A PHYSICAL CHEMICAL STUDY OF THE STABILITY AND KINETIC EFFECTS OF METAL ION COMPLEXES IN SOLUTION.

A THESIS

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by

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PREFACE

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

The writer wishes to express his sincere appreciation of the help and encouragement he has received from Doctors Dunsmore, Gelles and Nancollas under whose supervision this work was performed.

I am also indebted to the Nuffield Trust for the award of a Maintenance Grant from October 1959 to October 1962 which made the research possible.

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Part 1.

The metal-ion catalysed decarboxylation of oxaloacetic acid.

INTRODUCTION

Since the discovery that decarboxylation was a process of widespread occurrence in nature and of fundamental biological importance, much work has been done in the fields of metal-ion and amine catalysis of decarboxylation reactions,

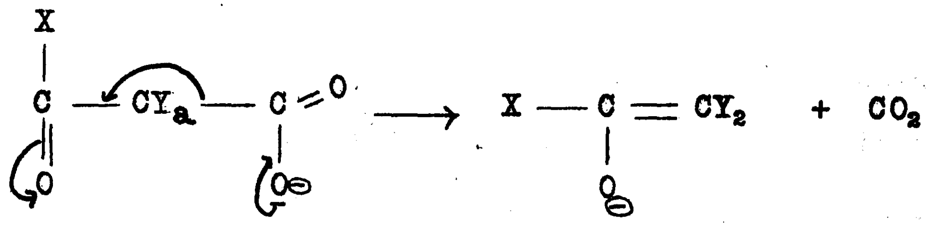
The decomposition of oxaloacetic acid in aqueous solution into pyruvic acid and carbon dioxide is an example of the decomposition exhibited by which β-keto carboxylic acids in general. The mechanism by which β-keto acids decarboxylate is now nearly completely understood, although much of the earlier kinetic work on the decarboxylation of organic acids in solution such as that carried out by Wiig[1] on acetonedicarboxylic acid, is of little value. The first order rate constants obtained are apparent constants for a system involving the simultaneous decomposition of the undissociated acid and its anions. An analysis of the kinetic data could not be made until the dissociation constants of the acids were measured. The concentration of the various species could then be calculated, and it was found, that the kinetics were quantitatively explained by an equation of the type[2]

$$k\ obs. = k_1[H_2A] + k_2[HA^-] + k_3[A^{2-}]$$

where k_1, k_2 and k_3 are specific first order rate constants for the undissociated acid, and its mono- and dianions.

The work on the mechanism of the process has now been reviewed by Brown[3]. It has been shown spectroscopically and by bromine titration that decarboxylation gives rise to an enolic intermediate. Since both αα-dimethyl acetoacetic[4] acid and αα-dimethyl oxaloacetic[5] acid, which cannot enolise, decarboxylate readily, it is concluded that the keto forms of these acids are unstable.

Westheimer and Jones[6] found that the rate of decarboxylation of αα-dimethyl acetoacetic acid is virtually independent of the dielectric constant of the solvent. Since a reaction which takes place by way of a polar intermediate should proceed more rapidly in a solvent of high dielectric constant, it was suggested that it is the hydrogen bonded form of the acid which is decarboxylated. If the β-keto acid is represented by $X.CO.CY_2.COOH$ the decarboxylation of the acid and anion can be represented by equations (1) and (2) respectively.



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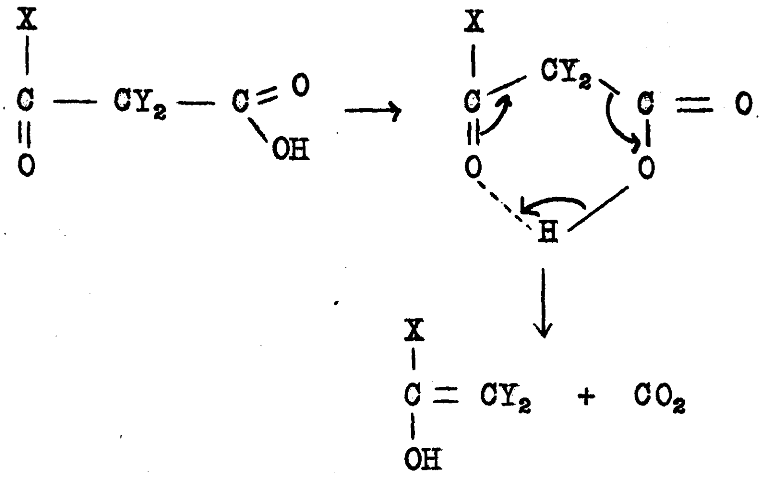
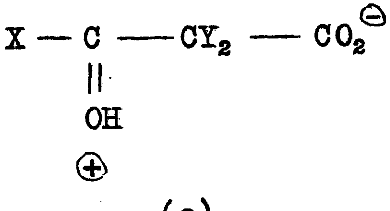


------------=(1)

The undissociated acid is regarded as decomposing through a hydrogen bonded form rather than as a zwitter ion (a) as originally suggested by Pedersen.[5]



$$X-C(=\overset{\oplus}{O}H)-CY_2-CO_2^{\ominus}$$

(a)

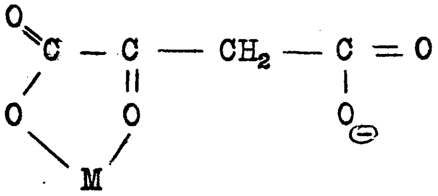
Gelles[7] discussed the difference in activation energies of acid and anion of oxaloacetic acid and malonic acid, and for other β-keto carboxylic acids. These differences are most easily interpreted in terms of the electronic effect of substituent groups X or Y on the stability of the activated complex, to which the enol $HO — C : CY_2$ or ion $^{-}O . CX : CY_2$ is a contributing structure. Electrophilic groups will stabilise the ion more than the enol, and electron releasing groups are expected to act in a reverse manner. As substituent groups become more electrophilic the relative stability of the activated complex of the anion increases and the activation energy is lowered more than that of the acid, so that the relative rate of decarboxylation of the anion increases. In malonic acid the anion would be expected to have a lower activation energy, as is the case, but the entropy effect causes the acid to react more rapidly. Increasing electrophilic substitution increases the difference in activation energies of the acid and anion until this effect overcomes the entropy effect, and leads to the anion reacting faster than the acid.

A variety of reactions are catalysed by metal ions, and one such reaction is the catalysed decomposition of oxaloacetic acid into pyruvic acid and carbon dioxide.

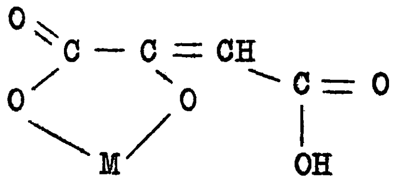
The primary role of the metal ion in chelate compounds undergoing chemical change is to withdraw electrons from the reaction centre of the substrate in order to facilitate the reaction. The catalytic effect of the metal ion is governed not only by the degree of interaction with the substrate in the initial state but also by the interaction in the transition state. Many examples of this type of reaction are known, the catalysed hydrolysis of simple peptides,[8] the halogenation of keto esters,[9] and as stated previously the decomposition of β-keto acids,[10] are specific examples.

The fact that the decarboxylation of oxaloacetic acid is catalysed by polyvalent cations notably Zn^{2+}, Cu^{2+} , Fe^{2+} etc., was first observed by Krebs[11] and Krampitz and Werkman.[12] In 1948, Komberg, Ochoa and Mehler[13] showed that the addition of Al^{3+} and Mn^{2+} , to solutions of oxaloacetic acid resulted in the formation of an intense absorption band in the region 260–290 mμ . which was interpreted as being due to the formation of a metal complex. In the same year this work was extended by Nossal[14] to Cu^{2+} and Fe^{3+} ions. Nossal showed that Cu^{2+} forms almost instantaneously a complex similar to that formed by Al^{3+}.

Steinberger and Westheimer[4] studied the decarboxylation of αα-dimethyl oxaloacetic acid and found that the reaction was catalysed by metal ions whilst the decarboxylation of the monoethyl ester $EtO_2C.CO.C(Me)_2CO_2H$ was not catalysed by metal ions. This indicated that the catalytically active species formed by αα-dimethyl oxaloacetic acid is a complex containing a five membered chelate ring [α-oxo carboxylate chelate compound].



(A)



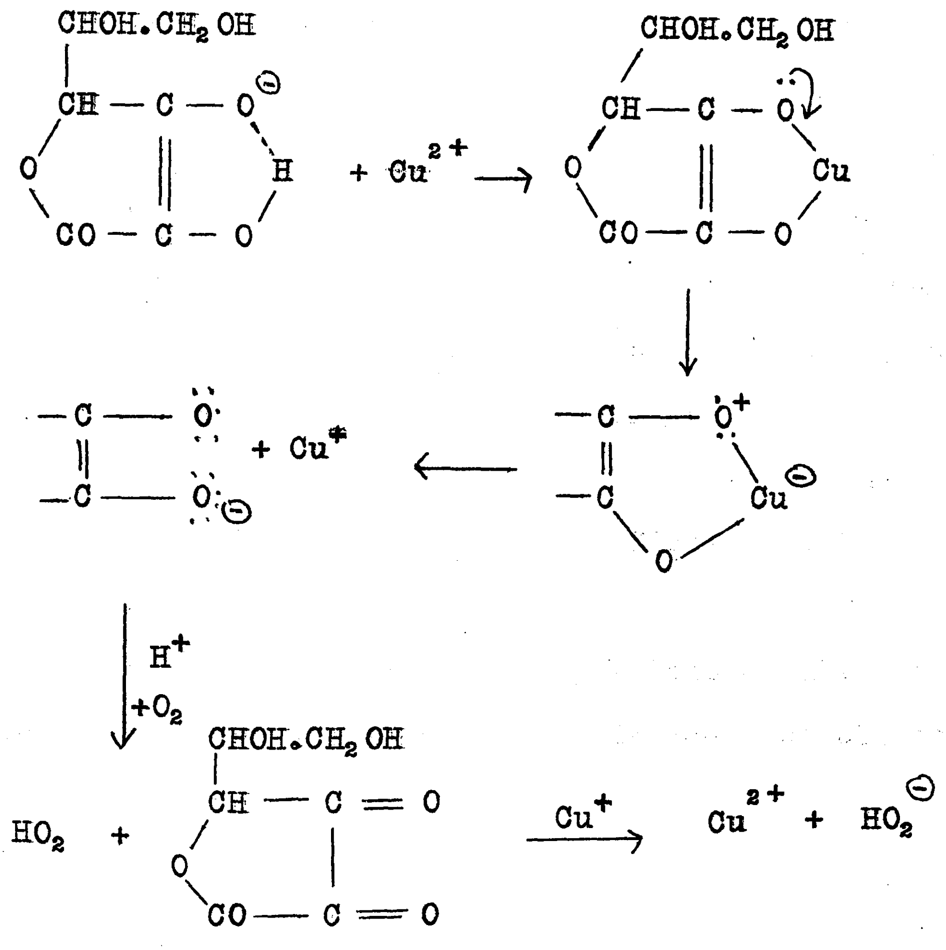
(B)

Dimethyloxaloacetic acid cannot form a complex of type (B) and so by analogy a ketonic complex (A) seemed to be the active species in the decarboxylation of oxaloacetic acid.

Pedersen[15] studied the kinetics of the copper and zinc catalysed decarboxylation of oxaloacetic acid, interpreting the results in terms of the first order decomposition of the acid, its two anions and a species MA, where M^{2+} is the metal ion and A^{2-} the oxaloacetate dianion. Salama and Gelles[16] extended this work, measuring potentiometrically the complexity constants of oxaloacetic acid with the transition metal ions Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, etc.

Homogeneous metal-ion catalysed reactions in solution can be divided into two general classifications; reactions in which the metal ion acts as an oxidation-reduction catalyst and reactions in which the metal ion acts as a generalised acid in the Lewis sense. Examples of the first class are, the oxidation of oxalate through the formation of the Mn(III) chelate and the oxidation of ascorbic acid by the Cu(II) ion.[17]

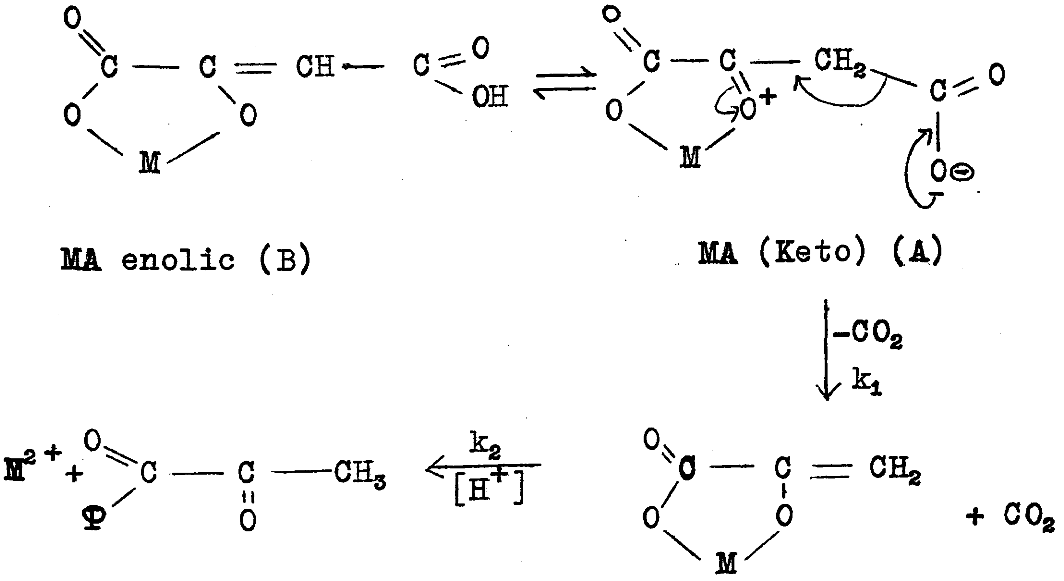
Ascorbic Acid Oxidation.



The metal-ion catalysed decarboxylation of oxaloacetic acid belongs to the second class. When a metal ion combines with an electron donor the resulting structure is a metal complex. However, if the ligand contains two or more donor groups, the resulting structure is a metal chelate. Since the ligand is an electron donor, it can be considered as a generalised base in the Lewis sense, while the metal ion acts as a generalised acid.

Due to the fact that aqueous metal ions behave as Lewis acids, it is to be expected that they would resemble other acids in the catalysis of many chemical reactions. The catalytic effect of a metal ion however, may be quite different from that of the hydrogen ion, because of its higher charge and its characteristic co-ordination tendencies. This gives rise to effects which are quite specific and selective in nature.

The mechanism by which metal ions catalyse the decarboxylation of β-keto acids has now been clarified and may be represented by



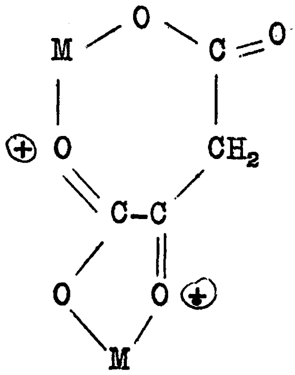
The metal ion forms an α-keto carboxylate (A) with the dianion of the acid. The charge produced on the oxygen atom then assists the electron transfer from the carboxyl group to the rest of the molecule, accelerating the reaction. Both oxaloacetic acid and acetone dicarboxylic acid react in this manner.

A large amount of experimental evidence suggests that in transition metal ion chelates, the order of stability of the chelate is practically independent of the nature of the ligand and is a function solely of the metal ion. Thus for many chelates which are sufficiently stable the order of stability is:[18]

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

The primary role of the metal ion is withdrawal of electrons from the reaction centre. Many reactions of this type are known, such as the catalysed hydrolysis of simple peptides and organic esters,[19] the halogenation of keto esters[29] and the decarboxylation of β-keto acids.

Inhibition of the decarboxylation of oxaloacetic acid has been noted, at high copper concentration and at pH $>$ 6. The latter effect is thought to be due to the formation of the inactive enolic complex (B) whilst the former is thought to be due to the formation of a second complex M_2A^{2+} of the structure.



M_2A^{2+}

It consists of a low stability seven membered ring causing binding of the carboxyl group lost during decarboxylation. Pedersen[21] has recently shown that a similar situation exists with acetosuccinic acid. Speck[68] has obtained similar results with Mn^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, in enzymatic decarboxylation which is thought to be of great importance in biochemical reactions.

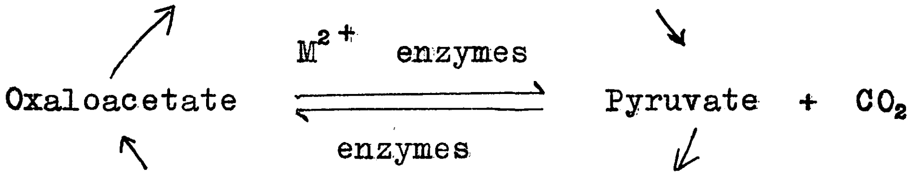
Now

$$K_{M_2A^{2+}} = \frac{[M_2A^{2+}]}{[MA][M^{2+}]}$$

and therefore

$$\frac{[M_2A^{2+}]}{[MA]} = [K_{M_2A^{2+}}][M^{2+}]$$

and the concentration of M_2A^{2+} should increase proportionally with the metal ion concentration. The interconversion of oxaloacetic acid and pyruvic acid occurs in the Krebs cycle.[22]



When the oxaloacetate reaches a low level, the $\frac{[M^{2+}]}{[\text{oxaloacetate}]}$ ratio will be large and decarboxylation will slow down. The concentration of oxaloacetate will then build up until the $\frac{[M^{2+}]}{[\text{oxaloacetate}]}$ ratio becomes small enough to allow rapid decarboxylation of the MA complex. The metal ion thus acts as a " governor" in the system. Further work is still necessary on the problem of inhibition before the true picture is known.

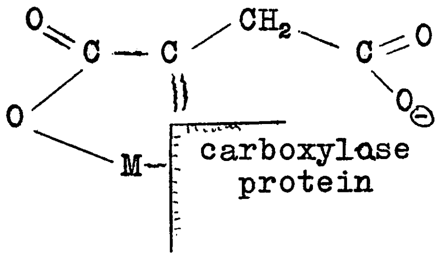
The importance of metal-ion and amine catalysis of β-keto dicarboxylic acids lies in the relationship between these comparatively simple reactions and the more complex reactions involving the metal-ion activated enzymatic decarboxylation reactions which occur in biological systems A number of enzymes are known to catalyse the decarboxylation of oxaloacetic acid and in each case, it was observed that divalent metal ions were necessary to activate the enzyme. Mehler[23] partially purified the enzyme, from M-lysodeiktious, and found it was quite inactive in the absence of metallic cations, but was activated by Mn^{2+}, Mg^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+}, Mn^{2+} being the most effective cation. This sort of catalysis seemed to involve an equilibrium of the type,

$$\text{Protein} + M^{2+} \rightleftharpoons \text{Enzyme}$$

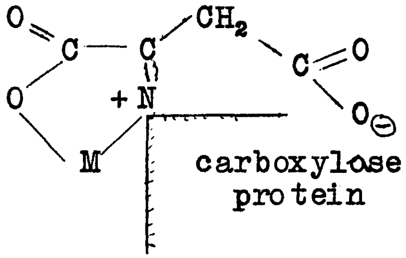
It is interesting to note that no metal-ion activation is necessary for the enzymatic decarboxylation of acetoacetic acid[24] but this reaction is catalysed by amines,[25] suggesting that the fundamental catalytic activity of the enzyme is supplied by the metal ion, which is bound both to the protein and substrate. The usual expression for an enzymatic reaction is:

$$E + S \rightleftharpoons E_S \rightleftharpoons EP \longrightarrow E + P$$ where E

is the enzyme, S the substrate, and P the products. In the last step the enzyme releases the products and so cannot bind the substrate too firmly since it would also bind the product, and the reaction would slow down. Several explanations for the role of the metal ion in metal activated enzymes have been put forward. Due to the tremendous reactivity shown by the aniline ketimine of oxaloacetic acid it has been suggested that a free amino group of the protein condenses with the carbonyl group of the keto acid the metal ion binding the protein and the substrate as in either (a) or (b).



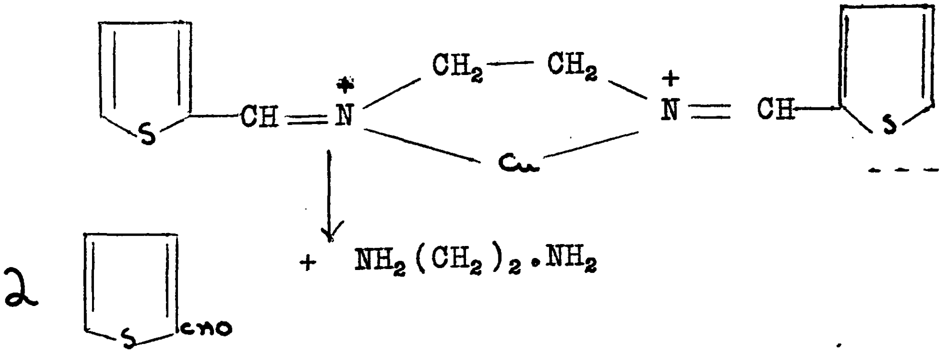
(a)



(b)

In structure (a) the metal ion would function primarily to bring the substrate and amino group of the protein into the correct stereochemical configuration. In (b) the metal ion would act as a catalyst by withdrawing electrons from the reaction centre, this structure being intensely active. The role of the metal ion in metal activated enzymatic reactions has also been explained by assuming a metal chelate bridge between the enzyme and the substrate molecule. Interaction of the peptide with the metal ion is viewed as resulting in an electron displacement rendering the bond susceptible to nucleophilic attack. It has been shown that Zn^{2+}, which activates several proteolytic enzymes, shows practically no tendency to interact with the peptide group, suggesting that if chelate formation with the peptide group of the substrate molecule with a resulting electron displacement is a necessary step in the mechanism of metal activated enzymes, the role of the metal ion must be considerably influenced by the protein molecule. Otherwise the metal ion, such as zinc, would not meet these requirements.

Recently Eichham and Trachtenberg[26] have found that ketimines are easily hydrolysed if made part of a chelate ring as in equation (1).



------(1)

This indicates that the metal ion might also play a role in removing the protein from the substrate after decarboxylation has taken place, by catalysing the hydrolysis of the ketimine bond. This would then allow the reaction to continue.

A consideration of the previous work done on the metal ion catalysed decarboxylation of oxaloacetic acid, suggested that the determination of the activation energies for the various decarboxylation reactions would be of considerable interest. Experiments were carried out with this aim in view and are described in detail in the following chapters.

EXPERIMENTAL

Standard solutions of hydrochloric acid, potassium chloride, cupric chloride and zinc chloride were made, using analar materials and Grade A volumetric apparatus. The oxaloacetic acid used (L. Light and Co.) was recrystallised in the following manner. 10 gms. of the acid was dissolved in 80 ml. of hot analar acetone and 130 ml. of benzene at 55°C was added to the nearly boiling solution. On cooling in an ice-salt bath, oxaloacetic acid crystallised. After filtration it was washed with analar benzene and dried in a vacuum dessicator (Yield 6.7 gms.). In order to ensure maximum yield it was necessary to heat the solution just long enough to ensure complete dissolution of the oxaloacetic acid. The molecular weight found by dissolving a sample in a small excess of sodium hydroxide and back titrating with hydrochloric acid was 132.6. The purity of the acid was determined by titrating against standard alkali (98%) and by carbon dioxide evolution (96.7%).

Measurement of the rate of decarboxylation.

(a) Manometric method.

The kinetics of the decarboxylation reactions were followed by measuring the rate of evolution of carbon dioxide. The apparatus (Fig.1) was an improved version of the one originally used by Bell and Trotman Dickenson.[27] In their experiments a lapse of 4 minutes was required between time of mixing of reactants and initial manometric readings. This time lapse was due to mixing of reactants outside the tube, evacuating and sealing. Measurements were made in a water thermostat at three temperatures, 25°C, 30°C, 37°C ± .03°C. The thermostat was fitted with an electrically operated rubber hammer (Fig.2) which struck the bulb of the apparatus at a rate of 100 times per minute, to prevent supersaturation of the solution with carbon dioxide.

Calibration of Apparatus.

The apparatus was calibrated using known quantities of sodium bicarbonate and hydrochloric acid, 16.8 mg. of bicarbonate being equivalent to the 26.4 mg., of oxaloacetic acid used in each run.

