223</td>
<td>8.326</td>
</tr>
<tr>
<td>$(HA')$</td>
<td>0.000929</td>
<td>0.002723</td>
<td>0.002792</td>
<td>0.003529</td>
</tr>
<tr>
<td>$(A'^{+})$</td>
<td>0.000002</td>
<td>0.000088</td>
<td>0.000108</td>
<td>0.000161</td>
</tr>
<tr>
<td>$(H_2A)$</td>
<td>0.000811</td>
<td>0.000175</td>
<td>0.000150</td>
<td>0.000157</td>
</tr>
<tr>
<td>$(M^{++})$</td>
<td>0.007973</td>
<td>0.008960</td>
<td>0.008973</td>
<td>0.007765</td>
</tr>
<tr>
<td>$(MA)$</td>
<td>0.002944</td>
<td>0.001540</td>
<td>0.001475</td>
<td>0.000678</td>
</tr>
<tr>
<td>$f_2(H^+)^{10^5}$</td>
<td>85.314</td>
<td>6.2137</td>
<td>5.1922</td>
<td>4.3883</td>
</tr>
<tr>
<td>$K_{MA}.10^4$</td>
<td>0.0158</td>
<td>1.30</td>
<td>1.69</td>
<td>5.11</td>
</tr>
</tbody>
</table>
Table (15) (continued)

<table>
<thead>
<tr>
<th>Cation</th>
<th>$\text{Cd}^{++}$</th>
<th>$\text{Mg}^{++}$</th>
<th>$\text{Ca}^{++}$</th>
<th>$\text{Ba}^{++}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_1$</td>
<td>.83073</td>
<td>.83710</td>
<td>.83750</td>
<td>.83710</td>
</tr>
<tr>
<td>$f_2$</td>
<td>.47625</td>
<td>.49104</td>
<td>.49194</td>
<td>.49104</td>
</tr>
<tr>
<td>$(\text{H}^+)10^5$</td>
<td>5.935</td>
<td>5.594</td>
<td>12.123</td>
<td>10.411</td>
</tr>
<tr>
<td>$(\text{HA}^+)$</td>
<td>.003517</td>
<td>.003659</td>
<td>.004080</td>
<td>.004113</td>
</tr>
<tr>
<td>$(\text{A}^{''})$</td>
<td>.000165</td>
<td>.000266</td>
<td>.000137</td>
<td>.000161</td>
</tr>
<tr>
<td>$(\text{H}_2\text{A})$</td>
<td>.000160</td>
<td>.000106</td>
<td>.000255</td>
<td>.000220</td>
</tr>
<tr>
<td>$(\text{M}^{++})$</td>
<td>.012071</td>
<td>.010623</td>
<td>.010809</td>
<td>.010886</td>
</tr>
<tr>
<td>$(\text{MA})$</td>
<td>.000632</td>
<td>.000494</td>
<td>.000080</td>
<td>.000031</td>
</tr>
<tr>
<td>$f_2(\text{H}^+)10^5$</td>
<td>4.2551</td>
<td>2.7467</td>
<td>5.9646</td>
<td>5.1120</td>
</tr>
<tr>
<td>$K_{\text{MA}}10^4$</td>
<td>6.63</td>
<td>13.8</td>
<td>45.0</td>
<td>141</td>
</tr>
</tbody>
</table>
Table (16).

Analysis of Succinate Buffers.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cu$^{++}$</th>
<th>Cd$^{++}$</th>
<th>Ni$^{++}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.034120</td>
<td>0.041409</td>
<td>0.035255</td>
</tr>
<tr>
<td>f$_1$</td>
<td>0.34225</td>
<td>0.33100</td>
<td>0.34039</td>
</tr>
<tr>
<td>f$_2$</td>
<td>0.50327</td>
<td>0.47637</td>
<td>0.49879</td>
</tr>
<tr>
<td>(H$^+$)$_10^5$</td>
<td>5.7070</td>
<td>4.3775</td>
<td>3.6242</td>
</tr>
<tr>
<td>(HA$'$)</td>
<td>0.002016</td>
<td>0.002679</td>
<td>0.002961</td>
</tr>
<tr>
<td>(A$''$)</td>
<td>0.000140</td>
<td>0.000257</td>
<td>0.000323</td>
</tr>
<tr>
<td>(H$_2$A)</td>
<td>0.001363</td>
<td>0.001351</td>
<td>0.001265</td>
</tr>
<tr>
<td>(M$^{++}$)</td>
<td>0.009049</td>
<td>0.012453</td>
<td>0.010415</td>
</tr>
<tr>
<td>(MA)</td>
<td>0.001067</td>
<td>0.000300</td>
<td>0.000330</td>
</tr>
<tr>
<td>f$_2$(H$^+$)$_10^5$</td>
<td>2.0720</td>
<td>2.0075</td>
<td>1.0077</td>
</tr>
<tr>
<td>K$_{MA}10^3$</td>
<td>323</td>
<td>2.42</td>
<td>2.60</td>
</tr>
</tbody>
</table>
Table (16) (continued)

<table>
<thead>
<tr>
<th>Cation</th>
<th>Co$^{++}$</th>
<th>Mn$^{++}$</th>
<th>Mg$^{++}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.034736</td>
<td>0.029036</td>
<td>0.035193</td>
</tr>
<tr>
<td>f$_1$</td>
<td>0.34121</td>
<td>0.35125</td>
<td>0.34050</td>
</tr>
<tr>
<td>f$_2$</td>
<td>0.50077</td>
<td>0.52510</td>
<td>0.49907</td>
</tr>
<tr>
<td>($H^+$)$_{10^5}$</td>
<td>4.1840</td>
<td>3.4967</td>
<td>3.6791</td>
</tr>
<tr>
<td>(HA')</td>
<td>0.002759</td>
<td>0.002947</td>
<td>0.002940</td>
</tr>
<tr>
<td>(A&quot;)</td>
<td>0.000263</td>
<td>0.000321</td>
<td>0.000320</td>
</tr>
<tr>
<td>(H$_2$A)</td>
<td>0.001364</td>
<td>0.001247</td>
<td>0.001276</td>
</tr>
<tr>
<td>(M$^{++}$)</td>
<td>0.010264</td>
<td>0.008288</td>
<td>0.010397</td>
</tr>
<tr>
<td>(MA)</td>
<td>0.000200</td>
<td>0.000155</td>
<td>0.000051</td>
</tr>
<tr>
<td>f$<em>2$($H^+$)$</em>{10^5}$</td>
<td>2.0951</td>
<td>1.8361</td>
<td>1.8314</td>
</tr>
<tr>
<td>$K_{MA} \cdot 10^3$</td>
<td>3.39</td>
<td>4.73</td>
<td>16.3</td>
</tr>
</tbody>
</table>
Table (17).

Analysis of Glutarate Buffers.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cu^{++}</th>
<th>Cd^{++}</th>
<th>Mn^{++}</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.034786</td>
<td>0.033676</td>
<td>0.030418</td>
</tr>
<tr>
<td>f_1</td>
<td>0.84115</td>
<td>0.83500</td>
<td>0.84877</td>
</tr>
<tr>
<td>f_2</td>
<td>0.50063</td>
<td>0.48613</td>
<td>0.51899</td>
</tr>
<tr>
<td>(H^+)10^5</td>
<td>4.4660</td>
<td>2.9157</td>
<td>2.4874</td>
</tr>
<tr>
<td>(HA')</td>
<td>0.001971</td>
<td>0.002541</td>
<td>0.002642</td>
</tr>
<tr>
<td>(A'')</td>
<td>0.000348</td>
<td>0.000708</td>
<td>0.000808</td>
</tr>
<tr>
<td>(H_2A)</td>
<td>0.001399</td>
<td>0.001161</td>
<td>0.001064</td>
</tr>
<tr>
<td>(M^{++})</td>
<td>0.010015</td>
<td>0.011223</td>
<td>0.008406</td>
</tr>
<tr>
<td>(MA)</td>
<td>0.000863</td>
<td>0.000171</td>
<td>0.000067</td>
</tr>
<tr>
<td>f_2(H^+)10^5</td>
<td>2.2360</td>
<td>1.4171</td>
<td>1.2909</td>
</tr>
<tr>
<td>K_{MA}10^3</td>
<td>1.01</td>
<td>10.9</td>
<td>27.3</td>
</tr>
</tbody>
</table>
Table (18).

Analysis of Glutarate Buffers using the value of $K_2$
obtained by Stock's method. $K_2 = 2.51 \times 10^{-6}$.

<table>
<thead>
<tr>
<th>Cation</th>
<th>$Cu^{++}$</th>
<th>$Cd^{++}$</th>
<th>$Mn^{++}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I$</td>
<td>.0334290</td>
<td>.037652</td>
<td>.029261</td>
</tr>
<tr>
<td>$f_1$</td>
<td>.34200</td>
<td>.33657</td>
<td>.35091</td>
</tr>
<tr>
<td>$f_2$</td>
<td>.50262</td>
<td>.48982</td>
<td>.52427</td>
</tr>
<tr>
<td>$(H^+)^{10^5}$</td>
<td>4.4487</td>
<td>2.8937</td>
<td>2.4623</td>
</tr>
<tr>
<td>$(A^\prime)$</td>
<td>.000222</td>
<td>.000451</td>
<td>.000515</td>
</tr>
<tr>
<td>$(H_2A)$</td>
<td>.001397</td>
<td>.001157</td>
<td>.001059</td>
</tr>
<tr>
<td>$(HA^\prime)$</td>
<td>.001975</td>
<td>.002548</td>
<td>.002650</td>
</tr>
<tr>
<td>$(M^{++})$</td>
<td>.009891</td>
<td>.010973</td>
<td>.008117</td>
</tr>
<tr>
<td>$(MA)$</td>
<td>.00987</td>
<td>.00424</td>
<td>.000356</td>
</tr>
<tr>
<td>$f_2(H^+)^{10^5}$</td>
<td>2.2360</td>
<td>1.4174</td>
<td>1.2909</td>
</tr>
<tr>
<td>$K_{MA} \cdot 10^3$</td>
<td>0.56</td>
<td>2.8</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Table (18) (continued)

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ni^{++}</th>
<th>Co^{++}</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.36291</td>
<td>0.35873</td>
</tr>
<tr>
<td>f_1</td>
<td>0.33871</td>
<td>0.33940</td>
</tr>
<tr>
<td>f_2</td>
<td>0.49486</td>
<td>0.49646</td>
</tr>
<tr>
<td>(H^+)10^5</td>
<td>2.2477</td>
<td>2.3603</td>
</tr>
<tr>
<td>(HA')</td>
<td>0.002780</td>
<td>0.002303</td>
</tr>
<tr>
<td>(A&quot;)</td>
<td>0.000627</td>
<td>0.000602</td>
</tr>
<tr>
<td>(H_2A)</td>
<td>0.000985</td>
<td>0.001047</td>
</tr>
<tr>
<td>(M^{++})</td>
<td>0.010421</td>
<td>0.010340</td>
</tr>
<tr>
<td>(MA)</td>
<td>0.00188</td>
<td>0.00123</td>
</tr>
<tr>
<td>f_2(H^+)10^5</td>
<td>1.1123</td>
<td>1.1718</td>
</tr>
<tr>
<td>K_{MA}10^3</td>
<td>8.5</td>
<td>12.0</td>
</tr>
</tbody>
</table>
Table (19).

Analysis of Adipate Buffers.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cu++</th>
<th>Cd++</th>
<th>Co++</th>
<th>Ni++</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.034040</td>
<td>0.039657</td>
<td>0.036276</td>
<td>0.036750</td>
</tr>
<tr>
<td>f_1</td>
<td>0.84240</td>
<td>0.83503</td>
<td>0.83973</td>
<td>0.83800</td>
</tr>
<tr>
<td>f_2</td>
<td>0.50359</td>
<td>0.48623</td>
<td>0.49490</td>
<td>0.49313</td>
</tr>
<tr>
<td>(H^+)10^5</td>
<td>4.0263</td>
<td>2.4406</td>
<td>2.2326</td>
<td>2.3310</td>
</tr>
<tr>
<td>(HA')</td>
<td>0.001856</td>
<td>0.002414</td>
<td>0.002487</td>
<td>0.002515</td>
</tr>
<tr>
<td>(A'')</td>
<td>0.000346</td>
<td>0.000769</td>
<td>0.000851</td>
<td>0.000827</td>
</tr>
<tr>
<td>(H_2A)</td>
<td>0.001452</td>
<td>0.001126</td>
<td>0.001970</td>
<td>0.001123</td>
</tr>
<tr>
<td>(M^++)</td>
<td>0.009787</td>
<td>0.011155</td>
<td>0.010321</td>
<td>0.010529</td>
</tr>
<tr>
<td>(MA)</td>
<td>0.000893</td>
<td>0.000236</td>
<td>0.000136</td>
<td>0.000081</td>
</tr>
<tr>
<td>f_2(H^+)10^5</td>
<td>2.0276</td>
<td>1.1867</td>
<td>1.1049</td>
<td>1.1495</td>
</tr>
<tr>
<td>K_{MA}10^3</td>
<td>0.963</td>
<td>8.59</td>
<td>15.8</td>
<td>26.1</td>
</tr>
</tbody>
</table>
Table (20).

Analysis of Adipate Buffers using a value for $K_2$
determined by Stock's method. $K_2 = 1.1 \times 10^{-6}$.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cu$^{++}$</th>
<th>Cd$^{++}$</th>
<th>Co$^{++}$</th>
<th>Ni$^{++}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.033692</td>
<td>0.036531</td>
<td>0.033920</td>
<td>0.034432</td>
</tr>
<tr>
<td>$f_1$</td>
<td>0.84300</td>
<td>0.83333</td>
<td>0.84300</td>
<td>0.83333</td>
</tr>
<tr>
<td>$f_2$</td>
<td>0.50503</td>
<td>0.49394</td>
<td>0.50406</td>
<td>0.50207</td>
</tr>
<tr>
<td>$(H^+)^{10^5}$</td>
<td>4.0148</td>
<td>2.4025</td>
<td>2.1920</td>
<td>2.2895</td>
</tr>
<tr>
<td>$(HA')$</td>
<td>0.001877</td>
<td>0.002445</td>
<td>0.002519</td>
<td>0.002541</td>
</tr>
<tr>
<td>$(A^-)$</td>
<td>0.000102</td>
<td>0.000227</td>
<td>0.000251</td>
<td>0.000243</td>
</tr>
<tr>
<td>$(HA)$</td>
<td>0.001441</td>
<td>0.001111</td>
<td>0.001055</td>
<td>0.001109</td>
</tr>
<tr>
<td>$(M^{++})$</td>
<td>0.009554</td>
<td>0.010628</td>
<td>0.009738</td>
<td>0.009953</td>
</tr>
<tr>
<td>$(MA)$</td>
<td>0.001126</td>
<td>0.000762</td>
<td>0.000719</td>
<td>0.000657</td>
</tr>
<tr>
<td>$f_2(H^+)^{10^5}$</td>
<td>2.0276</td>
<td>1.1867</td>
<td>1.1049</td>
<td>1.1495</td>
</tr>
<tr>
<td>$K_{MA} \cdot 10^4$</td>
<td>2.3</td>
<td>7.7</td>
<td>8.6</td>
<td>9.4</td>
</tr>
</tbody>
</table>
Table (20) (continued).

<table>
<thead>
<tr>
<th>Cation</th>
<th>Mn$^{++}$</th>
<th>Mg$^{++}$</th>
<th>Ca$^{++}$</th>
<th>Ba$^{++}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>l</td>
<td>0.028420</td>
<td>0.035888</td>
<td>0.035960</td>
<td>0.038091</td>
</tr>
<tr>
<td>f_1</td>
<td>0.85255</td>
<td>0.83935</td>
<td>0.83925</td>
<td>0.83591</td>
</tr>
<tr>
<td>f_2</td>
<td>0.52830</td>
<td>0.49637</td>
<td>0.49613</td>
<td>0.48824</td>
</tr>
<tr>
<td>(H^+)_{10^5}</td>
<td>1.8238</td>
<td>1.9865</td>
<td>1.9420</td>
<td>1.6685</td>
</tr>
<tr>
<td>(HA')</td>
<td>0.002681</td>
<td>0.002745</td>
<td>0.002773</td>
<td>0.002372</td>
</tr>
<tr>
<td>(A'')</td>
<td>0.000361</td>
<td>0.000306</td>
<td>0.000316</td>
<td>0.000338</td>
</tr>
<tr>
<td>(H_2A)</td>
<td>0.000957</td>
<td>0.001034</td>
<td>0.001021</td>
<td>0.000901</td>
</tr>
<tr>
<td>(M'')</td>
<td>0.007872</td>
<td>0.010435</td>
<td>0.010460</td>
<td>0.009752</td>
</tr>
<tr>
<td>(MA)</td>
<td>0.000601</td>
<td>0.000459</td>
<td>0.000434</td>
<td>0.000334</td>
</tr>
<tr>
<td>f_2(H^+)_{10^5}</td>
<td>0.9635</td>
<td>0.9861</td>
<td>0.9635</td>
<td>0.8146</td>
</tr>
<tr>
<td>K_{MA} \cdot 10^4</td>
<td>11.0</td>
<td>17.1</td>
<td>18.8</td>
<td>26.7</td>
</tr>
</tbody>
</table>
Table (21).

