I

UNCLASSIFIED

NYO-725

A POTENTIOMETRIC STUDY OF BETA-DIKETONE CHELATION TENDENCIES

by

LeGrand G. Van Uitert

January 10, 1951

The Pennsylvania State College
Contract No.AT(30-1)-907

School of Chemistry and Physics
Dr. George L. Haller, Dean

Department of Chemistry
Dr. W. Conard Fernelius, Head

State College, Pennsylvania
January 22, 1951

UNCLASSIFIED

MFC-23415

p.62

II

This report constitutes the thesis of Mr. LeGrand G. Van Uitert which has been submitted to the Graduate School of The Pennsylvania State College in partial fulfillment of the requirements for the degree of Master of Science to be granted January 27, 1951.

ABSTRACT:

The methods of procedure of Calvin and Wilson[1] for obtaining formation constants by potentiometric titrations have been substantiated. These methods have been extended to water-dioxane solutions containing more than 50 volume-percent of dioxane. The interpretation of the pH data obtained in these titrations has been clarified.

The effect of the ionic strength and the water-dioxane ratio upon the dissociation constants of the materials present in water-dioxane solutions has been demonstrated. The dissociation constants of a series of beta-diketones in 75 volume-percent dioxane solutions have been measured and related to the formation constants of their respective copper chelate compounds.

The existence of insoluble compounds of the general formula $M^{+2}(Ke)_2 \cdot M^{+1}Ke \cdot$dioxane, where Ke is the ionized acetylacetone molecule, has been demonstrated. This has been shown specifically for $NiKe_2 \cdot NaKe \cdot$ dioxane and $ZnKe_2 \cdot NaKe \cdot$dioxane.

The instability of trifluoro-beta-diketones in the presence of acid has been demonstrated.

TABLE OF CONTENTS

P-62-4

TABLE OF CONTENTS

INTRODUCTION

PREVIOUS INVESTIGATION

NYO - 725

In 1945 Calvin and Wilson[1] published a paper reporting the results of an investigation designed to determine the influence of structural factors of organic residues on their tendency to form chelate compounds with heavy metal ions. Their work was centered largely around o-hydroxy aromatic aldehydes and included several beta-diketones. Calvin and Wilson employed a solvent solution consisting of fifty volume-percent of water and fifty volume-percent of dioxane to study the chelation tendencies of the organic residues with the divalent copper ion. They had found a fortuitous situation to exist in 50-50 volume-percent water-dioxane solutions. They found that they could follow the course of a titration with base of acidic substances with a pH meter, employing a glass electrode and a saturated calomel electrode, without encountering any appreciable error in the hydrogen-ion concentrations so found. This observation of theirs has been termed fortuitous inasmuch as there are unevaluatable boundry potentials between the water solutions of the pH meter electrodes and the water-dioxane solvent medium.

The assumption appears to have been made by Maley and Mellor[2] that the pH meter behaves the same in water-dioxane solutions containing seventy volume-percent of dioxane. This has not been found to be the case in experiments that have been conducted in connection with this thesis. (See section 2 and note 3 of this section). Mellor and Maley worked with 8-hydroxyquinoline, salicylaldehyde, and acetylacetone. These materials were employed to compare the chelating abilities of a series of metal salts. This investigation was an extension of work done by Calvin and Melchior[3] with sodium 5-salicylaldehyde sulfonate in water

P-6r-6

solutions.

Recently further investigation of the chelating tendencies of several tri- and divalent metals with acetylacetone and other beta-diketones in 50-50 volume-percent water-dioxane solutions have been carried out at the Michigan State College. The investigators there have employed a new approach to the procurement and analysis of pH measurements in this solvent mixture.

Stites[4] in his dissertation has shown several peculiarities to exist that are connected with precipitation and hydrolysis phenomena that had not been previously reported by Calvin and Wilson or by Maley and Mellor. By allowing extensive periods of time to elapse between additions of base, Stites was able to show that plateaus would occur in a plot of pH vs. milliliters of base added (See graph 3 page 34). However, when the titration was performed quickly a smooth curve identical to those found by Calvin and Wilson could be obtained.

Stites chose to interpret the titration curves he obtained in terms of plateaus resulting from precipitation or from hydrolysis of the chelate compounds previously formed. The results he obtained by titrating solutions of zinc, copper, and nickel in the presence of acetylacetone will be compared to experimental results obtained in the development of this thesis (See section one). Miss Brilliantes[5] confirmed the work of Stites on the nickel and copper acetylacetonates. Therefore, her thesis is also considered in the present discussion.

PRESENT INVESTIGATION

The primary purposes of this investigation are: (1) to find what effect the sidegroups of a *beta*-diketone have upon its acid dissociation constant; (2) to find what relationship the dissociation constants of the *beta*-diketones have to their ability to form chelate compounds with divalent copper ion; and (3) to find what effect variations in solvent composition and ionic strength have on these abilities.

In order to complete the above stated primary requirements, two preliminary investigations became necessary. First, two controversial methods of obtaining and interpreting potentiometric titration curves determined in water-dioxane solutions have been presented. One is that of Calvin and Wilson[1], and the other is that of Stites[4]. The establishment of which of these interpretations is the better constitutes the first section of this thesis. Second, an empirical method of determining hydrogen-ion concentration in water-dioxane solutions in which there is more than fifty volume-percent of dioxane present has been developed. This is considered in the second section of this thesis. The third section is a discussion of the dissociation constants found for the *beta*-diketones under various conditions. The fourth section is concerned with the formation constants for the copper chelate compounds.