MANOMETRIC APPARATUS

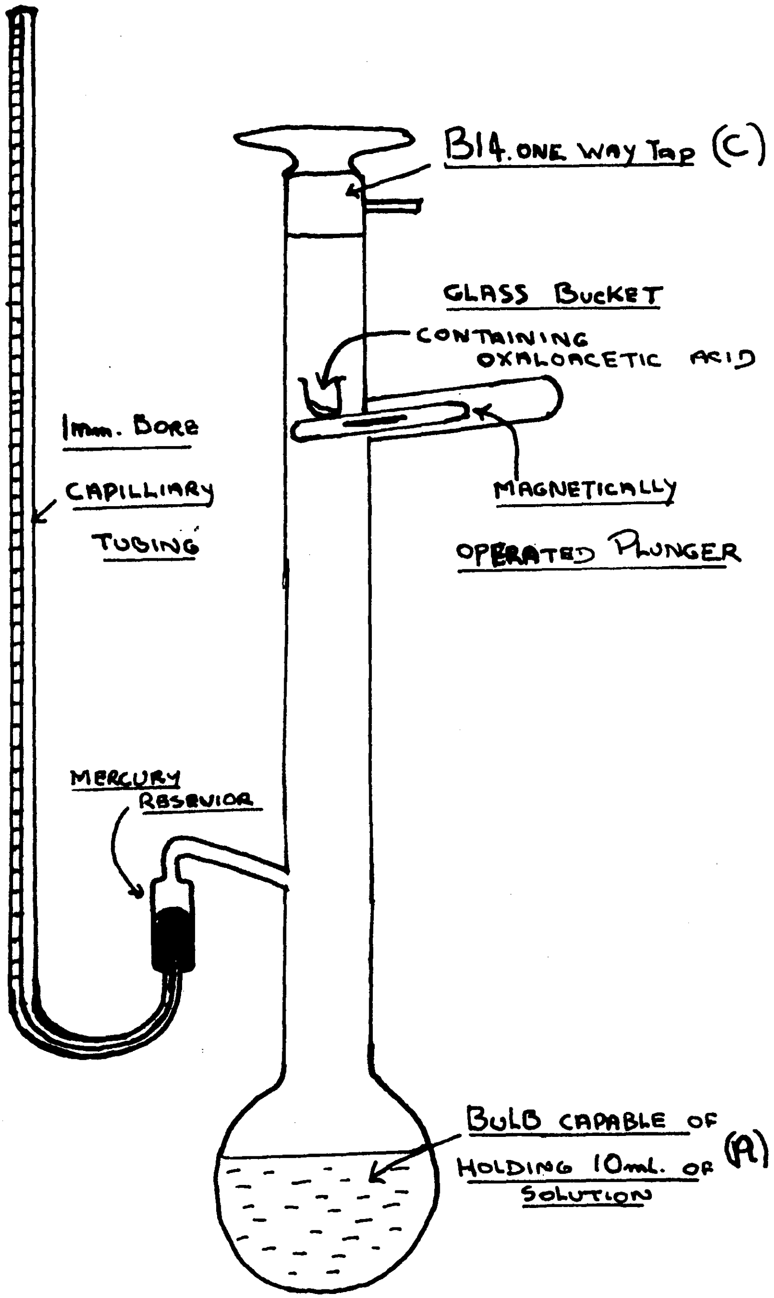
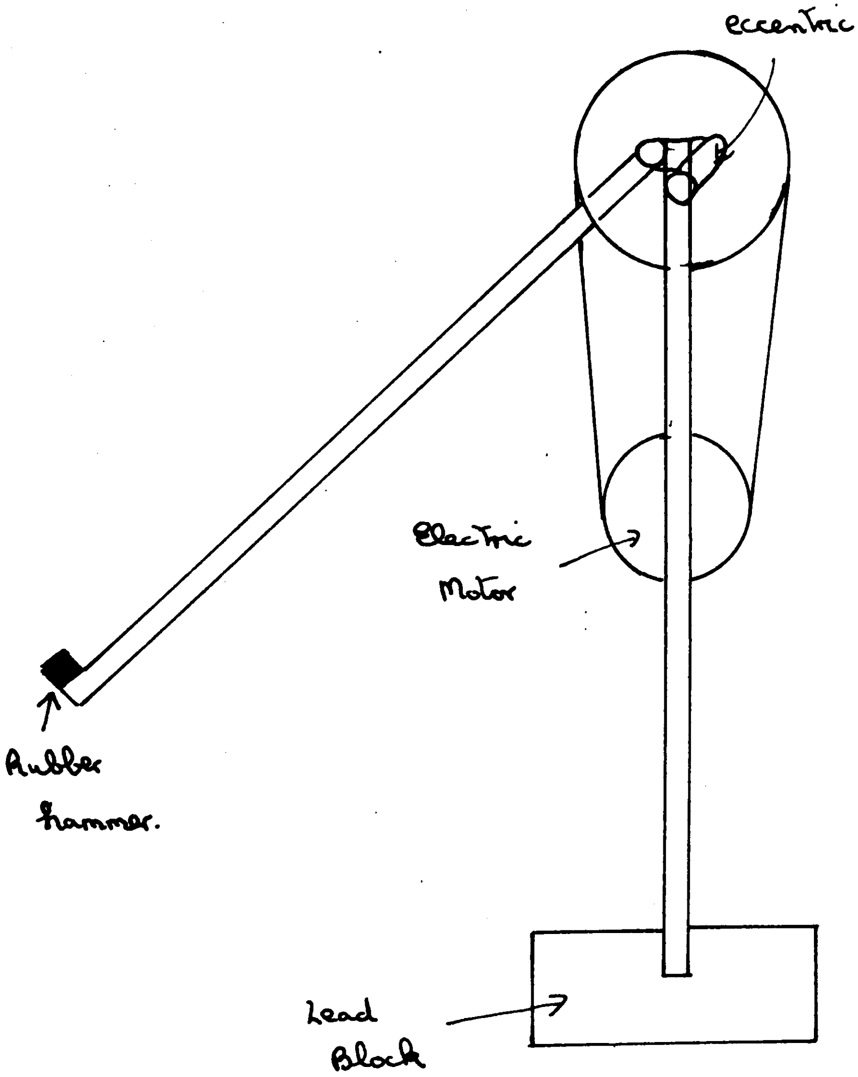


Fig 1

Fig 2.

Electrically operated rubber hammer



The calibration procedure was as follows. The sodium bicarbonate was weighed out in a small glass bucket; 10 ml. of $0.1\overline{N}$ hydrochloric acid was placed in the large bulb (B) of the apparatus and the bucket containing the sodium bicarbonate was placed in position (A) on top of the magnetically operated plunger which consisted of a small piece of soft iron sealed in glass. The tap (C) was lubricated with " Florube Grease W" , which was found to be quite stable at 37°C, and placed in position. The solution was then frozen in a solid carbon dioxide-acetone mixture, after which the apparatus was carefully evacuated, the tap (C) closed and the solution allowed to return to room temperature. The apparatus was then transferred to the thermostat and allowed to equilibrate for fifteen minutes. The reaction was then initiated by withdrawal of the plunger into the side arm. At this point the electrically operated hammer was started and pressure readings on the mercury manometer were taken every fifteen seconds or half-minute, until the reaction was complete. Excellent reproducibility was obtained, calibrations agreeing to 0.02 of a cm. This technique was employed with both the sodium bicarbonate and oxaloacetic acid and it was necessary to calibrate the kinetic gas apparatus at each temperature. Careful cleaning was observed with analar benzene, chromic acid and distilled water.

Potentiometric Measurements.

E.m.f. measurements were made with a glass electrode in the cell.

Ag/AgCl HCl(0.2m)/ glass/solution under study/saturated KCl/calomel electrode

pH measurements in solutions of hydrochloric acid, oxaloacetic acid, potassium chloride and copper chloride were made in order to determine the complex species present. The glass electrode was of the commercial screened type (E.I.L. Type GG33), and the cell was maintained at constant temperature by means of a "Colora ultra thermostat" unit which circulated water at a constant temperature within the annular space between the walls of the double walled vessel, in which the system was placed. E.m.f. measurements were made using a "Croydon" potentiometer and a "Vibron" electrometer. (E.I.L. Model 33B) as a null indicator; readings were reproducible to ± 0.1 mV. The electrode system was standardised before and after each set of measurements with solutions containing hydrochloric acid and potassium chloride at a constant ionic strength of 0.1M. Calibration curves of e.m.f. against log $[H^+]$ showed good linearity with slopes of 0.058 to 0.062 and unknown log $[H^+]$ could be obtained with an accuracy of ± 0.004.

A known weight of oxaloacetic acid was dissolved in 80 ml. of solution containing known concentrations of hydrochloric acid, potassium chloride and cupric chloride. The solutions were prepared immediately before use, and the copper solution was added only when the other reactants had been made up to nearly the required volume. When half the copper solution had been added, a stop watch was started; e.m.f. readings were taken at approximately 1 minute intervals and extrapolated to the time of mixing. In this way, the drift in e.m.f. accompanying decarboxylation amounting to some 4 m.v. per minute, was allowed for.

RESULTS AND DISCUSSION

Kinetic Measurements.

Measurements of the rate of the copper catalysed decarboxylation of oxaloacetic acid (0.02M) in aqueous solution were carried out over a range of copper and hydrochloric acid concentrations at a constant ionic strength of 0.1M. Linear first order plots with respect to oxaloacetic acid were obtained in every case and Fig.3 shows a typical plot of the results in Table I. The rate constants were evaluated from first order infinity plots and are quoted in min.$^{-1}$ Kinetic measurements were made at 25°C, 30°C and 37°C.

[illegible]	70.60	64.50	1.8096
40	72.50	6.250	1.7959
[illegible]	73.30	61.70	1.7903
[illegible]	74.60	60.50	1.7818

<u>Table I.</u> The decomposition of oxaloacetic acid in a solution of hydrochloric acid (0.01M), potassium chloride (.0885M) and cupric chloride (0.0005M). Ionic strength = 0.1M. Temperature 25°C.

Time (mins.)	Pt	Pα-Pt	log(Pα-Pt)
2	43.50	91.50	1.9614
3	44.00	91.00	1.9590
4	45.00	90.00	1.9542
8	47.75	87.20	1.9405
10	49.00	86.00	1.9345
15	51.50	83.50	1.9217
20	55.00	80.00	1.9031
26	58.40	76.60	1.8842
30	61.50	73.50	1.8663
35	64.30	70.70	1.8494
40	67.30	67.70	1.8306
45	70.50	64.50	1.8096
49	72.50	6.250	1.7959
51	73.30	61.70	1.7903
53	74.50	60.50	1.7818
54	74.90	60.10	1.7789

Time (mins.)	Pt	$P\alpha$-Pt	log($P\alpha$-Pt)
57	76.50	58.50	1.7672
59	78.00	57.00	1.7559
60	78.50	56.50	1.7520
62	79.80	55.20	1.7419
64	80.00	55.00	1.7404
67	81.50	53.50	1.7284
69	82.20	52.80	1.7226
73	84.00	51.00	1.7076
78	86.50	48.50	1.6857
81	87.80	47.20	1.6739
83	88.50	46.50	1.6675
86	89.80	45.20	1.6551
90	91.50	43.50	1.6385
95	93.50	41.50	1.6180
100	95.00	40.00	1.6021
105	96.90	38.10	1.5809
110	98.20	36.80	1.5658
115	100.00	35.00	1.5441
120	102.80	32.20	1.5079
135	105.00	30.00	1.4771
140	107.00	28.00	1.4472

Time (mins.)	Pt	Pα–Pt	log(Pα–Pt)
150	109.00	26.00	1.4150
188	116.10	18.90	1.2765
197	118.10	16.90	1.2279
205	119.00	16.00	1.2041
215	120.20	14.80	1.1703
231	122.00	13.00	1.1139
246	124.00	11.00	1.0414
270	125.00	10.00	1.0000
309	127.30	7.70	0.8865
331	128.30	6.70	0.8267

$K = 3.67 \times 10^{-3}$

Pt = Pressure readings at t minutes.

Pα = Infinity pressure reading.

Fig. 3.

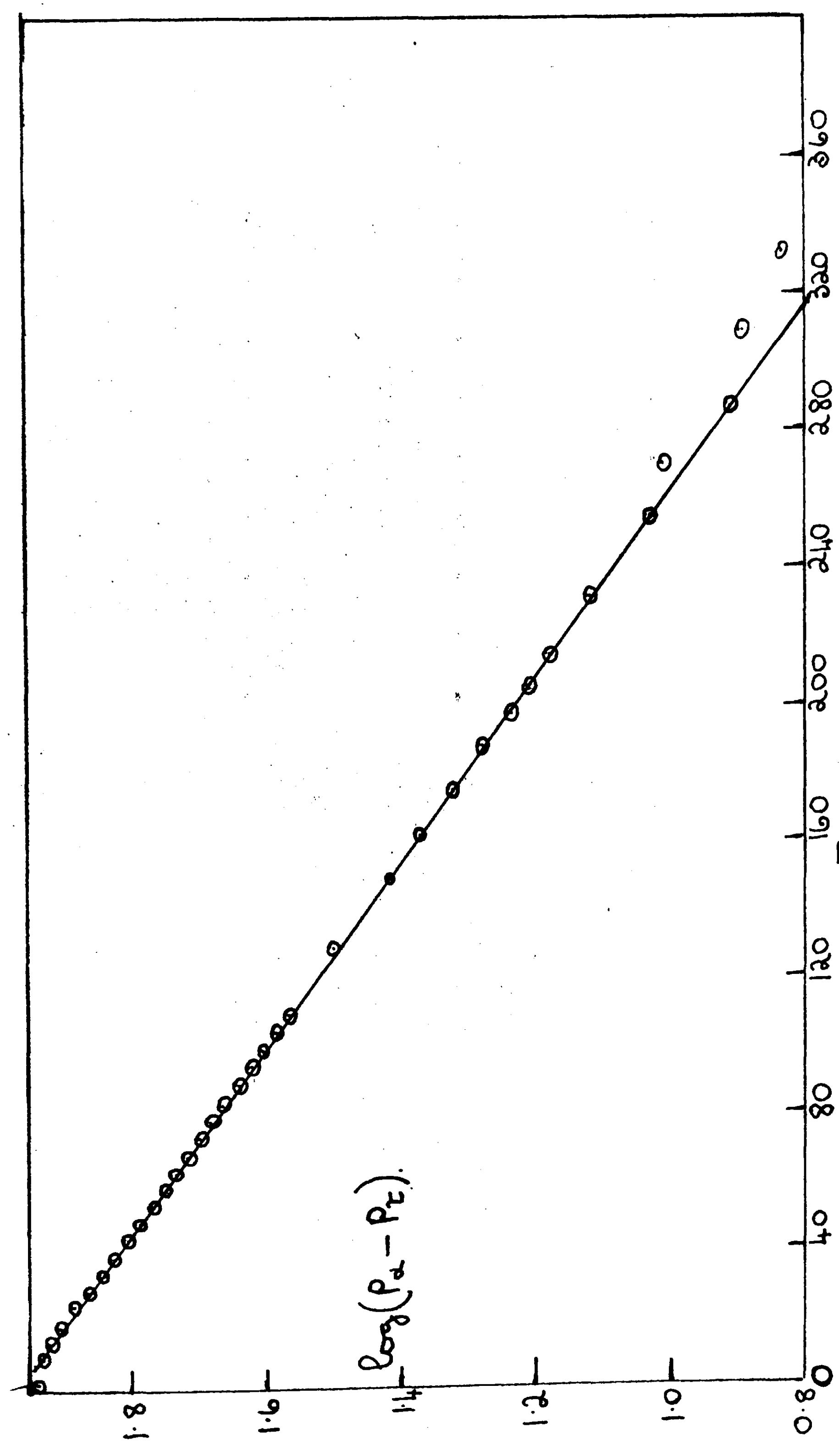
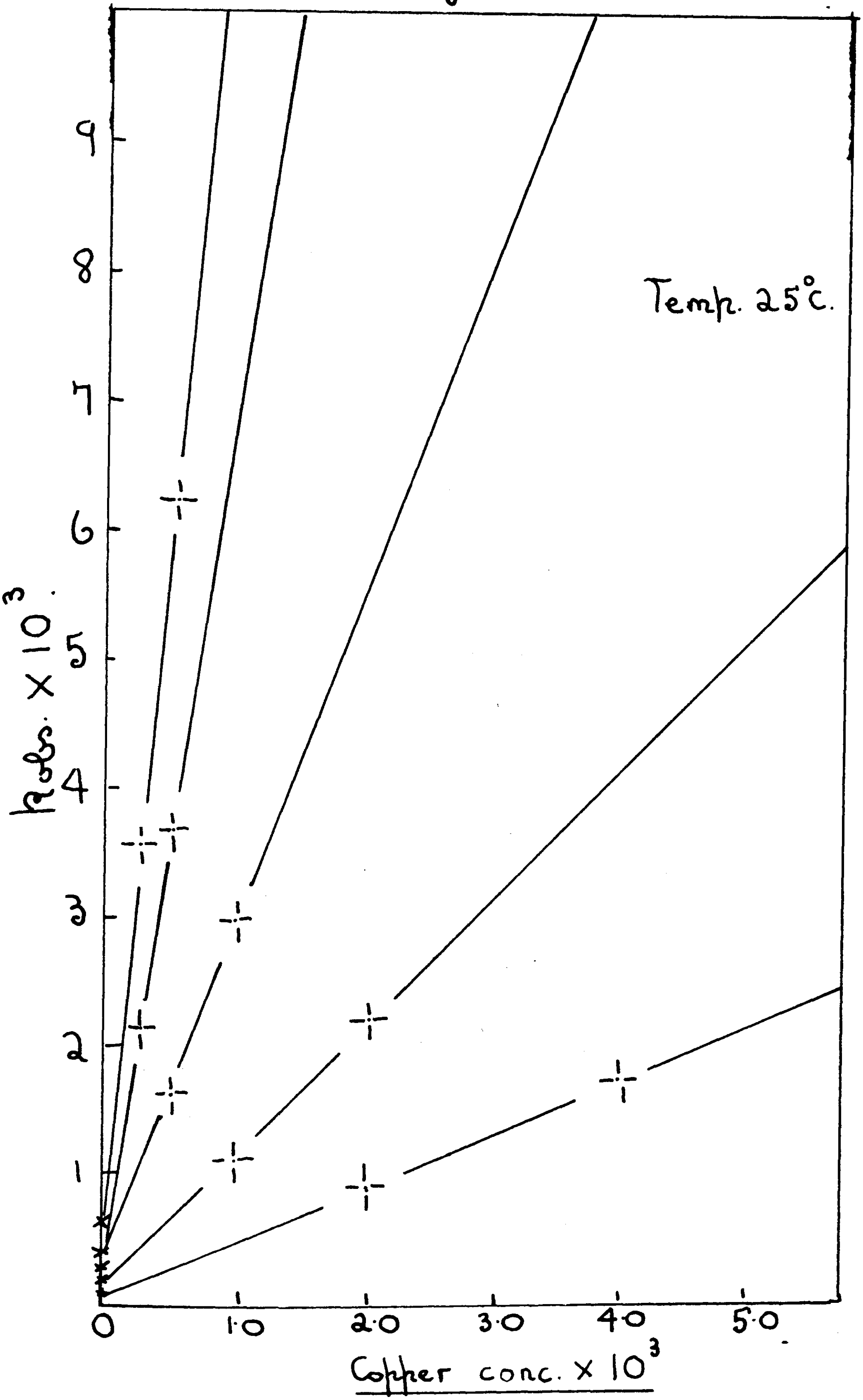

Log(Pα − Pt)
Time (mins.)
0
40
80
120
160
200
240
280
320
360
1.8
1.6
1.4
1.2
1.0
0.80

Fig. 4.



When the hydrogen ion concentration is constant, Fig.4 shows that there is a linear relationship between the velocity constants and the concentration of cupric chloride. Also the effect of the copper ion increases rapidly with decreasing hydrogen ion concentration. This metal ion catalysis may be explained quantitatively when it is assumed that unstable complexes of the composition CuA and $CuHA^+$ are formed in the solutions. The velocity of the decarboxylation of oxaloacetic acid may then be written in the following manner,

$$-\frac{dx}{dt} = k_0[H_2A] + k_1[HA^-] + k_2[A^=] + k_3[CuA] + k_4[CuHA^+] \text{ --(1)}$$

where $[H_2A]$ is the concentration of undissociated acid

$[HA^-]$ is the concentration of univalent ion,

$[A^=]$ is the concentration of divalent ion.

k_0, k_1, and k_2, are velocity constants for the spontaneous decarboxylation of the molecules H_2A, HA^-, and $A^=$ respectively.

The concentration of the unstable complexes are determined by the equilibria,

$$Cu^{++} + HA^- \rightleftharpoons CuA + H^+ \text{ ------------------(2)}$$

$$Cu^{++} + HA^{-} \rightleftharpoons CuHA^{+} \text{ ---------------------(3)}$$

When $K_3 = \frac{[CuA][H^+]}{[Cu^{++}][HA^-]}$ and $K_4 = \frac{[CuHA^+]}{[Cu^{++}][HA^-]}$

are the equilibrium constants for these reactions, the last two terms of expression (1) may be written

$$k_3K_3[Cu^{++}][HA^-][H^+]^{-1} + k_4K_4[Cu^{++}][HA^-]$$

From equations (2) and (3) it can be shown that

$$[CuA] = K_3[Cu^{++}][HA^-][H^+]^{-1} = K_3[Cu^{++}][H^+]^{-1}\alpha_1 x \text{ -----(4)}$$

and

$$[CuHA^+] = K_4[Cu^{++}][HA^-] = K_4[Cu^{++}]\,\alpha_1 x \text{ -------------(5)}$$

where α_1 is the degree of dissociation of oxaloacetic acid into the ion HA^-.

From equations (4) and (5), we find

$$[Cu^{++}] = \frac{C}{1 + \beta x} \quad \text{where } \beta = K_3\ \alpha_1[H^+]^{-1} + K_4\ \alpha_1$$

As x approaches zero, $[Cu^{++}]$ will approach C, and the reaction will approach a first order course with the velocity constant.

$$k \text{ obs.} = ku + kc \text{ ----------------------------(6)}$$

where $kc = k_3K_3C\alpha_1[H^+]^{-1} + k_4K_4C\alpha_1$ --------------------(7)

and ku is the contribution from the uncatalysed rate;

$$ku = k_0 + (k_1 - k_0)\alpha_1 + (k_2 - k_0)\alpha_2 \text{ ------------------(8)}$$

where α_1 and α_2 are the degrees of dissociation of oxaloacetic acid into the ions HA^- and $A^=$.

Thus $k \text{ obs.} = ku + k_3 K_3 C\alpha_1 [H^+]^{-1} + k_4 K_4 C\alpha_1$ ------------(9)

and rearranging,

$$\frac{k \text{ obs} - ku}{C\alpha_1} = k_3 K_3 [H^+]^{-1} + k_4 K_4 \text{ -----------------(10)}$$

k obs. is obtained from manometric measurements as described earlier, ku from equation (8), the values of k_0, k_1, and k_2 were those of Gelles.[7]

In order to calculate the total hydrogen ion present, the following procedure was adopted,

$$\underset{H_2A}{(a-x)} \rightleftharpoons \underset{HA^-}{(x-y)} + \underset{H^+}{(b+x+y)} \text{ --------------------(11)}$$

$$\underset{HA^-}{(x-y)} \rightleftharpoons \underset{A^=}{(y)} + \underset{H^+}{(b+x+y)} \text{ --------------------(12)}$$

From the above equilibria,

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]} f_1^2 = \frac{(b + x + y)(x - y)}{(a - x)} f_1^2 \text{ ------------(13)}$$

and

$$K_2 = \frac{[A^{=}][H^{+}]}{[HA^{-}]} f_2 = y\,\frac{(b + x + y)}{(x - y)} f_2 \text{ -------------(14)}$$

where a = concentration of oxaloacetic acid,

b = concentration of hydrochloric acid.

K_1 and K_2 were determined by Pedersen as a function of ionic strength from electrometric measurements. These were converted to the ionic strength used in the present work by means of equations (16-21); the values of K_1 and K_2 used being given in Table 2.

At 25°C,

$$-\log K_1 = 2.555 - 1.013I^{\frac{1}{2}} + 0.75I \text{ ------------(15)}$$

$$-\log K_2 = 4.370 - 2026I^{\frac{1}{2}} + 1.57I \text{ -------------(16)}$$

At 30°C

$$-\log K_1 = 2.511 - 1.026I^{\frac{1}{2}} + 0.80I \text{ ------------(17)}$$

$$-\log K_2 = 4.365 - 2047I^{\frac{1}{2}} + 1.60I \text{ -------------(18)}$$

At 37°C

$$-\log K_1 = 2.450 - 1.038I^{\frac{1}{2}} + 0.80I \text{ ------------(19)}$$

$$-\log K_2 = 4.359 - 2.076I^{\frac{1}{2}} + 1.65I \text{ ------------(20)}$$

where I = ionic strength.

Table 2.

Temperature	$K_1\ 10^3$	$K_2\ 10^4$
25°C	4.90	1.30
30°C	5.40	1.32
37°C	6.20	1.36

Hay[28] from spectrophotometric measurements obtained dissociation constants for oxaloacetic acid which agreed very closely with values obtained by use of the above equations.