Analysis of α-methyl Glutarate Buffers.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cu⁺⁺</th>
<th>Cd⁺⁺</th>
<th>Mn⁺⁺</th>
<th>Ni⁺⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.034308</td>
<td>0.040692</td>
<td>0.028491</td>
<td>0.035736</td>
</tr>
<tr>
<td>f₁</td>
<td>0.34195</td>
<td>0.3203</td>
<td>0.35239</td>
<td>0.33961</td>
</tr>
<tr>
<td>f₂</td>
<td>0.50252</td>
<td>0.47924</td>
<td>0.52791</td>
<td>0.49696</td>
</tr>
<tr>
<td>(H⁺)₁₀⁵</td>
<td>7.5929</td>
<td>5.3831</td>
<td>4.1814</td>
<td>4.2599</td>
</tr>
<tr>
<td>(HA⁺⁺)</td>
<td>0.001514</td>
<td>0.001971</td>
<td>0.002203</td>
<td>0.002223</td>
</tr>
<tr>
<td>(A⁺⁺)</td>
<td>0.000169</td>
<td>0.000331</td>
<td>0.000425</td>
<td>0.000446</td>
</tr>
<tr>
<td>(H₂A)</td>
<td>0.001866</td>
<td>0.001649</td>
<td>0.001536</td>
<td>0.001528</td>
</tr>
<tr>
<td>(M⁺⁺)</td>
<td>0.010143</td>
<td>0.012224</td>
<td>0.008129</td>
<td>0.010537</td>
</tr>
<tr>
<td>(MA)</td>
<td>0.000930</td>
<td>0.000529</td>
<td>0.000315</td>
<td>0.000281</td>
</tr>
<tr>
<td>f₂(H⁺)₁₀⁵</td>
<td>3.8156</td>
<td>2.5319</td>
<td>2.2086</td>
<td>2.1170</td>
</tr>
<tr>
<td>K₉MA·₁₀³</td>
<td>0.465</td>
<td>1.76</td>
<td>3.07</td>
<td>4.13</td>
</tr>
</tbody>
</table>
Table (22).

Analysis of β-methyl Glutarate Buffers.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cu&lt;sup&gt;++&lt;/sup&gt;</th>
<th>Cd&lt;sup&gt;++&lt;/sup&gt;</th>
<th>Mn&lt;sup&gt;++&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.034533</td>
<td>0.040772</td>
<td>0.028691</td>
</tr>
<tr>
<td>f&lt;sub&gt;1&lt;/sub&gt;</td>
<td>0.84159</td>
<td>0.83191</td>
<td>0.85201</td>
</tr>
<tr>
<td>f&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.50165</td>
<td>0.47899</td>
<td>0.52698</td>
</tr>
<tr>
<td>(H&lt;sup&gt;+&lt;/sup&gt;)&lt;sup&gt;10&lt;/sup&gt;</td>
<td>7.9252</td>
<td>5.5646</td>
<td>4.2019</td>
</tr>
<tr>
<td>(HA')</td>
<td>0.001761</td>
<td>0.002336</td>
<td>0.002547</td>
</tr>
<tr>
<td>(A&quot;)</td>
<td>0.000133</td>
<td>0.000252</td>
<td>0.000345</td>
</tr>
<tr>
<td>(H&lt;sub&gt;2&lt;/sub&gt;A)</td>
<td>0.001749</td>
<td>0.001524</td>
<td>0.001375</td>
</tr>
<tr>
<td>(M&lt;sup&gt;++&lt;/sup&gt;)</td>
<td>0.010228</td>
<td>0.012276</td>
<td>0.008223</td>
</tr>
<tr>
<td>(MA)</td>
<td>0.000845</td>
<td>0.000477</td>
<td>0.000221</td>
</tr>
<tr>
<td>f&lt;sub&gt;2&lt;/sub&gt;(H&lt;sup&gt;+&lt;/sup&gt;)&lt;sup&gt;10&lt;/sup&gt;</td>
<td>3.9757</td>
<td>2.6654</td>
<td>2.2143</td>
</tr>
<tr>
<td>K&lt;sub&gt;MA&lt;/sub&gt;&lt;sup&gt;10&lt;/sup&gt;</td>
<td>0.404</td>
<td>1.49</td>
<td>3.55</td>
</tr>
</tbody>
</table>
Table (22) (continued)

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ni$^{++}$</th>
<th>Co$^{++}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.034688</td>
<td>0.035083</td>
</tr>
<tr>
<td>$f_1$</td>
<td>0.84133</td>
<td>0.84070</td>
</tr>
<tr>
<td>$f_2$</td>
<td>0.50105</td>
<td>0.49952</td>
</tr>
<tr>
<td>$(H^+)^{10^5}$</td>
<td>4.2752</td>
<td>3.9132</td>
</tr>
<tr>
<td>$(HA')$</td>
<td>0.002557</td>
<td>0.002678</td>
</tr>
<tr>
<td>$(A''')$</td>
<td>0.000358</td>
<td>0.000411</td>
</tr>
<tr>
<td>$(H_2A)$</td>
<td>0.001369</td>
<td>0.001311</td>
</tr>
<tr>
<td>$(M^{++})$</td>
<td>0.010217</td>
<td>0.010332</td>
</tr>
<tr>
<td>$(MA)$</td>
<td>0.000203</td>
<td>0.000088</td>
</tr>
<tr>
<td>$f_2(H^+)^{10^5}$</td>
<td>2.1421</td>
<td>1.9547</td>
</tr>
<tr>
<td>$K_{M^+_A}^{10^3}$</td>
<td>4.52</td>
<td>12.0</td>
</tr>
</tbody>
</table>
### Analysis of ββ'-dimethyl Glutarate Buffers

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cu^{+ +}</th>
<th>Cd^{+ +}</th>
<th>Mn^{+ +}</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.035620</td>
<td>0.035936</td>
<td>0.036587</td>
</tr>
<tr>
<td>f_1</td>
<td>0.83980</td>
<td>0.83927</td>
<td>0.83325</td>
</tr>
<tr>
<td>f_2</td>
<td>0.49741</td>
<td>0.49618</td>
<td>0.49277</td>
</tr>
<tr>
<td>(H^+)_10^5</td>
<td>5.5166</td>
<td>6.6246</td>
<td>5.0163</td>
</tr>
<tr>
<td>(HA')</td>
<td>0.003441</td>
<td>0.003508</td>
<td>0.003720</td>
</tr>
<tr>
<td>(A'')</td>
<td>0.000055</td>
<td>0.000052</td>
<td>0.000074</td>
</tr>
<tr>
<td>(H A)_2</td>
<td>0.000704</td>
<td>0.000860</td>
<td>0.000689</td>
</tr>
<tr>
<td>(M^{+ +})</td>
<td>0.010410</td>
<td>0.010627</td>
<td>0.010796</td>
</tr>
<tr>
<td>(MA)</td>
<td>0.000390</td>
<td>0.000191</td>
<td>0.000128</td>
</tr>
<tr>
<td>f_2(H^+)_10^5</td>
<td>2.7440</td>
<td>3.2870</td>
<td>2.4719</td>
</tr>
<tr>
<td>K_{MA}10^3</td>
<td>0.366</td>
<td>0.716</td>
<td>1.51</td>
</tr>
</tbody>
</table>
Table (23) (continued)

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ni\textsuperscript{2+}</th>
<th>Co\textsuperscript{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.036510</td>
<td>0.034985</td>
</tr>
<tr>
<td>(f_1)</td>
<td>0.83887</td>
<td>0.84083</td>
</tr>
<tr>
<td>(f_2)</td>
<td>0.49403</td>
<td>0.49985</td>
</tr>
<tr>
<td>((H^+)\times10^5)</td>
<td>4.1761</td>
<td>7.1547</td>
</tr>
<tr>
<td>((H_4))</td>
<td>0.003836</td>
<td>0.003600</td>
</tr>
<tr>
<td>((A))</td>
<td>0.000091</td>
<td>0.000044</td>
</tr>
<tr>
<td>((H_2A))</td>
<td>0.000592</td>
<td>0.000096</td>
</tr>
<tr>
<td>((M'))</td>
<td>0.010739</td>
<td>0.010411</td>
</tr>
<tr>
<td>((Ma))</td>
<td>0.000092</td>
<td>0.000001</td>
</tr>
<tr>
<td>(f_2(H^+)\times10^5)</td>
<td>2.0631</td>
<td>3.5763</td>
</tr>
<tr>
<td>(K_{Ma}\times10^3)</td>
<td>2.60</td>
<td>12.1</td>
</tr>
</tbody>
</table>
Table (24).

\[ K_{MA} \times 10^4 \]

<table>
<thead>
<tr>
<th>Acid</th>
<th>Cu++</th>
<th>Ni++</th>
<th>Co++</th>
<th>Mn++</th>
<th>Cd++</th>
<th>Mg++</th>
<th>Ca++</th>
<th>Ba++</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malonic</td>
<td>0.0158</td>
<td>1.30</td>
<td>1.69</td>
<td>5.11</td>
<td>6.63</td>
<td>13.8</td>
<td>4.0</td>
<td>141</td>
</tr>
<tr>
<td>Succinic</td>
<td>3.28</td>
<td>33.9</td>
<td>260</td>
<td>47.3</td>
<td>24.2</td>
<td>163</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Glutaric</td>
<td>10.1</td>
<td>-</td>
<td>-</td>
<td>273</td>
<td>109</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>α-methyl Glutaric</td>
<td>4.65</td>
<td>47.3</td>
<td>-</td>
<td>30.7</td>
<td>17.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>β-methyl Glutaric</td>
<td>4.04</td>
<td>45.2</td>
<td>120</td>
<td>35.5</td>
<td>14.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ββ'-dimethyl Glutaric</td>
<td>3.66</td>
<td>26.0</td>
<td>121</td>
<td>15.1</td>
<td>7.16</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Adipic</td>
<td>9.63</td>
<td>261</td>
<td>158</td>
<td>-</td>
<td>85.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table (25).

Dissociation Constants of Copper Salts.

<table>
<thead>
<tr>
<th>Acid</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malonic</td>
<td>0.0158</td>
<td>0.0159</td>
<td>0.025</td>
</tr>
<tr>
<td>Succinic</td>
<td>3.27</td>
<td>4.7</td>
<td>2.71</td>
</tr>
<tr>
<td>Glutaric</td>
<td>10.1</td>
<td>6.9</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha$-methyl Glutaric</td>
<td>4.65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\beta$-methyl Glutaric</td>
<td>4.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\beta\beta'$-dimethyl Glutaric</td>
<td>3.66</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Adipic</td>
<td>9.63</td>
<td>4.2</td>
<td>-</td>
</tr>
</tbody>
</table>

I - present work, II - Peacock and James (9),
III - Stock and Davies (4)
(vii). Discussion of Results.

The dissociation constants of the bi-bivalent metal salts are collected in Table (24). There are only two sets of data with which comparison can be made: the values obtained by Stock and Davies (4) for the metal malonates, and by Peacock and James (9) for the copper salts of malonic, succinic glutaric and adipic acids. In general the values obtained in the present work are in good agreement with those published previously. For purposes of comparison all the published values for the dissociation constants of the copper salts are collected in Table (25).

The method suggested by Stock and Davies (4) has been carefully examined, and its usefulness tested by applying it to the determination of the dissociation constants of a considerable number of bi-bivalent salts. During the calculation of the results it became apparent that the method was suitable in the case of weak electrolytes (i.e. with dissociation constants of the order of $10^{-3}$ or less), but that for the more highly dissociated salts there was considerable uncertainty in the value of $K$. Stock (16) found that when the dissociation constants for the succinates were calculated, using the values for the primary and secondary thermodynamic dissociation constants given in the literature, in the case of the barium and calcium salts he was unable to obtain real values (i.e.}
the calculated concentration of the ion-pair was negative.)
This difficulty was overcome by determining an arbitrary value for \( K_2 \), by the colorimetric method discussed above. The same difficulty was encountered in the present work, but it was found that in some cases (e.g., calcium and barium glutarate) unreal values were obtained even when the arbitrary value of \( K_2 \) was used in the calculation. This is difficult to explain, as the \( K_2 \) value is calculated on the assumption that the potassium salt is completely dissociated. A possible explanation is that the values used for the individual ion activity coefficients are in error, and consequently incorrect values of \((A^-)\), \((H^+)\) and \((H_2A^-)\) are obtained.

Stock (16) demonstrated that for malonate and succinate buffers, equality of indicator colour means equality of \( f_2(H^+) \) if the colour change of the indicator is accompanying the second stage of dissociation of a dibasic acid indicator. In the present work it has been assumed that this relationship holds for all the acids used. This assumption appears to be justified by the good agreement between the values obtained for the primary and secondary thermodynamic dissociation constants of the acids by the colorimetric method, and the published values obtained conductimetrically and potentiometrically. The \( K_2 \) values calculated by Stock's method, using a \( K_1 \) determined conductimetrically, in some cases (e.g., adipic and glutaric acids) differ considerably from those obtained by the
modified Speakman method. This again seems to indicate some error in calculating the concentrations of the species $A^-$, $HA^+$ and $H_2A$, by Stock's method. No such calculation is involved in the Speakman method.

In five determinations of the dissociation constant of copper $\beta\beta'$-dimethyl glutarate a reproducibility of $\pm 0.2$ was obtained. With the stronger salts however, there was a much greater variation in the values obtained. This is not unexpected when the method of calculation is examined. The concentration of the ion-pair $MA$ is determined by difference. For the stronger salts this involves the subtraction of two figures of approximately the same value. There is therefore considerable uncertainty in the value derived for $\langle MA \rangle$. Calculations on pp. 50 - 54 show how the value obtained for the dissociation constant is affected by various experimental errors.

In the series $\text{COOH} \cdot (\text{CH}_2)_n \cdot \text{COOH}$ there is a general tendency for the stability of the metal dicarboxylate to decrease as $'n'$ increases, the decrease being greatest in going from the malonates to the succinates. For the salts of the alkyl substituted acids the stability is greater than for the unsubstituted ones. The adipates appear to be weaker than the glutarates. This has been noted by other authors (9, 14), but no explanation has been offered.
Bjerrum (25) calculated from the Boltzmann potential energy-concentration relationship that:

$$\log \frac{K_1}{K_2} - 0.6 = 3.1 \times 10^{-8}/r$$

where $K_1$ and $K_2$ are the primary and secondary thermodynamic dissociation constants of the acid, and $'r'$ the distance between the carboxyl groups. The Bjerrum formula gives values of $'r'$ which are of the right order, but no quantitative accuracy can be expected as a number of important factors are overlooked in the derivation. Gane and Ingold (36) considered these factors and concluded that when internally propagated polar factors are negligible, the Bjerrum formula will place the acids in the right order, but will not give physically accurate values for the intercarboxylic distances. A modified form of the Bjerrum equation was suggested by Gane and Ingold taking into account the interionic and solvent effects. Jones and Soper (44) later showed that when $'r' > 4\AA$, these corrections are not important.

The primary and secondary thermodynamic dissociation constants of a number of acids of the series $\text{COOH} \cdot (\text{CH}_2)_n \cdot \text{COOH}$ were determined potentiometrically by Gane and Ingold. From these values the intercarboxylic distance $'r'$ was calculated. Consideration of these values led the authors to suggest that the most appropriate model for the normal acids was a plane zig-zag. This model is also in accordance with the results of X-ray analysis of the crystalline compounds. When the results
for the β substituted acids were studied it was seen that the 'r' value for the normal acid was much larger than for the substituted acid. It was suggested that substitution on the methylene chain caused a departure from the zig-zag pattern, and that the molecule assumed a coiled configuration.

Since the size of the ions is one of the factors affecting the stability of an ion-pair, the results obtained in the present work are in agreement with the above. Although no data appear in the literature for the actual radii of the organic anions it can be inferred from the 'r' values that there is an increase along the series from malonic to adipic. If the effect of substitution on the methylene chain is to bend the chain, then it is reasonable to assume that the effective radius of the ion is reduced. This would lead to an enhanced stability of the ion-pair. The closer proximity of the carboxyl groups would also facilitate the formation of a covalent bond between the two ions, this again leading to a greater stability. This enhanced stability has in fact been observed; the α- and β-methyl glutarates are weaker than the normal glutarates. The introduction of a second substituent on the methylene chain should cause a further coiling of the molecule, and an ion-pair formed with this anion should have greater stability than one involving a monosubstituted anion. This has also been borne out in the present work; the β'-dimethyl glutarates are more stable than the α- and β-methyl glutarates.
Mellor and Maley (62) reported the dissociation constants of a number of bivalent metal complexes with salicylaldehyde in 50% dioxan, and noted that the order of stabilities was the same with various other ligands. Monk (63) from a study of the dissociation constants of a number of metal complexes with glycine, glycyl glycine and several carboxylic acids concluded that the tendency to form complexes was in the order:

\[ \text{Cu} > \text{Ni} > \text{Zn} > \text{Pb} \approx \text{Co} > \text{Mn} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}. \]

A study of all the available data for the stability of metal complexes however shows that the sequences given by Mellor and Maley, and by Monk are not invariable. For example the sequence \( \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba} \) does not hold for glycylglycine or for malic acid. Topp and Davies (14) also noted that the order \( \text{Mg} > \text{Ca} > \text{Ba} \) varied with the ligand.

Irving and Williams (64) observed that when the stability constants of a number of complexes of the first transition metals were plotted against the atomic number, there was a monotonic increase to a maximum at copper, irrespective of the ligand. This led them to suggest the 'Irving-Williams' order of stabilities \( \text{Cu} > \text{Ni} > \text{Co} > \text{Mn} \). An extensive survey of the existing data showed that this order held invariably for all metal chelates.

The stability of the transition metal complexes have been correlated with the cationic radii, and the second ionisation
potential, which is taken as a measure of the electron affinity of the cation (65). The radii of the cations decrease slightly from manganese to copper, which is the order of increasing stability. The second ionisation potential increases from manganese to copper. If the sequence is extended by including other bivalent metals, the order of decreasing ionic radii will not necessarily be that of increasing stability. This is seen when the stabilities of the alkaline earth metal complexes are considered. Although the radius of the magnesium ion is smaller than that of any of the transition metals, yet the stabilities of its complexes are much lower.