APPARATUS AND REAGENTS

DESCRIPTION OF APPARATUS
(See illustration one)

The titrations which have been performed in the course of gathering the information included herein were all carried out in the following apparatus:

A 250-ml. four-necked flask having three radial necks and one on top was employed to carry out the titrations. The flask was immersed in a thermostat set at 30° ± 0.02°.

A Beckman model "G" pH meter fitted with extension electrodes was employed to determine the pH values in the solutions being titrated. The saturated calomel electrode was used as a reference electrode and either the Beckman "Type E" high pH electrode or the Beckman (no. 290) plain glass electrode was used as the pH-determining electrode. The electrodes were fitted with stoppers so that tight connections could be made when they were inserted into two of the radial necks of the four-necked flask. The top neck was fitted with a microburette and the remaining radial neck accommodated a propeller and shaft connected to a stirring motor. All the titrations discussed herein were done in this apparatus. The materials involved in each titration and the titration techniques are varied and therefore are outlined for each group of experiments in the appropriate subsections.

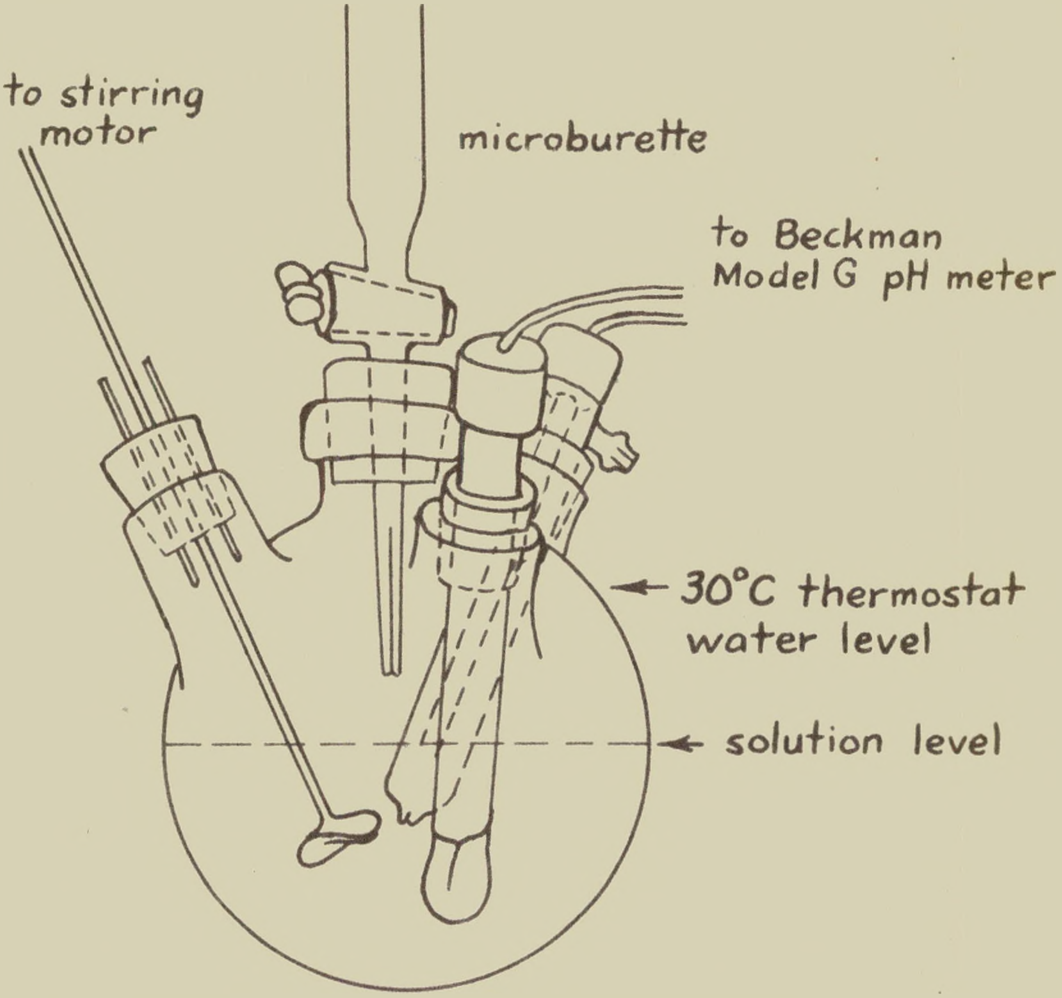
MATERIALS

Metal salts:

$CuCl_2 \cdot 2H_2O$	Mallinckrodt	C.P.
$NiCl_2 \cdot 6H_2O$	Fisher	C.P.
$ZnCl_2$	Fisher	C.P.

p-6r-9

Titration Apparatus



P-62-10

Beta-diketones

Acetylacetone	Eastman Kodak Company
Benzoylacetone	" " "
Dibenzoylmethane	" " "
2-Thenoylacetone	Robert Levine, Univ. of Pittsburgh
Benzoyl-2-thenoylmethane	" " " " "
Benzoyl-2-furoylmethane	" " " " "
Di-2-thenoylmethane	" " " " "
2-Thenoyl-2-furoylmethane	" " " " "
Beta-napthoyltrifluroacetone	" " " " "
Benzoyltrifluroacetone	" " " " "
Trifluroacetylacetone	" " " " "
2-Thenoyltrifluroacetone	" " " " "
2-Furoyltrifluroacetone	" " " " "
2-Pyridylacetone	" " " " "
4-Pyridylacetone	" " " " "
2-Pyridyl-2-thenoylmethane	" " " " "
4-Pyridyl-2-thenoylmethane	" " " " "
Hexafluroacetone dihydrate	Melvin Calvin, Univ. of California

DIOXANE: Carbide and Carbon-- technical grade

Purification of dioxane--

Technical grade dioxane was refluxed over metallic sodium for several hours. The solution was then fractionated through a 30-plate column. The forerun, up to 101°C., was carefully separated and discarded. The bulk of the material was then allowed to distill over and was used as a solvent for the titrations without further treatment.