Assuming that at the concentration of mineral acid used the bivalent ion ($A^=$) makes a very small contribution to the total rate of the reaction. y can be neglected and from equation (13) a value of x can be obtained. Substituting in equation (14) a corresponding value of y can be obtained and by successive approximations the true total hydrogen ion concentration calculated.

The degrees of ionisation α_1 and α_2 are given by equations (21) - (23).

$$\frac{\alpha_1}{1 - \alpha_1} = \frac{K_1}{[H^+]} \quad , \quad \frac{\alpha_2}{1 - \alpha_1 - \alpha_2} = \frac{K_1 \ K_2}{[H^+]^2} \text{ -----------(21),(22)}$$

and $\frac{\alpha_1}{1 - \alpha_1 - \alpha_2} = \frac{K_1}{[H^+]}$ -----------------------------(23)

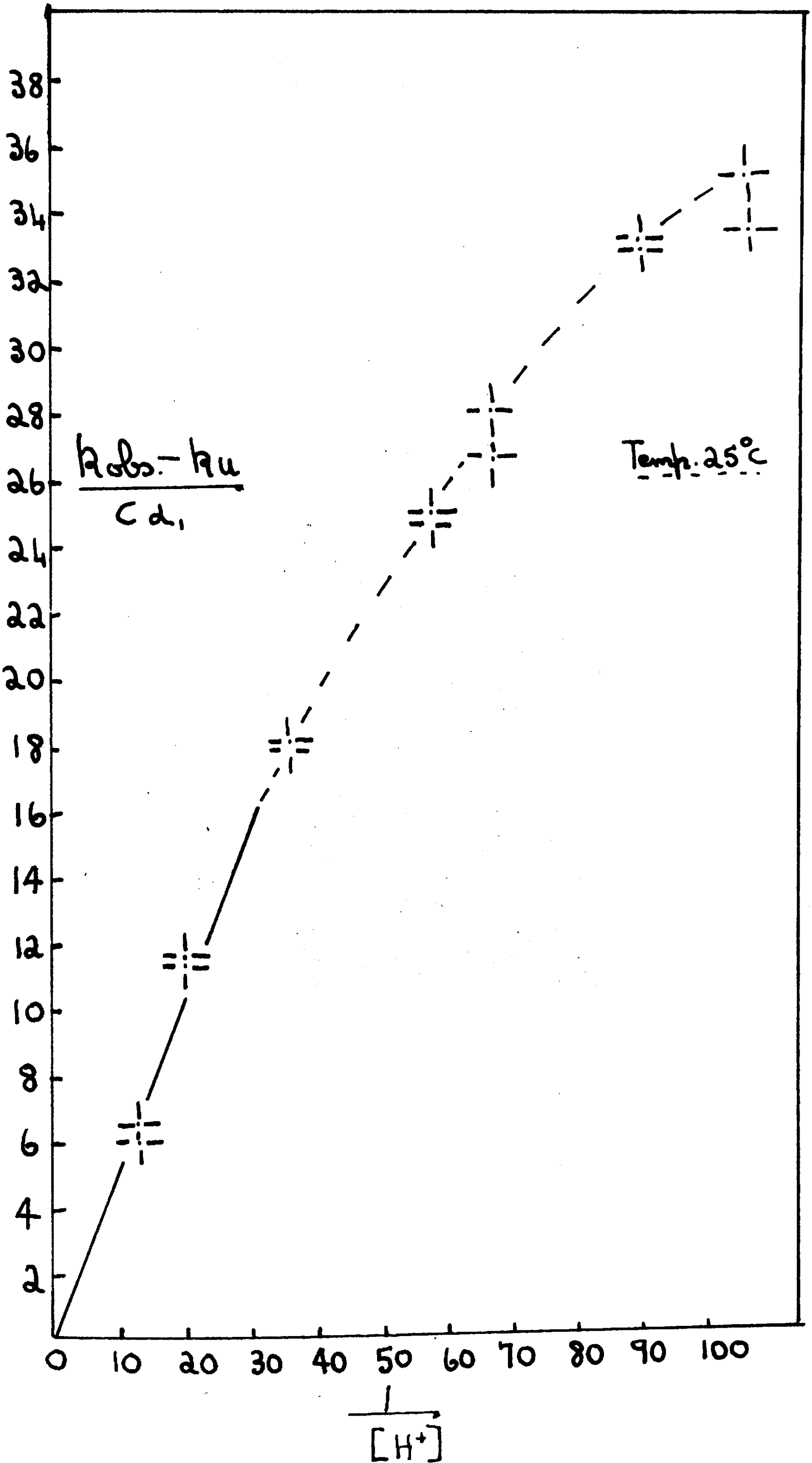
These are calculated at the beginning of the reaction, and are assumed constant.

From equation (10) it can be seen that plots of $\frac{K \text{ obs.} - ku}{C \ \alpha_1}$ against $\frac{1}{[H^+]}$ should give straight lines of gradient k_3K_3 and intercepts k_4K_4. These are shown in Figs. (5)-(7) and it is seen that although initially the plots are linear there is a very appreciable deviation at higher pH. This can be accounted for by the formation of greater amounts of complexes. The graphs appeared to go through the origin indicating that the term k_4K_4 is zero or very small.

The results obtained from the kinetic measurements at the three temperatures are given in Tables (3)-(5).

From the kinetic experimental results it is only possible to obtain the product k_3K_3 at each temperature. In order to separate them it is necessary to determine K_3 at the three temperatures.

Fig. 5



38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
10
20
30
40
50
60
70
80
90
100
$\frac{k_{obs.} - k_u}{C\alpha_1}$
Temp. 25°C
$\frac{1}{[H^+]}$

Fig. 6.

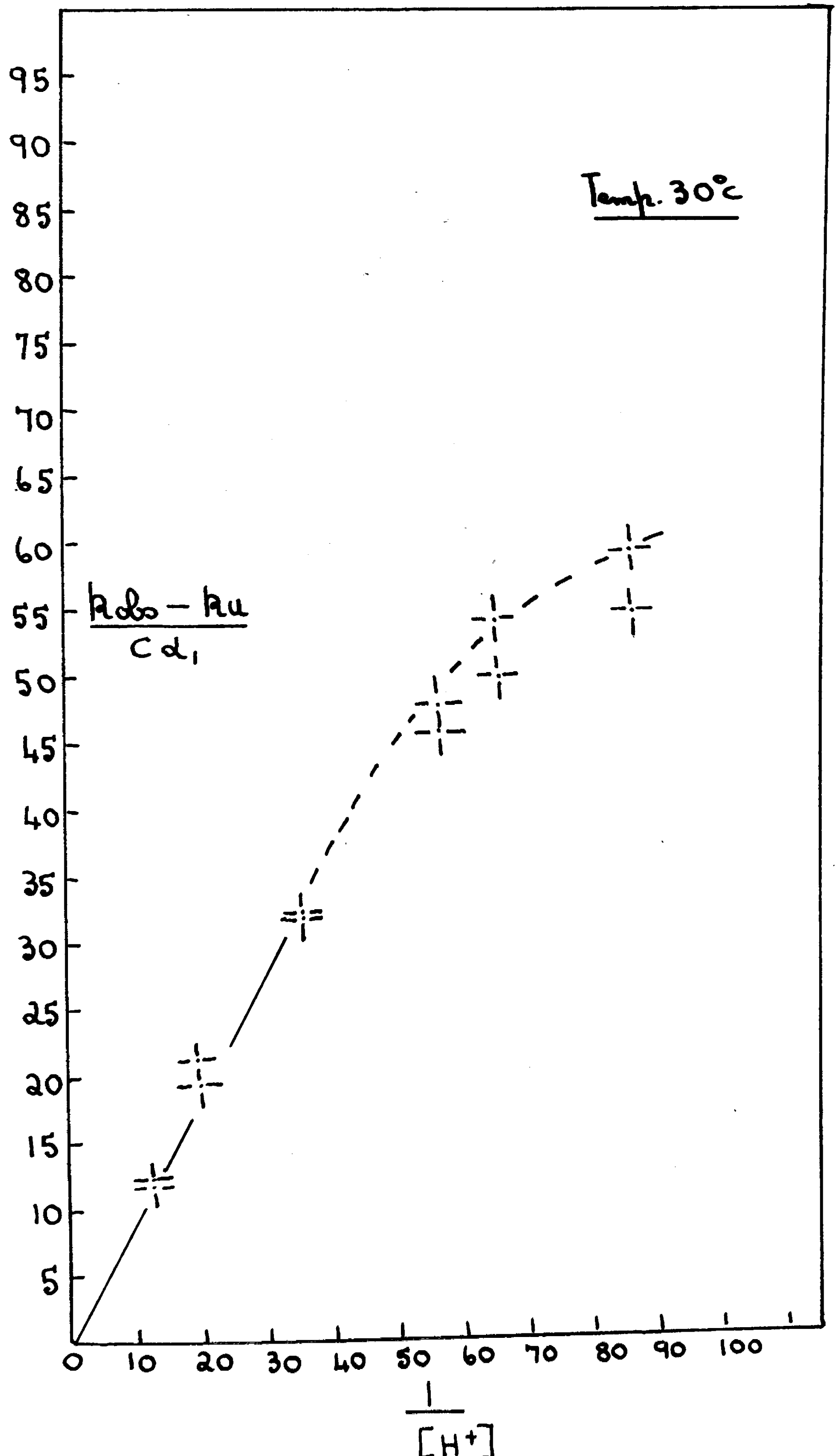
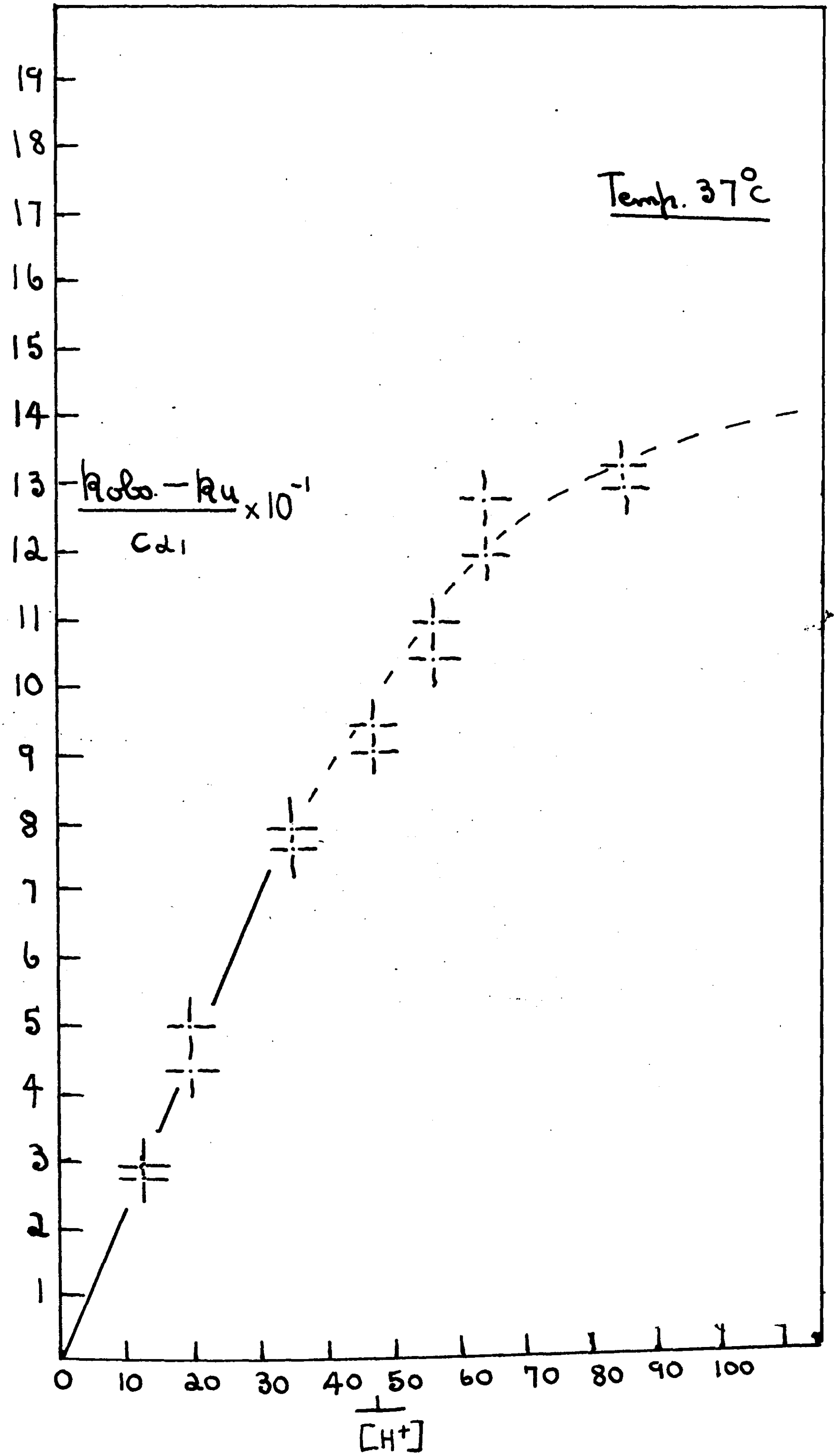

Temp. 30°c
$\frac{k_{obs} - k_u}{C\alpha_1}$
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
10
20
30
40
50
60
70
80
90
100
$\frac{1}{[H^+]}$

Fig. 7



Temp. 37°C
$\frac{k_{obs} - k_u}{C\alpha_1} \times 10^{-1}$
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
100
$\frac{1}{[H^+]}$

Kinetic measurements using zinc chloride in place of copper chloride at a constant ionic strength of 0.1M were also made. The results [Tables (6)-(7)] are plotted in Figs. (8) and (9). As in the case of the copper catalysed runs the values of k_4K_4 were very small.

The values of α_1 and α_2 are calculated thus.

From equation (21), where α_2 is assumed negligible, ie very little second dissociation, a value of α_1 found. This value substituted into equation (22) and α_2 found. Value of α_2 put into equation (23) and new value of α_1 obtained. By successive approximations the best values of α_1 and α_2 calculated.

Table 3. Decomposition of oxaloacetic acid (initial concentration
C molar cupric chloride, (0.1-h-3C) molar potassium

$C\ 10^{4}$	$h\ 10^{3}$	KCl	a_1	a_2	$[H^+]$
2.5	2.5	0.0968	0.3397	0.0047	0.0095
5.0	2.5	0.0960	0.3397	0.0047	0.0095
2.5	5.0	0.0943	0.3038	0.0035	0.0112
5.0	5.0	0.0935	0.3038	0.0035	0.0112
2.5	10.0	0.0890	0.2460	0.0021	0.0150
5.0	10.0	0.0885	0.2460	0.0021	0.0150
2.5	13.0	0.0863	0.2191	0.0016	0.0174
5.0	13.0	0.0855	0.2191	0.0016	0.0174
5.0	25.0	0.0735	0.1489	0.0007	0.0280
10.0	25.0	0.0720	0.1489	0.0007	0.0280
10.0	50.0	0.0470	0.0865	0.0002	0.0517
20.0	50.0	0.0440	0.0865	0.0002	0.0517
20.0	80.0	0.0140	0.0595	0.0001	0.0811
40.0	80.0	0.0080	0.0595	0.0001	0.0811

0.02 molar) at 25°C, in solvent, h molar hydrogen chloride, chloride.

10^3 k obs.	10^5 . ku	$\frac{k - ku}{C\,\alpha_1}$	$\frac{1}{[H^+]}$
3.52	52.17	35.31	105.73
6.20	52.17	33.43	105.73
3.00	46.93	33.31	89.53
5.50	46.93	33.11	89.53
2.12	38.50	26.68	66.78
3.67	38.50	26.68	66.78
1.72	34.59	25.10	57.38
3.10	34.59	25.14	57.38
1.60	24.08	18.25	35.73
2.94	24.08	18.10	35.73
1.18	15.32	11.82	19.33
2.22	15.32	11.98	19.33
0.90	11.40	6.61	12.32
1.80	11.40	6.67	12.32

Table 4. Decomposition of oxaloacetic acid (initial concen-
chloride, C molar cupric chloride, (0.1-h-3C) molar

$C\ 10^4$	$h\ 10^3$	KCl	a_1	a_2	$[H^+]$
2.5	5.0	0.0943	0.3183	0.0037	0.0115
5.0	5.0	0.0935	0.3183	0.0037	0.0115
2.5	10.0	0.0890	0.2606	0.0023	0.0152
5.0	10.0	0.0885	0.2606	0.0023	0.0152
2.5	13.0	0.0863	0.2333	0.0017	0.0177
5.0	13.0	0.0855	0.2333	0.0017	0.0177
5.0	25.0	0.0735	0.1605	0.0008	0.0282
10.0	25.0	0.0720	0.1605	0.0008	0.0282
10.0	50.0	0.0470	0.0942	0.0002	0.0519
20.0	50.0	0.0440	0.0942	0.0002	0.0519
20.0	80.0	0.0140	0.0623	0.0001	0.0812
40.0	80.0	0.0080	0.0623	0.0001	0.0812

tration 0.02 molar), at 30°C, in solvent h molar hydrogen potassium chloride.

10^3 k obs.	10^5 ku	$\frac{\text{k obs.-ku}}{C\ \alpha_1}$	$\frac{1}{[H^+]}$
5.30	96.59	54.46	86.95
10.40	96.59	59.27	86.95
3.98	79.92	49.11	65.49
7.86	79.92	54.18	65.49
3.50	72.26	47.82	56.49
6.03	72.26	45.46	56.49
3.10	51.49	32.22	35.08
5.68	51.49	32.18	35.08
2.35	32.62	21.48	19.27
3.93	32.62	19.09	19.27
1.75	23.55	12.15	12.31
3.23	23.55	11.99	12.31

Table 5. Decomposition of oxaloacetic acid (initial concen-
hydrogen chloride, C molar cupric chloride (0.1-h-3C)

$C\,10^4$	$h\,10^3$	KCl	α_1	α_2	$[H^+]$
2.5	5.0	0.0943	0.3410	0.0039	0.0119
5.0	5.0	0.0935	0.3410	0.0039	0.0119
2.5	10.0	0.0890	0.2817	0.0024	0.0157
5.0	10.0	0.0885	0.2817	0.0024	0.0157
2.5	13.0	0.0863	0.2541	0.0019	0.0181
5.0	13.0	0.0855	0.2541	0.0019	0.0181
2.5	17.0	0.0823	0.2234	0.0014	0.0215
5.0	17.0	0.0815	0.2234	0.0014	0.0215
5.0	25.0	0.0735	0.1780	0.0008	0.0286
10.0	25.0	0.0720	0.1780	0.0008	0.0286
10.0	50.0	0.0470	0.1062	0.0003	0.0521
20.0	50.0	0.0440	0.1062	0.0003	0.0521
20.0	80.0	0.0140	0.0707	0.0001	0.0814
40.0	80.0	0.0080	0.0707	0.0001	0.0814

tration 0.02 molar) at 37°, in solvent h molar molar potassium chloride.

10^3 k obs.	10^3 ku	$\frac{\text{k obs-ku}}{C\ a_1}$	$\frac{1}{[H^+]}$
13.33	2.39	128.30	84.02
24.60	2.39	130.28	84.02
11.00	1.99	127.88	63.51
18.83	1.99	119.53	63.51
8.44	1.82	104.25	55.14
15.83	1.82	110.30	55.14
6.69	1.51	90.83	46.51
12.17	1.61	94.46	46.51
8.35	1.32	79.03	34.99
15.00	1.32	76.87	34.99
5.50	0.86	43.84	19.18
11.50	0.86	50.18	19.18
4.83	0.61	29.81	12.28
8.50	0.61	27.88	12.28

__Table 6.__ Decomposition of oxaloacetic acid (initial concen-
chloride, C, molar zinc chloride, (0.1-h-3C) molar

$C\,10^3$	$h\,10^2$	KCl	α_1	α_2	$[H^+]$
5.0	1.0	0.0750	0.2606	0.0023	0.0153
10.0	2.5	0.0450	0.1605	0.0008	0.0282
10.0	5.0	0.0200	0.0942	0.0002	0.0518

__Table 7.__ Temperature 25°C

5.0	1.0	0.0750	0.2460	0.0021	0.0149
10.0	2.5	0.0450	0.1489	0.0007	0.0280
10.0	5.0	0.0200	0.0865	0.0002	0.0517

tration 0.02 molar) at 30°C, in solvent h molar hydrogen potassium.

10^5 k obs.	10^5 ku	$\frac{k-ku}{C\,\alpha_1}$	$\frac{1}{[H^+]}$
1.54	79.92	0.5377	65.49
1.00	51.49	0.3023	35.08
0.48	36.62	0.1473	19.27
1.025	38.50	0.5203	66.77
0.63	24.08	0.2580	35.72
0.28	15.32	0.1466	19.32

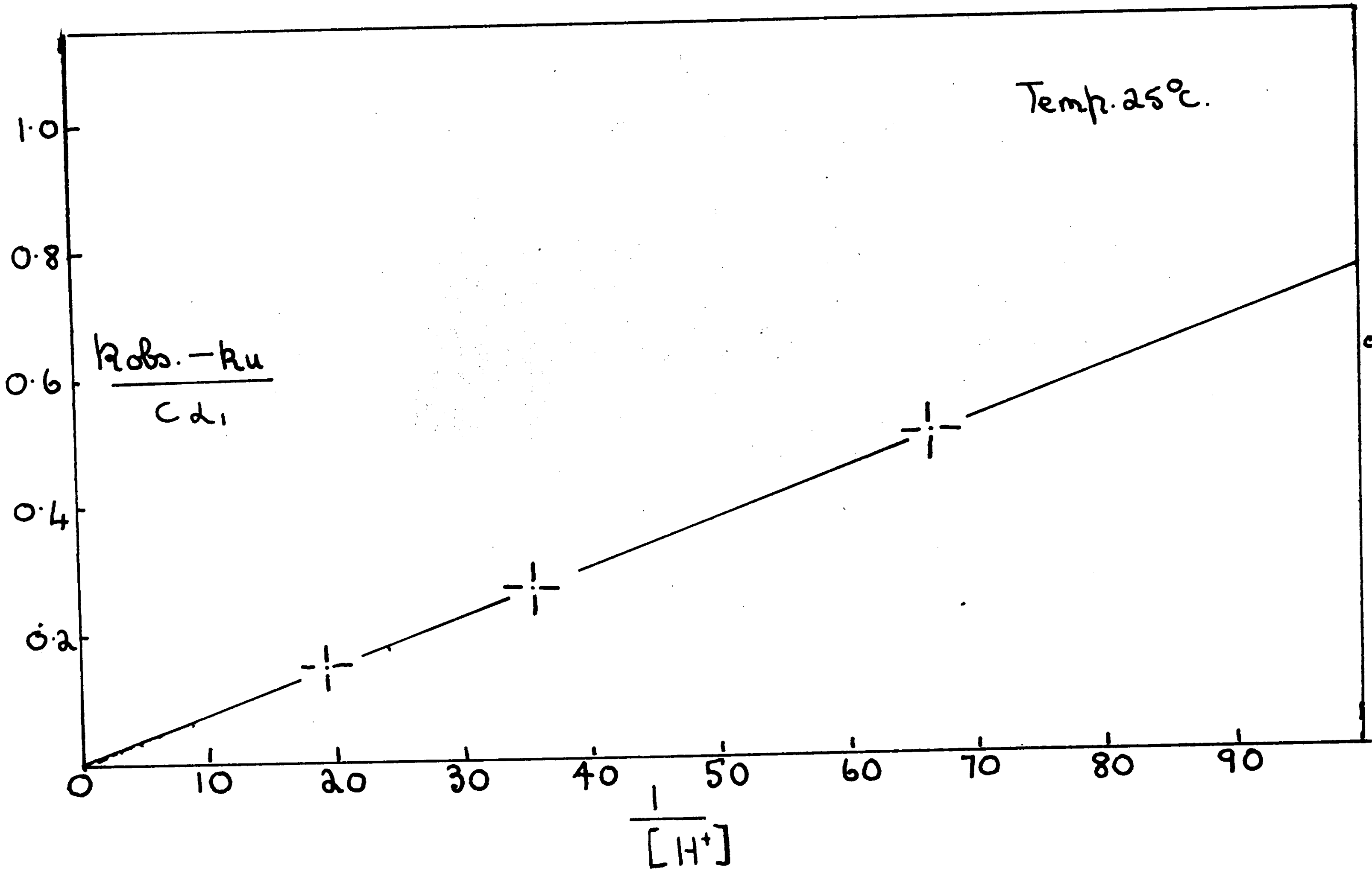
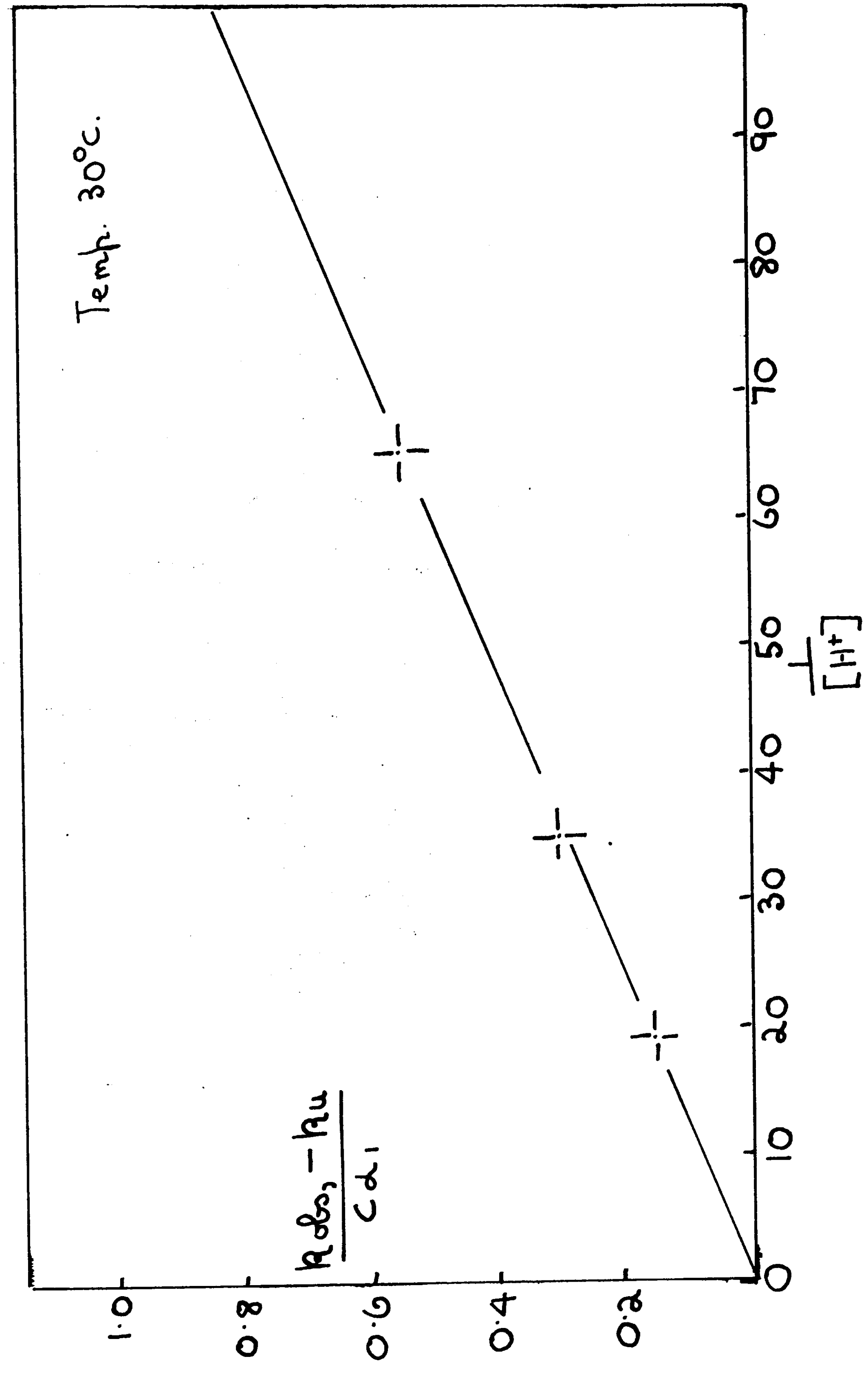