The stability of a complex depends on two main factors:

1. The hydration energy of the cation
2. The energy of interaction of the ions.

In most of the ion-pairs that have been studied in the present work it is apparent that the hydration energy plays relatively an insignificant part. When the order of stabilities follows that of the ionic radii, the interaction energy is the dominant factor. Deviations from this order can be attributed to the increasing contribution of the hydration energy. The anomalous position of magnesium in the series is due to its higher degree of hydration. The 'Irving-Williams' order of stabilities holds for most of the ligands studied, deviations appearing as the number of carbon atoms in the acid increases. The inclusion of a metal not of the transition family causes disruption of the
sequence as expected. Cadmium changes its position in the sequence as the ligand varies. Although the radius of the cadmium ion is greater than that of the nickel ion, its ionisation potential is approximately the same, so that one would expect the relative position of these two cations in the sequence to vary with the ligand.

Irving and Williams based their order of stabilities on a study of the data for compounds which were chelate in character. The corresponding order of stabilities found in the present work seems to indicate that chelation forces predominate in the salts studied. This is borne out by a study of the Bjerrum distances calculated from the dissociation constants, which shows that Bjerrum's assumption of Coulombic forces only between the ions is untenable. No data was obtained for alkaline earth metal salts other than the malonates. The stabilities of these salts are in the order of the bare cationic radii, indicating that the forces are chelate in character. This is in striking contrast to the order for the corresponding thiosulphates (66), where the forces are predominantly electrostatic. The absolute values for the adipates (using an arbitrary $K_2$) are probably incorrect, but it is interesting to note that the same order of stability holds $\text{Mg} > \text{Ca} > \text{Ba}$. In all cases copper forms the most stable ion-pair. This has been correlated with its ability to use the $\text{dsp}^2$ orbitals, although some doubt has been cast recently on the validity of this assumption (67).
Solubility Study of Copper Malonate.
Contents

(i) Introduction ........................................... (97)

(ii) Experimental ......................................... (102)

(iii) Tables and Graphs ................................. (111)

(iv) Calculations ........................................... (117)

(v) Discussion ............................................. (132)
(1) Introduction.

The anomalous solubility of bivalent metal oxalates in solutions of sodium and potassium oxalates has been explained on the basis of the formation in the solution of complex ions of the type $\text{MO}_x^2$. Money and Davies (18) showed that the solubility of manganese oxalate in solutions of potassium and sodium oxalate showed an initial fall to a minimum, with a subsequent rise. This they believed was due to the formation of $\text{MnO}_x^2$ by the process:

$$\text{MnO}_x + \text{O}_x^2 \rightleftharpoons \text{MnO}_x^2$$

Previous conductivity work by Scholder and Linstrom (69) provided a value for the dissociation constant of manganese oxalate which enabled Money and Davies to derive the instability constant for the complex anion $\text{MnO}_x^2$. Similar results were obtained by Clayton and Vosburgh (70) for zinc and cadmium oxalates. Topp (15) showed that magnesium oxalate exhibited the same enhanced solubility. He extended this work to manganese oxalate, and found that the solubility passed through a minimum in solutions of the corresponding metal chloride. This behaviour he was unable to explain. The solubility of manganese oxalate was measured in potassium nitrate solutions. Topp assumed that the only effect of the added salt was to increase the ionic strength, to modify the activity coefficients of the ions and perhaps change $\mu$ (the
activity coefficient of the undissociated ion-pair). A second series of measurements in 0.005 M MCl₂ plus KNO₃ was made. The object of the excess M⁺⁺ being to minimise the amount of simple ionisation, so that any increase in solubility could be attributed to a change in f_u.

In his manganese oxalate series Topp obtained fair agreement and concluded that f_u decreased with increasing I. However in the magnesium oxalate series the values of f_u varied between 1.0 and 1.1. He concluded that errors were present, both experimental and in the values of the constants he had taken for his calculations.

Stock repeated the calculations using a different equation for the activity coefficient, and allowing for undissociated potassium nitrate and KOX⁻. The results obtained were significantly different. He found no trend in the value for f_u, which he concluded could be regarded as unity up to an ionic strength of 0.1. In his manganese oxalate series Topp assumed that the MCl₂ and M(NO₃)₂ added was completely dissociated, and made no allowance for MCl⁺ and MNO₃⁺. Conductivity data appeared to justify this assumption in the case of the magnesium salt, but lack of suitable data made it impossible to say whether it was justified in the case of the manganese salt.

Assuming that f_u was equal to unity, and that the enhanced solubility of the manganese oxalate in KCl and KNO₃ could be
attributed wholly to the existence of MnCl\(^+\) and MnWO\(_3\)^+; Stock calculated the amounts of these species present and hence their dissociation constants. The values derived were reasonable constant, and indicated that these species were quite highly dissociated. For the solubility of manganese oxalate in manganese chloride solutions Stock propounded four hypotheses that could account for the enhanced solubility.

1. A decrease in \(f_u\).
2. The formation of mixed complex anions e.g. MnO\(_x\)Cl\(^-\).
3. The formation of mixed complex cations e.g. Mn\(_2\)O\(_x\)^{++}
4. A change in the composition of the solid phase.

Calculation showed that \(f_u\) would have to more sensitive to changes in ionic strength than a uni-valent ion for the first hypothesis to be the only cause of the enhanced solubility.

Topp had proved conclusively that (4) was unlikely. Calculations based on hypotheses (2) and (3) showed that either of them was capable of explaining the results. A further series of measurements of the solubility of manganese oxalate in potassium chloride were made in order to decide between the two. It was found that the increase in solubility in KCl was not comparable with that in MnCl\(_2\) of the same chloride concentration. Stock therefore concluded that the high solubility of manganese oxalate in manganese chloride was attributable mainly to the formation of Mn\(_2\)O\(_x\)^{++}. This was confirmed by similar measurements of solubility in manganese sulphate.
No similar data are available for bi-valent metal malonates, and the present work was undertaken in order to obtain such data for some of these salts, and to determine whether a similar state of affairs prevailed as in the oxalate solutions. The salt which has been examined is copper malonate. This choice was made for a variety of reasons. In order to use the solubility method the salt must have a low solubility in water, and also have a small dissociation constant. This results in the saturated solution having a low ionic strength, which facilitates the making of activity corrections. From the interpretation of the results a value for the dissociation constant of the salt is also necessary. Existing data indicated that copper malonate fulfilled most of these conditions, and would be suitable for this investigation.

A study of the electrical conductivities of aqueous solutions of the malonates of magnesium, copper, zinc and cadmium (71) indicated that copper malonate was an abnormally weak electrolyte. Ives and Riley (13) carried out extensive conductivity and electrometric measurements on aqueous solutions of transition metal malonates and alkyl malonates in order:

"......(1) to determine whether or not there is any definite relationship between the dissociation of a simple salt MA, and that of the corresponding complex anion $M(A)_x^{x-}$.

(2) to determine the extent to which transition metal cations control the degree of dissociation."
(3) to determine the effect of changes in the nature of the
anion upon the degree of dissociation of transition metal salts.

They calculated the dissociation constants of the copper
salts of malonic and alkyl malonic acids, but regarded their
values as being only relatively correct, as there was considerable
uncertainty in the values used for $\Lambda_o$ for the various salts.
The dissociation constant of copper malonate was recalculated
from their data by Davies, who obtained a value of $2.5 \times 10^{-6}$.
Peacock and James (9) also give conductivity data for copper
malonate, and report a dissociation constant of $1.59 \times 10^{-6}$.
They also recalculated the Ives and Riley data using a value
of 118.3 for the conductivity at infinite dilution in comparison
with a value of 113.8 used in the original publication. The value
obtained for $K_{CuMal}$ was $1.77 \times 10^{-6}$. The Peacock and James values
for the dissociation constant are in agreement with the value
($1.58 \times 10^{-6}$ - obtained in the present work by a colorimetric
method. Stock and Davies (4) also using a colorimetric method
report a value of $2.5 \times 10^{-6}$ in agreement with the Davies value.
Gelles and Nancollas (21) quote a value of $2.0 \times 10^{-6}$ arrived at
by a polarographic method. This is in fair agreement with the
conductimetric and potentiometric values of Peacock and James.

In the present work data are given for the solubility of
copper malonate in water, and in aqueous solutions of sodium
malonate, malonic acid and copper sulphate.
(ii) Experimental.

(a) Preparation of Copper Malonate.

The copper malonate was prepared by the method of Ives and Riley (13). Electrolytic copper was dissolved in concentrated nitric acid. The solution was evaporated until crystals formed, these were dried at the pump and then recrystallised from dilute nitric acid. The crystals thus formed were decomposed by heating to give cupric oxide. This was washed several times with distilled water to remove any trace of copper nitrate.

The malonic acid used was B.D.H. Commercial grade, recrystallised thrice from distilled water. The pure sample melted at 136°C (lit. value 136°C).

The cupric oxide was heated on a water bath with a 10% solution of malonic acid in distilled water, over a period of five hours. The hot solution was filtered, and the residual cake of copper oxide washed thoroughly with hot distilled water. The filtrate was evaporated to two thirds of its original volume and kept in a cool place overnight. The crystals obtained were recrystallised from a 0.1% malonic acid solution, and thoroughly washed, first with alcohol to remove any acid, and then with distilled water.

Copper malonate was formed as blue, cubic crystals, which on exposure to air for some time, appeared to effloresce. In
order to ascertain the purity of the copper malonate a perfectly dry sample of the hydrated salt had to be obtained. This was achieved by standing the moist salt in a vacuum desiccator over a sample of the partially dehydrated salt. Constant weight was attained after one month. Analysis of the sample showed a copper content of 29.17% which is in good agreement with the calculated value of 29.2% for the trihydrate. A sample placed in a vacuum desiccator over concentrated sulphuric acid continued to lose weight after two months. In view of the fact that dehydration occurs on standing in air, the bulk of the copper malonate was kept as a slurry with distilled water.

The copper sulphate used in this work was B.D.H. AnalaR quality recrystallised from conductivity water. The sodium malonate was B.D.H. Commercial grade, recrystallised several times from conductivity water.
(b) **Apparatus.**

In most of the previous work on solubility the Brønsted-Davies saturator has been used. This apparatus has the disadvantage of requiring relatively large quantities of the salt under examination. Furthermore at least two sources of error are present:

1. Incomplete saturation of the solution.
2. Evaporation in the withdrawal tube.

The apparatus used in the present investigation overcomes these disadvantages. It consists essentially of a disc to which are attached by means of clips, six small glass bottles of about 45 mls. capacity. The disc is completely immersed in a water thermostat, the level of the water in which is adjusted so that the necks of the bottles just project out of the water as the disc is rotated at a suitable speed by means of an electric motor. The temperature of the water was kept at 25° ± 0.05 by means of a Mercury-Toluene regulator. The bottles were cleaned with concentrated chromic acid, and by means of the "alcohol-nitric" reaction, and thoroughly washed with distilled water.

The copper malonate was sucked dry at the pump, and washed four or five times with the solvent to be used. Samples were then introduced into the bottles which had also been washed several times with the solvent. The bottles were then filled
with the solvent, and securely stoppered with rubber bungs. These had been previously cleaned by successive boiling in

(a) sodium carbonate solution
(b) dilute HCl
(c) distilled water.

Samples were withdrawn from the bottles by means of a calibrated pipette fitted with a piece of glass tubing containing a plug of glass wool. This prevented the passage into the pipette of small crystals of copper malonate. The pipette was kept at 25°C in an air jacket immersed in the thermostat.

By making successive withdrawals at intervals of one hour, after an initial period of three hours, it was found that with distilled water as the solvent complete saturation was obtained after eight hours. The samples were therefore allowed to saturate for at least twelve hours, and in the case of copper sulphate solutions as solvent, were left overnight. It will be noted that the time taken for complete saturation is quite appreciable; using a Brønsted-Davies saturator it would probably be unduly long.

Before analysis the pH of each solution was measured using a glass electrode, a calomel half-cell and a pH meter used as a voltmeter. The instrument was calibrated at 25°C using the McIlvaine buffers, and the value of the pH of the saturated solution obtained by interpolation on the graph of E.M.F. against pH.
(c) Analysis of the saturated solution.

The copper content of the solution was determined by electrodeposition on platinum electrodes. To test the accuracy of the method a standard solution of pure copper sulphate was analysed by two methods.

1. Electrodeposition
2. Precipitation as thiocyanate.

The percentage copper obtained by the first method was in exact agreement with the calculated value, whilst that by the second method deviated by 0.5%. The second method was also much more tedious.

The technique of electrodeposition.

The copper was deposited from an acid solution of pH approximately 2.5 using platinum electrodes. These consisted of two concentric gauze cylinders. The inner electrode was rotated at a speed which produced good stirring of the solution without causing any spilling or splashing. The copper was deposited on the stationary outer electrode. It was found that excellent deposits were obtained when 0.15 ml of concentrated nitric acid 0.5 gm. of solid ammonium nitrate and 2 ml. of ethyl alcohol were added to each 25 ml. of solution. The ethyl alcohol reduces the possibility of oxidation occurring, whilst a high concentration of NO$_3^-$ produces a depolarising effect at the cathode.

$$\text{NO}_3^- + 10\text{H}^+ + 8\text{e} = \text{NH}_4^+ + 3\text{H}_2\text{O}$$
The reduction potential of the nitrate ion is lower than the discharge potential of hydrogen, and therefore hydrogen is not liberated in the free state. A distinct fading of colour occurred on adding the concentrated nitric acid to the saturated solution of copper malonate. This was probably due to the decomposition in strongly acid solution of the species $\text{CuMal}_2^-$.

As deposition continued the colour of the solution became less intense until it became colourless when all the copper had been deposited. To verify the completeness of deposition a few mls. of distilled water were added to the solution, thus raising the level by 2 or 3 mms. If the surface of the platinum newly immersed remained bright after about 15 minutes, then deposition was taken as being complete.

With the current still running, the rotation of the inner electrode was stopped, and the beaker lowered whilst a stream of distilled water was directed on the upper rim of the cathode. As soon as the cathode was completely out of the electrolyte the current was switched off and the cathode well washed, first with distilled water, and then with a few mls. of pure acetone. It was then dried for ten minutes in an oven at 110°C and allowed to cool in a desiccator.

A current of 0.5 amps increasing to 1.5 amps after ten minutes, and an e.m.f. of 3.5 volts was used. Deposition was complete in 45 minutes.
Ives and Riley (13) described the preparation of the copper salts of alkyl malonic acids, and made qualitative statements about their relative solubilities. With the exception of ethyl malonic acid, none of the alkyl malonic acids are produced commercially today. A sample of ethyl malonic acid was purchased from Messrs. B.D.H., but was found to be contaminated with butyric acid. Attempts at purifying the acid by recrystallisation from several organic solvent failed. A synthesis of the acid was attempted, this involving the alkylation of diethyl malonate with subsequent hydrolysis. The final product was a viscous syrup which eventually crystallised. This again was found to be contaminated with butyric acid.

In order to determine whether they were suitable for solubility work a number of other metal malonates were prepared.

Magnesium malonate was prepared by adding A.R. magnesium oxide to an aqueous solution of malonic acid until no more effervescence occurred. The solution was then filtered. A portion of it was placed in an evaporating dish on a steam bath, but it was found that extensive hydrolysis took place, with the precipitation of magnesium hydroxide. Another portion of the solution was placed in a vacuum desiccator over concentrated sulphuric acid. No crystals formed after leaving for several days. Analysis of the solution for magnesium showed that the solubility of magnesium malonate was too high for our purpose.
Similar results were obtained with nickel malonate prepared by dissolving nickel hydroxide in an aqueous solution of malonic acid.

An attempt was made to prepare the copper salt of glutaric acid in the hope that this might have a suitable solubility. The first attempt was by the method of Ives and Riley (13) for the preparation of the copper salts of malonic acids. It was found however that hydrolysis occurred on heating the copper oxide with an aqueous solution of the acid, and that some copper hydroxide was precipitated. The second method proved more successful. It has been used by Ploquin (72) for the preparation of the copper and nickel salts of oxalic, malonic, glutaric, succinic, adipic and pimelic acids.

Theoretically it is possible to prepare the copper salt by the double decomposition of the disodium salt of the acid and copper chloride or sulphate. In practice however the addition of the sodium salt to a copper sulphate solution results in the precipitation of copper hydroxide. In order to prevent this the following procedure was adopted.

An approximately N/10 solution of the acid was prepared and the pH of the solution adjusted to about 5 by the addition of sodium carbonate. To this was added a fairly concentrated solution of copper sulphate. The precipitation of copper glutarate as a bright green powder occurred after about thirty
minutes. Analysis showed this to be the anhydrous salt. Copper succinate was prepared by the same method, and was precipitated as a fine powder, much lighter in colour. Attempts to determine the solubility in water at 25°C failed because of the extensive hydrolysis that occurred.

It appears therefore that copper malonate is the only salt of the ones examined suitable for study by the solubility method. Its solubility has been determined in water, sodium malonate and copper sulphate solutions. In both of the latter solvents malonic acid had to be added in order to suppress the hydrolysis. Further data were obtained by measuring the solubility in aqueous malonic acid solutions, calculations using these figures would not be complicated by consideration of the hydrolysis of the copper malonate.

The value given for the solubility of copper malonate in water is the mean of ten determinations; all the other measurements were made in triplicate.
(iii) Tables and Graphs.

(all concentrations are expressed in g.mol/litre)
Table (26).