P-62-11

The *beta*-diketones received from the University of Pittsburgh were prepared by Martin W. Farrer and James K. Sneed working under the direction of Dr. Robert Levine. The methods followed for their synthesis were essentially those of Reid and Calvin[14] and are outlined in the report "*Studies on the Zirconium Derivatives of Beta-diketones*".[15]

P-62-12

SYMBOLS

The following symbols will be used throughout this thesis:

Symbol	Significance
KeH	The concentration of chelating agent
Ke^-	The concentration of ionized chelating agent
H^+	The concentration of hydrogen ion
$CuKe^+$	The concentration of copper monochelate
$CuKe_2$	The concentration of copper dichelate
K_d	The "apparent" dissociation constant of the chelating agent
K_1	The first formation constant of the chelate compound
K_2	The second formation constant of the chelate compound
K(av)	The average formation constant of the chelate compound
pH	The negative log. of the hydrogen ion concentration
pKe^-	The negative log of Ke^-
pK_d	The negative log. of K_d
T_{KeH}	The total concentration of chelating agent (combined and uncombined)
$T_{Cu^{++}}$	The total concentration of Cu^{++} (combined and uncombined)
$\bar{n}$	The average number of chelating agent molecules coordinated to a metal ion
$[H^+]$	The "apparent" hydrogen ion activity as measured by the pH meter
U_{H^+}	A defined function, $U_{H^+} = [H^+]/H^+$ (see section 2)

The above defined concentration symbols are to be considered as molar quantities when they are employed in chemical equations.

SECTION ONE

AN EVALUATION OF TITRATION METHODS

General:

This section is devoted primarily to resolving the differences in the interpretation of the data obtained by Calvin and Wilson[1] and those obtained by Stites[4] concerning the curves for pH vs. ml. base added derived by titrating copper in the presence of acetylacetone in a solvent medium consisting of 50 volume-percent water and 50 volume-percent dioxane. The phenomena encountered by Stites in his dissertation and by Miss Brilliantes[5] in her thesis in regards to the titration of nickel in the presence of acetylacetone are also explained.

Calvin and Wilson successfully calculated the formation constants for several copper dichelates by means of an adaptation of the procedures of Bjerrum.[6] The calculations employed by them are outlined in part two of this section.

Stites felt that the titration curves obtained by Calvin and Wilson were unreliable inasmuch as they apparently were not equilibrium measurements. In repeating their copper acetylacetone titration, Stites was able to show that certain plateaus in this curve and others would become evident provided long time intervals were allowed between additions of base. He chose, in the copper acetylacetone formation titration to designate the first such plateau (pH 2.7) as the precipitation plateau and the second plateau (pH 6.7) as the hydrolysis ($CuKe_2 + OH^- \longrightarrow CuKe(OH) + Ke^-$) plateau. Stites also obtained a plateau after the second chelation in the titrations of acetylacetone in the presence of the divalent nickel and zinc ions. These plateaus were also designated by him as hydrolysis plateaus.

Miss Brilliantes, expanding the work of Stites, made an analysis of the hydrolized (?) chelate products occurring at these plateaus.

The fundamental errors occurring in the work and assumptions of Stites and Miss Brilliantes along with experimental and mathematical evidence in support of the methods employed by Calvin and Wilson will constitute the major portion of this section. The effect of the erroneous assumption made by Maley and Mellor will be discussed in note 4 of this section.

Titration procedure:

The basic procedure is as follows: Fifty milliliters of dioxane and fifty milliliters of water are combined to act as a solvent medium for a copper salt ($CuCl_2 \cdot 2H_2O$) and acetylacetone. The copper salt, the acetylacetone and the metal chelate product are all soluble in the mixture. The solution is then titrated with an approximately one-normal solution of sodium hydroxide and the resulting changes in pH are followed by means of a pH meter.

The increments of base added and the time allowed between additions are variable in the experiments outlined in this thesis. In general, small increments of base were added in the course of the titrations where stochiometry was to be observed and larger increments where the specific pH values measured were of secondary importance. The time allotted between adding increments of base range from a few seconds to several hours as dictated by the attainment of equilibrium as indicated by a steady reading of the pH meter.

An Analysis of Stites Titration Curves

Stites reports that for the titration of a solution consisting of 50 ml. of dioxane, 50 ml. of water, 2×10^{-3} moles of cupric chloride and 8×10^{-3} moles of acetylacetone (see graph 3) there are two plateaus in his pH curve. The first plateau was located at a pH of 2.7 and the second at a pH of 6.7. The first of these plateaus to be considered will be that one which occurs at pH 6.7.

If one adds 2×10^{-3} moles of copper chloride to the water-dioxane solution, the solution exhibits a pH of about 4.0. If the acetylacetone is added alone, the pH of the solution is approximately 5.5. However, when both are added to the same solution, the pH of the solution is found to be 1.87.