Temp. 25°c.
$\frac{k_{obs.} - k_u}{C\alpha_1}$
1·0
0·8
0·6
0·4
0·2
0
10
20
30
40
50
60
70
80
90
$\frac{1}{[H^+]}$

Fig. 8

Fig. 9.


Temp. 30°C.
$\frac{k_{obs.} - k_u}{C\alpha_1}$
$\frac{1}{[H^+]}$
0
10
20
30
40
50
60
70
80
90
0·2
0·4
0·6
0·8
1·0

Potentiometric Measurements.

In the pH range investigated, the e.m.f. data could be satisfactorily interpreted in terms of only the complex CuA, according to the equilibrium,

$$Cu^{2+} + A^{2-} \rightleftharpoons CuA; \quad K_{CuA} = \frac{[CuA]}{[Cu^{2+}][A^{2-}]f_2^2} \text{ -------(24)}$$

The experiments were made at the three temperatures 25°C, 30°C, 37°C, and the thermodynamic association constants determined at each temperature.

In the presence of copper the pH changed with time because of decarboxylation of the copper chelate compound; measurements could be made only over a limited range of pH and metal-ion concentration. The pH-time curve was extrapolated to the time of addition of metal ion.

$$Ta = [H_2A] + [HA^-] + [A^{2-}] + [CuA] \text{ -----------------(25)}$$

and for the total concentration of metal ion,

$$Tm = [Cu^{2+}] + [CuA] \text{ ----------------------------(26)}$$

By subtraction

$$Tm - Ta = [Cu^{2+}] - [H_2A] - [HA^-] - [A^=] \text{ -------------(27)}$$

or

$$[Cu^{2+}] = Tm - Ta + [H_2A] + [HA^-] + [A^=] \text{ ----------------(28)}$$

Electroneutrality requires

$$[H^+] + 2[Cu^{2+}] = [HA^-] + 2[A^=] + [Cl^-] \text{ ----------------(29)}$$

and by substituting equation (28) in (29),

$$\begin{aligned}[H^+] + 2[Tm - Ta + [H_2A] + [HA^-] + [A^=]\ ] &= \\ = [HA^-] + [2A^=] + [Cl^-] & \text{ -----------------------(30)}\end{aligned}$$

$$\therefore\ [H^+] + 2Tm - 2Ta + 2[\frac{[H^+][HA^-]}{K_1} f_1^2] + [HA^-] - [Cl^-] = 0 \text{ -----------(31)}$$

$$\therefore\ [HA^-] = \frac{2Ta - 2Tm - [H^+] + [Cl^-]}{\frac{2[H^+]f_1^2}{K_1} + 1} \text{ -----------------(32)}$$

Hence we can obtain concentrations of all ion species and K_{CuA} can be calculated. The results are given in Tables (8-9-10) and in view of the quite rapid decarboxylation of the chelate the constancy of the association constants must be regarded as satisfactory over the range of pH studied. The presence of only one complex in this region is in agreement with the findings of the kinetic work, and the value of the association constant at 37°C is in close agreement with that obtained by Pedersen, which is 9.5×10^4.

acid ≐ 0.01M. Ionic Strength = 0.1.

$[A^{=}]$	[CuA]	$K_{3\,\text{therm.}} \times 10^{-3}$
0.000053	0.0007	60.0
0.000049	0.0010	59.3
0.000044	0.0013	62.3
0.000040	0.0015	62.0
0.000028	0.0025	68.3
0.000019	0.0035	64.3

Mean $K_{3\,\text{therm.}} = 62.7 \times 10^{3}$

Table 9. Potentiometric Results at 30°C. Oxaloacetic

$K_1 = 3.08 \times 10^{-3}$, $K_2 = 4.32 \times 10^{-5}$.

Tm 10^3	HCl 10^3	KCl	$[H^+]$	$[HA^-]$
2.50	2.5	0.0900	0.0079	0.0036
3.75	2.5	0.0863	0.0083	0.0033
5.00	2.5	0.0825	0.0087	0.0031
6.25	2.5	0.0787	0.0092	0.0029
10.00	2.5	0.0675	0.0098	0.0026
12.50	2.5	0.0600	0.0105	0.0024

acid = 0.01M. Ionic Strength = 0.1,

$[A^{=}]\ 10^5$	$[CuA]$	$K_3\ 10^{-3}$
5.00	0.0008	77.1
4.78	0.0012	74.0
4.25	0.0015	77.7
3.79	0.0018	83.9
3.21	0.0024	74.5
2.68	0.0028	81.5

Mean K_3 **therm.** $= 78.1 \times 10^3$

Table 10. Potentiometric Results at 37°C. Oxaloacetic

$K_1 = 3.55 \times 10^{-3}$, $K_2 = 4.38 \times 10^{-5}$.

Tm 10^3	HCl 10^3	KCl	$[H^+]$	$[HA^-]$
2.50	2.5	0.0900	0.0081	0.0037
3.75	2.5	0.0863	0.0087	0.0035
5.00	2.5	0.0825	0.0092	0.0032
6.25	2.5	0.0787	0.0095	0.0030
10.00	2.5	0.0675	0.1050	0.0026
12.50	2.5	0.0600	0.0170	0.0024

acid = 0.01M. Ionic Strength = 0.1

$[A^{=}]\ 10^{5}$	[CuA]	$K_3\,10^{-3}$
5.40	0.0009	92.7
4.79	0.0013	87.8
4.24	0.0017	92.0
3.76	0.0020	97.0
3.02	0.0027	91.6
2.66	0.0030	91.1

Mean $K_{3\,\text{therm.}} = 92.0 \times 10^{3}$

We are now in a position to calculate the approximate free copper ion present in the kinetic experiments from the following equations, (Tables 11, 12, 13).

$$T_{Cu^{2+}} = [Cu^{2+}] + [CuA] \text{ --------------------------(33)}$$

$$\therefore T_{Cu^{2+}} = [Cu^{2+}] + K_3[Cu^{2+}][A^{=}] \text{ ------------------(34)}$$

$$\therefore T_{Cu^{2+}} = [Cu^{2+}][1 + K_3[A^{=}]] \text{ ------------------(35)}$$

$$\therefore [Cu^{2+}] = \frac{T_{Cu^{2+}}}{1 + K_3[A^{=}]} \text{ ------------------(36)}$$

Substituting these values in equation (10), new plots of $\frac{k\ obs - ku}{C\ \alpha_1}$ against $\frac{1}{[H^+]}$ are obtained (Figs. 10, 11, 12)

It is seen that now straight lines passing through the origin are obtained over the whole pH range studied, confirming the presence of only one complex and the accuracy of the K_3 values.

Table 11. Calculated free copper-ion concentrations measurements at 25°C.

Tm 10^4	HCl 10^3	$[A^{=}]\ 10^6$	$[Cu^{2+}]\ 10^4$
2.5	2.5	11.25	1.47
5.0	2.5	11.25	2.93
2.5	5.0	8.37	1.64
2.5	10.0	5.07	1.89
5.0	10.0	5.07	3.80
2.5	13.0	3.91	2.01
5.0	13.0	3.91	4.01
5.0	25.0	11.65	4.53
10.0	25.0	1.65	9.04

($[Cu^{2+}]$) and new values of $\frac{k\ obs.-ku}{C\ \alpha_1}$ for kinetic

$C\ \alpha_1\ 10^5$	$\frac{K\ obs.-ku}{C\ \alpha_1}$ t	$\frac{1}{[H^+]}$
4.99	60.05	105.73
9.95	57.05	105.73
4.98	50.79	89.53
4.66	37.12	66.78
9.34	35.16	66.78
4.38	31.46	57.38
8.79	30.74 31.31	57.38
6.75	20.14	35.73
1.35×10^{-4}	20.05	35.73

Table 12. Calculated free copper ion concentration kinetic measurements at 30°C.

Tm 10^4	HCl 10^3	$[A^=]$ 10^6	$[Cu^{2+}]$ 10^4
2.5	5.0	8.74	1.50
5.0	5.0	8.74	2.99
2.5	10.0	5.37	1.77
5.0	10.0	5.37	3.54
2.5	13.0	4.14	1.90
5.0	13.0	4.14	3.79
5.0	25.0	1.76	4.40
10.0	25.0	1.76	8.80

$[Cu^{2+}]$ and new values of $\frac{k\ obs.-ku}{C\ \alpha_1}$ for

$C\ \alpha_1\ 10^5$	$\frac{k\ obs.-ku}{C\ \alpha_1}$	$\frac{1}{[H^+]}$
4.76	9.107	86.95
9.51	99.16	86.96
4.61	68.85	65.49
9.23	76.54	65.49
4.42	62.79	56.48
8.84	59.97	56.48
7.07	36.58	35.08
14.13	36.54	35.08

Table 13. Calculated free copper ion concentration kinetic measurements at 37°C.

Tm 10^4	HCl 10^3	$[A^=]$ 10^6	$[Cu^{2+}]$ 10^4
2.5	5.0	9.16	1.35
5.0	5.0	9.16	2.71
2.5	10.0	5.71	1.64
5.0	10.0	5.71	3.27
2.5	13.0	4.47	1.77
5.0	13.0	4.47	3.54
2.5	17.0	3.31	1.92
5.0	17.0	3.31	3.83
5.0	25.0	1.98	4.27
10.0	25.0	1.98	8.25

$[Cu^{2+}]$ and new values of $\frac{k\ obs.-ku}{C\ \alpha_1}$ for

$C\ \alpha_1\ 10^5$	$\frac{k\ obs.-ku}{C\ \alpha_1}$	$\frac{1}{[H^+]}$
4.62	237.00	84.02
9.23	240.50	84.02
4.61	195.30	63.51
9.21	182.80	63.51
4.49	147.26	55.14
8.96	155.81	55.14
4.27	118.58	46.51
8.58	123.28	46.51
7.59	93.51	34.99
15.05	90.94	34.99

Fig. 10.

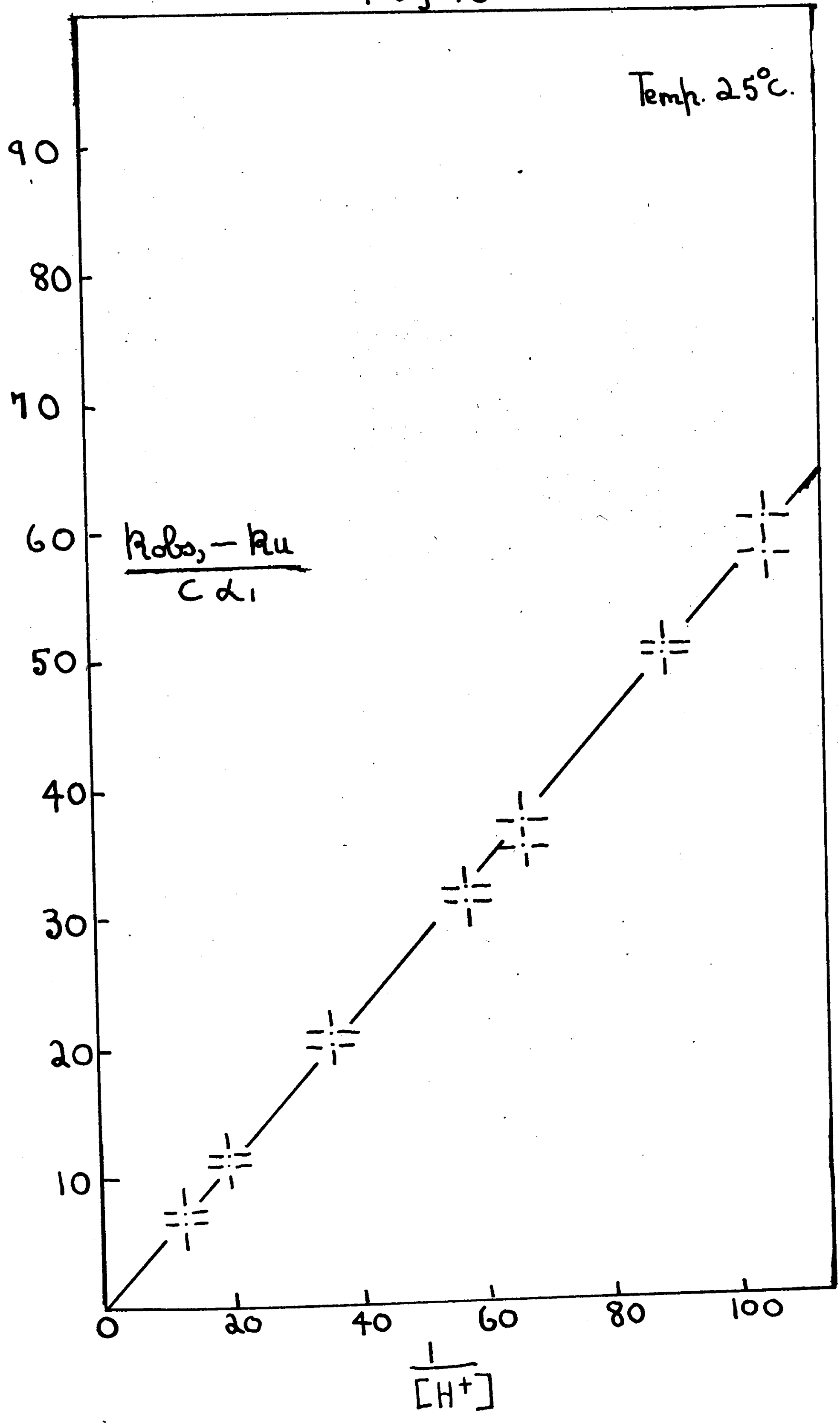

Temp. 25°C.
$\frac{k_{obs.} - k_u}{C\alpha_1}$
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
$\frac{1}{[H^+]}$

Fig. 11.

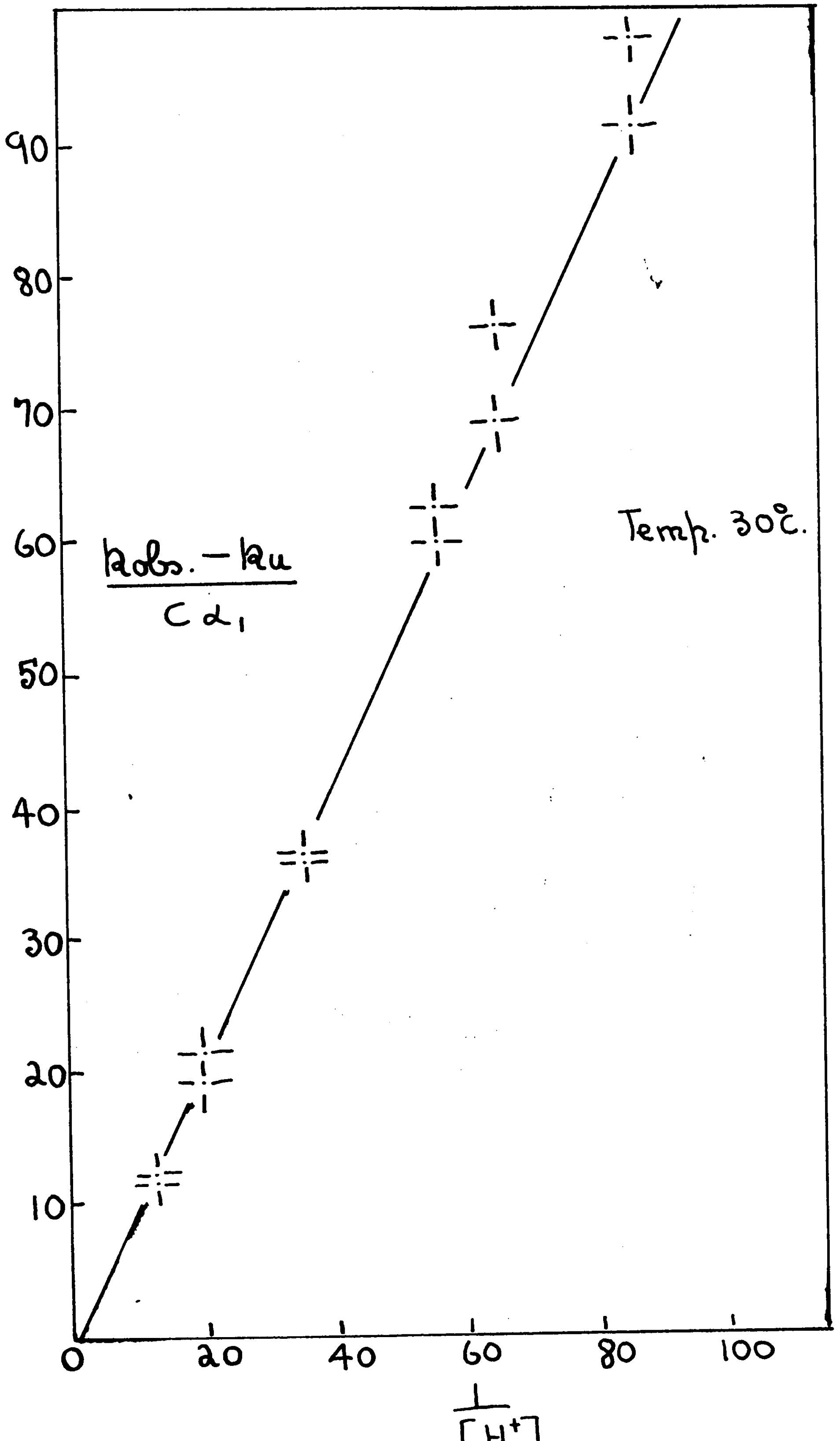
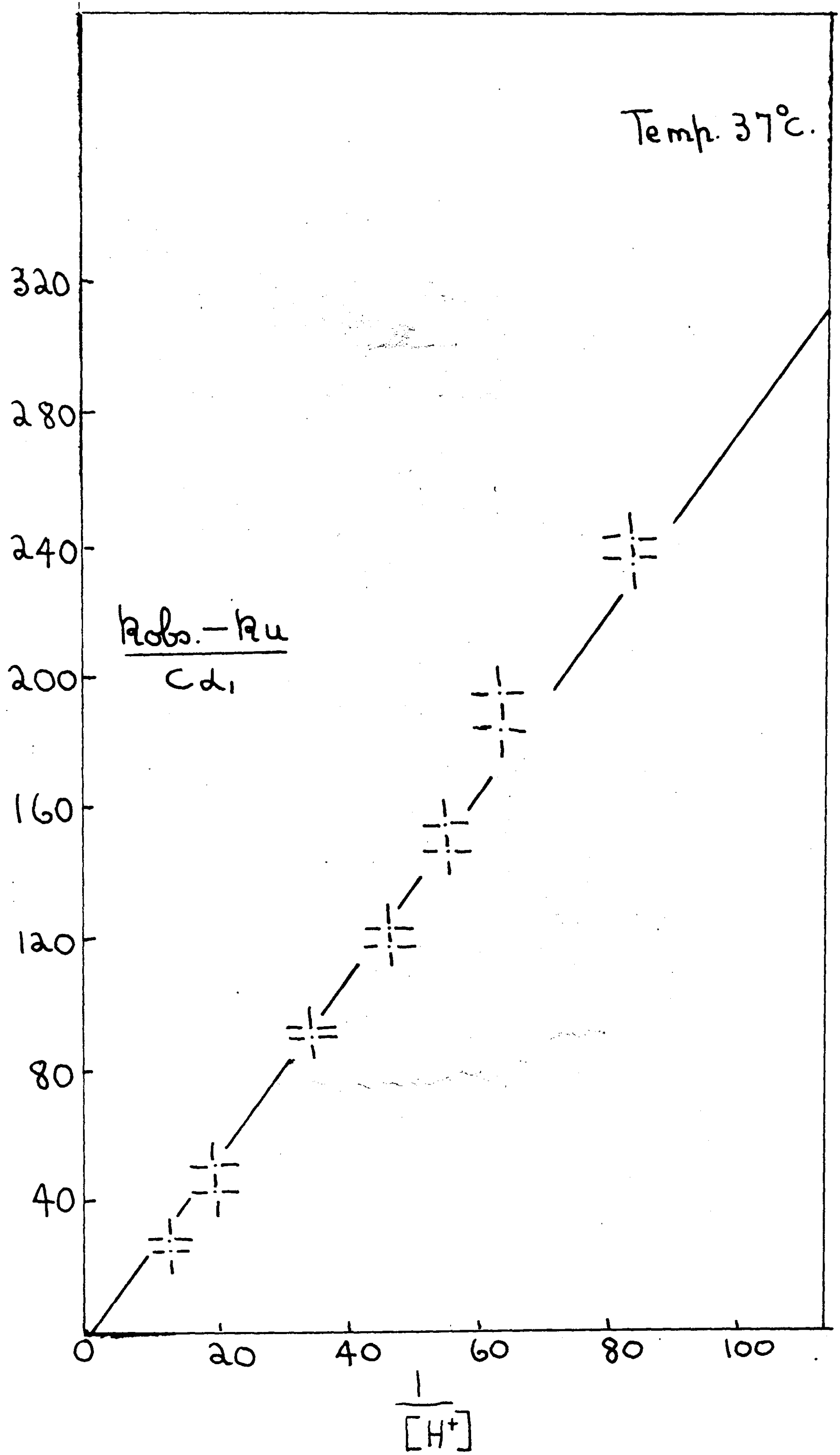

90
80
70
60
50
40
30
20
10
$\frac{k_{obs.} - k_u}{C\alpha_1}$
Temp. 30°C.
0
20
40
60
80
100
$\frac{1}{[H^+]}$

Fig. 12.