Solubility of Copper Malonate in Malonic Acid Solutions

<table>
<thead>
<tr>
<th>(Malonic Acid)</th>
<th>(Copper Malonate)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>.04667</td>
<td>4.80</td>
</tr>
<tr>
<td>.00514</td>
<td>.04840</td>
<td>3.37</td>
</tr>
<tr>
<td>.00960</td>
<td>.04990</td>
<td>3.10</td>
</tr>
<tr>
<td>.02118</td>
<td>.05341</td>
<td>2.79</td>
</tr>
<tr>
<td>.03236</td>
<td>.05511</td>
<td>2.73</td>
</tr>
<tr>
<td>.04832</td>
<td>.05755</td>
<td>2.53</td>
</tr>
<tr>
<td>.06431</td>
<td>.05928</td>
<td>2.52</td>
</tr>
</tbody>
</table>
COPPER MALONATE IN MALONIC ACID SOLUTIONS

FIG. 7

SOLUBILITY g.mol/litre

MALONIC ACID g.mol/litre

9 mol/litre - 0.045
Table (27).

Solubility of Copper Malonate in Sodium Malonate solutions containing .00482 M Malonic Acid.

<table>
<thead>
<tr>
<th>(Sodium Malonate)</th>
<th>(Copper Malonate)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>.03619</td>
<td>.07706</td>
<td>4.47</td>
</tr>
<tr>
<td>.02147</td>
<td>.06219</td>
<td>4.20</td>
</tr>
<tr>
<td>.01154</td>
<td>.05307</td>
<td>4.08</td>
</tr>
<tr>
<td>.00900</td>
<td>.05090</td>
<td>4.00</td>
</tr>
<tr>
<td>.00580</td>
<td>.04830</td>
<td>3.91</td>
</tr>
<tr>
<td>.00259</td>
<td>.04742</td>
<td>3.80</td>
</tr>
</tbody>
</table>
COPPER MALONATE IN SODIUM MALONATE SOLUTIONS PLUS 0.0004817M MALONIC ACID

FIG. 8
Table (28).

Solubility of Copper Malonate in Copper Sulphate solutions.

<table>
<thead>
<tr>
<th>(Copper Sulphate)</th>
<th>(Copper Malonate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.04761</td>
<td>.04861</td>
</tr>
<tr>
<td>.02926</td>
<td>.04661</td>
</tr>
<tr>
<td>.03861</td>
<td>.04821</td>
</tr>
<tr>
<td>.02572</td>
<td>.04679</td>
</tr>
<tr>
<td>.01016</td>
<td>.04541</td>
</tr>
<tr>
<td>.03118</td>
<td>.04654</td>
</tr>
<tr>
<td>.00408</td>
<td>.04566</td>
</tr>
<tr>
<td>.06693</td>
<td>.05633</td>
</tr>
<tr>
<td>.03108</td>
<td>.04701</td>
</tr>
<tr>
<td>.04736</td>
<td>.04968</td>
</tr>
<tr>
<td>.03497</td>
<td>.04714</td>
</tr>
<tr>
<td>.04999</td>
<td>.04855</td>
</tr>
<tr>
<td>.05664</td>
<td>.04911</td>
</tr>
<tr>
<td>.01932</td>
<td>.04661</td>
</tr>
</tbody>
</table>

The pH of all the solutions remained approximately constant at 4.8.
COPPER MALONATE IN COPPER SULPHATE SOLUTIONS

SOLUBILITY
\[ \text{g.mol/litre} \]

COPPER SULPHATE
\[ \text{g.mol/litre} \]

FIG. 9
Table (29).

<table>
<thead>
<tr>
<th>(Copper Sulphate)</th>
<th>(Copper Malonate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00514</td>
<td>0.04764</td>
</tr>
<tr>
<td>0.01229</td>
<td>0.04794</td>
</tr>
<tr>
<td>0.02406</td>
<td>0.04810</td>
</tr>
<tr>
<td>0.03287</td>
<td>0.04886</td>
</tr>
<tr>
<td>0.04278</td>
<td>0.04999</td>
</tr>
<tr>
<td>0.04770</td>
<td>0.05068</td>
</tr>
</tbody>
</table>

The pH of all the solutions remained approximately constant at 3.19.
COPPER MALONATE IN COPPER SULPHATE PLUS 0.00499M MALONIC ACID.

FIG. 10

SOLUBILITY
\[ \text{g mol/litre} \]

COPPER SULPHATE \[ \text{g mol/litre} \]
Table (30).

The dissociation constant of the complex cation $\text{Cu}_2\text{Mal}^{++}$. 

<table>
<thead>
<tr>
<th>Solubility</th>
<th>0.05755</th>
<th>0.05511</th>
<th>0.05341</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Malonic Acid)</td>
<td>0.04832</td>
<td>0.03236</td>
<td>0.02118</td>
</tr>
<tr>
<td>I</td>
<td>0.03260</td>
<td>0.02729</td>
<td>0.02401</td>
</tr>
<tr>
<td>$f_1$</td>
<td>0.8451</td>
<td>0.8547</td>
<td>0.8615</td>
</tr>
<tr>
<td>$f_2$</td>
<td>0.5120</td>
<td>0.5341</td>
<td>0.5510</td>
</tr>
<tr>
<td>($H^+$)</td>
<td>0.00295</td>
<td>0.00215</td>
<td>0.00181</td>
</tr>
<tr>
<td>($H\text{Mal}'$)</td>
<td>0.02341</td>
<td>0.01895</td>
<td>0.01443</td>
</tr>
<tr>
<td>($H_2\text{Mal}$)</td>
<td>0.03503</td>
<td>0.02111</td>
<td>0.01367</td>
</tr>
<tr>
<td>($\text{Mal}''$)</td>
<td>0.00003</td>
<td>0.00003</td>
<td>0.00003</td>
</tr>
<tr>
<td>($\text{CuMal}$)</td>
<td>0.04635</td>
<td>0.04635</td>
<td>0.04635</td>
</tr>
<tr>
<td>($\text{Cu}_2\text{Mal}^{++}$)</td>
<td>0.00147</td>
<td>0.00051</td>
<td>0.00005</td>
</tr>
<tr>
<td>($\text{Cu}^{++}$)</td>
<td>0.00827</td>
<td>0.00773</td>
<td>0.00695</td>
</tr>
<tr>
<td>$K_{\text{Cu}_2\text{Mal}^{++}}$</td>
<td>0.26</td>
<td>0.64</td>
<td>0.61</td>
</tr>
</tbody>
</table>
(iv) Calculations.
(a) **Calculation of the Solubility Product of copper malonate in water.**

Solubility at 25°C = 0.04667 g·mol/litre

The following species only are assumed to be present in the aqueous solution:

Cu++, Mal", H+, OH', CuMal, CuOH+, HMal', and H₂Mal.

The calculation is based on the following equations:

(a) Total copper = solubility = (Cu++) + (CuMal) + (CuOH+)

(b) Total malonate = solubility = (Mal") + (CuMal) + (HMal') + (H₂Mal)

(c) \[ K_1 = \frac{f_1^2 \cdot (H^+)(OH^)}{H_2 Mal} = 1.40 \times 10^{-3} \] (30)

(d) \[ K_2 = \frac{f_2^2 \cdot (H^+)(Mal")}{(HMal')} = 2.01 \times 10^{-6} \] (30)

(e) \[ K_{CuMal} = \frac{f_2^2 \cdot (Cu++)(Mal")}{(CuMal)} = 1.59 \times 10^{-6} \] (9)

(f) \[ K_w = (H^+)(OH').f_1^2 = 1.008 \times 10^{-14} \]

(g) \[ K_{CuOH^+} = \frac{(Cu++)(OH')}{(CuOH^+)} = 3.4 \times 10^{-7} \] (60)

(h) \[ 2(Cu++) + (H^+) + (CuOH^+) = 2(Mal") + (OH') + (HMal') \]

( electroneutrality )

(i) Ionic Strength = \( \frac{1}{2} \left\{ 4(Cu++) + 4(Mal") + (H^+) + (OH') + (CuOH^+) \right\} + (H²Mal') \)
\[ \log f_1 = -\frac{1}{3} \left[ f(I) \right] \]
\[ f(I) = \left\{ \frac{4I}{1 + \sqrt{I}} - 0.2 \right\} \]
\[ \log f_1 = -f(I) \quad \log f_2 = -2f(I) \]
\[ \log f_2 = -4f(I) \]

(k) \[ K_{\text{CuMal}} = \frac{S_0}{(\text{CuMal})} \]

Multiply equation (a) by 2 and subtract (h)
\[ 2(\text{CuMal}) + (\text{CuOH}^+) - (H^+) = 2S - (\text{HMal}') - 2(\text{Mal}^\prime\prime) - (OH') \]

or

\[ 2(\text{CuMal}) = 2S - (\text{HMal}') - 2(\text{Mal}^\prime\prime) - (OH') + (H^+) - (\text{CuOH}^+) \]

Multiply (h) by 2 and substitute for 2CuMal from (1)
\[ 2(\text{Mal}^\prime\prime) + 2(\text{HMal}') + 2(\text{H}_2\text{Mal}) + 2S - (\text{HMal}') - 2(\text{Mal}^\prime\prime) - (OH') \]
\[ - (\text{CuOH}^+) = 2S \]

or

(m) \[ (\text{HMal}') + 2(\text{H}_2\text{Mal}) + (H^+) = (\text{CuOH}^+) + (OH') \]

The method of successive approximations was used to solve the above equations. An approximate value was given to \((H^+)\) (from pH measurement) and to \((\text{Cu}^{++})\). The activity coefficients were neglected in the first few approximations. Knowing \((H^+)\) and \((\text{Cu}^{++})\), the concentrations of the other species were calculated as follows: \((OH')\) from (f), \((\text{CuOH}^+)\) from (g), \((\text{CuMal})\) from (a), \((\text{H}_2\text{Mal})\) from (c) and (m), \((\text{HMal}')\) from (c), \((\text{Mal}^\prime\prime)\) from (d), \((\text{Cu}^{++})\) from (e) and \((H^+)\) from (h).
These two new values for \((\text{Cu}^{++})\) and \((\text{H}^+)\) should then be used to recalculate the concentrations of the other species, making corrections for the activity coefficients from equations (i) and (j). Normally constant values should be obtained after a few approximations. Unfortunately in this case the approximations were not convergent, and random values for \((\text{H}^+)\) and \((\text{Cu}^{++})\) had to be tried, repeating the cycle of calculations until reasonably constant values were obtained. After numerous approximations the following values were deduced for the concentrations of the various species present:

\[
\begin{align*}
(\text{H}^+) &= 2.53 \times 10^{-7}; \\
(\text{OH}^-) &= 4.313 \times 10^{-8}; \\
(\text{CuOH}^+) &= 3.441 \times 10^{-5}; \\
(\text{CuMal}) &= 4.6312 \times 10^{-2}; \\
(\text{H}_2\text{Mal}) &= 5.71 \times 10^{-9}; \\
(\text{HMal}^+) &= 3.419 \times 10^{-5}; \\
(\text{Mal}^-) &= 3.1839 \times 10^{-4}; \\
(\text{Cu}^{++}) &= 3.182 \times 10^{-4}. \\
\end{align*}
\]

Ionic strength = 0.001307.

\[
S_0 = f_2^2 \cdot (\text{Cu}^{++})(\text{Mal}^-)
= 7.36 \times 10^{-8}.
\]

It will be noted that there is a considerable discrepancy between the calculated \((\text{H}^+)\) and that derived from the pH measurement. This may be due to the neglect in the calculation of the effect of \(\text{H}_2\text{CO}_3\) and \(\text{HCO}_3^-\).

The solubility was measured to an accuracy of ± 0.00006. A second value of \(S_0\) was calculated using a value of 0.04660 for the solubility of copper malonate in water. In this case
\[(\text{Cu}^{++}) = 0.0003179, \quad (\text{Mal}^-) = 0.0003182, \quad (\text{CuMal}) = 0.046248\]

and \(S_0 = 7.35 \times 10^{-8}\). The only effect of the change in solubility was on the concentration of the undissociated CuMal.

Another value of \(S_0 = 1.384 \times 10^{-7}\) was calculated using the value of Stock and Davies (4) for the dissociation constant of copper malonate.
(b) **Calculation of** $S_0$ **for copper malonate assuming the presence in aqueous solution of the species** $Cu^{++}$, $Mal^-$ **and CuMal only.**

In previous solubility work (15, 16) a value for $S_0$ was calculated neglecting all species other than $M^{++}, A^-$, and MA. A similar calculation has been attempted in the case of copper malonate. The relevant equations are:

(a) $f_2^2 \cdot (Cu^{++})(Mal^-) = 1.59 \times 10^{-6}$ \hspace{1cm} (9)

(b) $(CuMal) + (Mal^-) = \text{total malonate} = \text{solubility}$

(c) $(Cu^{++}) = (Mal^-) \hspace{1cm} \text{electroneutrality}$

$(Cu^{++})$ was given an approximate value; from this a value of I was obtained and hence $f_1$ and $f_2$. This enabled a value for $(CuMal)$ to be calculated from (a) and a new value of $(Mal^-)$ from (b). The calculations were repeated until constant values were obtained. Six approximations, which in this case were convergent, were sufficient to give a constant value of $3.1418 \times 10^{-4}$ for $(Cu^{++})$. The ionic strength was .001257, hence $S_0 = 7.370 \times 10^{-8}$ \hspace{1cm} (c.f. p 120, $S_0 = 7.36 \times 10^{-8}$)

It appears therefore that neglecting all species other than $Cu^{++}$, $Mal^-$ and CuMal does not introduce an appreciable error in the value of $S_0$, although this agreement may be due, to a certain extent, to a cancellation of errors.
A similar calculation using a value of \(2.5 \times 10^{-6}\) for \(K_{CuMal}\) gave \(S_0 = 1.295 \times 10^{-7}\).

Since the value of \(1.59 \times 10^{-6}\) for the dissociation constant of copper malonate, derived by Peacock and James (9) was in close agreement with the value \((1.58 \times 10^{-6})\) arrived at in Section 1 by a colorimetric method, the solubility product of copper malonate was, for use in subsequent calculations, taken to be \(7.36 \times 10^{-8}\).
(c) Calculation of $K_{\text{CuMal}_2^2}$ from the solubility of copper malonate in malonic acid solutions.

The enhanced solubility of copper malonate in malonic acid solutions is attributed solely to the formation of the complex anion $\text{CuMal}_2^2$. The species present in solution are assumed to be: $\text{Cu}^{++}$, $\text{Mal}^-$, $\text{CuMal}$, $\text{CuMal}_2^2$, $\text{HMal}'$, $\text{H}_2\text{Mal}$ and $\text{H}^+$.

The equations on which the calculations are based are:

(a) \[(\text{Cu}^{++}) + (\text{CuMal}) + (\text{CuMal}_2^2) = \text{solubility}\]

(b) \[2(\text{Cu}^{++}) + (\text{H}^+) = 2(\text{Mal}^-) + (\text{HMal}') + 2(\text{CuMal}_2^2)\]

or \[(\text{HMal}') = 2(\text{Cu}^{++}) + (\text{H}^+) - 2(\text{Mal}^-) - 2(\text{CuMal}_2^2)\]

(electroneutrality)

(c) \[(\text{CuMal}) + (\text{Mal}^-) + 2(\text{CuMal}_2^2) + (\text{HMal}') + (\text{H}_2\text{Mal}) = \text{solubility} + \text{added malonic acid}\]

(d) \[
\frac{f_1^2(\text{H}^+)(\text{HMal}')}{(\text{H}_2\text{Mal})} = 1.40 \times 10^{-3}
\]

or \[(\text{HMal}') = \frac{1.40 \times 10^{-3}(\text{H}_2\text{Mal})}{f_1^2(\text{H}^+)}\]

(e) \[
\frac{f_2^2(\text{H}^+)(\text{Mal}^-)}{(\text{HMal}')} = 2.01 \times 10^{-6}
\]

or \[(\text{Mal}^-) = \frac{2.01 \times 10^{-6}(\text{HMal}')}{f_2^2(\text{H}^+)}\]

(f) \[S_0 = f_2^2(\text{Cu}^{++})(\text{Mal}^-) = 7.36 \times 10^{-8}\]
A value was assigned to \( H^+ \) and to \( \text{Mal}^{"} \). From equations (d) and (e) (H\text{Mal}') and (H\text{Mal} \text{Mal}) were calculated. (Cu\text{Mal}) was constant in all solutions and was known from the previous calculation. Equation (c) then gave (Cu\text{Mal} \text{2} \text{Mal}) and equation (a) (Cu^{+++}). A new value for (\text{Mal}^{"}) was then calculated from equation (f) - the activity coefficient \( f_2 \) being given an approximate value. These approximations again proved to be non-convergent, and random values of (\text{Mal}^{"}) had to be tried until the initial value of (\text{Mal}^{"}) agreed with that derived from equation (f). When this agreement was attained, (H\text{Mal}') was calculated from the electroneutrality equation. If this value for (H\text{Mal}') did not agree with that derived from equation (e) the whole cycle of calculations was repeated using a new value for (H^+). This procedure was tried with the most concentrated solutions, but it was impossible to get agreement between the two values of (H\text{Mal}') derived from equations (b) and (e). The value derived from equation (b) was consistently smaller than that derived from (e), indicating that another term involving a positive ion, probably 2(Cu\text{2}\text{Mal}^{+++}), should be introduced in equation (b).
(d) **Calculation of** $K_{\text{Cu}_2\text{Mal}^{++}}$ **from the solubility of copper malonate in malonic acid solutions.**

The enhanced solubility of the copper malonate is attributed solely to the formation of the complex cation $\text{Cu}_2\text{Mal}^{++}$. The species present in solution are: $\text{H}^+$, $\text{Cu}^{++}$, $\text{Cu}_2\text{Mal}^{++}$, $\text{HMal}'$, $\text{Mal}''$, and $\text{H}_2\text{Mal}$.