The number of hydrogen ions which are released in the chelating process is a measure of the amount of chelation that has occurred: [i.e., $HKe + Cu^{++} \longrightarrow H^{+} + CuKe^{+}$]. When sufficient base has been added to complete chelation, there will be a sharp rise in the pH curve. For 2×10^{-3} mole copper this should require 4×10^{-3} equivalents of base (see graph 3). At this point there should be 4×10^{-3} mole acetylacetone left in solution and therefore an additional 4×10^{-3} mole of base should be required to titrate it. It may be observed (graph 1 page 32) that, when Eastman Kodak Acetylacetone of recent purchase is used, the sharp rise is in agreement with the calculated end of chelation. Approximately 4×10^{-3} moles of acetylacetone must be accounted for from this point to the end of the acetylacetone titration (allowing for transfer and evaporation losses). Stites curve was plotted (graph 3) on the basis of an equal number of moles of NaOH added, starting from the point where both solutions are at the same pH. The data as plotted by Stites, start at a slightly lower pH but the base added to arrive at the starting point of this graph can be discounted as it, in effect, is only neutralising excess acid that was added by Stites. At the same pH, the degree of chelation for either titration is essentially the same.

Stites considers the end of the plateau at pH = 2.7 to represent the end of chelation. This is also in agreement with the calculated end point. Over the next 4 x 10^{-3} equivalents of base added, all three curves represented on graph 3 indicate that the excess chelating agent has been completely titrated. One should conclude then that any phenomenon observed in this area is a peculiarity of the chelating agent used. The curve obtained using acetylacetone purchased from Carbide and Carbon illustrates this. It was found upon titrating the Carbide and Carbon product that a dip ending at the same pH as that of Stites' plateau, pH = 6.7, was obtained, titrating the acetylacetone by itself the same phenomenon was observed (see graph 2). The dip terminating at approximately pH 7 proved to be due to acetic acid possibly present in the acetylacetone as acetic anhydride since it is used in the process of acetylacetone manufacture. The boiling points are 139°C. (746 mm.) for acetylacetone and 139.6°C. for acetic anhydride.[7]

Separation of these materials by fractionation was attempted with a twelve plate column. The best fraction obtained at a constant thermometer reading still showed acetic acid to be present when titrated with base (see graph 2). Purification of this acetylacetone was carried no further as in the meantime it had been found that Eastman Kodak acetylacetone was of a satisfactory degree of purity (see graph 1). Stites reports that he used "freshly distilled acetylacetone" purchased from the Eastman Kodak Company. If this acetylacetone was not of a purity comparable to that recently produced by Eastman Kodak a discrepancy similar to that found in the titration of fractionated

P-62-17

Carbide and Carbon acetylacetone might well result. There is also a very strong possibility that the long periods of time that Stites allowed his solutions to stand at low pH values resulted in the hydrolysis of part of the acetylacetone present to acetic acid.

To check for the presence of impurities, Stites' data for his acetylacetone titration were plotted on the basis of equal numbers of moles of sodium hydroxide added along with a titration curve obtained by titrating recently purchased Eastman Kodak acetylacetone. The divergence of the two curves is evident. The slope of Stites' curve is comparable to that for the Carbide and Carbon fraction and the few points plotted can well mask the acetic acid dip. As little as 0.02 ml. of one-normal base is enough to change the pH from 3 to 7 when uncontaminated acetylacetone is used.

The failure of Stites to take the possibility of the hydrolysis of the chelating agent into consideration is especially evident in his trifluro-beta-diketone titrations. To determine the dissociation constants of trifluroacetylacetone and thenoyltrifluroacetone, he titrated 0.924 gm. (6 x 10^{-3} moles) of the former and 0.44 gm. (2 x 10^{-3} moles) of the latter with 1.0672-N. NaOH. It is obvious that approximately 6 ml. of base are required to titrate the trifluroacetylacetone and 2 ml. of base are required to titrate the thenoyltrifluroacetone. However, Stites shows a plateau equal to 3.5 ml. of base in the first case and equal to 1.0 ml. of base in the second--the remainders had been titrated 3 to 4 pH units lower. Stites had acidified these solutions before titrating. This probably resulted in hydrolysis producing trifluroacetic acid, a strong acid, which will titrate at the lower pH. It should be noted also that Calvin and Wilson, who also worked with trifluro-beta-diketones made no mention of hydrolysis.

P-6r-18

Chelate Compound Hydrolysis

Stites attributed the plateau pH 6.7 in his titration of copper in the presence of acetylacetone (graph 3) to the hydrolysis of the copper dichelate to yield copper monochelate hydroxide. This is very interesting in view of the fact (Sidgwick[5]) that all previous investigation has shown only the dichelates to exist. To check this an attempt to prepare the hydrolyzed product was made.

If Cu(acac)OH is a precipitable product in the media employed it was reasoned that titrating a solution of 2 x 10^{-3} moles of copper chloride and 2 x 10^{-3} moles of acetylacetone with sodium hydroxide would allow this precipitate to form (see graph 5A & table 8A- solution A). Three titrations were made. Titration A contained 2 x 10^{-3} moles $CuCl_2$ plus 2 x 10^{-3} moles acetylacetone. Base equivalent to one-half of the copper ion present was added to the break in the curve representing the completion of the first chelation, $Cu^{++} + Ke^{-} \longrightarrow CuKe^{+}$. The rest of the curve corresponds to 1.5 x 10^{-3} equivalents of base 3/4 of that which would be expected to form Cu(acac)OH.