Temp. 37°C.
320
280
240
200
160
120
80
40
0
20
40
60
80
100
$\frac{k_{obs.} - k_u}{C\alpha_1}$
$\frac{1}{[H^+]}$

From the kinetic and potentiometric measurements we have obtained values for k_3 at the three temperatures. Application of the Arrhenius equation ($k = Ae^{-E_A/RT}$) gives the results in Table 14.

Table 14.

Temperature	k_3K_3	$K_3 \times 10^3$ (therm)	K_3 (conc.) 10^4	K_3 (mass action)	k_3	E_A(K cal/ mole)
37°C	2.27	92.0	1.20	1.63	1.40	15.9
30°C	1.00	78.1	1.00	1.33	0.75	15.2
25°C	0.525	62.7	0.82	1.06	0.49	16.6

Average $E_A \approx 16$ K cal mole

The activation energies for the decarboxylation of the undissociated acid, its anion and the copper complex CuA are given in Table 15.

Table 15.

	Acid	Anion	Complex CuA
E(K cal/ mole)	25.8	23.1	16

The activation energy for the complex CuA is considerably lower than that of the undissociated acid or anion.

INTRODUCTION

[illegible] study of hydrolytic equilibria in general, has been [illegible]ed by a number of authors over the last sixty [illegible] and today knowledge of the subject is quite exten[illegible] [illegible] examined in [illegible] [illegible] hydrolysi[illegible]

Part 2.

The Hydrolysis of the Uranyl ion UO_2^{2+} in a nitrate medium.

INTRODUCTION

The study of hydrolytic equilibria in general, has been treated by a number of authors over the last sixty years, and today knowledge of the subject is quite extensive.

If an iron salt, say ferric nitrate, is dissolved in water, the solution has an acidic reaction, the reaction of the iron salt with the water being called " hydrolysis" ,

$$XFe^{3+} + YH_2O \rightleftharpoons Fe_x(OH)_y^{(3x-y)} + yH^+ \text{ ---------------(1)}$$

Iron is by no means unique in this respect. Many metallic cations undergo this reaction in aqueous solution, e.g., UO_2^{2+}, Cu^{2+}, Be^{2+}, Al^{3+}.

In 1907, both Werner[29] and Pfeiffer[30] put forward the same explanation for the above, when they suggested that protons are split off from the water molecules bound to the cation, (" aquo-acidity").

$$\text{e.g., } Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5OH^{2+} + H_3O^+ \text{ --------(2)}$$

or more briefly

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \text{ ----------------(3)}$$

As a result of supporting evidence obtained by Bjerrum[31] and Bronsted and Volquartz,[32] it was assumed that reactions such as (3) are the general explanation of cation hydrolysis.

In 1908, Bjerrum[33] found that the hydrolysis of Cr^{3+} also gives polynuclear complexes, nevertheless, and in spite of the fact that polynuclear complexes had long been recognised among the hydrolysis products from anions such as molybdate and silicate, the concept of aquo-acidity with mononuclear products predominated for many years. In 1936, Jander,[34] from diffusion measurements obtained qualitative evidence for the presence of polynuclear complexes of many cations.

In this part of the thesis, the work has dealt specifically with the study of the hydrolysis of the uranyl ion UO_2^{2+} in a nitrate medium, in order to determine the polynuclear complexes present in solution.

One of the earliest workers on uranyl hydrolysis was Britton,[35] who extended the work carried out by Hildebrand.[36] Britton showed that hydrolysis of the uranyl ion (UO_2^{2+}) occurred when the pH of a solution of uranyl nitrate was raised above 2.5. In 1949, Ahrland[37] published an investigation on the hydrolysis of the uranyl ion in 1 molar sodium perchlorate, the data obtained being more accurate and covering a wider range than any published previously. From his results Ahrland concluded that the uranyl ion (UO_2^{2+}) forms mainly polynuclear complexes at low acidities.

Although about a score of studies on the hydrolysis of the uranyl ion have been published in the last fifteen years, many of the schemes postulated agree in little more than the fact that polymeric species are formed but even this has been disputed by several authors.[38] Other workers, whilst postulating the presence of the same species have quoted stability constants differing by a factor of 10,[39] or even 100 as in the case of UO_2OH^+.[40]

One of the main schools of research engaged in the study of hydrolytic equilibria is the Sillén school in Sweden. In 1954, Sillén[41] published a series of papers in which he discussed the mathematical laws for the formation of polynuclear complexes, both under rather general assumptions and also for a few special mechanisms. This has been called the " core + links" hypothesis, in which all complexes that are produced in appreciable amounts have a composition corresponding to a certain core +

a various number of links. It was also shown how experimental data may be treated to find the nature of reaction products. In the same year Hietanen and Sillén[42] applied the general equations to the special case of hydrolysis. Applying this more general scheme, Arhland, Hietanen and Sillén,[43] reinterpreted the earlier data of Ahrland. In this interpretation all hydrolysed species were postulated to have the general "core + links" formula, $M[(OH)_tM]_n$ where t is a constant and where n is the number of links. Three possibilities were offered,

(a) a limited series, having complexes with $n = 1 \rightarrow 3$,
(b) a limited series, having complexes with $n = 1 \rightarrow 4$,
(c) an unlimited series where n can have several integral values.

The last possibility of continuous polymerisation was preferred by the authors. A few years later Hietanen and Sillén[44] modified this picture to account for the introduction of the additional species $(UO_2)_2OH^{3+}$. Recently Peterson[45] has used the "core + link" hypothesis to interpret e.m.f. data in uranyl sulphate solutions.

Many other ions have been studied by e.m.f. methods. The results seem to indicate, that when applied over a wide concentration range and with a constant ionic medium, sufficient information is obtained from these methods to allow reliable conclusions to be drawn about the species present and the equilibrium constants.

Recently Rush, Johnson and Kraus,[46] in the light of results obtained from ultracentrifuge measurements on the hydrolysis of several ions, have suggested that there is an alternative hydrolysis scheme which is consistent with both e.m.f. and ultracentrifuge measurements, and which does not require a "core + link" system nor a continuous polymerization scheme. They also carried out acidity measurements on hydrolysed uranyl solutions in 1 molar total chloride, their results being in most accord with those of Sutton.[47]

On the basis of e.m.f. measurements there is a strong suggestion that the hydrolytic schemes of uranyl hydrolysis in chloride and perchlorate media differ. Hydrolytic species in 1 molar sodium perchlorate are $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^{+}$ whilst in chloride there appears to be the additional species $(UO_2)_3(OH)_4^{2+}$. The differences in hydrolytic schemes have been suggested as being the reason for the large differences in the phase diagrams in these media. Baes and Meyer[48] have suggested that in a nitrate medium the hydrolysis scheme should resemble more closely that of perchlorate, a conclusion which is consistent with the phase diagrams.

In the light of all the controversy arising in the literature, experiments were carried out in this laboratory to study by means of acidity measurements the hydrolysis of the uranyl ion UO_2^{2+} in 1 molar nitrate media. This work was carried out over as wide a range of uranyl concentrations as was practicable in order to determine the species formed and the corresponding equilibrium constants.

It is interesting to note, that schemes put forward or suggested for uranyl hydrolysis seem to depend on the media in which the hydrolysis was performed, indicating that the medium used, in some way influences the formation of the complex species. At the present time it is impossible to determine the activity coefficients for the different species, as the amount and type of complexes are unknown. It has therefore been necessary to carry out the experimental work in a 1 molar nitrate medium enabling activity factors to be assumed constant. It is expected however, with the advent of higher speed electronic computers, the hydrolysis will be able to be carried out at low ionic strength.

[illegible] the precipitate [illegible] then [illegible] was washed [illegible] three times [illegible] of chloride ions. [illegible] cylinder nitrogen [illegible] through two wash bottles containing 10% [illegible] sodium hydroxide and [illegible] through two wash bottles [illegible] of potassium [illegible]

[illegible] 0.5 normal solution of [illegible] hydroxide was [illegible] red by dissolving a [illegible] of potassium hydroxide [illegible]) under a [illegible] of nitrogen. the [illegible] made up with [illegible] distilled wa-

EXPERIMENTAL

Materials and Analysis.

The uranyl nitrate [$UO_2(NO_3)_2 6.H_2O$] used was a spectroscopically pure material (Johnson, Matthey and Co. Ltd.). The total uranium concentration of a solution being verified by precipitation with oxine, the solution filtered and the precipitate ignited to U_3O_8. The uranium present was then determined. Analar materials were used in all cases but it was necessary to recrystallize the potassium nitrate three times from conductivity water to ensure the absence of chloride ions. All the water used was carbonate free. Cylinder nitrogen was washed by bubbling it through two wash bottles containing 10% sulphuric acid and 10% sodium hydroxide and then pre-saturated by bubbling through two wash bottles each containing a 1 molar solution of potassium nitrate.

An approximately 0.5 normal solution of potassium hydroxide was prepared by dissolving x gms. of potassium hydroxide pellets (Analar) under a stream of nitrogen, the solution being made up with boiled out distilled water and kept under nitrogen in a polythene bottle. Portions of stock solution were blown out with purified nitrogen, as required. An approximately 1 normal solution of nitric acid was prepared from Analar nitric acid and standardised against sodium bicarbonate using screened methyl orange as the indicator. The stock solution of potassium hydroxide was standardised against potassium hydrogen phthalate and also constant boiling hydrochloric acid using phenolphthalein as indicator. The stock solutions of nitric acid and potassium hydroxide were then checked against each other using phenolphthalein as indicator, and potentiometrically using a Gran[53] extrapolation to determine the exact equivalence point. From these stock solutions, other solutions of nitric acid and potassium hydroxide which were 1 molar in nitric were prepared and standardised. Agreement between standardisations was found to be within 0.1%. A stock solution of 1 molar potassium nitrate and one of silver nitrate-potassium nitrate [20 mM Ag^+, 980 mMK^+, 1000 mM NO_3^-] was prepared.

Experimental Details.

A study of the hydrolysis of the uranyl ion in a nitrate medium was carried out as a series of potentiometric titrations, Leden[50] being first to use this technique in the study of cadmium complexes. By this method it is possible to obtain in a limited time a much larger number of experimental results than could be obtained by the older point-wise method. All solutions were made up to be 1 molar in nitrate with potassium nitrate to ensure that the ionic medium remained as constant as possible.

The work was carried out in a room which was thermostatically controlled at 25°C ± 1°C. Measurements were made in a paraffin oil thermostat maintained at 25°C ± 0.02°C by a Sunvic Thermoregulator. (Proportioning Head Type Tol.3B).

All pipettes, burettes and flasks were calibrated under experimental conditions with water and 1 molar potassium nitrate. Provided the liquid was allowed to drop slowly no difference was found in the volumes of water and solution delivered from burettes. Rate of addition from pipettes was controlled by a "Pumpette". Before each run all glass apparatus was cleaned with alcoholic potassium hydroxide, chromic acid and distilled water.

In the set of experiments two forms of titration were used.

(a) Constant B titrations, i.e., titrations in which the total uranyl concentration B remained constant whilst the concentration of hydrogen ion was varied.

(b) Constant Z titrations, i.e. titrations in which Z, the average number of hydroxyl groups bound per uranyl ion was kept approximately constant. This was done by adding successively calculated amounts of uranyl nitrate solution to a 1 molar potassium nitrate solution.

The free hydrogen ion concentration, (h) was measured with a commercial screened glass electrode (E.I.L type GG33), the e.m.f. measurements being made on a Croydon potentiometer, a Vibron electrometer (E.I.L. model 33e) acting as a null indicator. Readings were reproducible to ± 0.1 mV. A Wilhelm[51] type salt bridge (Fig.1b) was used and the cell can be written as

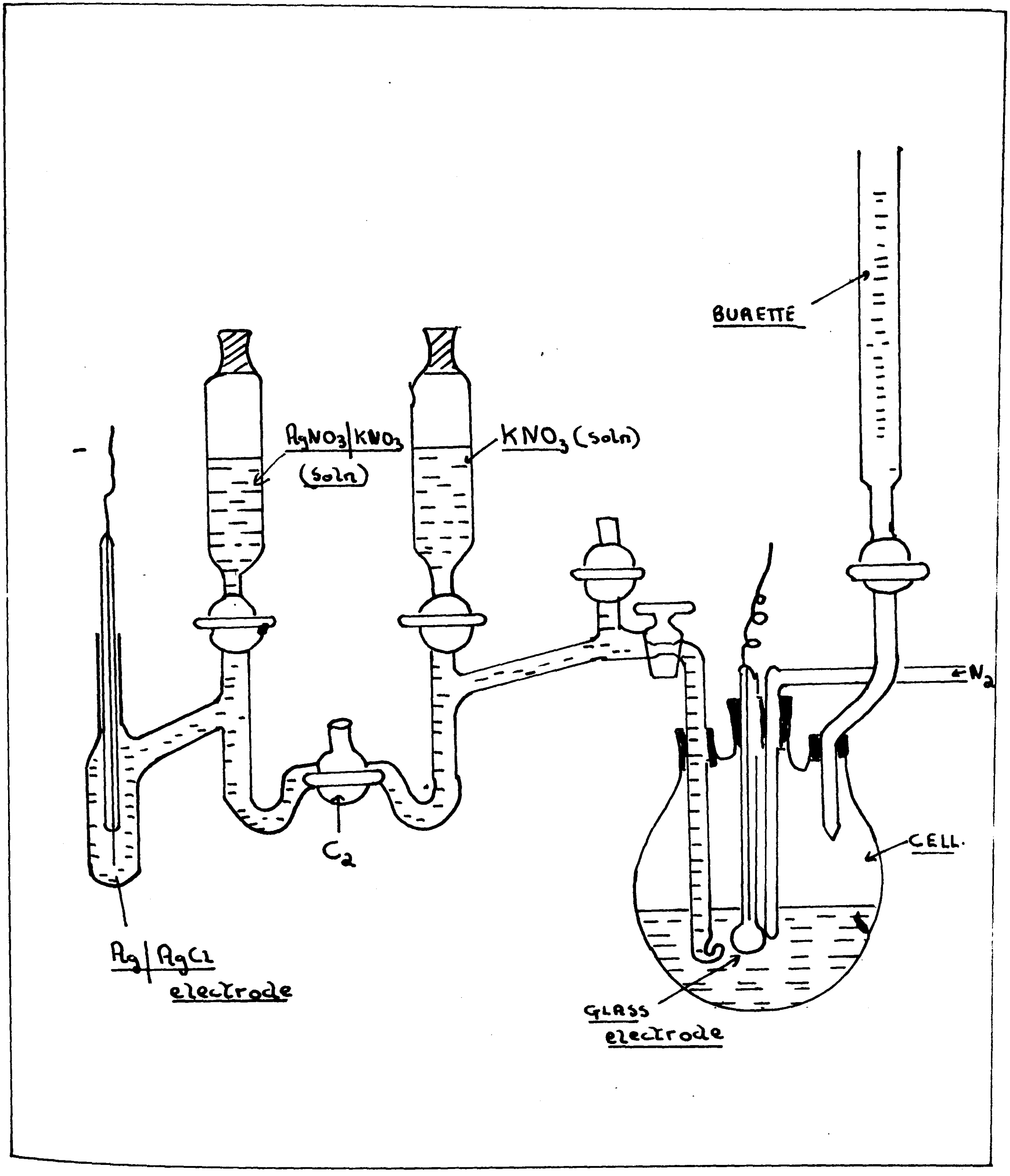
$$- \text{Glass electrode} / \text{solution under study} / \text{SE}^+$$

SE, the reference electrode was

$$\text{Ag}/\text{AgCl}/\text{20mM Ag}^+, \text{980mM K}^+, \text{1000mM NO}_3^- / \text{1000mM KNO}_3$$

The silver/silver chloride reference electrode was prepared by the method of Brown,[49] the platinum wire being

Fig 1b.



BURETTE
AgNO3|KNO3 (soln)
KNO3 (soln)
-
N2
C2
CELL.
Ag|AgCl electrode
GLASS electrode

coated with silver by electrolysis in a solution of 1% potassium argentocyanide [$KAg(CN)_2$] for four to five hours at a current of 0.5 mA . The electrodes were then washed with ammonium hydroxide, stored in water for sixteen hours to remove all traces of cyanide and then coated with silver chloride by electrolysis in 0.1 normal hydrochloric acid for thirty minutes at a current of 2mA.

For the cell used assuming that activities are constant, the e.m.f. can be expressed as,

$$E = E^{\circ} - 59.15 \log h + E_j \quad \text{------------------------------(A)}$$

where h is in mM.

The junction potential Ej, has been found to be small and proportional to the acidity of the solution, but can be neglected above pH 3.5,[52]

$$E_j = kh \quad \text{--------------------------------------(B)}$$

For each titration E° was determined by the following method. E^1, the calculated value of E° obtained by neglecting Ej was plotted against h, to find the proportionality constant k. E^1 was then corrected for kh where this was significant to give E°.

Titration Procedure (Constant B titrations).

25 ml. of an acid solution of known normality was added to the cell (Fig.1b). To this solution, additions of standard potassium hydroxide were made until approximately pH 1.70, readings being taken after each addition of alkali. This initial part of the titration enabled the glass electrode to be calibrated. At this stage in the titration an equal volume of 2x normal uranyl nitrate solution, which contained a small amount of standard nitric acid, was added to the cell, giving a total uranium concentration of x. This addition of a small amount of nitric acid to the stock solution of uranyl nitrate is necessary, in order to suppress hydrolysis, the acidity of the uranyl solution being taken into account in all the calculations. The titration was continued, equal volumes of the potassium hydroxide and uranyl nitrate solutions being added to the solution; the total uranium concentration remaining constant during the titration. When a sharp drop in the e.m.f. of the solution was observed, indicating the precipitation had commenced, the titration was stopped and the electrodes carefully cleaned. During the complete run, nitrogen was bubbled constantly at

a slow rate through the solution, serving as a stirrer and also excluding carbon dioxide from the system. Before the titration was started the liquid junction at C_2 (Fig.1b) was renewed by flushing alternatively with potassium nitrate from resevoir A, and the silver nitrate-potassium nitrate solution from B. While the titration was in progress the stopcock at C_2 remained open. During the run local precipitation was observed on addition of potassium hydroxide. This soon redissolved on mixing and constant e.m.f. readings obtained. Several titrations were performed in the opposite direction, starting well below the point of precipitation, and no difference was observed in the graphs for corresponding titrations. It was therefore concluded that equilibrium was being reached on each addition during the titrations.

At each uranyl concentration 160, 80, 40, 20, 10 and 5 mM UO_2^{2+} several titrations were carried out and agreement between the curves was better than 0.01 pH unit.

Constant Z titrations.

25 ml. of 1 molar potassium nitrate was added to the cell (Fig.1b). To this solution additions of successively calculated amounts of a standard uranyl nitrate solution were

made. The uranyl solution contained a known volume of a standard nitric acid solution, this enabling the acidity of the uranyl solution to be calculated. After each addition the e.m.f. was taken. It was found that by this titration technique Z was kept approximately constant throughout the titration as the addition of acid to the uranyl solution kept the ratio $\frac{H}{B}$ constant in the equation $Z = \frac{H - h}{B}$. Also in the uranyl solution there was a known volume of a standard solution of potassium hydroxide to allow hydrolysis to occur.

SYMBOLS AND FORMULAE

The symbols adopted are mainly those used by other workers in this field.

B = total UO_2^{2+} concentration
b = concentration of unhydrolysed UO_2^{2+}
h = H^+ concentration
H = analytical hydrogen concentration
Z = average number of OH^- bound per UO_2^{2+}
x = $\log B - 2 \log h$
Y = $0.5Z$
K_n = equilibrium constant for the reaction
$(n+1)(UO_2^{2+}) + 2nH_2O \rightleftharpoons UO_2[(OH)_2UO_2]_n^{2+} + 2n H^+$
U = $h^{-t}b$
g = $\sum KnU^n = K_1U + K_2U^2 + \dots\dots\dots$
η = $\log \frac{B}{b}$
E = e.m.f.
Ej = liquid junction potential
g^1 = $\frac{dg}{dU}$
n = number of links per complex
k = constant in $Ej = kh$

Calculations and Results.

The hydrolysis of the uranyl ion (UO_2^{2+}) was studied by a series of potentiometric titrations at 25°C. The free concentration of hydrogen ion will be denoted by,

$$[H^+] = h$$

B is the total concentration of uranium in the solution and H is the analytical excess of hydrogen ion, assuming that no hydrolysis has taken place. H is therefore negative in the latter parts of the titrations. The quantities B and H are known from analytical data.

In each constant B titration, H was varied and h measured. The average number of OH^- bound per UO_2^{2+} could then be calculated

$$Z = \frac{(h - H)}{B} \text{ -----------------------------(1)}$$

The measured e.m.f. of the cell can be written,

$$E = E^\circ - 59.15 \log h + Ej \text{ -----------------(2)}$$

The junction potential, Ej, was found to be small and to vary slightly between titrations with different B, the value being determined for each titration by measurement in a region where no hydrolysis occurred. E was corrected for Ej where Ej was significant. For each titration E° was determined (Table 1b) and found to remain fairly constant during the series of experiments. Z and log h were then calculated and a family of curves (- log h, Z) was drawn (Fig.2b). The data are given in Table 2b.

Table 1b.

St[illegible] [illegible] electrodes: B = 5mM $[NO_3^-]$ = 100mM.

Table 1b.

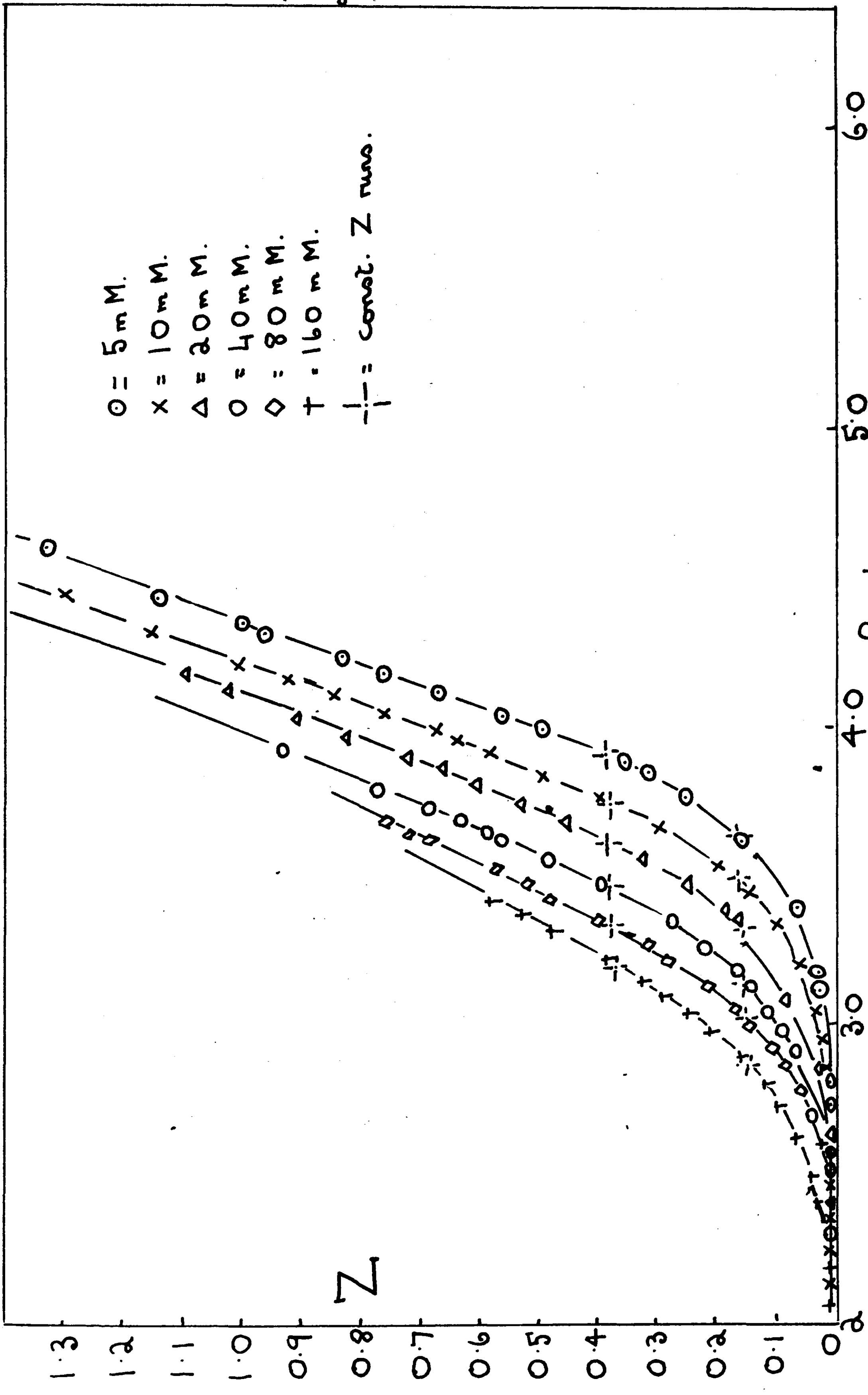
Standardisation of electrodes. B = 5mM $[NO_3^-]$ = 1000mM.