The calculation is based on the following equations:

(a) $\text{(Cu}^{++}) + (\text{CuMal}) + 2(\text{Cu}_2\text{Mal}) = \text{solubility}$

(b) $2(\text{Cu}^{++}) + 2(\text{Cu}_2\text{Mal}^{++}) + (\text{H}^+) = 2(\text{Mal}''') + (\text{HMal}')$

(c) total malonate = solubility + added malonic acid

$$= (\text{CuMal}) + (\text{Mal}'''') + (\text{Cu}_2\text{Mal}^{++}) + (\text{HMal}') + (\text{H}_2\text{Mal})$$

and equations (d), (e) and (f) on p. 124, which remain unchanged.

An approximate value was given to $(\text{H}^+)$, $(\text{Mal}'''')$ and I. This enabled first approximate values to be obtained for $(\text{HMal}')$, $(\text{H}_2\text{Mal})$, (from (d) and (e)); $(\text{Cu}_2\text{Mal}^{++})$ from (c); $(\text{Cu}^{++})$ from (a) and a new value for $(\text{Mal}'')$ from (f). This process was repeated until the initial value of $(\text{Mal}'''')$ agreed with the value calculated from equation (f). When this agreement was attained $(\text{HMal}')$ was calculated from the electroneutrality equation (b). If this value did not agree with that calculated from equation (e), a new value of $(\text{H}^+)$ was tried and the whole
process repeated until self consistent values were obtained for the concentrations of all the species present. A new value of I was then calculated, and if the new activity coefficients were significantly different from the first values, the whole cycle of calculations was repeated. The values arrived at for the three more concentrated solutions are shown in table (30).
(e). Calculation of $K_{\text{CuMal}_2^-}$ from the solubility of copper malonate in sodium malonate solutions containing malonic acid.

The enhanced solubility of the copper malonate is attributed solely to the formation of CuMal$_2^-$. The species assumed to be present are: H$^+$, Cu$^{++}$, HMal', Mal'$, H$_2$Mal, CuMal$_2^-$ and Na$^+$. 

The relevant equations are:

(a) $(\text{Cu}^{++}) + (\text{CuMal}) + (\text{CuMal}_2^-) = \text{solubility}$

(b) $2(\text{Cu}^{++}) + (\text{H}^+) + (\text{Na}^+) = 2(\text{Mal}^-) + (\text{HMal}') + 2(\text{CuMal}_2^-)$

or $(\text{HMal}') = 2(\text{Cu}^{++}) + (\text{H}^+) + (\text{Na}^+) - 2(\text{Mal}^-) - 2(\text{CuMal}_2^-)$

(c) total malonate = solubility + added malonic acid + added sodium malonate

\[ = (\text{CuMal}) + (\text{Mal}^-) + 2(\text{CuMal}_2^-) + (\text{HMal}') + (\text{H}_2\text{Mal}) \]

Equations (d), (e) and (f) (p 124) remain unchanged.

The method of calculation is exactly as in the previous example.

In a solution of 0.02147 M sodium malonate containing 0.004817 M malonic acid the solubility of copper malonate was 0.06219 g·mol/litre. After many approximations the concentrations of the various ionic species were calculated to be as follows
\[ (H^+) = 0.000297; \quad (HM\text{al}^+) = 0.009432; \quad (H_2\text{Mal}) = 0.0001363 \]
\[ (Cu\text{Mal}_2^{"}) = 0.015605; \quad (Cu^{++}) = 0.000235; \quad (\text{Mal}^{"}) = 0.00139 \]
\[ I = 0.04339; \quad f_1 = 0.8284; \quad f_2 = 0.4705 \]

\[ K_{\text{CuMal}_2^{"}} = \frac{(\text{CuMal})(\text{Mal}^{"})}{(\text{CuMal}_2^{"})} \]
\[ = \frac{0.04635 \times 0.001352}{0.015605} \]
\[ = 4.02 \times 10^{-3} \]
(f) Re-calculation of $K_{\text{CuMal}_2^{\text{"}}}$ from the solubility of copper malonate in sodium malonate solutions allowing for the presence of $\text{Cu}_2\text{Mal}^{++}$.

The species assumed to be present are:

$\text{Cu}^{++}$, $\text{H}^+$, $\text{Na}^+$, $\text{Cu}_2\text{Mal}^{++}$, $\text{CuMal}$, $\text{CuMal}_2^{\text{"}}$, $\text{HMal}'$, $\text{Mal}^{\text{"}}$, $\text{H}_2\text{Mal}$

The relevant equations are:

(a) $(\text{Cu}^{++}) + (\text{CuMal}) + (\text{CuMal}_2^{\text{"}}) + 2(\text{Cu}_2\text{Mal}^{++}) = \text{solubility}$

(b) $\text{Na}^+ + 2(\text{Cu}^{++}) + (\text{H}^+) + 2(\text{Cu}_2\text{Mal}^{++})$

\[ = 2(\text{CuMal}_2^{\text{"}}) + 2(\text{Mal}^{\text{"}}) + (\text{HMal}') \]

(c) total malonate = solubility + added sodium malonate + added malonic acid

\[ = (\text{CuMal}) + (\text{Mal}^{\text{"}}) + (\text{Cu}_2\text{Mal}^{++}) + 2(\text{CuMal}_2^{\text{"}}) + (\text{HMal}') \]

\[ + (\text{H}_2\text{Mal}) \]

Equations (d), (e) and (f) p 124 remain unchanged.

\[ (\text{Cu}^{++})(\text{CuMal}) = (\text{Cu}_2\text{Mal}^{++}) \]

Approximate values were first given to $(\text{H}^+)$, $(\text{Mal}^{\text{"}})$ and I, and $\text{Cu}_2\text{Mal}^{++}$ was neglected in the first few approximations. $(\text{HMal}')$ and $(\text{H}_2\text{Mal})$ were obtained from equations (d) and (e). $(\text{CuMal}_2^{\text{"}})$ from equation (c). Equation (a) then gave $(\text{Cu}^{++})$, and from equations (g) and (f) $(\text{Cu}_2\text{Mal}^{++})$ and $(\text{Mal}^{\text{"}})$ respectively were obtained. The calculations were repeated until reasonably
constant values were obtained.

In a solution of .02147 M sodium malonate containing .004817 M malonic acid the solubility of copper malonate was .06219 g.mol/litre. The concentrations of the various ionic species were calculated to be as follows:

\[
\begin{align*}
(H^+) &= .000294; \\
(Mal^{-}) &= .001375; \\
(HMal') &= .009509; \\
(H_2Mal) &= .000136; \\
(Cu_2Mal^{++}) &= .000019; \\
(CuMal^{-}) &= .015543; \\
(Cu^{++}) &= .000257; \\
(CuMal) &= .0463 \\
(Mal^-) &= .001375 \\
(CuMal_2^{-}) &= .01556 \\
K_{CuMal_2^{-}} &= \frac{(CuMal)(Mal^-)}{(CuMal_2^{-})} \\
&= \frac{.0463 \times .001375}{.01556} \\
&= 4.8 \times 10^{-3}.
\end{align*}
\]
(v) **Discussion.**

Data for the solubility of copper malonate in water, sodium malonate, malonic acid and copper sulphate solutions are given in tables 26 - 29, and the relevant graphs are shown in figs 7-10.

As a first step in the interpretation of the results the solubility product of copper malonate in water was calculated. The calculation is shown in detail on p. 118. It was assumed that the only species present in the aqueous solution were: $\text{Cu}^{++}$, $\text{CuMal}$, $\text{Mal}^-$, $\text{HMal}^-$, $\text{H}_2\text{Mal}$, $\text{CuOH}^+$, and $\text{OH}^-$. As there were no reliable values available for the dissociation constants of the species $\text{CuMal}_2^-$ and $\text{Cu}_2\text{Mal}^+$, these could obviously not be taken into consideration in the first calculation. The measured pH of the solution was found to be 4.80. Since cupric hydroxide is precipitated at a pH of about 5, it was thought desirable for a complete analysis of the solution to take into account the presence of the ion $\text{CuOH}^+$. This inclusion introduced considerable uncertainty into the calculation as the only two published values for $K_{\text{CuOH}^+}$ (60, 94) differ quite considerably. The value given by Davies (60) has been used in the present calculation.

In previous solubility work on the oxalates (15, 16) no pH measurements appear to have been made. A solution of sodium oxalate in water would certainly have a pH $> 5$ at the concentrations used, and a correction should have been made for the
presence of MOH⁺. When an attempt was made to measure the solubility of copper malonate in sodium malonate solutions, it was seen that cupric hydroxide was precipitated in considerable quantities. The solubility was then measured in sodium malonate solutions containing a fixed concentration of malonic acid. No precipitation occurred in these solutions. Using a Brønsted-Davies saturator it would have been very difficult to detect visually the formation of the hydroxide, whereas it was easily done using the rotating disc apparatus. It may be that precipitation occurred in the oxalate solutions, but that it remained undetected in the Brønsted-Davies saturator.

As is shown on p.120 a value of 7.37 x 10⁻₈ was obtained for the solubility product of copper malonate in water. A second calculation assuming the presence of Cu⁺⁺, Mal" and CuMal only, proved to be far less involved and gave a value of S₀ in close agreement with the first. Another value was derived (1.38 x 10⁻⁷) using the dissociation constant for copper malonate arrived at by Stock and Davies (4). Since the value for K_CuMal determined colorimetrically in Section 1 is in very good agreement with that obtained by Peacock and James (9), the value of 7.37 x 10⁻₈ for the solubility product of copper malonate was adopted for use in the subsequent calculations.

A series of measurements was also made in malonic acid solutions, and the change in the solubility of copper malonate
with increasing concentrations of malonic acid is shown in fig. 7. The most logical assumption to make was that this increased solubility was due to the formation of a complex anion Cu\text{Mal}_2^-. Calculations based on this assumption were made (see p. 124) in order to obtain a value for $K_{\text{CuMal}_2^-}$. The calculations were however not successful, although many approximations were made, no constancy being attained in the values for the concentrations of the various species. In the calculation two values were obtained for (H\text{Mal}'), one from the equation for $K_2$ for the acid, and the other from the electroneutrality equation. The value from the latter was consistently smaller than that from the former. It was obvious from these calculations that the increased solubility could not be attributed wholly to Cu\text{Mal}_2^-.

Another series of calculations was tried (see p. 126) assuming that the enhanced solubility in the malonic acid solutions was due entirely to the complex cation Cu$_2$\text{Mal}$$^\text{++}$. These calculations proved to be more tractable and values were obtained for $K_{\text{Cu}_2\text{Mal}^\text{++}}$ from the three most concentrated solutions. Calculations for the less concentrated solutions showed the concentration of Cu$_2$\text{Mal}$$^\text{++}$ to be too low for any significance to be attached to the $K$ values derived for these points. The dissociation constant of Cu$_2$\text{Mal}$$^\text{++}$ was calculated to be approximately 0.6.
The very considerable increase in the solubility of copper malonate in solutions of sodium malonate is shown in fig. 8. In these solutions the malonate ion is in excess, so that the enhanced solubility can almost certainly be attributed to the formation of the complex anion CuMal$_2$". The calculation (see p. 128) again proved to be long, and no absolutely constant values for the concentrations of the species present were obtained. Nevertheless, it was concluded that an approximate value for K$_{CuMal_2"}$ could be calculated from the data. This value was 4.0 x 10$^{-3}$.

Using the K value derived for Cu$_2$Mal$^{++}$ from the solubility measurements in malonic acid, a second attempt was made to obtain a value for K$_{CuMal_2"}$ based on the solubility data in sodium malonate solutions. The value derived was 4.08 x 10$^{-3}$. If K$_{CuMal_2"}$ is about 4.0 x 10$^{-3}$, it should be possible, using this value, to calculate the concentration of CuMal$_2"$ in the solutions of copper malonate in malonic acid, e.g. for the point S = .05341, pH = 2.79

$$(\text{CuMal}_2") = \frac{(\text{CuMal})(\text{Mal}")}{4.0 \times 10^{-3}} = \frac{.0463 \times .000029}{4.0 \times 10^{-3}}$$

$$= .000034.$$ 

In this solution the concentration of Cu$_2$Mal$^{++}$ was calculated to be .000053 assuming that no CuMal$_2"$ was present. It would be possible, although undoubtedly unprofitable, to approximate
between these two values to get mutually consistent pairs of K's for the complex cation and anion. However, from the values already obtained it is possible to say that in the sodium malonate solutions the concentration of Cu₂Mal⁺⁺ is negligible, and it has been shown that the $K_{CuMal_2}$ derived from the sodium malonate data is not seriously affected by neglecting Cu₂Mal⁺⁺ in its derivation. In the malonic acid series, when the enhanced solubility was attributed solely to CuMal⁺⁺ no consistent results were obtained, (the very small concentration of Mal⁺⁺ playing too great a part in the calculations), whereas when it was attributed to Cu₂Mal⁺⁺, reasonable results were obtained; in this calculation the concentration of Mal⁺⁺ was less important. Whilst the length and complicated nature of the calculations made it impossible to arrive at self-consistent values for $K_{CuMal_2}$ and $K_{Cu₂Mal⁺⁺}$ it is not unreasonable to suggest that these values are of the order of $4.0 \times 10^{-3}$ and 0.6 respectively.

The solubility of copper malonate in copper sulphate solutions was also measured. The data are plotted in fig. 9, and it will be noted that there is considerable scatter of the points. The measured pH of the solutions remained constant at approximately 4.8. Since Cu(OH)₂ is precipitated at a pH of 5 - 5.5, it is likely that this scatter is due to the hydrolysis of the cupric ion in the solutions. A further series of measurements in copper sulphate solutions containing
added malonic acid confirmed this opinion. All the points in this series lie on a smooth curve (fig. 10). In view of the uncertainties introduced by the necessity for taking into consideration the species CuSO₄ and HSO₄⁻, and the dubious values for the activity coefficients, no quantitative treatment of the data for the copper sulphate solutions was attempted. Since the pH of the solutions remained nearly constant at 3.19 the concentration of Mal⁻ remained nearly constant in all the solutions, and the presence of CuMal₂⁻ can safely be neglected. The effect of the added Cu⁺⁺ is fourfold:

1. the ionic strength is increased, which of itself tends to increase the solubility of a sparingly soluble salt by the lowering of the activity coefficients;

2. the ionisation of CuMal will be suppressed, and the solubility lowered by the common ion effect;

3. the formation of CuMal₂⁻ will be suppressed;

4. the concentration of Cu₂Mal⁺⁺ will be increased.

Since, however, the dissociation constant of Cu₂Mal⁺⁺ is high, the effect of this complex cation will be very small, and the increase in solubility slight. If the value derived for K₁₉Mal₂⁻ were used for the data in malonic acid to derive another value for K₁₉₂Mal⁺⁺, this value would in all probability be greater than 0.8, and the K₁₉Mal₂⁻ would not be greatly affected. This calculation was attempted, and the concentration of Cu₂Mal⁺⁺ proved to be smaller than that first calculated. No satisfactory
constant values for the concentrations of the various species were obtained. Superposing the curve for the solubility of copper malonate in copper sulphate solutions (+ constant concentration of Malonic acid) on the corresponding curve for the solubility in sodium malonate solutions it is apparent that the solubility in the copper sulphate solutions can be attributed almost entirely to CuMal as the only complex containing copper present in significant amounts.

All the above calculations were based on a value for the solubility product derived by neglecting the presence of CuMal$_2^{-}$ and Cu$_2$Mal$^{++}$ in the aqueous solution. Preliminary values having been derived for the dissociation constants of these species, a new solubility product should, logically, be calculated making allowance for them. This new $S_0$ should then be used to derive new dissociation constants for CuMal$_2^{-}$ and Cu$_2$Mal$^{++}$, and the process repeated until constant values are obtained. If all the dissociation constants involved in the calculations (those of CuMal, H$_2$Mal and HMal') were known to be absolutely correct, as well as the solubility of the salt, and most importantly the individual ionic activity coefficients, then the complete calculations would be likely to lead to conclusions of quantitative value. However, in view of the uncertainties involved it was deemed that further approximations were not justified.
From the work of Topp (15) and Stock (16) on the oxalates of magnesium and manganese, there is evidence of the existence of quite reasonably stable complex anions of the type $\text{MO}_x^-$, and of less stable complex cations $\text{M}_2\text{O}_x^{++}$. Copper malonate has been shown to be much less dissociated in aqueous solution than either magnesium or manganese oxalates. The dissociation constants are respectively:

$$1.59 \times 10^{-6}; \quad 3.7 \times 10^{-4} \quad \text{and} \quad 1.22 \times 10^{-4}.$$  

The Bjerrum distance for copper malonate is 1.3 Å, an impossibly small value, indicating that the molecule is chelate in character. Since $K_{\text{CuMal}} < K_{\text{MnOx}}$ one would expect that there would be less polar attraction between the Cu part of CuMal and a Mal$^-$ (to give CuMal$^-_2$) and between the Mal$^-$ part and Cu$^{++}$ (to give Cu$_2$Mal$^{++}$) than there would be between the corresponding parts in manganese oxalate. It would then be expected that $K_{\text{CuMal}_2^-} > K_{\text{MnOx}_2^-}$ and $K_{\text{Cu}_2\text{Mal}^{++}} > K_{\text{Mn}_2\text{Ox}^{++}}$.

Similarly in the case of MgOx and MnOx (these two are more comparable as they have an ion in common), as $K_{\text{MgOx}} > K_{\text{MnOx}}$ one would expect $K_{\text{MgOx}_2^-} < K_{\text{MnOx}_2^-}$. The values given for these two K's (15, 16) show them to be equal (.037), but as these values may be in error it is quite likely that the order of stability is as indicated above.