A similar curve was obtained for a solution containing 2 x 10^{-3} moles benzoylacetone plus 2 x 10^{-3} moles $CuCl_2$ (graph 5C & table 8A, solution C). However, it was noted that in titration (A), at the previously mentioned break in the pH curve, a pale white cloudy precipitate formed. The same white precipitate coprecipitated in the case of benzoylacetone, along with a green crystalline precipitate identifiable as the copper dichelate. A third titration was made using 2 x 10^{-3} moles $CuCl_2$ with sufficient HCl to get a starting pH of 2.00 (graph 5B & table 8A, solution B). The plateau in this run proved to be equivalent to 3 x 10^{-3} moles of NaOH and the same pale white cloudy precipitate formed. This again showed that 3 equivalents of base precipitate 4 equivalents of copper. This result is simply explained by identifying the pale

P-62-19

white precipitate as $Cu(OH)_{1.5}$ $Cl_{0.5}$, copper trihydroxychloride, which will form more readily than $Cu(OH)_2$ at this pH (Näsänen and Tamminen[9])

Calculations will show (see note 4 section one) that copper acetylacetonate is soluble to the extent of 1×10^{-3} moles in this solution. Observing the end products of the titrations (A) and (C) shows that the supernatant liquid above (A) is deep blue. This color indicates that the $Cu(acac)_2$ is in solution while $Cu(OH)_{1.5}$ $Cl_{0.5}$ alone has precipitated. The supernatant liquid above (C) is quite clear but a mixed precipitation of $Cu(OH)_{1.5}$ $Cl_{0.5}$ and $Cu(bzac)_2$ has occurred. (see note 2 at end of this section)

The evidence thus far shown cannot be reconciled with Stites' claim that Cu(acac)OH is formed by hydrolysis. Further, if this hydrolysis did occur additional base would be used up (see graph 3) in Stites' titration to the limiting extent of 2×10^{-3} equivalent. This does not appear to be the case even on Stites' curve.

The contention that the hydrolysis of a chelate compound below the pH level at which the excess chelating agent titrates will result in a plateau in the pH curve is fundamentally unsound. This is readily shown to be the case as follows:

Consider the relationship:

$$\frac{Ke^- \times H^+}{KeH} = K_d \quad \text{(dissociation constant)}$$

In a titration, for example, which originally contained 1×10^{-3} moles of divalent metal ion (M^{++}), and 4×10^{-3} moles of acetylacetone which had been carried forward to where 1×10^{-3} moles MKe_2 and 2×10^{-3} moles KeH were present in solution at pH = 6,

The moles of Ke^- at this point would be,

$Ke^- = 2 \times 10^{-10} \times \frac{2 \times 10^{-3}}{10^{-6}} = 4 \times 10^{-7}$. An addition of 4×10^{-5} moles of NaOH at this point, provided all of it reacted with the di-

P-62-20

chelate present to cause hydrolysis, $MKe_2 + OH^- \longrightarrow M(OH)Ke + Ke^-$, would cause the appearance of 4×10^{-5} moles of Ke^-.

The resulting solution would contain 4×10^{-5} moles of Ke^-, and 2×10^{-3} moles of KeH inasmuch as all the NaOH reacted to cause hydrolysis.

Then, $$\frac{Ke^- \times H^+}{KeH} = 2 \times 10^{-10} = \frac{4 \times 10^{-5}H}{2 \times 10^{-3}}$$

$$H = \frac{4 \times 10^{-13}}{4 \times 10^{-5}} = 10^{-8} \qquad pH = 8$$

From the above it is evident that any hydrolysis occurring below the level of titration of the molecular chelating agent present will result in a rapid rise in pH. If only part of the added base caused hydrolysis, the rest would ionize part of the excess chelating agent resulting in the same vertical pH rise. This simple equilibrium constant shows that the plateaus described by Stites cannot be due to hydrolysis as he proposes.

Returning to the equilibrium equation

$$\frac{Ke^- \times H^+}{KeH} = K_d$$

we find that a possible source of pH plateaus could lie in the removal of Ke^-. A 90% removal of Ke^- present could cause a pH drop of 1-pH unit. This is essentially what happens when nickel or zinc replaces copper in a chelation titration with acetylacetone. (graph 10A & B, and tables 7A). In graph 10A a pH drop of 1.5 units is observed. In this case the Ke^- must have been reduced to 1/30 of its former value. There is no sharp rise again in the pH curve until a third equivalent of Ke^- has been ionized. This shows that the additional Ke^- ionized was largely removed from solution as it formed.

In graph 10B, the moles of $Ke^- = 1.2 \times 10^{-3}$ before precipitation. The pH drop of 0.56 pH units indicates the concentration of Ke^- has been reduced to 1/3.6 of the former amount or approximately to

0.3 x 10^{-3} moles. Thus (1.2 - 0.3) x 10^{-3} or 0.9 x 10^{-3} moles of chelating agent ions have left the solution (10A). This along with graph 10A indicates that 3 moles of Ke^- leave the solution per one mole of Ni^{++}. To check this the precipitate in run 10B was filtered off and the filtrate acidified to pH = 3.1 and retitrated. This titration showed a maximum of 1 x 10^{-3} moles of unassociated KeH to be present, confirming the above evidence that 3 KeH = 1 Ni^{++} in this case.

The above evidence strongly suggests that a compound consisting of the double salt $NaKe \cdot NiKe_2 \cdot C_4H_8O_2$ is precipitated.