E.m.f. (volts)	Total $[H^+]$mM	log$[H^+]$	−log h
0.3850	91.06	$\bar{2}.959$	1.04
0.3886	76.57	$\bar{2}.883$	1.12
0.3926	63.86	$\bar{2}.805$	1.19
0.3970	52.84	$\bar{2}.722$	1.28
0.4020	43.11	$\bar{2}.634$	1.37
0.4045	38.65	$\bar{2}.587$	1.41
0.4100	30.53	$\bar{2}.484$	1.52
0.4167	23.20	$\bar{2}.365$	1.63
0.4206	19.85	$\bar{2}.297$	1.70

Average value of E° = 319.1 mV.

$0.05915 \log [H^+]$	E^1(volts)	K	E° volts
-0.0616	0.3234	0.046	0.3192
-0.0660	0.3226	0.046	0.3191
-0.0708	0.3218	0.046	0.3189
-0.0755	0.3215	0.046	0.3191
-0.0808	0.3212	0.046	0.3192
-0.0836	0.3209	0.046	0.3191
-0.0896	0.3204	0.046	0.3190
-0.0967	0.3200	0.046	0.3189
-0.1007	0.3199	0.046	0.3190

Fig. 2b.



Z
− log h
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
2.0
3.0
4.0
5.0
6.0
⊙ = 5 mM.
× = 10 mM.
△ = 20 mM.
○ = 40 mM.
◇ = 80 mM.
+ = 160 mM.
-¦- = const. Z runs.

Table 2b. Experimental data. Z. - log h.

Titration 1. B = 5mM.

Z	-log h
0	2.291
0	2.316
0	2.423
0.001	2.506
0.002	2.543
0.003	2.730
0.005	2.901
0.020	3.134
0.023	3.188
0.069	3.409
0·138	3·628
0.154	3.624
0.253	3.770
0.314	3.851
0.356	3.885
0.491	4.002
0.564	4.049
0.671	4.120

Z.	-log h
0.766	4.183
0.832	4.233
0.961	4.313
0.995	4.345
1.150	4.445
1.155	4.463
1.331	4.604

Titration 2. B = 10mM

Z	$-\log h$
0	2.054
0	2.135
0	2.233
0	2.349
0.003	2.504
0.007	2.719
0.013	2.867
0.024	2.969
0.027	3.035
0.055	3.217
0.097	3.353
0.144	3.457
0.149	3.459
0.194	3.547
0.295	3.674
0.315	3.696
0.394	3.775
0.491	3.849
0.494	3.854

Z	-log h
0.583	3.927
0.633	3.971
0.673	3.995
0.759	4.059
0.783	4.076
0.843	4.113
0.923	4.169
1.004	4.225
1.154	4.333
1.295	4.451
Back Titration	
0.7134	4.034
0.545	3.907
0.368	3.755
0.172	3.554
0.061	3.231
0.024	2.911
0.014	2.741
0.007	2.619
0	2.530

Titration 3. B = 20 mM.

Z.	-log h
0	1.899
0	1.995
0	2.146
0	2.279
0.003	2.387
0.007	2.563
0.006	2.507
0.015	2.664
0.029	2.854
0.035	2.942
0.090	3.175
0.107	3.216
0.168	3.351
0.188	3.381
0.256	3.471
0.268	3.493
0.325	3.564
0.344	3.579
0.399	3.637
0.420	3.653
0.534	3.758

Z	**-log h**
0.553	3.770
0.616	3.816
0.645	3.851
0.729	3.904
0.761	3.939
0.834	3.975
0.927	4.038
1.091	4.039
1.030	4.130
1.104	4.183

Titration 4. B = 40 mM.

Z	-log h
0	1.885
0	1.988
0	2.063
0	2.228
0.004	2.194
0.006	2.281
0.007	2.380
0.012	2.490
0.019	2.612
0.029	2.739
0.052	2.916
0.063	2.918
0.082	2.987
0.101	3.047
0.139	3.136
0.160	3.187
0.222	3.265
0.279	3.354
0.393	3.479
0.486	3.567
0.564	3.635
0.573	3.655
0.629	3.692

Z	-log h
0.685	3.736
0.776	3.797
0.932	3.932
	[illegible]
	[illegible]
	[illegible]
	[illegible]
	[illegible]
	[illegible]
	[illegible]
	[illegible]
	[illegible]
	[illegible]
	3.194
	3.141
	3.222
	[illegible]
	[illegible]

Titration 5. B = 80 mM.

Z	-log h
0	1.768
0	1.923
0.003	2.139
0.005	2.364
0.010	2.544
0.015	2.507
0.032	2.693
0.056	2.786
0.070	2.849
0.100	2.921
0.111	2.945
0.144	3.007
0.163	3.053
0.187	3.087
0.214	3.134
0.217	3.141
0.282	3.224
0.315	3.273
0.349	3.304
0.407	3.374

Z.	**-log h**
0.477	3.422
0.493	3.457
0.575	3.530
0.591	3.537
0.698	3.625
0.717	3.657
0.799	3.708

Titration 6. B = 160 mM.

Z	-log h
0	1.639
0	1.749
0	1.892
0.003	2.083
0.009	2.215
0.014	2.315
0.021	2.399
0.038	2.507
0.047	2.593
0.058	2.637
0.083	2.732
0.109	2.805
0.157	2.908
0.157	2.911
0.203	2.984
0. 246	3.049
0.286	3.102
0.328	3.148
0.389	3.236

Z.	**-log h.**
0.478	3.327
0.528	3.376
0.573	3.424

Constant Z titrations.

Titration 1.

Z.	-log h
0.075	3.410
0.058	3.214
0.047	3.006
0.037	2.799
0.029	2.593
0.022	2.401

Titration 2.

Z.	-log h
0.170	3.672
0.167	3.511
0.165	3.356
0.164	3.204
0.163	3.039
0.163	2.915

Titration 3.

Z	-log h
0.354	3.855
0.346	3.713
0.339	3.560
0.334	3.415
0.331	3.273
0.327	3.151

Titration 4.

Z	-log h
0.359	3.907
0.394	3.765
0.391	3.623
0.390	3.481
0.389	3.337
0.389	3.219

The systematic " core and links " treatment developed by Sillén[41] will be used in the first part of the discussion. It has frequently been observed that the products formed by the hydrolysis of metal ions can be described by a general " core and links " formula, i,e. $M[(OH)_tM]_n$ where t is a constant and n may be a constant or have several integral values. If all the complexes can be described by the " core and links " hypothesis, the curves $Z(\log h)_B$ must form a family of parallel curves with a constant spacing along the log h axis. From Fig.2b it can be seen that the family of curves obtained from the data on the hydrolysis of the uranyl ion are roughly parallel with each other. This indicates that the system studied is polynuclear and can probably be explained in terms of the " core and links " hypothesis.

If the complexes can be expressed by the general formula $UO_2[(OH)_tUO_2]_n$ then t, the number of OH^- groups in the link, can be obtained from the spacing of the curves $(\log B, -\log h)_Z$

$$\left(\frac{\partial \log B}{\partial \log h}\right)_Z = t \quad \text{-----------------------------} (3)$$

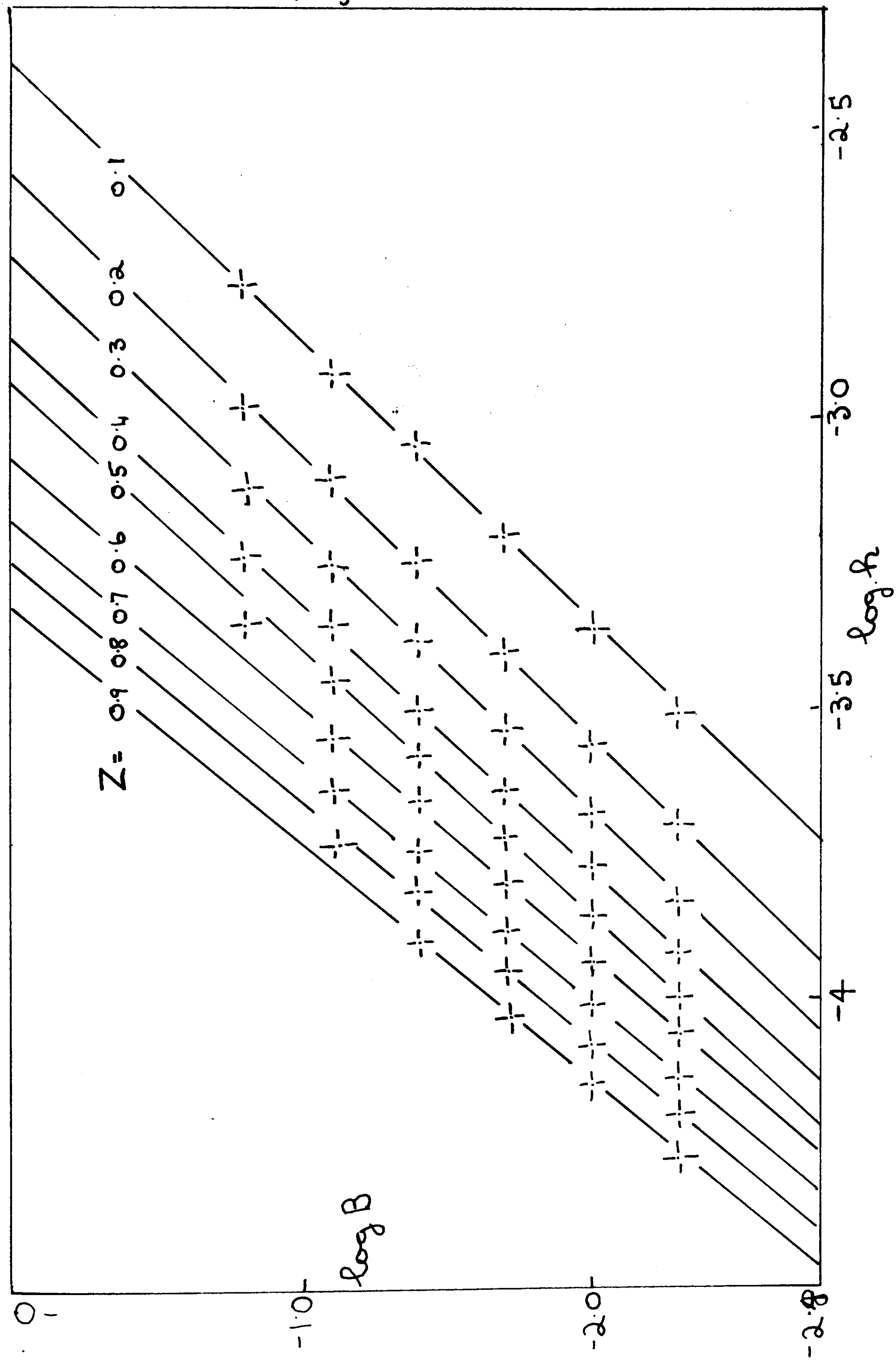
i.e. Z = function of $[\log B - t \log h]$.

It follows from equation (3) that the value of t may be obtained directly from the slope of the curves $(\log B, \log h)_Z$ given in Fig.3b. The values of t obtained from the data (Table 3b) varied from 2 at low Z values to 2.5 at high Z values.

The value of t obtained at low Z values was tested by plotting Z against $\log B - t \log h$. Since the limitation to "core + links" species requires Z to be a function of the single variable $U = bh^{-t}$ and $Bh^{-t} = f(U)$, Z is a function of the variable Bh^{-t}. The data (Table 4b) is most conveniently plotted as $Y = \frac{Z}{2}$ versus $X = \log(Bh^{-t})$ or $X = \log B - 2 \log h$, (Fig.4b.). This is equivalent to displacing the curves $Z(\log h)_B$ along the log h axis to see if they coincide.

Fig.4b shows that at the lowest y values there is a single curve which indicates that hydrolysis starts by a " core and links" mechanism but the fanning out at higher y-values suggests the existence of complexes other than those of the " core and links" series. This is in agreement with the explanation for the variation of t from $2 \rightarrow 2.5$ in Fig.3b. Since the deviation from the

Fig. 3b.



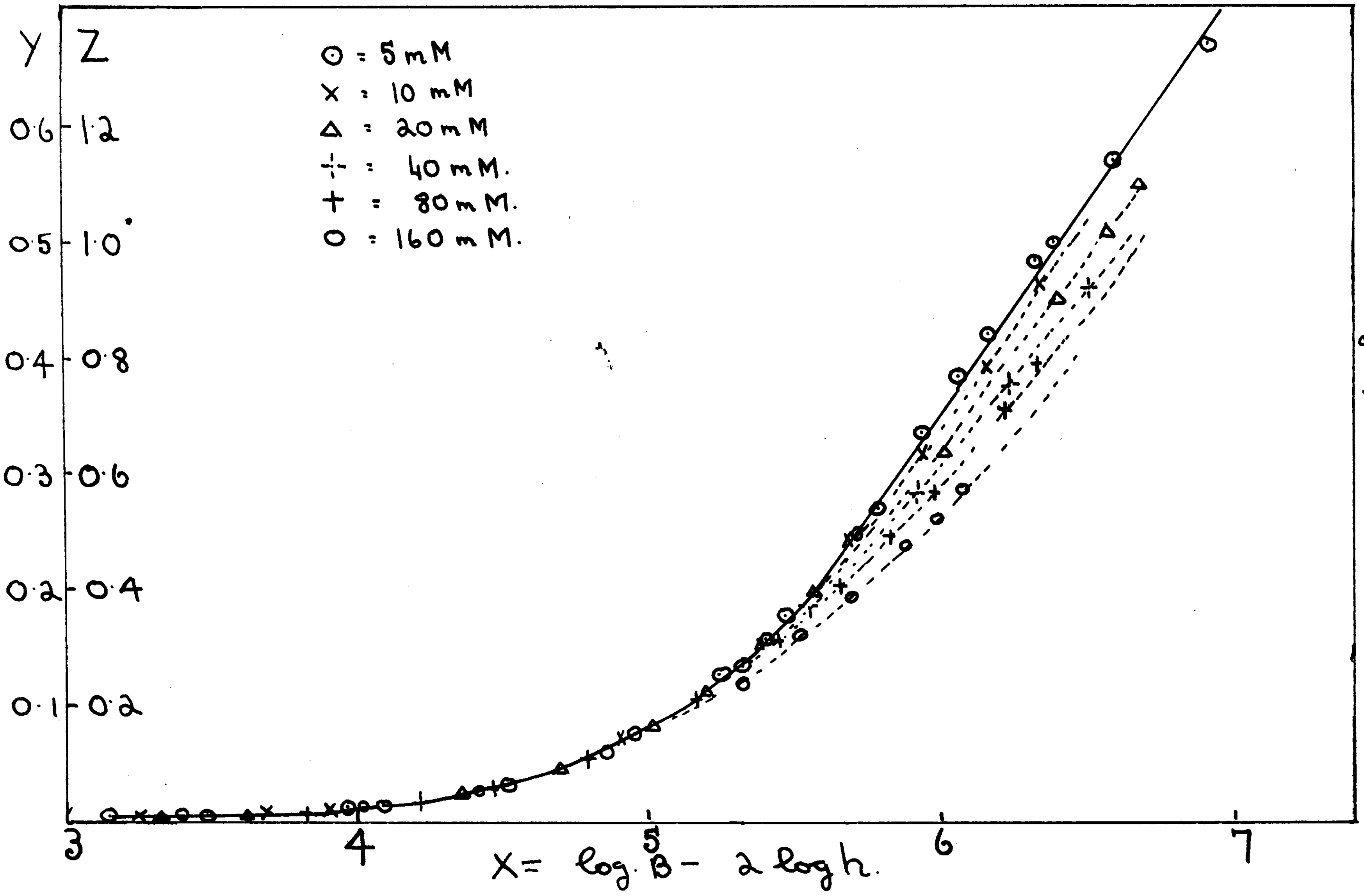

Y
Z
⊙ = 5 mM
× = 10 mM
△ = 20 mM
-¦- = 40 mM.
+ = 80 mM.
o = 160 mM.
0·6
1·2
0·5
1·0
0·4
0·8
0·3
0·6
0·2
0·4
0·1
0·2
3
4
5
6
7
X = log B − 2 log h.

Fig. 4b.

Z →	0.9	0.8	0.7	0.6
log B	-log h	-log h	-log h	-log h
-0.7959	-	-	-	-
-1.0969	-	3.73	3.64	3.55
-1.3979	3.90	3.81	3.75	3.66
-1.6990	4.03	3.96	3.88	3.80
-2.000	4.15	4.08	4.02	3.94
-2.3010	4.28	4.20	4.14	4.07
t(slope) →	2.5	2.5	2.33	2.35

0.5 -log h	0.4 -log h	0.3 -log h	0.2 -log h	0.1 -log h
3.35	3.24	3.12	2.98	2.79
3.46	3.36	3.25	3.10	2.92
3.58	3.50	3.38	3.25	3.04
3.72	3.64	3.53	3.40	3.21
3.86	3.77	3.68	3.56	3.36
4.00	3.92	3.83	3.70	3.51
2.22	2.22	2.22	2.00	2.00

" core and links " hypothesis appears to depend on the acidity of the solution, it seemed best to try and reduce the importance of the extra complexes by extrapolating some function back to zero acidity. The limiting values of X thus obtained were plotted against Y. (Fig.5b).

As outlined by Sillén[41] it is possible to calculate equilibrium constants for the " core and links " complexes directly from the experimental data Y(X).

If K_n is defined as the equilibrium constant for the reaction,

$$(n+1)UO_2^{2+} + 2nH_2O \rightleftharpoons UO_2[(OH)_2UO_2]_n^{2+} + 2nH^+ \text{------}(4)$$

then

$$\begin{aligned} B &= b + \sum (n+1)UO_2[(OH)_2UO_2]_n^{2+} \\ &= b + \sum (n+1)(K_n h^{-2n} b^{n+1}) \text{-------------------------}(5) \end{aligned}$$

Substituting $U = (h^{-2}b)$ into equation (5)

$$B = b(1 + \sum (n+1)K_n U^n) \text{---------------------------}(6)$$

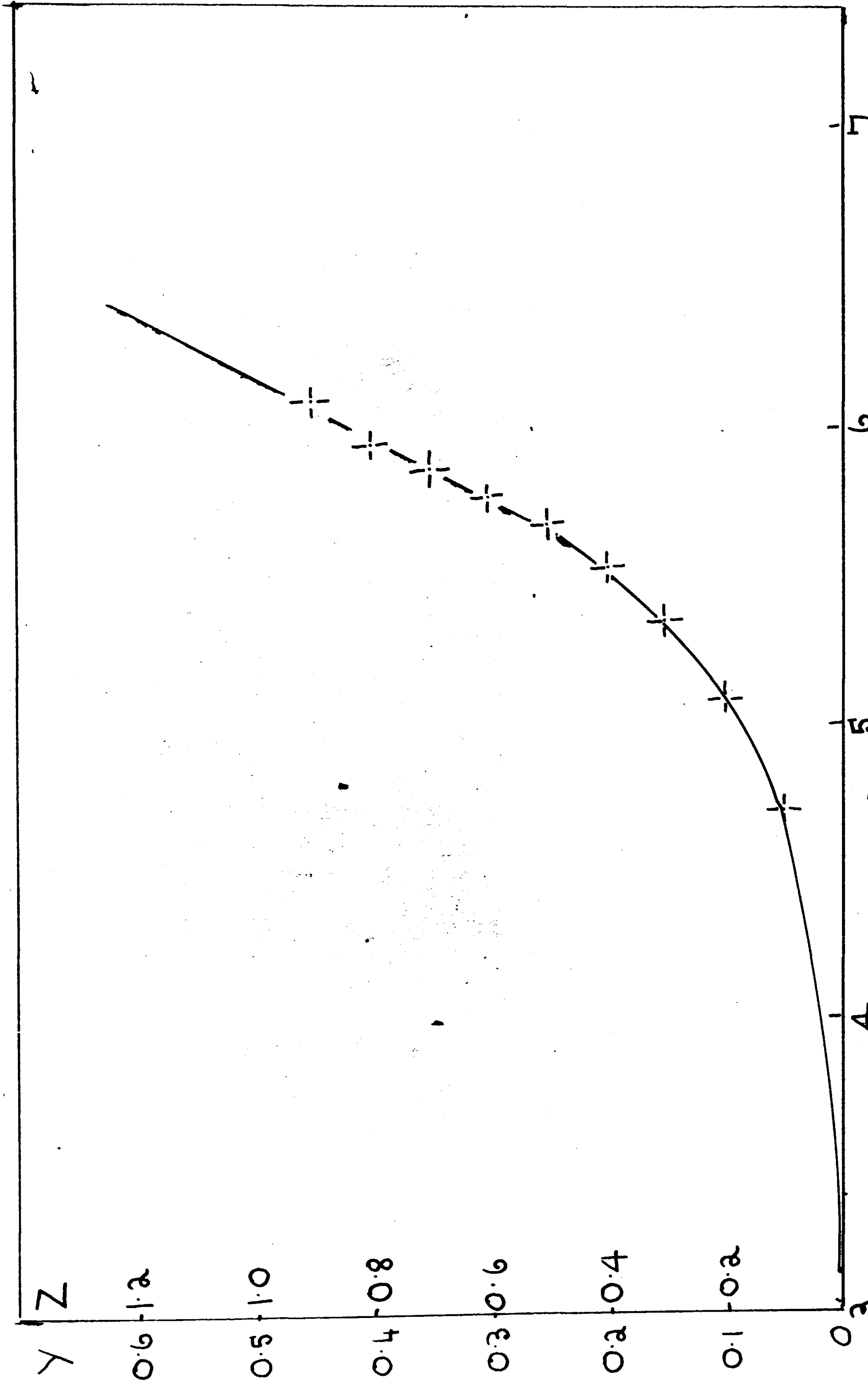
~~Now~~ if $g = \sum K_n U^n$, $\frac{dg}{dU} = g^1$, and substitution into (6) gives

$$B = b\,\frac{d}{dU}(U + Ug) = b(1 + g + Ug^1) \text{-------------------}(7)$$

From equation 7, it is seen that,

$$(1 + g) = U^{-1} \int_0^U Bb^{-1}\,dU = U^{-1} \times \int_0^U 10\,\eta\,dU \text{-------}(8)$$

Fig. 5b.



It follows directly from the definitions of U, X and η that

$$\log U = X - \eta \quad \text{------------------------------(9)}$$

η can be obtained directly from the $Y(X)$ data by using the equation

$$\eta = Y \log e + \int_{-\infty}^{X} Y \, dX \quad \text{----------------(10)}$$

together with

$$\log U = X - \eta \quad \text{------------------------------(9)}$$

Although g(U) may be obtained direct from equation (8), it is simpler to apply the equation,

$$\log (1+g) = \eta + \log (1-Y) \quad \text{----------------------(11)}$$

Equation (11) is derived in the following way. The total number of bound OH^- groups per liter of solution is given by the equation,

$$\begin{aligned} BZ &= \sum 2n[UO_2[(OH)_2UO_2]_n^{2+} \\ &= 2b \sum nK_nU^n = 2b\, Ug^1 \quad \text{----------------------(12)} \end{aligned}$$

Substituting $Z = 2Y$, $Bb^{-1} = (1+g+Ug^1)$ and $Bb^{-1} = 10^{\eta}$ (definition) and eliminating Bb^{-1} and Ug^1 gives

$$(1+g) = 10\,\eta\,(1-\bar{y}) \text{ -----------------------------(13)}$$

Taking logarithms we obtain

$$\log (1+g) = \eta + \log (1-\bar{y}) \text{ ---------------(14)}$$

Therefore from equations (11), (10) and (9) values of $\frac{B}{b}$, log g, and log U were calculated, the integration in equation (10) being performed graphically.

In order to evaluate the polynuclear complexity constants, the function $gU^{-1} = K_1 + K_2U^{+}$---------- was plotted versus U in Fig.6b. The intercept and slope give the values for the first two equilibrium constants, $\log K_{22} = -6.00$ and $\log K_{43} = -11.24$. The data for gU^{-1} and U are given in Table 5b.

It can be seen from fig.6b that the first few points do not lie on the line. This could be due to
(a) the extrapolation to zero h being incorrect, or
(b) the " core and links" mechanisms being inadequate.

Fig. 6b.