In aqueous solution the Cu$^{++}$ is attached to four molecules of water, so that it is less likely that a Cu$^{++}$ can get near enough to the negative end of the dipolar CuMal to form Cu$_2$Mal$^{++}$.
than it is for a Mal" to attach itself to the positive end. This is borne out by the high value of $K_{Cu_2Mal^{++}}$ and the low value of $K_{CuMal_2^{"}}$. No value has been calculated for $K_{Mg_2Cx^{++}}$ but inspection of the solubility data indicates that it is greater than $K_{Mn_2Cx^{++}}$ (.05). Examination of the available data shows

$$K_{MnCx_2^{"}} < K_{MgCx_2^{"}} > K_{CuMal_2^{"}}$$

and

$$K_{Cu_2Mal^{++}} > K_{Mn_2Cx^{++}}$$

The anomalous position of $CuMal_2^{"}$ seems to indicate that the forces binding the second Mal" to the CuMal are more covalent in character than the corresponding forces in $MgCx_2^{"}$ and $MnCx_2^{"}$.
Section 3.

Spectrophotometric Study of some Copper Salts.
Contents

(i) Introduction ....................................... (143)
(ii) Theory ............................................. (152)
(iii) Errors in Spectrophotometric Measurements (158)
(iv) Experimental ................................. (160)
(v) Tables and Graphs .............................. (164)
(vi) Discussion ................................. (170)
(i) Introduction.

When a parallel monochromatic beam of light passes through a homogeneous absorbing medium, the absorption of radiation occurs in such a way that the intensity transmitted by the medium is a constant fraction of that incident on it, irrespective of the absolute value of the latter.

Each successive layer of the medium absorbs an equal fraction of the radiation, so that the rate of decrease of the intensity $I$ with the path length is proportional to the intensity at that particular point.

$$\frac{-dI}{dl} = aI$$

If the initial intensity is $I_0$ and the intensity of radiation after passing through a length $l$ of the medium is $I$, then:

$$\ln \frac{I_0}{I} = al$$

or

$$I = I_0 e^{-al}$$

where 'a' is a constant for the medium at one particular wavelength and is called the 'absorption coefficient'. This relationship is known as Lambert's Law (73). Converting the logarithms to the base 10 the above expression becomes

$$\log \frac{I_0}{I} = Kl$$

$$I = I_0 \times 10^{-Kl}$$

where $K$ is the 'extinction coefficient',

$$a = K \ln 10 = 2.3026 K$$
log $I_0/I$ is known as the extinction, or the optical density of the medium, the value for unit path length being the extinction coefficient.

A second law discovered by Beer (74) states that the absorption is proportional to the number of molecules through which the radiation passes. If a substance is dissolved in a non-absorbing medium, the absorption will be proportional to the concentration. Whilst Lambert's Law is obeyed in most cases deviations from Beer's Law are frequently encountered. The two relationships are combined in what is know as the Lambert-Beer Law, which may be expressed:

$$I = I_0 10^{-scl}$$

where $s$ is the molecular extinction coefficient i.e. the extinction coefficient for a solution containing 1 g.mol/litre. 'c' is the concentration in g.mols/litre and 'l' the path length in cms.

The constancy in the value of $s$ for an ion with varying ionic concentrations was one of the earliest pieces of evidence for the complete dissociation of strong electrolytes. Further work showed that the absorption coefficient was not affected by Debye-Hückel interactions. Association between the ions can however cause changes in the absorption coefficients, and these changes have been utilised for examining equilibria in electrolyte solutions.
Job (75) devised a simple spectrophotometric method of determining the composition of metal chelate compounds. This technique has been called the Method of Continuous Variation. If the complex $AB_n$ is formed from the metal ion A and the complexing agent B

$$A + nB \rightleftharpoons AB_n$$

$$k = \frac{(AB_n)}{(A)(B)^n}$$

By making $(A) + (B)$ constant in all cases, it can be shown that when the concentration of $AB_n$ is a maximum

$$\frac{(B)}{(A)} = n$$

or

$$\frac{d(AB_n)}{d(A)} = 0$$

This means that the concentration of $AB_n$ will be a maximum when A and B are present in the ratio in which they occur in the complex.

If $AB_n$ is the only absorbing species present, the optical density of the solution will be proportional to the concentration of the complex, and a plot of the optical density against the composition of the solution will have a maximum at the composition corresponding to the formula of the complex. When other species are present which absorb light in the same region as $AB_n$ a modified method must be employed. The difference between the observed optical density of the solution, and that
which would be observed in the absence of association is plotted against the composition. Job was of the opinion that the method was applicable only to a system containing not more than one complex.

Vosburgh and Cooper (76) suggested a method whereby it is possible to determine whether or not more than one compound is formed by measuring the optical densities at a series of wavelengths. If similar results are obtained at different wavelengths they concluded that only a single complex is formed. The method was applied to the formation of the acid chromate and dichromate ions, and to the complex ions formed by nickel and o-phenanthroline and ethylene-diamine, and by copper and ammonia.

Following the publication of Job's results, numerous other papers appeared reporting investigations by his method. Fromherz et alia (77) used ultra violet spectrophotometry in investigation of the dissociation of lead, thallous, stannous and other metal halides in solution. Schmidt and Gastinger (78) studied the absorption of the unstable ion $\text{HS}_2\text{O}_3^-$ in the region 2336 - 2807 A.U., and Cathala and Cluzel (79) studied the hydrolysis of ferric salts.

Bobtelsky and Jordan (80) in a study of the character and behaviour of metallic oxy-complexes in dilute aqueous and 50\% alcoholic solutions, established the existence of 1:1 complexes of copper and nickel tartrates and citrates. Their measurements
were made using colour filters.

Many authors noted the marked influence of the chloride ion on the extinction coefficient of the cupric ion in aqueous solution in the range 230 - 400 μm. Of the many investigations of this association the most satisfactory are those of Bjerrum (81) and McConnell and Davidson (82). Bjerrum using a spectrophotometric method and making rough activity corrections was able to calculate the stability constants of the various complexes formed.

McConnell and Davidson repeated his work in an attempt to obtain more accurate data. They describe a spectrophotometric study of the equilibria

\[
\text{Cu}^{++} + n\text{Cl}^{-} \rightleftharpoons \text{CuCl}^{(n-2)}^{+}
\]

in a solution containing cupric perchlorate, hydrochloric acid and perchloric acid. The ionic strength of all the solutions was fixed at unity in order to minimize the variation in the activity coefficients as the composition of the solution was varied. Their results were interpreted on the assumption that these variations were negligible. This assumption was not valid in the previous investigations which had been carried out at high and varying ionic strengths. In order to be able to determine the dissociation constants of \(\text{CuCl}^{+}\) and \(\text{CuCl}_2\) fairly concentrated solutions had to be used, as these two species were found to be highly dissociated in dilute aqueous solution.
Bobtelsky and Bar-Gadda (83) report a study of the copper complexes of malonic, succinic, maleic, phthalic, salicylic, and lactic acids. They employed two methods: the spectrophotometric method, and what they called the 'heterometric method' (a photometric study of suspensions). The spectrophotometric method was used to:

(1) study the effect of various anions on the absorption spectrum of the cupric ion.
(2) determine the composition of the complexes formed by applying Job's method of continuous variation.
(3) calculate the dissociation constants.

The absorption measurements were made in the wavelength range 340 - 680 μm. In some cases (e.g. copper succinate) the salt was precipitated. Although the authors have calculated by some method, not specified in the paper, values for the dissociation constants of a number of copper complexes, it is difficult to attach any real significance to the values quoted. No attempt was made to maintain a constant ionic strength, neither was there any correction for the activities. The authors used as their source of the cupric ion an approximately 0.2 M solution of copper sulphate, presumably assuming in their calculations the complete dissociation of the salt at this concentration. To this solution were added varying concentrations of 0.2 M sodium or potassium dicarboxylate. The pH of the alkali metal salt solutions being greater than 7, extensive hydrolysis.
of the cupric ion would occur. It is probable that Bobtelsky and Bar-Gadda's solutions contained appreciable quantities of CuOH$^-$ and possibly colloidal Cu(OH)$_2$. These constituents would have a considerable effect on the optical density, and a correction for them would probably make a significant difference in the values of the dissociation constants of the copper complexes.

Peacock and James (9) had previously made a qualitative study on similar lines. They also used a copper sulphate solution as the source of the cupric ion. An appreciable increase in the absorption was observed on adding sodium malonate, whilst the increase on adding the sodium salts of maleic, fumaric, phthalic, and tartaric acids was much less. Copper succinate, glutarate, and adipate were found to be too insoluble for any measurements to be made. Job's method of continuous variation was applied at a series of wavelengths in the range 680 - 840 μm. Sharp breaks in the plots of optical density against \((A^\infty)/(M^{++})\) were obtained with copper malate and lactate. With the malonate solutions the results were less satisfactory as the breaks were not very sharp and their location varied with the wavelength. This was attributed to the presence of CuMal and CuMal$^2$. Peacock and James did not attempt to calculate the dissociation constants.

In calculating the various dissociation constants all the authors mentioned above neglected activity coefficients. Most of the work involved high and varying ionic strengths.
Rabinowitch and Stockmayer (84) determined the absorption spectra of ferric salt solutions under controlled conditions of acidity, ionic strength and temperature, and attempted to calculate the thermodynamic dissociation constants of the various ionic species present. By keeping the ionic strength at a constant value by adding perchloric acid they felt justified in assuming that the activity coefficients of the various ions remained unchanged. Similar assumptions were made by Evans and Nancollas (85) who studied the formation of ion-pairs by the cobaltic ion with chloride, bromide, iodide and azide ions at an ionic strength of .054.

The dissociation of copper acetate was studied by Doucet and Marion (86), by both the spectrophotometric and conductivity methods. The optical density of an aqueous solution of copper acetate was measured in the region of 670 mu. The acetate ion was added in the form of acetic acid, which also suppressed the hydrolysis of the cupric ion. In calculating the dissociation constant an approximate form of the Debye-Hückel equation was used, the K value obtained being in agreement with that previously determined from conductivity measurements.

In a study of metal amine formation in aqueous solution, Bjerrum (82) developed a method for the determination of all the complexity constants of a system. The primary assumption made in this method was that it was possible to carry out the
investigation at a constant concentration of a highly dissociated neutral salt, and at a low concentration of the complex-forming substance. Under such conditions the activity coefficients would remain constant, and the law of mass action could be applied. When the system is of slight complexity, this condition cannot be fulfilled, because of the high and varying concentration of the ligand, and the activity coefficients must be taken into consideration. Bjerrum (82) made some approximate activity corrections which were reasonable at high ionic strengths, but inapplicable at low ionic strengths. Nåsanen (87) in a spectrophotometric study of complex formation in copper sulphate solutions suggested a new method which permitted the determination of the first complexity constant over wide limits of ionic strengths. The value calculated for the dissociation constant of copper sulphate was not however in good agreement with values obtained by other methods.

Monk et alia in a series of papers (88 - 92) have examined various methods of making suitable activity corrections. By measuring the optical densities of a number of solutions of constant ionic strength a value for \( \frac{1}{(\varepsilon_2 - \varepsilon_1)} \) was obtained, where \( \varepsilon_2 \) and \( \varepsilon_1 \) are the molecular extinction coefficients of the ion-pair and the absorbing ion respectively. Copper sulphate was examined by this method (90), and a value for \( K \) in good agreement with the conductivity value was obtained.
If solutions of cupric perchlorate and sodium dicarboxylate are mixed, the ion-pair CuA is formed by the reaction

\[ \text{Cu(ClO}_4\text{)}_2 + \text{Na}_2\text{A} \rightarrow \text{CuA} + 2\text{NaClO}_4 \]

Assuming that in the spectral region chosen Cu\(^{++}\) and CuA are the only species absorbing radiation, then from the Lambert-Beer Law:

\[
D_1 = l \cdot \varepsilon_1 (a - x) + l \cdot \varepsilon_2 x \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (1)
\]

\[
D_2 = l \cdot \varepsilon_1 a \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (2)
\]

'a' is the molarity of the cupric perchlorate solution, 'x' that of the ion-pair CuA in the presence of 'b' molar Na\(_2\)A. \(\varepsilon_1\) and \(\varepsilon_2\) are the molecular extinction coefficients of Cu\(^{++}\) and CuA respectively. \(D_1\) and \(D_2\) are the optical densities of solutions 'a' and 'a + b' in cells of path length 'l' cm's. It is assumed that the cupric perchlorate is completely dissociated at the concentrations employed, and that no higher association products e.g. CuA\(_2\) are present. This assumption is probably justified if the concentration of Cu\(^{++}\) is very much greater than that of the added A\(^-\). The contribution to the optical density of CuHA\(^+\) has also to be neglected, this being justified, at least in the case of copper oxalate and copper malonate, by the following processes:

\[
\text{CuHA} \rightleftharpoons \text{Cu}^{++} + \text{HA'}
\]

\[
\text{Cu}^{++} + \text{HA'} \rightleftharpoons \text{CuA} + \text{H}^+
\]
The dissociation constant of CuA is given by:

\[ K = \frac{(Cu^{++})(A^-) \cdot f_1 f_2}{(CuA) \cdot f_3} \]

\[ = \frac{(a - x)(b - x - y_1 - y_2 - \cdots) \cdot f_1 f_2}{x \cdot f_3} \] ... (3)

where \( y_1, y_2 \) etc. are the concentrations of any other non-absorbing ion-pairs formed by the anion \( A^- \), and cations other than \( Cu^{++} \). \( f_1, f_2, f_3 \) are the activity coefficients of \( Cu^{++}, A^- \), and CuA respectively.

From equations (1), (2), and (3)

\[ x = \frac{D_1 - D_2}{1 \cdot \left( \varepsilon_2 - \varepsilon_1 \right)} \] .......... (4)

\[ K = \frac{\alpha l(b - x - y_1 \cdots) \cdot f_1 f_2}{(\varepsilon_2 - \varepsilon_1) \cdot (D_1 - D_2) \cdot f_3} - \frac{(b' - x' - y_1 \cdots) \cdot f_1 f_2}{(\varepsilon_2 - \varepsilon_1) \cdot f_3} - \frac{\beta f_1 f_2}{f_3} \]

\[ = \frac{\alpha f_1 f_2}{f_3} - \frac{\beta f_1 f_2}{f_3 \cdot (\varepsilon_2 - \varepsilon_1)} \]

A plot of \( \alpha f_1 f_2 / f_3 \) against \( \beta f_1 f_2 / f_3 \) has a slope of \( 1/(\varepsilon_2 - \varepsilon_1) \) and an intercept on the y-axis of \( K/(\varepsilon_2 - \varepsilon_1) \). Since 'x' is not known, \( K \) cannot be obtained directly, neither can \( y_1, y_2 \) etc be calculated.

If various molarities of Cu(ClO\(_4\))\(_2\) and Na\(_2\)A are used keeping the total ionic strength constant with sodium perchlorate.
the activity coefficients can be regarded as being constant. A plot of \( \frac{ab1}{(D_1 - D_2)} \) against 'b' should give a value of \( \frac{1}{(e_2 - e_1)} \) and \( \frac{K'}{(e_2 - e_1)} \), where \( K' \) is the concentration dissociation constant at one ionic strength. This preliminary value of \( (e_2 - e_1) \) can then be used to obtain an approximate value of 'x' (from (4)), and hence \( y_1 \) etc. From these values an approximate value for the ionic strength I can be deduced. This enables the activity coefficient to be calculated using some suitable equation such as the Davies equation. A second plot of \( \frac{al(b - x - y_1 \cdots f_1 f_2)}{(D_1 - D_2) f_3} \) against \( (b - x - y_1 \cdots) f_1 f_2 \) will give a second value for \( \frac{1}{(e_2 - e_1)} \). These calculations can then be repeated until constant values are obtained. If the optical densities of a second series of solutions of varying ionic strengths are measured, the value of \( \frac{1}{(e_2 - e_1)} \) obtained by the constant ionic strength method can be used to calculate \( K \) for each solution. The correct value of \( C \) in the Davies equation, required to give constant \( K \) values, can be determined by trial and error.

The above procedure was adopted by Bale, Davies and Monk (90) in their study of copper sulphate. In systems of higher complexity a number of difficulties arise. If the ion-pair has a very small dissociation constant, it is difficult to maintain constant ionic strength. There is ample evidence that cupric salt solutions are susceptible to hydrolysis, so that in order to prevent the
formation of CuOH\(^+\) and Cu(OH)\(_2\) sufficient acid must be present. If the anion A\(^n\) is derived from an organic dicarboxylic acid, a further complication arises due to the association between H\(^+\) from the acid and A\(^n\) to give HA\(^{+}\) and H\(_2\)A. This results in \(y_1\) and \(y_2\) etc in equation (3) having quite appreciable values, and the first approximation (neglecting \(x, y_1\) etc.) giving impossible results.

In the present work no attempt has been made to maintain an absolutely constant ionic strength. The copper oxalate and copper malonate solutions contained an excess of perchloric acid, so that the ionic strength in all solutions was approximately constant. The low pH of the solution precluded the presence of any of the hydrolysis products. In the succinate and glutarate solutions however, the presence of the acid decreased the association of Cu\(^{++}\) and A\(^n\) to such an extent that (\(D_1 - D_2\)) was too small to be accurately measured. This is understandable when the K values for HA\(^{+}\) and CuA are compared. Preferential association occurs between the H\(^+\) and the anion. A\(^n\) constant concentration of sodium perchlorate was maintained in each of the succinate and glutarate solutions. Since there is no excess acid in these solutions, allowance must be made for CuOH\(^+\) formed by hydrolysis. It was assumed that as the solutions remained clear, no cupric hydroxide was formed.
In a solution which contains \( \text{Cu}^{++} \) and \( \text{CuOH}^+ \) only
\[
D = \varepsilon_1(\text{Cu}^{++}) + \varepsilon_2(\text{CuOH}^+) \quad \ldots \ldots (5)
\]
where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the molecular extinction coefficients of \( \text{Cu}^{++} \) and \( \text{CuOH}^+ \) respectively. The path length is taken as unity.