It is proposed that a salt in which only two chelate groups are directly coordinated by the metal ion is precipitated for the following reason:

The dissociation of the third precipitated acetylacetonate molecule of Ke^- and H^+ is not influenced by the nickel ion present in solution. This is inferred inasmuch as the curves (A and B) show that prior to precipitation the KeH titration follows that of acetylacetone when titrated alone. Note that a granular precipitate is formed, quite unlike the waxy crystals of $Cu(acac)_2$.

The above described phenomena also occur when the metal ion is zinc. The description of the resulting curves for zinc would be entirely analogous.

Miss Brilliantes was able to reproduce the titration curves obtained by Stites in the cases for copper acetylacetonate and nickel acetylacetonate. Some insight into the conditions under which the titrations performed by Stites as well as by her can be gained from her discussion of her titration procedures.

Point of interest:

(1) Miss Brilliantes assumed that the information presented by Stites was correct.

(2) Therefore, stating, "Equilibrium is said to have been reached when the addition of more sodium hydroxide did not show a change in pH on the curve plotted for pH vs. added sodium hydroxide, a plateau was observed for this."

(3) Further, "Evaporation took place during the time necessary for a titration. A ten percent loss of solution was noted in approximately twenty-four hours."

Curve A of graph 10 was determined for the same set of materials as Miss Brilliantes' "fast" nickel acetylacetone titration. She refers to the pH drop she encountered in her titration as a "hump" that is of unknown origin--possibly occurring as a consequence of not obtaining equilibrium prior to that point. The text referring to graph 10 adequately shows that the "hump" is a result of supersaturation and consequent precipitation of a $NiKe_2 \cdot NaKe$ compound. Further, the above points (2) and (3) explain the vagaries of Stites' and Miss Brilliantes' titration curves. Precipitation is of course dependent upon the temperature and the constitution of the solvent. If one waits long enough at any point while titrating a saturated solution of metal dichelate that has not been maintained at a constant temp-

p-62-23

erature and protected from evaporation losses, additional precipitation is bound to occur. This will also be shown, in the next subsection, to lead to falling pH values for the dichelate and hence, by proper choice of time intervals, to any desired pH curve.

The Phenomena Occurring at the Crystallization Point in Copper-acetylacetone Chelation Titrations

(See graphs 3 & 4 and table 1A)

The copper-acetylacetone titration discussed by Stites was repeated using the same amounts of water and dioxane, (50 ml. of each), and the same concentrations of copper ion (0.02 molar) amd acetylacetone (0.08 molar). A suggestion of Stites' precipitation plateau was obtained (See graph 4). The pH drop observed can be shown to be a predictable phenomenon and will be accounted for in the following calculations.

First, the calculation methods will be outlined. They are based upon the methods of Bjerrum.[6]

Stated simply, for a solution consisting of 50 ml. H_2O and 50 ml. dioxane, the pH of the solution containing copper chloride alone or acetylacetone alone is close to 4.0 and 5.5 respectively, but when they are added to the same solution the pH falls to 1.87. This indicates the formation of 1.36×10^{-3} moles of hydrogen ion by the mechanism $Cu^{++} + KeH \longrightarrow CuKe^{+} + H^{+}$. The hydrogen ion concentration is, therefore, a measure of the amount of chelate formed before base is added. Upon the addition of base, the hydrogen ion concentration is reduced so that additional chelation can occur: i.e.

$OH^{-} + H^{+} \longrightarrow H_2O$ followed by $Cu^{++} + KeH \longrightarrow CuKe^{+}\ H^{+}$.

It can be seen that the moles of NaOH added, Na^{+}, plus the moles

p-62-rx

of protons present are equivalent to the amount of chelation that has occurred. This value divided by the total amount of copper atoms in solution gives a value for ($\bar{n}$), which is the average number of chelate groups attached per copper atom.

The K_d value, where $K_d = \frac{H^+ \times Ke^-}{KeH}$ is obtained from the midpoint of the plateau of the acetylacetone titration. This is at pH = 9.7; here (Ke^-) = (HKe) and therefore $K_d = H^+ = 10^{-9.7} = 2 \times 10^{-10}$. Also the concentration of uncoordinated acetylacetone KeH equals $8 \times 10^{-3} \times \frac{1000}{100} \times \frac{100}{vol} - Na^+ + H^+$, where Na^+ equals a concentration equivalent and the amount of base that has been added. The value $1/Ke^-$ is now solved for and the log of this function plotted as an absicca against ($\bar{n}$) as an ordinate (See graph 6 and table 2A). Note that the above statements only apply when pK_d is much larger than the pH at which chelation is occurring. See note 6 of this section for the mathematical development.

In these calculations, the activities of all species in the solution are assumed to be equal to their concentrations. This is to say that the constants solved for are concentration constants and admittedly somewhat in error. However, the values so obtained can be considered to be fairly accurate and quite adequate for comparison work.

The values of pKe^- (see graph 6) where $\bar{n}$ equals 1.50, 1.00, and 0.50 are, respectively, the values of K_2, K average, and K_1 for the formation constants. At $\bar{n}$ = 1.50 on graph 6 a distinct break is observed in the chelate formation curve. This break corresponds to the crystallization point (see graph 4, ml. NaOH = 2.25). The crystallization of material out of solution in this case is associated with a drop in pH. This behavior can be explained by a few simple calculations.

First, assume that upon the addition of base to the solution, the prodominate reactions will be the most rapid ones. These are

(1) $H^+ + OH^- \longrightarrow H_2O$ and

(2) $KeH + OH^- \longrightarrow H_2O + Ke^-$ followed by

$CuKe^+$ (or Cu^{++}) $+ Ke^- \longrightarrow CuKe_2$ (or $CuKe^+$).