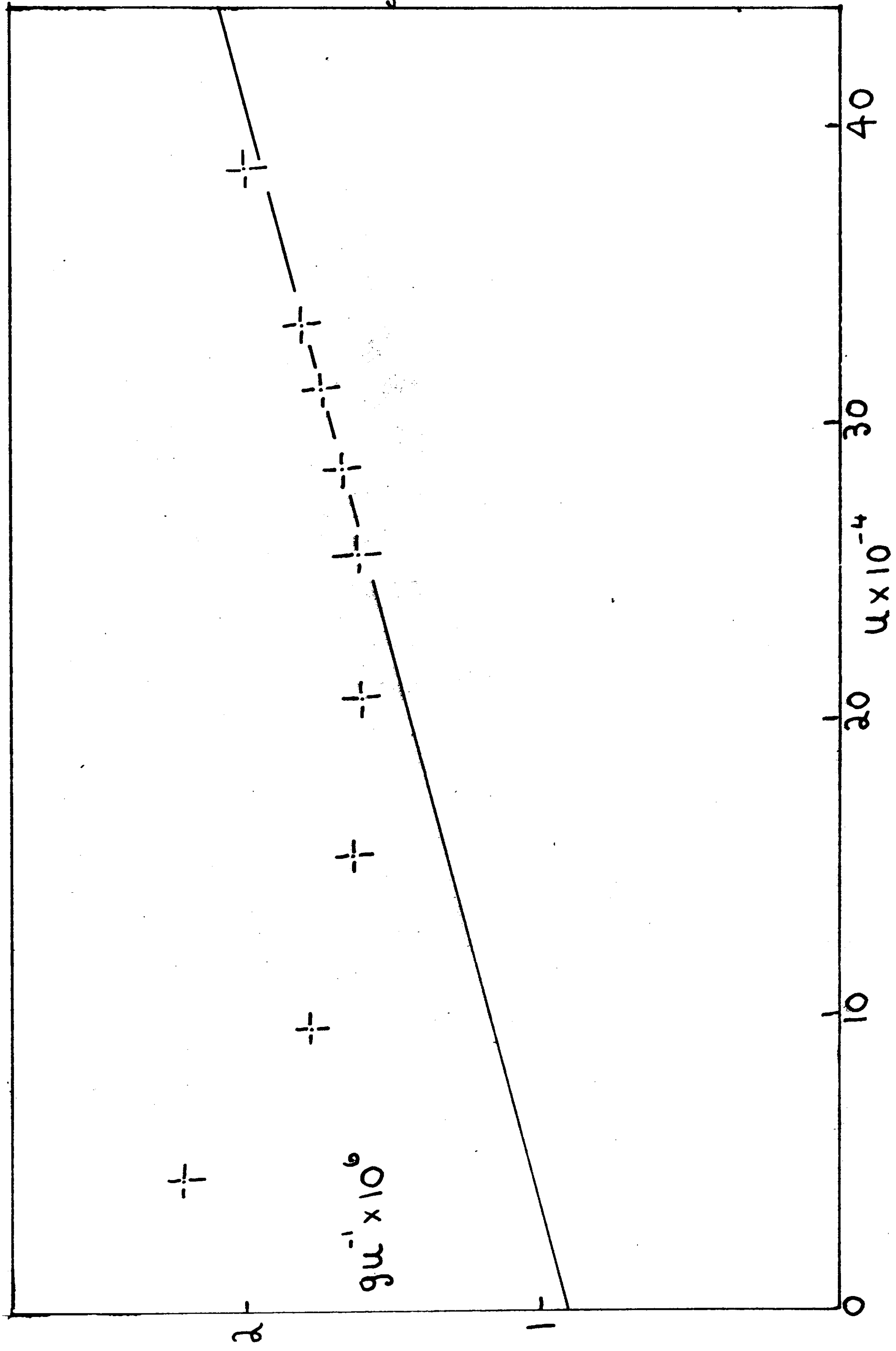


Table 5b. Direct Analysis of curve Y(X).

Y	X	$gU^{-1} \times 10^{6}$	$U \times 10^{-4}$
0.0	3.007	–	0.1017
0.05	4.720	2.258	4.523
0.10	5.097	1.785	9.605
0.15	5.360	1.640	15.520
0.20	5.540	1.610	20.780
0.25	5.685	1.632	25.600
0.30	5.7800	1.673	28.500
0.35	5.8700	1.738	31.230
0.40	5.950	1.813	33.330
0.45	6.100	2.044	38.670

By application of the " core and links" treatment and the " direct approach" , as devised by Sillén, it was possible by mainly a graphical treatment to deduce the formulae and approximate equilibrium constants of the main products present in solution.

In order to refine these equilibrium constants and determine formulae and stability constants for species present in smaller amounts, a series of programmes for high speed electronic computers,[54] which have proved useful in investigations on equilibria with polynuclear complexes were used. These programmes are so constructed that when a new system is studied only a small part (the S.P.) of the programme has to be rewritten, the main part (the H.P.) being used without change.

The programme " Kuska" was primarily designed for calculations on equilibria with polynuclear complexes. It calculates for a given set of complexes, equilibrium constants and a given B, Z as a function of -log h.

On the basis of e.m.f. measurements there is a strong suggestion that the hydrolytic schemes of uranyl hydrolysis in chloride and perchlorate differ. Hydrolytic species in 1 molar sodium perchlorate are $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^{+}$

whilst in chloride there appears to be the additional species $(UO_2)_3(OH)_4^{2+}$. Kraus[48] has suggested that in a nitrate medium the hydrolysis scheme should resemble more closely that of perchlorate. In order to test this suggestion, theoretical curves for the complexes $(UO_2)_2(OH)_2^{+2}$ and $(UO_2)_3(OH)_5^{+}$ were computed but showed no resemblance to the experimental curves (Fig. 2b). On addition of the complex $(UO_2)_3(OH)_4^{+2}$ there was a significant trend of the theoretical curves (Fig.7b) towards the experimental curves suggesting that the complexes present in solution are the (2,2), (5,3) and (4,3) species. This shows that in the nitrate medium the hydrolysis scheme resembles more closely that of chloride, differing from the concept put forward by Kraus, who suggested it would resemble perchlorate. The data for the best values obtained for the equilibrium constants of the above species are,

$\log K_{22} = -6.0$ $\qquad$ $\log K_{43} = -11.8$

$\log K_{53} = -16.5$

Fig. 7b.

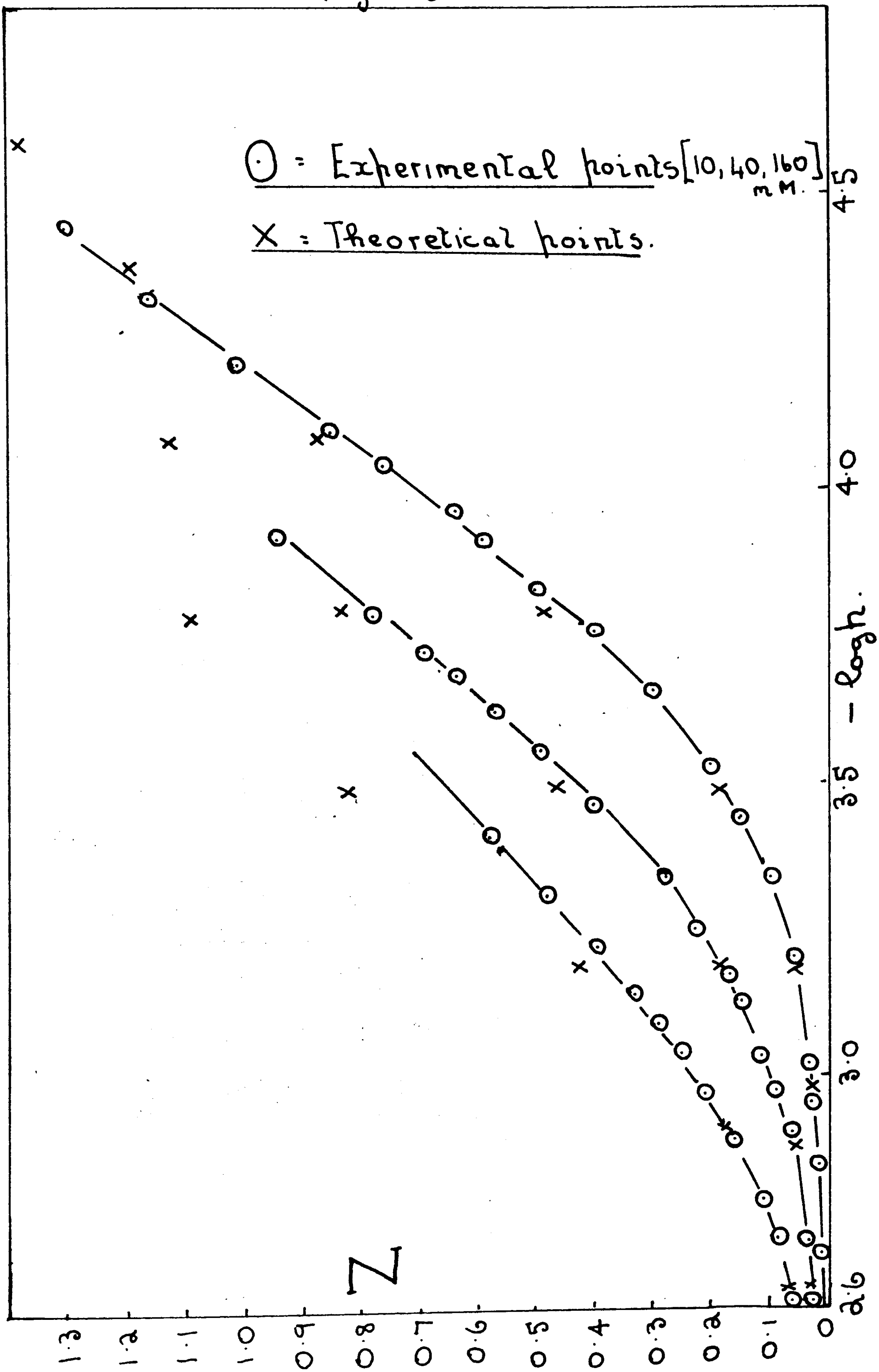

⊙ = Experimental points [10, 40, 160] mM.
X = Theoretical points.
4.5
4.0
3.5
3.0
2.6
− log h
Z
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3

Table 6b. Theoretical values of Z and -log h for the stability constants,

$\log K_{22} = -6.0$ $\log k_{43} = -11.8$

and

$\log K_{53} = -16.5$

B = 1 0mM	Z	-log h
	0.001	2.600
	0.004	2.900
	0.019	3.200
	0.104	3.500
	0.434	3.800
	0.888	4.100
	1.207	4.400
	1.398	4.700
	1.514	5.000
	1.583	5.300
B = 4 0mM	Z	-log h
	0.004	2.600
	0.019	2.900
	0.103	3.200
	0.423	3.500
	0.859	3.800

Z	-log h
1.159	4.100
1.337	4.400
1.453	4.700
1.536	5.000
1.592	5.300

B = 16 0mM

Z	-log h
0.019	2.600
0.108	2.900
0.418	3.200
0.843	3.500
1.129	3.800
1.291	4.100
1.395	4.400
1.478	4.700
1.456	5.000
1.596	5.300

Table 4b. X and Y values, where $X = \log B - 2 \log h$ and $Y = 0.5Z$

B = 5mM

Z(= 2Y)	X
0.003	3.159
0.005	3.499
0.020	3.968
0.069	4.519
0.138	4.955
0.253	5.239
0.356	5.469
0.491	5.702
0.564	5.797
0.766	6.064
0.832	6.166
0.961	6.325
0.995	6.389
1.149	6.588
1.155	6.625
1.331	6.906

B = 1 0mM

Z.	=	I
0.003		3.007
0.007		3.437
0.013		3.735
0.027		4.069
0.055		4.434
0.097		4.705
0.144		4.915
0.194		5.094
0.295		5.347
0.394		5.550
0.494		5.709
0.583		5.855
0.672		5.989
0.759		6.118
0.843		6.227
1.004		6.450
1.154		6.666
1.295		6.903

B = 20mM

<u>Z</u>	<u>Y</u>
0.007	3.426
0.035	4.814
0.107	4.732
0.188	5.063
0.268	5.287
0.344	5.459
0.420	5.607
0.553	5.841
0.616	5.932
0.729	6.108
0.834	6.250
0.927	6.379
1.029	6.561
1.104	6.666

B = 4 0mM

Z	X
0.004	2.990
0.006	3.163
0.007	3.366
0.012	3.582
0.019	3.826
0.030	4.079
0.063	4.438
0.082	4.576
0.101	4.695
0.139	4.874
0.222	5.131
0.279	5.310
0.393	5.560
0.486	5.736
0.564	5.887
0.629	5.986
0.685	6.074
0.776	6.196
0.932	6.480

B = 80mM

Z	X
0.010	3.991
0.032	4.289
0.070	4.600
0.100	4.745
0.144	4.918
0.187	5.077
0.214	5.171
0.282	5.351
0.350	5.510
0.477	5.746
0.591	5.976
0.698	6.152
0.799	6.318

B = 160mM

Z	X
0.003	3.369
0.009	3.633
0.014	3.833
0.021	4.002
0.038	4.218
0.047	4.390
0.058	4.478
0.083	4.668
0.109	4.813
0.157	5.019
0.208	5.171
0.246	5.303
0.286	5.408
0.328	5.499
0.389	5.675
0.478	5.858
0.528	5.956
0.573	6.051

Part III

Complex formation in solutions of Lanthanum Tartarate.

INTRODUCTION

In any comprehensive treatment of the thermodynamic properties of electrolytic solutions, it is necessary to take into account the forces involved such as the long range (Coulombic) interionic attractive forces and the shorter interactions between ions and solvent molecules. Debye and Hückel,[55] introduced the concept of an " ionic atmosphere" , of ions of one type around a central ion of opposite charge, and showed that for strong electrolytes, deviations from ideality could be interpreted in terms of a potential arising from the arrangement of the surrounding ions. When the ions are close together, so that the energy of their mutual attraction is greater than the thermal energy which permits random motion, it is considered that they form a new entity in solution, the ion-pair or complex, which is stable enough to withstand collisions with solvent molecules.

The ion association reaction may be described by the equilibrium,

$$M^{n+}\ aq. + X^{m-}\ aq. \rightleftharpoons MX^{(n-m)+}\ aq. \text{ ------------(1)}$$

where M^{n+} aq. and X^{m-} aq. etc., are the hydrated ionic species present in the solution.

Bjerrum[56] developed a theory to account for ion association by considering the formation of ion-pairs in terms of purely electrostatic forces between ions, but it should be remembered that the model used in Bjerrum's theory contains a number of simplifying assumptions; the ions are regarded as spherically symmetrical and unpolarisable, and the solvent as a medium of uniform dielectric constant. Non-polar quantum mechanical bonds as well as ion-solvent interactions are excluded. He suggested that ions within a certain minimum distance " q" of one another are " associated" into ion-pairs, though in reality a fast moving ion might come within this distance of another without associating. If we consider a solution of a symmetrical electrolyte, the average distribution of negative ions will be greater in the vicinity of a given positive ion than in the bulk solution. The number of negative ions in a shell of thickness " dr" at a distance " r" from the positive ion can be obtained from the Boltzmann expression

$$N\text{-}\exp\left(-\frac{Z_1 e \psi}{KT}\right) . \, 4\pi r^2 . \, dr$$

where $Z_1 e \psi$ is the electrical potential energy of the negative ions of valency Z_1, and n- the bulk concentration of the negative ions. If r is small, then the potential of the central ion will be dominant and interionic forces can be neglected, so that $\psi = \frac{Ze}{\varepsilon r}$ where ε is the dielectric constant of the medium, and substitution in the above expression gives the number of negative ions in the shell to be,

$$4\pi \, n\text{-}\exp\left(-\frac{Z^2 e^2}{\varepsilon k Tr}\right) . \, r^2 \, dr$$

If a series of such shells is considered, the number of ions in each shell can be estimated on a time average basis. With increasing distance from the central ion, the probability of finding a negative ion in any unit volume decreases, but since the total volume considered is progressively increasing, the two opposing effects combined to give a critical distance in which there is a minimum probability of finding a negative ion anywhere in the sphere surrounding the positive ion. This distance " q " is the ionic separation at which the mutual potential energy of the ions is equal to 2KT.

$$q = \frac{Z^2 e^2}{2KT\varepsilon} = Z^2 / 3.57 / \text{Å} \quad \text{in water at } 25°\text{C} \text{ ------------- (2)}$$

The association constant for equation (1),

$$K = \frac{\{Mx^{(n-m)+}\}}{\{M^{n+}\}\{x^{m-}\}}$$ may be written

$$K = \frac{[Mx^{(n-m)+}]}{[M^{n+}][X^{m-}]} \cdot \frac{f.Mx^{(n-m)+}}{f.M^{n+}.fX^{m-}} \text{-----------------} (3)$$

where the braces enclose activities, square brackets concentrations, and f's are the corresponding activity coefficients. The expression derived by Debye-Hückel for the activity coefficients is given by

$$\log f_{\pm} = \frac{-A\,|Z_1 Z_2|\,I^{\frac{1}{2}}}{1 + B\mathring{a}\,I^{\frac{1}{2}}} \text{-------------------------} (4)$$

where A and B are constants depending on the temperature and dielectric constant of the medium and å is the distance of closest approach of the ions. The equation represents observed mean-activity coefficients with good accuracy by the choice of suitable å values. In the derivation of the equation, ions are treated as rigid spheres, both long range coulombic forces and short range interactions being taken into account. In an actual solution, there will be ion-solvent interaction to consider as well as other forces resulting from the deformation of the spherical model. These are thought to be of a type causing linear variation of log f with I and have led to extended equations of the type,[57,58]

$$\log f_{\pm} = \frac{A\,|Z_1 Z_2|\,I^{\frac{1}{2}}}{1 + B\mathring{a}\,I^{\frac{1}{2}}} + \beta I \text{ ------------------------(5)}$$

The advantage of these equations is that they can be used in solutions containing mixed electrolytes for which it is thermodynamically unsound to use equation (4). An equation proposed by Davies,

$$\log f_{\pm} = -A\,|Z_1 Z_2|\,[\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.2I\,] \text{ -----------(6)}$$

has been found very suitable for a number of electrolytes of different charge types and an equation of this form was used in the present work.

In this part of the thesis potentiometric measurements were made to determine the equilibrium constants of the complex species present in solutions of lanthanum tartrate.

EXPERIMENTAL

Preparation of constant boiling hydrochloric acid.

This was prepared by the method of Foulk and Hollingworth[59], and Shaw[60] using the modification of Titus and Smith.[61] A.R. concentrated hydrochloric acid was diluted to a specific gravity of 1.14 with conductivity water in a Pyrex " Quickfit" distilling flask (3 litre capacity) surmounted with a splash bulb and connected to a pyrex Leibig condenser having a 75 cm. long water jacket and a 1 cm. inner bore. About 0.7 gm. of scrap platinum wire was put in, to prevent bumping, and the body and neck of the flask was covered with asbestos fibre. Uniform heating was ensured by using a heating mantle and distillation was continuous at a steady rate of less than 5 ml. per minute. The distillate was collected in a pyrex stock flask, which had been previously cleaned with chromic acid, ethanolic potassium hydroxide, washed thoroughly with water and steamed for at least one hour. The receiver was cooled in an ice bath. After rejecting the first 25% of the distillate the next 1600 ml. was collected and redistilled again discarding the first 25%. The final 800 ml. was collected as a constant boiling hydrochloric acid and the barometric pressure was noted.

Preparation of Sodium Hydroxide Solution.

Saturated solutions of sodium hydroxide were prepared from " Analar" sodium hydroxide pellets, which were mechanically shaken in distilled water for 24 hours. Solutions of sodium hydroxide were prepared from the saturated solution by dilution with carbon dioxide-free distilled water in an atmosphere of nitrogen. The hydroxide solution was stored in a flask connected to an automatic burette fitted with soda-lime guard tubes. Samples of the solution were titrated against weighed samples of potassium hydrogen phthalate. Agreement was better than 0.1%.

Preparation of Lanthanum Chloride.

Solutions of lanthanum chloride were prepared by the addition of excess lanthanum oxide (Spec., pure, Johnson, Matthey and Co. Ltd.) to a solution of constant boiling hydrochloric acid. The solution was filtered and diluted in a standard flask with carbon dioxide-free conductivity water. Lanthanum was estimated by precipitating with ammonium oxalate. After filtering, the precipitate was ignited to the oxide and the lanthanum present determined. Chloride was estimated as silver chloride and duplicate determinations agreed to better than ± 0.02%.

Potentiometric Measurements.

E.M.F. measurements were made with a glass electrode in a cell of the type,

Ag | AgCl.HCl (0.2m) | glass | solution under study/
saturated KCl | calomel

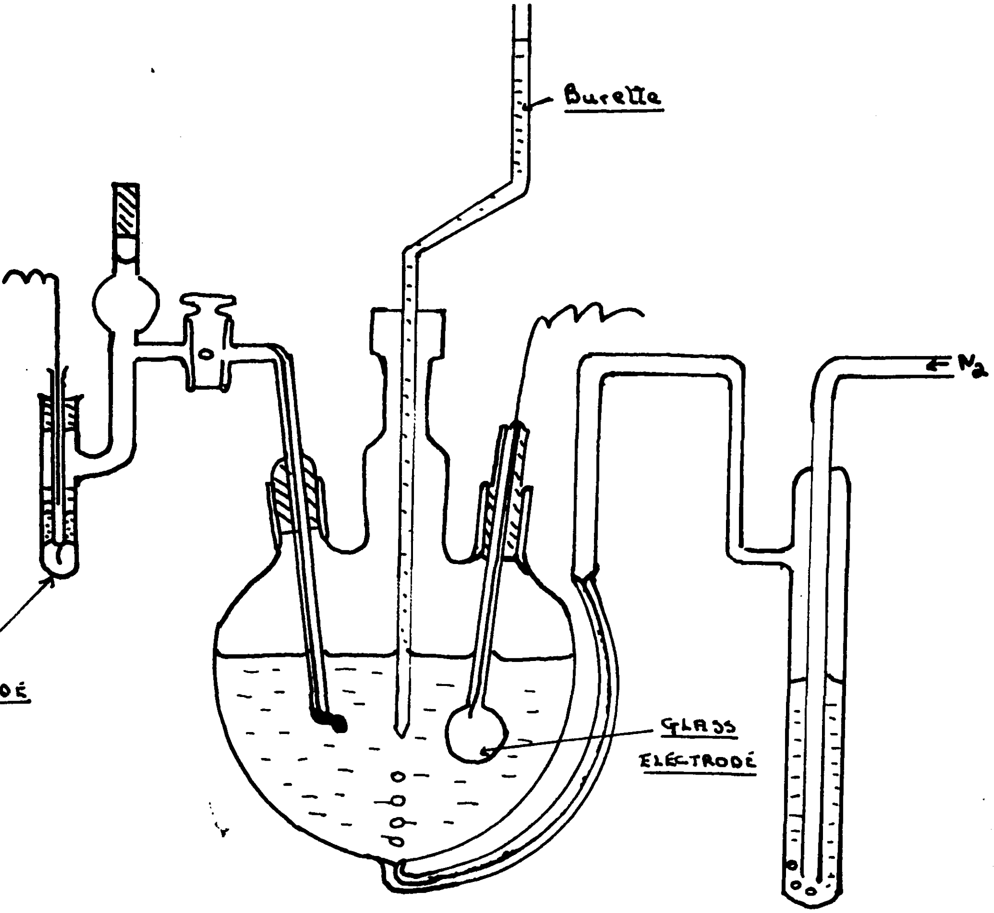
using a Croydon Potentiometer, and a Vibron electrometer, (E.I.L. model 33B) as a null indicator; readings were reproducible to ± 0.1 m.v. The cell Fig.2c contained a calomel electrode and a pair of commercial screened glass electrodes (E.I.L. type G.G.33) so that any irregularity in the behaviour of any one was immediately detectable. The thermostat containing paraffin oil was maintained at 25°C ± 0.02°C by means of a mercury-toluene regulator.

Standardisation of electrodes.

(a) At low ionic strength $I \longrightarrow 0$.

Before and after each run, the electrode system was calibrated with buffer solutions of known pH (0.05m potassium hydrogen pthalate, pH = 4.0005,[62] and B.D.H. tabloid phosphate buffer, pH = 6.99).

Fig. 2c.



Cell and electrodes.

(b) At Constant Ionic Strength.

For these runs, the electrode system was calibrated before and after each experiment with hydrochloric acid solutions of known concentrations in 1 molar potassium nitrate. The e.m.f. values were plotted against $\log[H^+]$ and unknown $\log[H^+]$ could be obtained by interpolation to within ± 0.005.

Experimental Procedure.

Grade A glassware was used for all experiments. A known volume of a standard solution of tartaric acid was added to the cell along with known volumes of standard sodium hydroxide and carbon dioxide free distilled water. The solution was allowed to equilibrate for twenty minutes with nitrogen bubbling, and successive additions of known volumes of lanthanum chloride were made. The steady e.m.f. readings were taken after each addition. Experiments were made over as wide range of metal and acid concentration as possible and great care was taken in cleaning the cell and electrodes. The same procedure was adopted for both the low and constant ionic strength runs. In the latter all the solutions were made up to be 1 molar in potassium nitrate.