For the process:
\[
\text{Cu}^{++} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+
\]
\[
K_h = \frac{(\text{CuOH}^+)(\text{H}^+)}{(\text{Cu}^{++})}
\]
If under experimental conditions \( (\text{Cu}^{++}) \gg (\text{CuOH}^+) \) and \( (\text{H}^+) \gg (\text{CuOH}^+) \) then
\[
D = \varepsilon_1(\text{Cu}^{++})c + \varepsilon_2K_h(\text{Cu}^{++})c \quad \ldots \ldots (6)
\]
where \( (\text{Cu}^{++})c \) is the total copper concentration, and \( (\text{H}^+)c \) the concentration of the hydrogen ions due to the perchloric acid present, neglecting the concentration produced by the hydrolysis.

\[
D = \overline{\varepsilon}(\text{Cu}^{++})c
\]
Dividing throughout in equation (6) above will give
\[
\overline{\varepsilon} = \varepsilon_1 + \frac{\varepsilon_2K_h}{(\text{H}^+)c}
\quad \ldots \ldots \ldots (7)
\]
According to this equation, measurement of the optical density of a solution containing \( \text{Cu}^{++} \) and \( \text{CuOH}^+ \) can only give the product \( \varepsilon_2K_h \) and not \( \varepsilon_2 \). If however a value can be assigned to \( K_h \) then \( \varepsilon_2 \) can be calculated.

If the optical densities of solutions containing a constant
concentration of copper, varying concentrations of acid, and having constant ionic strength (maintained by adding sodium perchlorate), are measured, a plot of $\varepsilon$ against $1/(H^+)$ should give a straight line of slope $\varepsilon_2 K_h$. Two values of $K_h$ are quoted in the literature: that calculated by Davies (60) from the conductivity data of Owen and Gurry (93) for copper sulphate, and that given by Berecki-Biedermann (94) determined by a pH titration method. There is considerable discrepancy between the two values, Davies giving the dissociation constant of CuOH$^+$ as $3.4 \times 10^{-7}$, whilst Berecki-Biedermann gives $(1.0 \pm 0.2) \times 10^{-8}$. 


(iii). Errors in Spectrophotometric Measurements.

Many departures from absorption theory in photoelectric spectrophotometry have been reported in the literature. Factors which can account for these departures can be divided into three classes. (96, 97)

(1) Chemical.

(2) Instrumental.

(3) Technique.

(1). Chemical Factors.

(a) Any turbidity present in the solutions may escape casual observation, and may vary with time and temperature. It can generally be removed either by filtering or centrifuging the solution before it is introduced into the cell.

(b) The absorption due to the solvent can introduce an appreciable error, but if it is only slight its effect is negligible as it is incorporated in the cell correction.

(c) Any photochemical reaction that can take place in the solution will have a considerable effect on the absorption. This was noted by Bisikalova (98), in his study of complex oxalates. A definite variation in the dissociation constant with the wavelength of the light used for measurement, was observed.
(2) **Instrumental Factors.**

These may be listed briefly as follows:

(a) **Spectral Impurities.** It is very difficult to obtain 100% monochromatic light.

(b) **Multiple reflections of the light from the absorption cell faces,** causes the light to pass through the cell several times.

(c) **Non-parallelism of the light beam** gives rise to errors in the effective path length of the cells, and in the failure of some of the multiple reflected light to fall on the photocell.

Provided that the solution is not too dilute, so that spectral impurities cannot be absorbed, at constant wavelength, slit width and using the same cell, the errors can be represented by a constant factor.

(3) **Errors in Technique.**

The cells must be scrupulously clean and the cell windows free from contamination. Greater constancy in the results is obtained if the cells are filled 'in situ' in the cell carrier.

The temperature in the cell carrier can be controlled by enclosing it in a water jacket maintained at a constant temperature. A less satisfactory method is to use the instrument in a thermostated room.
(iv) **Experimental.**

**Preparation of Solutions.**

(a) **Cupric Perchlorate.**

Cupric oxide was prepared as described in Section 2. The oxide was washed several times with distilled water, and then digested on a steam bath with concentrated perchloric acid. The deep blue solution formed was filtered to remove excess cupric oxide. This filtrate after standing for a few days was found to deposit cupric hydroxide, formed by hydrolysis. This was prevented by adding a known concentration of perchloric acid. Solutions used in the actual experiments were prepared from the stock solution by dilution. The copper content was determined by electrodeposition on platinum electrodes (Section 2 p.106).

(b) **Sodium Salts of the Dicarboxylic Acids.**

A.R. sodium oxalate was recrystallised thrice from distilled water. The sodium salts of malonic, succinic and glutaric acids were prepared by dissolving a weighed quantity of the pure acids (purified as described in Section 1.) in an equivalent volume of standard sodium hydroxide, with subsequent dilution to give suitable concentrations. As these solutions were found to be susceptible to bacterial attack they were freshly prepared before each run.
(c) Sodium Perchlorate.

This was prepared by carefully neutralising a solution of perchloric acid with the calculated quantity of standard sodium hydroxide.

There is little evidence of ionic association in aqueous solutions of metal perchlorates. These salts are therefore frequently used in spectrophotometric work. In order to ascertain that in the present work it was justifiable to assume complete dissociation of cupric perchlorate, the effect of adding perchlorate ions, in the form of perchloric acid, to a solution of cupric perchlorate of fixed concentration, was examined. The added acid caused a slight decrease in the optical density, indicating the removal of an absorbing species. This decrease continued until a critical acidity was attained, when no further change was observed. This can be attributed to the presence of CuOH\(^+\) and perhaps colloidal Cu(OH)\(_2\). As the test solutions in the oxalate and malonate series contained added acid, these hydrolysis products would be absent. In the succinate and glutarate series no acid was present so that CuOH\(^+\) was probably present. As the solutions remained perfectly clear, it was assumed that Cu(OH)\(_2\) was absent.

Preliminary experiments showed that a cupric perchlorate solution of approximately 0.002 M would give suitable values for the optical densities, measured in cells of path length 4 cms.
In order to choose a suitable wavelength region, the absorption spectrum of copper perchlorate was measured from 220 - 760 μm. This proved to have a high peak in the ultraviolet region, and a smaller one in the 450-600 μm region. Between 270 and 350 μm the absorption due to the Cu^{++} ion was very small. It was therefore decided to measure the optical densities at 270, 275, and 280 μm as the absorption at these wavelengths would be due mainly to the ion-pair CuA. It was also shown that none of the species A^-, HA, and H₂A absorbed radiation in this region.

In the copper oxalate series there was such a large change in the optical density on adding relatively small concentrations of the sodium oxalate, that further measurements were made at 305, 310, and 315 μm. It was deemed wise to measure the optical densities at more than one wavelength as there is evidence (98) that the dissociation constant can vary with the wavelength.

The test solutions were made up to contain a constant concentration of cupric perchlorate, and varying concentration of the sodium salt. In the oxalate and malonate series, a known excess of perchloric acid was added, and in the succinate and glutarate solutions a fixed concentration of sodium perchlorate. A second series of oxalate solutions was prepared adding the sodium oxalate from a micro-burette. The optical densities of these solutions were measured at 270, 275, and 280 μm.
The measurements were made on an Unicam S.P. 500 spectrophotometer. The solutions were contained in silica cells of path length 4 cm. Errors which can arise in spectrophotometric measurements have already been discussed. In order to minimise the 'stray light' error, the reference solution was cupric perchlorate of the same copper concentration as the test solution. To compensate for any differences in the cells, they were interchanged, and a further set of readings taken in each case.

Various authors have suggested methods of filling the cells. It has been claimed (97) that filling the cells 'in situ' in the spectrophotometer leads to greater constancy in the readings. This procedure was therefore adopted. Before filling, each cell was washed several times with the solution. This was done by means of a pipette, the possibility of contaminating the cell windows being thus reduced to a minimum. The cells were cleaned with chromic acid before each run, followed by successive washing with distilled water before being used.

The spectrophotometer was used in a room maintained at 25°C, the solutions being kept at this temperature overnight in a thermostated water bath before being transferred to the cells.
ABSORPTION CURVE
0.002 M COPPER PERCHLORATE
4 cm. cell

Optical Density

Wavelength μm

FIG. 11
Table 31.

**Molecular Extinction Coefficient of Cu**

<table>
<thead>
<tr>
<th>(Cu&lt;sup&gt;++&lt;/sup&gt;)</th>
<th>D&lt;sub&gt;270&lt;/sub&gt;</th>
<th>(\varepsilon_{270})</th>
<th>D&lt;sub&gt;275&lt;/sub&gt;</th>
<th>(\varepsilon_{275})</th>
<th>D&lt;sub&gt;280&lt;/sub&gt;</th>
<th>(\varepsilon_{280})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00794</td>
<td>0.131</td>
<td>4.128</td>
<td>0.105</td>
<td>3.288</td>
<td>0.087</td>
<td>2.738</td>
</tr>
<tr>
<td>0.01589</td>
<td>0.275</td>
<td>4.330</td>
<td>0.221</td>
<td>3.469</td>
<td>0.181</td>
<td>2.848</td>
</tr>
<tr>
<td>0.02466</td>
<td>0.430</td>
<td>4.359</td>
<td>0.330</td>
<td>3.345</td>
<td>0.257</td>
<td>2.605</td>
</tr>
<tr>
<td>0.03289</td>
<td>0.579</td>
<td>4.403</td>
<td>0.441</td>
<td>3.352</td>
<td>0.342</td>
<td>2.600</td>
</tr>
<tr>
<td>0.04111</td>
<td>0.729</td>
<td>4.435</td>
<td>0.554</td>
<td>3.369</td>
<td>0.426</td>
<td>2.591</td>
</tr>
</tbody>
</table>

\[ \bar{\varepsilon}_{270} = 4.351 \]
\[ \bar{\varepsilon}_{275} = 3.364 \]
\[ \bar{\varepsilon}_{280} = 2.676 \]
Optical Density

FIG. 12

(\(\text{Na}_2\text{Ox}\))^{10^4}_M

(1) 0.23
(2) 1.14
(3) 2.85
(4) 5.82
(5) 8.55
(6) 14.25
Table 32.

Copper Oxalate.
(Cupric Perchlorate) = \(0.002005\) g mol/litre
(Sodium Oxalate) = \(b\) g mol/litre.

\[D = D_1 - D_2\]

<table>
<thead>
<tr>
<th>(b \times 10^3)</th>
<th>(D_{305})</th>
<th>(D_{310})</th>
<th>(D_{315})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4160</td>
<td>0.645</td>
<td>0.436</td>
<td>0.292</td>
</tr>
<tr>
<td>0.8495</td>
<td>0.388</td>
<td>0.260</td>
<td>0.173</td>
</tr>
<tr>
<td>0.5946</td>
<td>0.287</td>
<td>0.200</td>
<td>0.133</td>
</tr>
<tr>
<td>0.2832</td>
<td>0.128</td>
<td>0.076</td>
<td>0.048</td>
</tr>
<tr>
<td>0.1155</td>
<td>0.035</td>
<td>0.021</td>
<td>0.010</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(b \times 10^3)</th>
<th>(D_{270})</th>
<th>(D_{275})</th>
<th>(D_{280})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1155</td>
<td>0.553</td>
<td>0.429</td>
<td>0.321</td>
</tr>
<tr>
<td>0.1036</td>
<td>0.547</td>
<td>0.432</td>
<td>0.297</td>
</tr>
<tr>
<td>0.0906</td>
<td>0.385</td>
<td>0.297</td>
<td>0.220</td>
</tr>
<tr>
<td>0.0685</td>
<td>0.335</td>
<td>0.258</td>
<td>0.192</td>
</tr>
<tr>
<td>0.0476</td>
<td>0.200</td>
<td>0.154</td>
<td>0.115</td>
</tr>
<tr>
<td>0.0227</td>
<td>0.102</td>
<td>0.084</td>
<td>0.061</td>
</tr>
</tbody>
</table>
Table 33.

Copper Oxalate.

\[ X = \frac{abl}{D} \quad l = 4 \text{ cms.} \]

<table>
<thead>
<tr>
<th>( b \cdot 10^3 )</th>
<th>( x_{305} \cdot 10^6 )</th>
<th>( x_{310} \cdot 10^6 )</th>
<th>( x_{315} \cdot 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4160</td>
<td>17.365</td>
<td>26.047</td>
<td>38.890</td>
</tr>
<tr>
<td>.8495</td>
<td>17.559</td>
<td>26.204</td>
<td>39.382</td>
</tr>
<tr>
<td>.5946</td>
<td>16.916</td>
<td>23.844</td>
<td>34.556</td>
</tr>
<tr>
<td>.2832</td>
<td>17.745</td>
<td>29.886</td>
<td>47.319</td>
</tr>
<tr>
<td>.1036</td>
<td>16.750</td>
<td>21.592</td>
<td>29.887</td>
</tr>
<tr>
<td>.0906</td>
<td>15.190</td>
<td>19.234</td>
<td>31.997</td>
</tr>
<tr>
<td>.0685</td>
<td>18.975</td>
<td>24.468</td>
<td>23.032</td>
</tr>
<tr>
<td>.0475</td>
<td>16.403</td>
<td>21.293</td>
<td>28.620</td>
</tr>
<tr>
<td>.0227</td>
<td>17.809</td>
<td>21.625</td>
<td>29.779</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( b \cdot 10^3 )</th>
<th>( x_{270} \cdot 10^6 )</th>
<th>( x_{275} \cdot 10^6 )</th>
<th>( x_{280} \cdot 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1155</td>
<td>16.750</td>
<td>21.592</td>
<td>29.887</td>
</tr>
<tr>
<td>.1036</td>
<td>15.190</td>
<td>19.234</td>
<td>27.976</td>
</tr>
<tr>
<td>.0906</td>
<td>18.975</td>
<td>24.468</td>
<td>33.032</td>
</tr>
<tr>
<td>.0685</td>
<td>16.403</td>
<td>21.293</td>
<td>28.620</td>
</tr>
<tr>
<td>.0475</td>
<td>19.076</td>
<td>24.773</td>
<td>33.175</td>
</tr>
<tr>
<td>.0227</td>
<td>17.809</td>
<td>21.625</td>
<td>29.779</td>
</tr>
</tbody>
</table>
Table 34.

Copper Malonate

(Cupric Perchlorate) = 0.001986 g mol/litre
(Sodium Malonate) = \( b \) g mol/litre

<table>
<thead>
<tr>
<th>( b \cdot 10^3 )</th>
<th>( D_{270} )</th>
<th>( D_{275} )</th>
<th>( D_{280} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5989</td>
<td>0.165</td>
<td>0.128</td>
<td>0.101</td>
</tr>
<tr>
<td>0.7187</td>
<td>0.200</td>
<td>0.152</td>
<td>0.117</td>
</tr>
<tr>
<td>0.8984</td>
<td>0.248</td>
<td>0.189</td>
<td>0.141</td>
</tr>
<tr>
<td>1.0181</td>
<td>0.283</td>
<td>0.214</td>
<td>0.162</td>
</tr>
<tr>
<td>1.1978</td>
<td>0.341</td>
<td>0.257</td>
<td>0.193</td>
</tr>
<tr>
<td>1.3775</td>
<td>0.391</td>
<td>0.289</td>
<td>0.211</td>
</tr>
</tbody>
</table>

\[ X = \frac{a b l}{D} \quad l = 4 \text{ cms} \]

<table>
<thead>
<tr>
<th>( b \cdot 10^3 )</th>
<th>( X_{270} \cdot 10^5 )</th>
<th>( X_{275} \cdot 10^5 )</th>
<th>( X_{280} \cdot 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5989</td>
<td>2.884</td>
<td>3.717</td>
<td>4.711</td>
</tr>
<tr>
<td>0.7187</td>
<td>2.855</td>
<td>3.757</td>
<td>4.880</td>
</tr>
<tr>
<td>0.8984</td>
<td>2.878</td>
<td>3.777</td>
<td>5.062</td>
</tr>
<tr>
<td>1.0181</td>
<td>2.858</td>
<td>3.780</td>
<td>4.993</td>
</tr>
<tr>
<td>1.1978</td>
<td>2.791</td>
<td>3.791</td>
<td>4.931</td>
</tr>
<tr>
<td>1.3775</td>
<td>2.799</td>
<td>3.787</td>
<td>5.187</td>
</tr>
</tbody>
</table>
COPPER MALONATE
270 m\text{u.}

FIG. 14

3.1
3.0
2.9
2.8
2.7
0.6
0.8
1.0
1.2
b \cdot 10^3
\frac{a b l}{10^5} D
Table 35.

Copper Succinate.

conc. Cu(ClO₄)₂ = .002005 g mol/litre, (Na₂Succ) = b g mol/litre

<table>
<thead>
<tr>
<th>b·10⁴</th>
<th>D₂70</th>
<th>D₂75</th>
<th>D₂80</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1997</td>
<td>.123</td>
<td>.076</td>
<td>.059</td>
</tr>
<tr>
<td>1.4991</td>
<td>.170</td>
<td>.132</td>
<td>.102</td>
</tr>
<tr>
<td>1.7996</td>
<td>.227</td>
<td>.177</td>
<td>.132</td>
</tr>
<tr>
<td>2.0995</td>
<td>.296</td>
<td>.223</td>
<td>.171</td>
</tr>
<tr>
<td>2.4594</td>
<td>.364</td>
<td>.283</td>
<td>.215</td>
</tr>
<tr>
<td>2.6994</td>
<td>.433</td>
<td>.337</td>
<td>.257</td>
</tr>
<tr>
<td>2.9994</td>
<td>.507</td>
<td>.395</td>
<td>.303</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b·10⁴</th>
<th>X₂70·10⁷</th>
<th>X₂75·10⁷</th>
<th>X₂80·10⁷</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4997</td>
<td>7.075</td>
<td>9.321</td>
<td>12.062</td>
</tr>
<tr>
<td>1.7996</td>
<td>6.353</td>
<td>8.341</td>
<td>11.185</td>
</tr>
<tr>
<td>2.0995</td>
<td>5.689</td>
<td>7.555</td>
<td>10.073</td>
</tr>
<tr>
<td>2.4594</td>
<td>5.419</td>
<td>7.130</td>
<td>9.335</td>
</tr>
<tr>
<td>2.6994</td>
<td>5.000</td>
<td>6.572</td>
<td>8.617</td>
</tr>
<tr>
<td>2.9994</td>
<td>4.745</td>
<td>6.229</td>
<td>8.121</td>
</tr>
</tbody>
</table>
FIG. 16

COPPER SUCCINATE

$\frac{a b l}{D} \cdot 10^7$

280 mu.