These reactions appear to be quick and complete within a few seconds of stirring time. Let us consider the point ml. of NaOH = 2.25 (the crystallization point). The following values apply at this point:

The volume of the solution equals 103.2 ml.

The pH of the solution equals 3.11.

The hydrogen ion concentration in the solution equals 0.00078.

The moles of hydrogen ion present in solution equals 0.00078 x $\frac{103.2}{1000}$ = 0.000081, and $\bar{n}$ = 1.485 (Table 2 A)

The $\bar{n}$ value equals 1.485.

Now if one allows sufficient time for crystal growth from the supersaturated solution present, a pH drop to 3.00 will be observed. (After crystallization, then the following values apply;) The hydrogen ion concentration equals 0.00100 and the moles of hydrogen ion present in solution equals 0.00100 x $\frac{103.2}{1000}$ = 0.000103. Subtracting the moles of hydrogen ion present before crystallization from the moles present after crystallization (0.000103 - 0.000081 = 0.000022) we find 0.000022 moles of protons have appeared. To explain this mathematically we must derive the appropriate relationships first. Keeping in mind that the formation constants being solved for are concentration constants, we must recognize that after crystallization has occurred, the simple formula for $\bar{n}$, $\bar{n} = \frac{Na^+ \ x \ H^+}{T_{Cu^{++}}}$, no longer holds — $\bar{n}$ being concerned with the average number of acetylacetone molecules chelated per atom of copper in solution. However, the relationship

P 62-26

$\bar{n} = \frac{Na^+ + H^+ - 2a}{T_{Cu^{++}} - a}$, where a = moles of copper acetylacetone precipitated, should hold.

The values for n may be in error for the points taken after crystallization but the absicca values of pKe^- are pH dependent alone and therefore are accurate. Assuming that the line found (see graph 6) for the chelate formation curve while all the material was still in solution (this will be called the solution curve) is correct, we can drop down from the $\bar{n}$ value on the curve measured after crystallization (the crystallization curve) to the same pKe^- value on the solution curve and find the $\bar{n}$ value for the material in solution. These two $\bar{n}$ values enable us to calculate the theoretical amount of precipitate formed.

On the crystallization curve $\bar{n} = 1.50$ and dropping down, we find $\bar{n} = 1.43$ in the solution. The value of $\bar{n}$ on the crystallization curve is a measure of the average number of acetylacetone molecules chelated per copper atom including those in the precipitate as well as those in the solution. Hence, as the number of moles of copper originally added equals 2×10^{-3} moles and $Na^+ + H^+ = TKe$ (the total amount of acetylacetone chelated);

$$\frac{TKe^- - 2a}{T_{Cu^{++}} - a} = \bar{n} \text{ (in solution)} = \frac{\bar{n} \text{ cryst.} \times TCu - 2a}{TCu^{++} - a}$$

solving $\frac{1.5 \times 2 \times 10^{-3} - 2a}{2 \times 10^{-3} - a} = 1.43$

$$3 \times 10^{-3} - 2a = 2.86 \times 10^{-3} - 1.43; \quad 0.14 \times 10^{-3} = 0.57a$$

we find $a = 0.246 \times 10^{-3}$ moles of precipitate predicted. This is the amount of precipitate that would be expected to separate at the crystallization point. An obvious equilibrium may now be set up. Assuming that $Cu(acac)_2 + H^+ \rightleftharpoons Cu(acac)^+ + KeH$

we may write a constant $\frac{Cu(acac)^+ \times KeH}{Cu(acac)_2 \times H^+} = K_A$

As the crystallization occurring influences only slightly the concentrations of acetylacetone and water present, these two values can be assumed to be constant and we have the relationship.

Case I before crystallization $$\frac{Cu(acac)^{+}_{I}}{Cu(acac)_{2\,I} \times H^{+}_{I}} = \frac{Cu(acac)^{+}_{II}}{Cu(acac)_{2\,II} \times H^{+}_{II}}$$ Case II after crystallization

Case I

Before precipitation; $n = 1.485$, pH = 3.11
let d = the concentration of $CuKe_2$
and b = the concentration of CuKe

then $d + b = 2 \times 10^{-3} \times \frac{1000}{103}$ = the total copper concentration, and

$\frac{2d + b}{d + b} = \frac{\text{total chelated acetylacetone}}{\text{total copper}} = \bar{n}$ (solution) = 1.485 substituting $d = 2 \times 10^{-3} \times \frac{1000}{103} - b$ into $\frac{2d + b}{d + b} = 1.485$; $\frac{2(2/103 - b)}{2/103}\, b = 1.485$

and solving, $b = 1.00 \times 10^{-2} = Cu(acac)_2$

and $d = 0.94 \times 10^{-2} = Cu(acac)^{+}$. We also know the pH is 3.11 and therefore the hydrogen ion concentration is 0.000776.

Case II

After precipitation, n for the solution has been shown to be 1.43

Solving as above.

$$\frac{2d + b}{d + b} = 1.43 \qquad d + b = (2 - 0.246) \times 10^{-3} \times \frac{1000}{103}$$

Note that here the total copper concentration is diminished by the amount of precipitate 0.246×10^{-3} moles.