RESULTS AND DISCUSSION

Before studying lanthanum tartrate, it was necessary to obtain the values of the dissociation constants of tartaric acid. This was done by the method of Speakman.[63]

The thermodynamic dissociation constants of a dibasic acid H_2A, may be defined by

$$K_1 = \frac{\{H^+\}[HA^-]f_1}{[H_2A]} \tag{1}$$

and

$$K_2 = \frac{\{H^+\}[A^=]f_2}{[HA^-]f_1} \tag{2}$$

where $[H_2A]$ is the concentration of undissociated acid,

$[HA^-]$ is the concentration of univalent ion,

$[A^=]$ is the concentration of divalent ion,

and f_1 and f_2 are the activity coefficients of the uni- and di-valent species respectively. In a solution of total acid concentration Ta (molar),

$$Ta = [H_2A] + [HA^-] + [A^=] \tag{3}$$

and when a strong monobasic base, which may be taken as completely dissociated has been added to give a molar concentration b, electroneutrality requires that

$$b + [H^+] = [HA^-] + 2[A^=] + [OH] \quad \text{------------}(4)$$

If we define L, M, and N by the equations

$$L = b + [H^+] - [OH^-] \qquad (=[HA^-] + 2[A^=]) \quad \text{--------}(5)$$

$$M = Ta - b - [H^+] + [OH^-] \quad (=[H_2A] - [A^=]) \quad \text{--------}(6)$$

$$N = 2Ta - b - [H^+] + [OH^-] \quad (=2[H_2A] + [HA^-]) \quad \text{-------}(7)$$

then it can easily be shown that,

$$\frac{\{H^+\}^2 \; L\, f_2}{N} = \frac{K_1[\{H^+\}Mf_2]}{Nf_1} + K_1K_2 \quad \text{---------------}(8)$$

which may be rewritten,

$$X = K_1Y + K_1K_2 \quad \text{------------------------------}(9)$$

X and Y may be evaluated from experimental data and a plot of X against Y should give a straight line of slope K_1 and intercept K_1K_2. The results Table (1c) are plotted in Fig.1c, and the values for the dissociation constants were,

$$K_1 = 9.70 \times 10^{-4}\ , \quad K_2 = 4.\overset{64}{\cancel{\text{[illegible]}}} \times 10^{-5}.$$

Table 1c. K_1 and K_2 at low ionic strength.

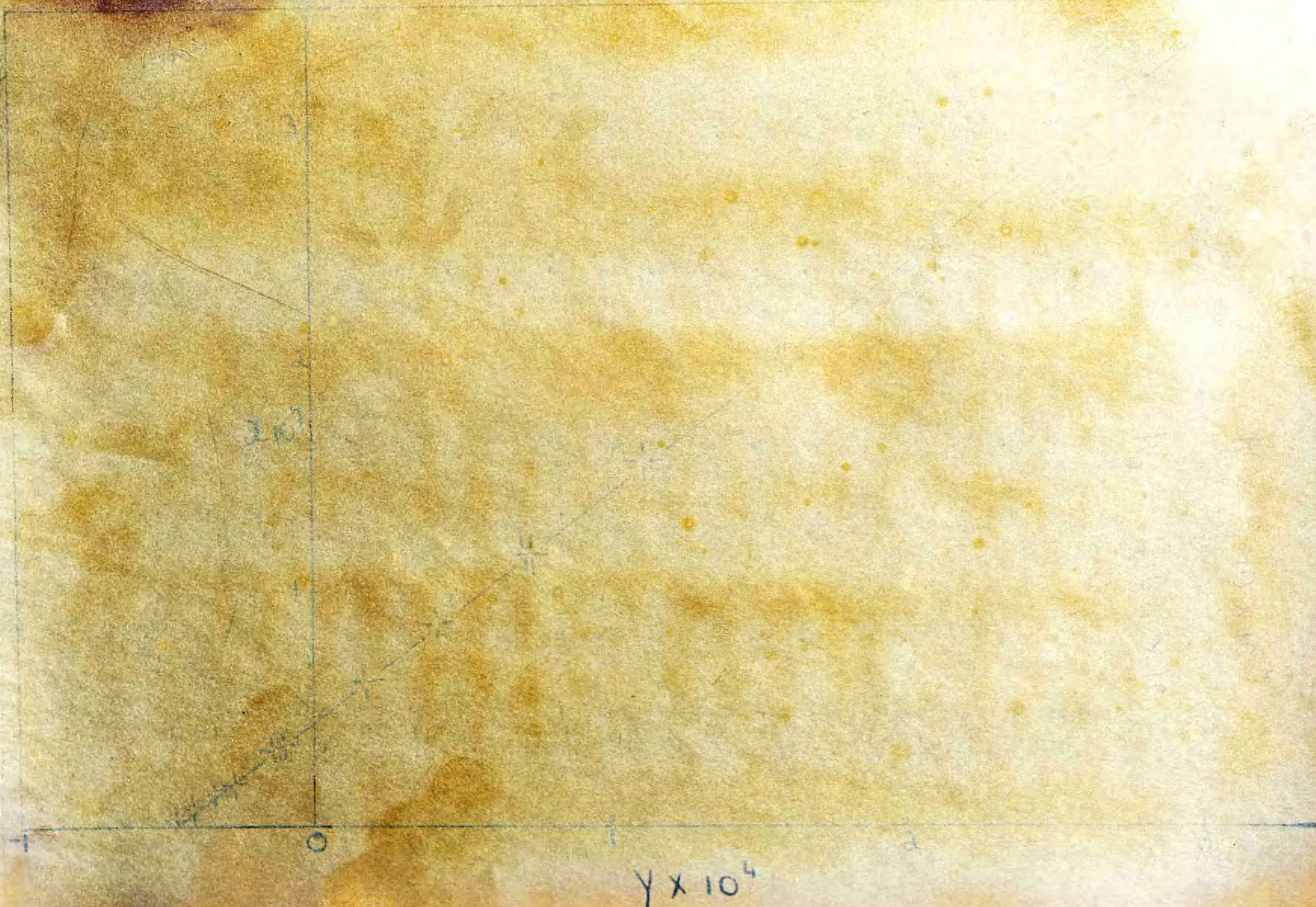
E.M.F.	p H.	$HA^- \; 10^{+3}$	$A^=$	$I \times 10^3$
0.0404	2.934	1.427	6.209×10^{-5}	1.613
0.0443	3.000	1.528	8.442×10^{-5}	1.781
0.0485	3.071	1.633	1.105×10^{-4}	1.965
0.0501	3.156	1.765	1.218×10^{-4}	2.1310.
0.0532	3.150	1.747	1.361×10^{-4}	2.155
0.0581	3.233	1.851	1.749×10^{-4}	2.376
0.0599	3.321	1.942	2.277×10^{-4}	2.625
0.0634	3.323	1.947	2.238×10^{-4}	2.619
0.0691	3.420	2.024	2.896×10^{-4}	2.892
0.0750	3.519	2.067	3.793×10^{-4}	3.205
0.0808	3.617	2.059	5.026×10^{-4}	3.567
0.0844	3.734	2.036	6.349×10^{-4}	3.940
0.0885	3.748	2.057	6.209×10^{-4}	3.920
0.0955	3.866	1.975	7.895×10^{-4}	4.343
0.1022	3.980	1.839	9.899×10^{-4}	4.808
0.1105	4.120	1.687	1.198×10^{-3}	5.281
0.1142	4.236	1.467	1.447×10^{-3}	5.807
0.1179	4.245	1.471	1.443×10^{-3}	5.802
0.1262	4.386	1.239	1.698×10^{-3}	6.332
0.1321	4.537	0.986	1.964×10^{-3}	6.876
0.1369	4.567	0.991	1.959×10^{-3}	6.871
0.1490	4.771	0.722	2.233×10^{-3}	7.423
0.1581	4.975	0.438	2.516×10^{-3}	7.986

$K_1 = 9.90 \times 10^{-4}$

$K_2 = 4.64 \times 10^{-5}$

$Ta\ 10^3$	$Na^+ 10^3$	X	Y
3.115	0.319	3.84×10^{-7}	3.44×10^{-4}
3.105	0.636	3.18×10^{-7}	2.74×10^{-4}
3.098	0.952	2.58×10^{-7}	2.12×10^{-4}
3.086	1.265	1.96×10^{-7}	1.57×10^{-4}
3.086	1.265	2.02×10^{-7}	1.58×10^{-4}
3.077	1.576	1.57×10^{-7}	1.11×10^{-4}
3.067	1.886	1.19×10^{-7}	7.30×10^{-5}
3.067	1.886	1.18×10^{-7}	7.29×10^{-5}
3.058	2.194	8.68×10^{-8}	4.18×10^{-5}
3.049	2.499	6.31×10^{-8}	1.73×10^{-5}
3.040	2.803	4.67×10^{-8}	$- 1.68 \times 10^{-5}$
3.030	3.106	3.18×10^{-8}	$- 1.52 \times 10^{-5}$
3.030	3.106	2.97×10^{-8}	$- 1.43 \times 10^{-5}$
3.021	3.406	2.03×10^{-8}	$- 2.38 \times 10^{-5}$
3.012	3.705	1.43×10^{-9}	$- 3.09 \times 10^{-5}$
3.003	4.001	8.73×10^{-9}	$- 3.32 \times 10^{-5}$
2.994	4.296	6.66×10^{-9}	$- 3.85 \times 10^{-5}$
2.994	4.296	6.39×10^{-9}	$- 3.77 \times 10^{-5}$
2.985	4.589	4.27×10^{-9}	$- 3.98 \times 10^{-5}$
2.976	4.880	2.86×10^{-9}	$- 4.20 \times 10^{-5}$
2.976	4.880	2.49×10^{-9}	$- 3.91 \times 10^{-5}$
2.967	5.170	1.41×10^{-9}	$- 3.88 \times 10^{-5}$
2.958	5.458	9.93×10^{-10}	$- 4.53 \times 10^{-5}$

Fig 1c



In solutions containing lanthanum and tartarate ions, assuming only one complex LaA^+, the concentration of ionic species may be calculated using the equations for the total concentration of acid,

$$Ta = [H_2A] + [HA^-] + [A^=] + [LaA^+] \tag{9}$$

and for the total metal concentration,

$$Tm = [La^{3+}] + [LaA^+] \tag{10}$$

Subtracting (9) from (10),

$$Tm - Ta = [La^{3+}] - [H_2A] - [HA^-] - [A^=] \tag{11}$$

$$\therefore [La^{3+}] = Tm - Ta + [H_2A] + [HA^-] + [A^=] \tag{12}$$

Electroneutrality requires

$$[Na^+] + [LaA^+] + [H^+] + 3[La^{3+}] = [HA^-] + 2[A^=] + [OH^-] + [Cl^-] \tag{13}$$

By substitution in equation (12),

$$[H^+] + 2[La^{3+}] + Tm + [Na^+] = [HA^-] + 2[A^=] + [OH^-] + 3Tm \tag{14}$$

$$\therefore [H^+] + 2[La^{3+}] + [Na^+] = [HA^-] + 2[A^=] + [OH^-] + 2Tm \tag{15}$$

and substituting for La^{3+} from equation (12)

$$[H^+] - 2Ta + 2[H_2A] + [HA^-] + [Na^+] - [OH^-] = 0 \tag{16}$$

Substituting for $[H_2A]$ from equation (1),

$$[HA^-] = \frac{2Ta - [H^+] - [Na^+] + [OH^-]}{\frac{2[H^+]f_1^2}{K_1} + 1} \text{ ------------------(17)}$$

The ionic strength of the solution is given by,

$$I = \tfrac{1}{2} \left[[H^+] + [Na^+] + [HA^-] + 4[A^=] + [Cl^-] + [LaA^+] + 9[La^{3+}] \right] \text{ -----------(18)}$$

An approximate value for the ionic strength ($[H^+]$ + $[Na^+]$ + 3Tm) is first used to calculate activity coefficients from the equation

$$-\log f_Z = Az^2 \left[\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - \beta I \right] \text{ -----------------(19)}$$

in which 'A' is the Debye-Huckel constant (0.5092 at 25°C) and 'β' is a parameter which is given the value of 0.2 by Davies. Using these approximate activity coefficients the concentration of all the ion species are calculated and used to derive a more accurate value of I from equation 18. This process is repeated until a constant I value is obtained. Values for the thermodynamic complexity constant K_3,

$K_3 = \frac{[LaA^{+}]f_1}{[La^{3+}][A^{=}]f_3 f_2}$, varied from 3.20×10^4 to 5.81×10^4 over the pH range investigated. Such a variation in K_3 could be due to the presence of other complexes or else errors arising in the calculated activity coefficients for ions of such high charge type.

In order to test whether other complexes were present, $LaHA^{+}$, LaA_2^{-} and $La\,H(A)_2$ were allowed for in the calculations but did not account for the drift in K_3. It was therefore decided to design experiments in which the activity effects could be assumed constant. For this, work was done in a constant ionic medium, 1 molar potassium nitrate. It was first necessary to obtain the corresponding acid dissociation constants at this ionic strength and the method of Speakman was again used. The results are given in Table 2c and plotted in Fig.3c; the values for the dissociation constants were,

$$K_1^{\prime} = 2.06 \times 10^{-3}, \quad K_2^{\prime} = 2.07 \times 10^{-4}$$

(The primed letters now refer to quantities at constant ionic strength). Similar experiments in the presence of La^{3+} ions were done at constant ionic strength and the results are given in table 3c, from which it is seen that $K_3{}^1$ is now constant.

This suggested that the drift in K_3 obtained at low ionic strength was due to uncertainties in the activity coefficients. Calculations, using a high speed electronic computer, were made giving β values of 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 in equation 19. It was found that the value of 0.4 led to K_3 values which were satisfactorily constant. These are given in table 4c and the average K_3 value has a mean deviation of only ± 0.08. The use of $\beta = 0.4$ in equation 19, leads to the satisfactory constant values for K_3 in table 4c, which summarises the results of experiments at low ionic strength.

Although the Davies equation has been used extensively in the evaluation of association constants of 2:2 electrolytes a value for β of 0.4 is not at all unlikely for these highly charge species. Davies[64] himself has proposed a universal value of 0.3 instead of 0.2. Guggenheim[65] goes so far to suggest that a β of 2 for 2:2 electrolytes should be used. This defines the distance of approach of the ions in association as about 9Å, but this value of 2.0 has been found to be unsatisfactory for divalent metal sulphates.[66] Rosseinsky [67] has attributed the able 2c.

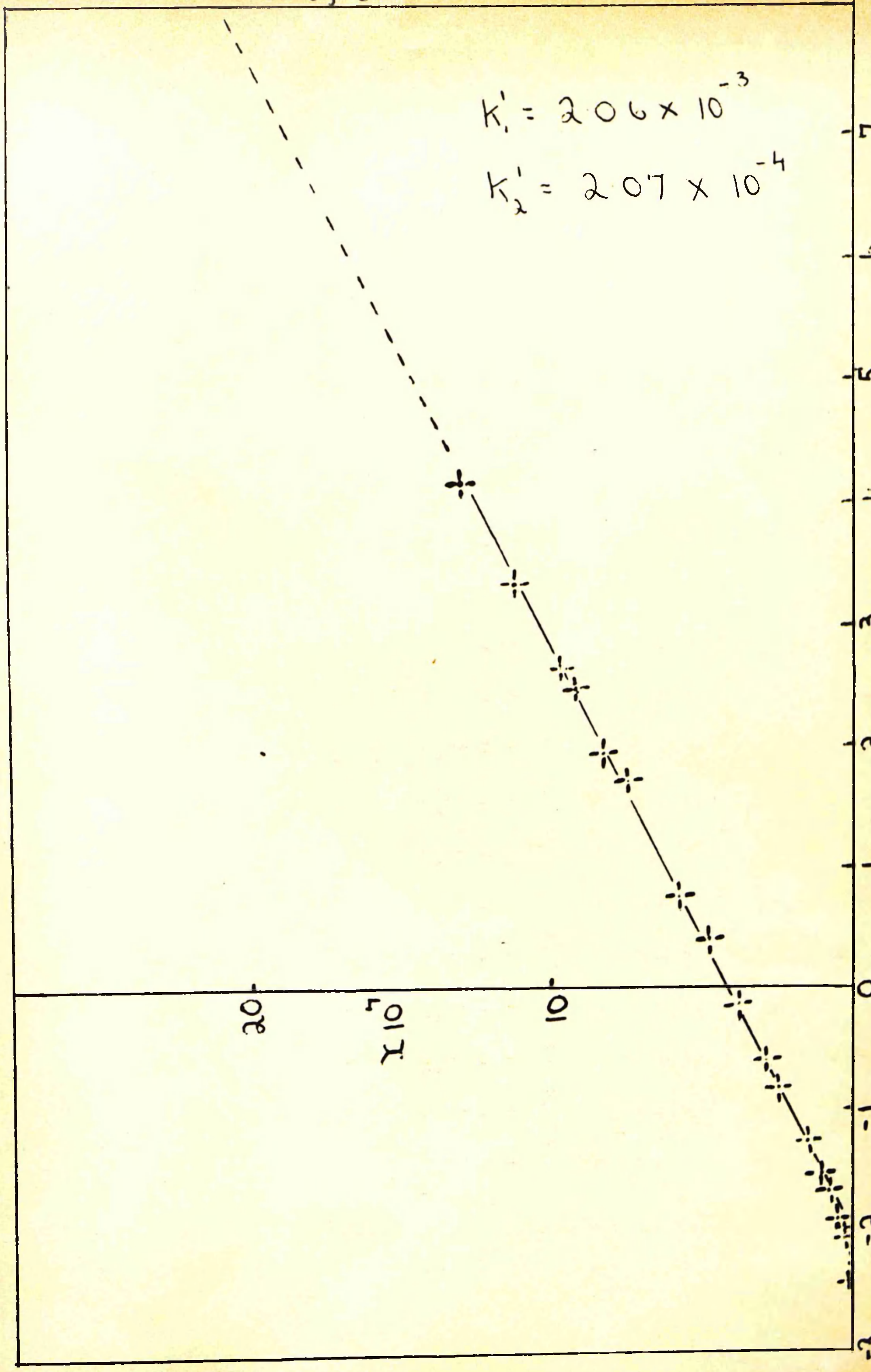
Acid Dissociation constants K_1' and K_2' at constant ionic strength.

E.M.F.	-log (H+)	Ta x 10^3	b	X	Y
0.0250	2.78	2.933	2.97×10^{-4}	1.31×10^{-6}	4.16×10^{-4}
0.0281	2.84	2.924	5.92×10^{-4}	1.13×10^{-6}	3.36×10^{-4}
0.0313	2.89	2.915	8.86×10^{-4}	9.73×10^{-7}	2.62×10^{-4}
0.0321	2.91	2.053	2.97×10^{-4}	9.24×10^{-7}	2.48×10^{-4}
0.0346	2.95	2.907	1.18×10^{-3}	8.35×10^{-7}	1.93×10^{-4}
0.0364	2.98	2.047	5.92×10^{-4}	7.42×10^{-7}	1.73×10^{-4}
0.0421	3.07	2.890	1.76×10^{-3}	5.81×10^{-7}	7.69×10^{-5}
0.0455	3.13	2.035	1.18×10^{-3}	4.87×10^{-7}	4.03×10^{-5}
0.0505	3.22	2.874	2.33×10^{-3}	3.88×10^{-7}	-1.40×10^{-5}
0.0565	3.32	2.023	1.76×10^{-3}	2.90×10^{-7}	-5.80×10^{-5}
0.0596	3.37	2.857	2.89×10^{-3}	2.55×10^{-7}	-8.34×10^{-5}
0.0696	3.54	2.012	2.33×10^{-3}	1.58×10^{-7}	-1.26×10^{-4}
0.0772	3.66	2.006	2.61×10^{-3}	1.12×10^{-7}	-1.51×10^{-4}
0.0821	3.75	2.825	4.00×10^{-3}	9.20×10^{-8}	-1.67×10^{-4}
0.0862	3.82	2.000	2.89×10^{-3}	7.49×10^{-8}	-1.68×10^{-4}
0.0972	4.00	2.809	4.55×10^{-3}	4.82×10^{-8}	-1.91×10^{-4}
0.1072	4.17	2.801	4.82×10^{-3}	3.18×10^{-8}	-1.99×10^{-4}
0.1207	4.40	2.793	5.09×10^{-3}	1.84×10^{-8}	-2.08×10^{-4}
0.1414	4.74	2.786	5.36×10^{-3}	9.16×10^{-9}	-2.45×10^{-4}

$K_1' = 2.06 \times 10^{-3}$

$K_2' = 2.07 \times 10^{-4}$

Fig 3c



$K_1' = 2.06 \times 10^{-3}$
$K_2' = 2.07 \times 10^{-4}$
$Y \times 10^4$
-3
-2
-1
0
1
2
3
4
5
6
7
$X\ 10^5$
10
20

success of the activity coefficient expression containing a low $\overset{o}{a}$ to the neglect of an activity coefficient for the ion pair, which arises from interaction between the ion pair and other ions. The problem of understanding activity coefficients and pK values is clearly a complex one, and at an interesting stage where more experimental study is desirable.

Table 3c.

K_3 values at constant ionic strength.

$[H^+]\,10^4$	$T_m\,10^3$	$T_a\,10^3$	$HA^-\,10^4$	$A^=\,10^4$
3.089	6.907	1.369	3.752	2.517
3.211	8.015	1.362	3.592	2.318
3.338	9.110	1.355	3.430	2.130
3.552	11.265	1.340	3.156	1.841
3.721	13.375	1.326	2.933	1.634
4.132	1.395	1.509	7.930	4.152
4.569	2.648	1.501	7.680	3.853
4.957	3.886	1.491	7.088	3.215
5.254	5.109	1.482	6.587	2.754
5.547	6.317	1.474	6.207	2.449
5.766	7.512	1.465	5.845	2.184
5.971	8.693	1.457	5.570	2.002

$Na^+ 10^3$	$La^{3+} 10^{+3}$	$LaA^+ 10^4$	$K_3' \times 10^{-2}$
1.942	6.220	6.864	4.38
1.932	7.299	7.151	4.26
1.921	8.366	7.432	4.17
1.901	10.47	7.861	4.07
1.881	12.55	8.164	3.97
1.529	6.103×10^{-4}	1.531	4.39
1.520	1.194	2.018	4.16
1.511	2.335	3.125	4.15
1.502	3.487	3.985	4.12
1.493	4.650	4.585	4.04
1.484	5.804	5.132	3.95
1.476	6.960	5.517	3.97

$$\text{Average } K_3' = 4.12 \times 10^2$$

Table 4c.

K_3 values at Ionic strength I → 0

E.M.F.	I 10^3	Tm 10^3	Ta 10^3	LaA^+ 10^4	Na+ 10^3
0.0630	5.377	1.061	1.579	6.284	1.618
0.0603	6.658	1.325	1.577	6.960	1.616
0.0573	8.686	1.719	1.574	7.736	1.613
0.0560	10.111	1.982	1.572	8.083	1.611
0.0536	13.746	2.634	1.567	8.749	1.606
0.0611	21.194	3.927	1.557	9.497	1.596
0.0499	28.693	5.203	1.547	9.889	1.586
0.0491	36.145	6.464	1.358	10.165	1.576
0.0488	43.566	7.710	1.529	10.287	1.567
0.0484	50.884	8.940	1.519	10.436	1.557
0.0450	58.152	10.150	1.510	10.488	1.548
0.0441	28.08	5.267	2.784	14.981	2.853
0.0434	31.302	5.836	2.776	15.262	2.845
0.0422	37.868	6.964	2.761	15.752	2.830
0.0415	44.443	8.081	2.746	16,042	2.814
0.0400	63.830	11.350	2.701	16.667	2.768

La^{3+} 10^3	HA^- 10^4	$A^=$ 10^5	(H^+) 10^4	K_3 10^{-4}
0.433	6.236	8.954	4.407	4.10
0.629	5.676	7.512	4.932	4.09
0.946	5.040	6.128	5.600	4.21
1.173	4.757	5.607	5.929	4.20
1.759	4.22	4.730	6.601	4.26
2.977	3.323	3.941	7.439	4.29
4.215	3.297	3.606	7.930	4.24
5.448	3.058	3.381	8.296	4.26
6.681	2.927	3.031	8.491	4.13
7.896	2.777	3.188	8.710	4.15
9.107	2.693	3.160	8.820	4.04
3,769	7.097	6.261	9.774	4.07
4.309	6.844	5.995	10.110	4.10
5.389	6.403	5.544	10.716	4.21
6.476	6.120	5.315	11.124	4.20
9.690	5.463	4.980	12.068	4.27

Mean $K_3 = 4.11 \times 10^4$

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