15.0

10.0

4.0

$10^4$

2.0  4.0  6.0  8.0  9.0  10.0
Table 36.

Copper Glutarate.

concen. Cupric Perchlorate = .00205 g mol/litre.

(Sodium Glutarate) = b g mol/litre

<table>
<thead>
<tr>
<th>b \cdot 10^4</th>
<th>D_{270}</th>
<th>D_{275}</th>
<th>D_{280}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3511</td>
<td>.513</td>
<td>.364</td>
<td>.169</td>
</tr>
<tr>
<td>1.0508</td>
<td>.407</td>
<td>.292</td>
<td>.143</td>
</tr>
<tr>
<td>.9007</td>
<td>.358</td>
<td>.258</td>
<td>.124</td>
</tr>
<tr>
<td>.7506</td>
<td>.289</td>
<td>.210</td>
<td>.104</td>
</tr>
<tr>
<td>.6005</td>
<td>.237</td>
<td>.172</td>
<td>.088</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b \cdot 10^4</th>
<th>X_{270} \cdot 10^7</th>
<th>X_{275} \cdot 10^7</th>
<th>X_{280} \cdot 10^7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3511</td>
<td>21.124</td>
<td>29.770</td>
<td>43.002</td>
</tr>
<tr>
<td>1.0508</td>
<td>20.707</td>
<td>28.362</td>
<td>40.714</td>
</tr>
<tr>
<td>.9007</td>
<td>20.179</td>
<td>28.000</td>
<td>39.692</td>
</tr>
<tr>
<td>.7506</td>
<td>20.331</td>
<td>28.667</td>
<td>40.403</td>
</tr>
<tr>
<td>.6005</td>
<td>20.322</td>
<td>28.002</td>
<td>39.157</td>
</tr>
</tbody>
</table>
(vi) Discussion of Results.

The absorption spectrum of cupric perchlorate is shown in fig. (11). In order to determine whether the Lambert-Beer Law was valid, the optical densities of a number of solutions of cupric perchlorate of varying concentrations were measured. For each one the molecular extinction coefficient of the cupric ion was calculated from the relationship $D = \varepsilon x$, where $x$ is the concentration of the cupric ion. The results are set out in table 31. It is seen that there is an increase in $\varepsilon$ as the concentration of the cupric ion increases. This, at first sight might be taken as an indication that association was taking place between the $\text{Cu}^{++}$ and $\text{ClO}_4^-$ ions. However, if $\varepsilon$ is calculated from the relationship suggested by Monk (91)

$$\varepsilon' = \frac{D_n - D_m}{c_n - c_m}$$

where $D_n$ and $D_m$ are the optical densities of two solutions of concentrations $c_n$ and $c_m$ respectively, constancy is obtained in the value of $\varepsilon$.

The very considerable effect on the absorption of the cupric perchlorate solution of adding relatively small concentrations of sodium oxalate is shown in fig (12). Smaller changes were observed with malonate, succinate, and glutarate. Fig (13) shows a plot of $(D_1 - D_2)$ against the concentration of added malonate for four wavelengths.
As a basis for calculating the dissociation constants of the various copper salts, the method used by Bale, Davies and Monk (90) was adopted. The main difficulty in using this method is to obtain a value for \(1/(e_2 - e_1)\). As a first approximation, all ion-pairs are neglected, and a preliminary plot of \(a/(D_1 - D_2)\) against \(b\) made, where \(a\) = concentration of cupric perchlorate, and \(b\) = concentration of the added sodium salt. This should give a value of \(1/(e_2 - e_1)\), and did in fact do so in the case of the relatively strong salt copper sulphate, but when this was tried in the present work it was found that in the case of the oxalate solutions a straight line of negative slope was obtained. For the malonate solutions a line of negative slope was obtained at 270 mu, but at 275 and 280 mu the slope became positive. For the succinates the slopes were negative at all wavelengths, a change in the slope occurring at the higher concentrations of the sodium salt. The graphs for copper malonate are shown in figs. 14, 15, and those for copper succinate in fig (16). A negative slope implies that the molecular extinction coefficient of the ion-pair \((e_2)\), is less than that for the cupric ion \((e_1)\), and therefore the optical density should decrease on adding the sodium dicarboxylate. This is contrary to what is observed experimentally. From the positive slopes obtained in the case of copper malonate, the value of \(x\) (the concentration of the ion-pair) deduced from the value of \(1/(e_2 - e_1)\) was greatly in excess of the total malonate concentration: an obviously meaningless conclusion.
The results can be explained, if one takes into account the extensive ion association that is known to occur in these solutions. 'x' therefore must have a very high value so that its neglect in the first approximation cannot be justified. In the acid solutions, association between the H⁺ and A⁻ ions makes the concentration of HA⁺ and H₂A appreciable, whereas in the systems studied by Bale, Davies and Monk (90) association of this type was considerably less important. Another assumption which is probably not justified, is the neglect of any of the higher association products. Although the concentration of CuA₂⁻ may be very small, if the species has a high molecular extinction coefficient then it will make considerable contribution to the optical density. The malonate solutions were strongly acid, and therefore since association occurs between the malonate and hydrogen ions, as well as between the malonate and cupric ions, the concentration of CuMal present is small. As e decreases with increasing wavelength, the change in the slope of the graph is easily explained.

In the graph of abl/D against b for copper succinate, fig (16) there is a change in the slope at high values of b. This can probably be attributed to the formation of a new species in the solution, in all probability CuSuco₂⁻. The slopes of the abl/D v b curves for copper glutarate were positive at all wavelengths, indicating a lesser degree of association than in the succinate solutions. This is in accord with the values obtained in Section 1
COPPER SUCCINATE

FIG. 17

\[ \frac{1}{b} \times 10^{-4} \]
for the dissociation constants of these two salts. It is apparently impossible to obtain a satisfactory value for $1/(e_2-e_1)$ by this method.

Klotz and Loh Ming (99) adopted another method for determining the molecular extinction coefficient of the ion-pair. When the value of $b$ was infinity, they assumed that all the metal ions were taken up in the ion-pairs, so that $x = a$. By plotting $D$ against $1/b$ and extrapolating to $1/b = 0$ (i.e. $b = \infty$) a value for $e_2$ could be obtained since $D = ae_2$.

This extrapolation method has been tried in the present work, but it was impossible to extrapolate the curves obtained with any degree of certainty. The plot of $D$ against $1/b$ for copper succinate at three wavelengths is shown in fig (17). A plot of log $D$ against $1/b$ was also tried, but although this appeared to be a straight line, an extrapolation gave an impossible value for $D$ and hence for $'x'$. A specimen graph is shown in fig (18) for copper oxalate. Although it is obviously possible to draw a mean straight line through all these points, absence of data for low values of $1/b$ make it impossible to extrapolate with any certainty, and it must be concluded that the graph is almost certainly not linear.

Two other methods of calculation were tried. The first one is similar to the method adopted by Posey and Taube (100).
At constant \( I \), \( K' = \frac{(a - x)(b - x - \ldots)}{x} \)

where \( a, b, x \) etc have the same meaning as before.

\[
\frac{K'}{(b-x-\ldots)} = \frac{(a - x)}{x}
\]

\( D_1 = \varepsilon_1(a - x) + \varepsilon_2x \)

\( (a - x) = \frac{D_1 - \varepsilon_2x}{\varepsilon_1} \)

and \( D_1 - D_2 = x(\varepsilon_2 - \varepsilon_1) \)

Therefore

\[
\frac{K'}{(b-x-\ldots)} = \frac{(D_1 - \varepsilon_2x)(\varepsilon_2 - \varepsilon_1)}{\varepsilon_1(D_1 - D_2)}
\]

or

\[
\frac{(D_1 - D_2)K's_1}{(b-x-\ldots)(\varepsilon_2 - \varepsilon_1)} = D_1 - \varepsilon_2x
\]

A plot of \( \frac{(D_1 - D_2)}{(b-x-\ldots)} \) against \( D_1 \) extrapolates to a value \( D'_1 \)

whence \( x = \frac{(D_1 - D_2)}{(D_1 - D'_1)} \cdot a \)

The quantity measured experimentally was \( (D_1 - D_2) \). \( D_1 \) was found calculating a value for \( D_2 \) from the experimentally determined value of \( \varepsilon_{Cu^{++}} \). In this method again 'x' was too high to be ignored in the first approximation, and no useful information could be obtained from the graph of \( D_1 \) against \( (D_1 - D_2)/b \).
A second method suggested was to assume a value for $K$, and then, by trial and error, to find what value of $(D_1 - D_2)$ gave the same value of $K$ for one set of data. This value of $D$ could then be used to calculate $K$ for the other points. For using the data for copper malonate at 270 μ, and Stock and Davies's $K$ for copper malonate (4), $D$ is approximately 3.0, so that $x = \frac{(D_1 - D_2)}{3.0}a$ (where $a$ is the total copper concentration). This method although it appeared to be unsatisfactory was tried, again with no success.

The extensive ion-association that occurs in these solutions makes it impossible to obtain accurate values for the dissociation constants of the copper salts from the data available. The following method has been suggested (101) as likely to give better results.

If $a = \text{(copper perchlorate)}$  
$b = \text{(sodium dicarboxylate)}$  
$c = \text{(perchloric acid)}$  
$x = \text{(CuA)}$;  
$y = \text{(HA')}$  
$z = \text{(H}_2\text{A)}$

from the condition for electroneutrality

$$2(Cu^{++}) + (Na^+) + (H^+) = 2(A'^+) + (HA') + (ClO_4')$$

$$2(a-x) + 2b + (H^+) = 2(b-x-y-z) + y + 2a + c$$

$$(H^+) = c - y - 2z \quad \cdots \cdots \cdots \cdots (1)$$
If \( (H^+) \) can be measured for one of the solutions by some method, e.g. the spectrophotometric null-point indicator method (92), then \( (c-y-2z) \) can be obtained from equation (1). 'x' can then be determined from (2) and (3) by successive approximations, and from (5) \( (\varepsilon_2 - \varepsilon_1) \) can be calculated. This value of \( (\varepsilon_2 - \varepsilon_1) \) can be used in subsequent calculations.

Knowing 'x', \( K_{CuA} \) could also be calculated from (4), so that two independent sets of \( K \) values could be obtained. Further experiments will be performed to test the applicability of the above method.
Appendix A.

Equations for the Activity Coefficients.

The mean rational activity coefficient $f_+^*$ of an electrolyte is given on the Debye-Hückel theory by

$$\log f_+^* = - \frac{Az_1z_2\sqrt{I}}{1 + B\sqrt{I}} \quad \cdots \cdots \cdots (1)$$

where $\bar{a}$ is the distance of closest approach of the ions, and $A$ and $B$ are constants involving the absolute temperature and dielectric constant of the solvent. At very high dilutions the term $B\sqrt{I}$ will become negligible compared with unity and the above equation will approach the limiting form

$$\log f_+^* = - Az_1z_2\sqrt{I} \quad \cdots \cdots \cdots \cdots (2)$$

This is the Debye-Hückel limiting law. It cannot be expected that it will be obeyed at the experimental concentrations usually employed, since the product $B\sqrt{I}$ is always nearly unity. In a $10^{-3}M$ solution of a 1:1 electrolyte $(1 + B\sqrt{I})$ is about 1.03, and $\log f_+^*$ differs by 3% from the limiting value.

In equation (1) above the term $-Az_1z_2\sqrt{I}$ gives the effect of the long-range coulomb forces, while $(1 + B\sqrt{I})$ represents the effect of short-range interactions between the ions, which are assumed to be non-deformable spheres of equal radii. In any solution there will also be short-range interactions between the ions and the solvent molecules, and also interactions between ions which cannot be adequately be represented by the rigid sphere.
model. These can be corrected for by modifying (1) by the addition of a term $bI$

$$ \log f_\pm = \frac{-Az_1z_2\sqrt{I}}{1 + b\sqrt{I}} + bI \quad \cdots \cdots (3) $$

where $b$ is a constant which can be adjusted to fit the experimental data.

A simpler form of equation (3) was suggested by Güntelberg (102). For aqueous solutions at 25°C he writes

$$ \log f_\pm = -\frac{Az_1z_2\sqrt{I}}{1 + \sqrt{I}} \quad \cdots \cdots (4) $$

This equation gives a fair representation up to an ionic strength of 0.1.

Banks, Righellato and Davies, (103) examined the existing data then available for ternary electrolytes in water, and found that the experimentally determined activity coefficients $\gamma_\pm$ differed considerably from each other even at low concentrations. Conductimetric evidence indicated that the salts examined were not completely dissociated, and when the activity data were corrected for incomplete dissociation the mean activity coefficients for the different salts were found to lie on a common curve. It was further shown (6) that in solubility measurements corrections for ionic association had the effect of almost eliminating completely the deviations from the requirements of the simple Debye-Hückel theory. Davies considered
it likely therefore that an equation could be derived which could express within specified limits of uncertainty the mean activity coefficient of any electrolyte at fairly low ionic strengths. He proposed that the mean activity coefficient of an electrolyte in water at 25°C be given by

\[
\log f_+ = 0.50 z_1 z_2 \left\{ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.20 \right\}
\]

where \(z_1, z_2\) are the valencies of the ions, and \(I\) the ionic strength. At sufficiently high dilutions, the equation reduces to the Debye-Hückel limiting formula.

An equation of similar form was suggested by Guggenheim (104-5). If the constant 0.2 in the Davies equation is replaced by an adjustable parameter, the formula accurately expresses the stoichiometric activity coefficients of both dissociated and undissociated salts up to an ionic strength of 0.1.

A survey of all the available data showed that the mean activity coefficients of an electrolyte can be calculated from the Davies equation with an uncertainty not greater than 2\% at a concentration of 0.1 M.

Although Davies proposed the above equation for the mean activity coefficient of an electrolyte, it has been subsequently used by various authors, including Davies himself (4), to calculate the individual ion activity coefficient. It has been used for that purpose in the present work.
Appendix B.

The Method of Least Squares.

In the determination of the primary and secondary dissociation constants of dicarboxylic acids (Section 1, p 25) it was necessary to obtain the slope and intercept given by the experimental points. The method of least squares was used for this purpose.

Taking two variables \((x, y)\) of which \(n\) observed pairs of values are \((x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)\), and supposing that in theory these pairs lie on a straight line, then this line will be of the form

\[ y = a + bx \]

The unknown constants \(a\) and \(b\) are to be determined on the assumption that the sum of the squares of the residuals is a minimum; a residual being the difference between an observed value of \(y\) and its value given by the straight line for the same value of \(x\). This is the case when the values of \(x\) are chosen and accurately known while the values of \(y\) are subject to error.

Then:

\[ S = \sum (y_r - a - bx_r)^2 \]

For \(S\) to be a minimum

\[ \sum (y_r - a - bx_r)^2 \frac{dS}{db} = 0 \]
That is:

\[-2 \sum (y_r - a - bx_r) = 0\]

or

\[\sum y_r = na + b \sum x_r \quad \ldots \ldots \ldots \ldots (1)\]

Also:

\[-2 \sum x_r (y_r - a - bx_r) = 0\]

or

\[\sum x_r y_r = a \sum x_r + b \sum x_r^2 \quad \ldots \ldots (2)\]

Let \( \bar{x} \) and \( \bar{y} \) be the arithmetic mean of the observed values of \( x \) and \( y \).

Then equation (1) becomes:

\[\bar{y} = a + bx \quad \ldots \ldots \ldots (3)\]

This shows that the required line passes through the centroid of \( n \) points.

Eliminating \( a \) from equations (1) and (2) gives:

\[b = \frac{\sum xy - \bar{y} \sum x}{\sum x^2 - \bar{x} \sum x}\]

The value of the constant \( a \) is obtained from equation (3).

Should the dependent variable be \( x \), then the constant \( b \) is given by:

\[b = \frac{\sum y^2 - \bar{y} \sum y}{\sum xy - \bar{x} \sum y}\]

(For a detailed treatment of the method see ref (106).)
References.

1) Debye and Hückel, Phys. Z. 1923, 24, 185.
(50) Jones and Bradshaw, J. Amer. Chem. Soc., 1930, 55, 1780.
(58) Holmes and Snyder, J. Amer. Chem. Soc., 1925, 47, 221.
(59) Vles, Comp. Rend., 1925, 180, 584.
(64) Irving and Williams, J. Chem. Soc., 1953, 3192.
(69) Scholder and Linstrom, Ber., 1930, 63, 2831.
(74) Beer, 'Grundriss des photometrischen Calculs', Brunswick, 1854, 91, p 86.
(76) Vosburgh and Cooper, J.Amer.Chem.Soc., 1941, 63, 437.
(79) Cathala and Cluzel, Comp.Rend., 1939, 209, 43.
(84) Rabinowitch and Stockmayer, J.Amer.Chem.Soc., 1942, 64, 335.
(86) Doucet and Marion, Comp.Rend., 1955, 240, 1616.
(101) Monk, Private communication.
(104) Guggenheim, Phil.Mag., 1935, 19, 588.
(105) Guggenheim, Phil.Mag., 1936, 22, 322.