Hence $\frac{2(1.754/103) - b}{1.754/103} = 1.43$ solving $b = 0.0098 = Cu(acac)_2$

$d = 0.0072 = Cu(acac)$

now solving for the hydrogen ion concentration after precipitation

$$\frac{1}{H^{+}_{II}} = \frac{Cu(acac)^{+}_{I} \times Cu(acac)_{2\,II}}{Cu(acac)_{2\,I} \times Cu(acac)^{+}_{II}\; H^{+}_{I}}$$

$$\frac{1}{H^+_{II}} = \frac{1.00 \times 10^{-2} \times 0.72 \times 10^{-2}}{0.94 \times 10^{-2} \times 0.98 \times 10^{-2} \times 7.76 \times 10^{-4}} = 1.001 \times 10^{-3}$$

$$\log \frac{1}{H^+} = \log 1 \times 10^{-3} = 3.00$$

The pH has been calculated to be 3.00. This checks with the pH measured by the pH meter at the end of precipitation for this point. It can therefore be assumed that the solution was supersaturated with all the components effectively in solution just prior to precipitation.

The equilibrium constant, K_A, for the previous equation leads to the equation for K_2, which is the second chelation constant. Here, $\frac{1}{Ke} = \frac{CuKe^+}{CuKe_2} \cdot K_2$ so that by assuming values for $\frac{CuKe^+}{CuKe_2}$ we can solve for the values of $\bar{n}$ and pKe^-. (See table 5)

This also can be done for K_1 which is the first chelation constant. Here $\frac{1}{Ke^-} = \frac{Cu^{++}}{CuKe^+} \cdot K_1$ (See table 5A)

The entire chelate formation curve, therefore, can be found by extrapolating the experimental points found while all the material is in solution to find K_1 and K_2 and then solving for the remaining points of the curve (See graph 7). The points thus found lying above $\bar{n} = 1.5$ and below $\bar{n} = 0.5$ for the calculated curves should give values comparable to those that would be found experimentally. This is seen in the closeness with which a solution 1×10^{-2} M in $CuCl_2$ and 4×10^{-2} M in acetylacetone duplicates the calculated curve (See graph 8 and tables 3A and 4A).

From the foregoing it appears that the best data obtainable for comparison of the formation constants can be obtained by titrating at a normal rate allowing 10 to 20 seconds between additions of base.

P-62-29

The farther the titration can be carried into the supersaturated region of the curve without the occurrence of crystallization, the better the results will be. It is only while all the material is still in solution that the values for the chelate formation curve can be calculated with accuracy and, since the equilibria with which we are concerned are rapid, no error will be encountered by not waiting for crystallization to occur. However, once crystallization has begun care must be taken to allow sufficient time for its completion or else to look only for stochiometric relationships beyond that point. After crystallization occurs, points may be taken when no further change is shown by the pH meter. This will take about 2 hours per addition of base. It should be expected that, inasmuch as the amount of precipitation formed can be calculated from the crystallization curve $\bar{n}$ values and the corresponding solution $\bar{n}$ values, by weighing the fractional precipitates that the proper solution $\bar{n}$ values may be determined. This was done for a titration duplicating that of graph 4 (See table 6A).

For accurate work the true concentration of hydrogen ions must be known inasmuch as this will have a large effect on the calculations. An estimate of the "apparent" hydrogen ion activity function ($U_H^+ = 1/1.1$) has been employed inasmuch as calibration has shown this is a probable value (See table 2 and graph 9). It is expected that a proper determination of U_H^+ will enable satisfactory calculations of chelate formation curves to be made by this method for materials that precipitate due to oversaturation. Solubility data for varying pH values can also be gained this way (See note 4 of this section).

P-62-30

Conclusions

The treatment of this section has been designed to accentuate the following facts.

(1) The rules of stochiometry should be carefully observed in titrating any solution. Where the stochiometry is not obvious, special means must be employed to establish it. This may involve increasing the concentration of reactants or special means of analysis.

(2) Carefully controlled conditions must be maintained in regards to temperature and evaporation.

(3) The formation curves, in agreement with those obtained by Bjerrum, are regular -- approaching definite integral values asymptotically for mononeucleate chelate compounds. It has been shown experimentally that the formation curves are linear over those parts of the curves that lie between the midpoints of the first and the last chelations in those cases in which the successive formation constants are not greatly different. This statement is made in a general way to indicate that irregularities in the above described pattern are more apt to be the fault of the experimentor than a consequence of the reactions involved.

(4) In those chelation titrations in which precipitation is possible, correct data for the formation-constant curves can be gathered as long as all the materials involved are in solution -- including a state of supersaturation.

(5) The method of titration of a solution should be a matter of judgment and observation rather than following any set pattern.

(6) The interpretation of phenomena occurring in the course of

a chelation titration should be mathematically substantiated or else considered to be questionable.

(7) With a reservation concerning the hydrolysis of trifluro-*beta*-diketones the methods of Calvin and Wilson have been substantiated.

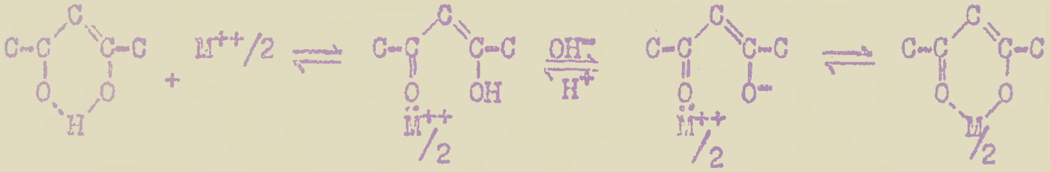
(8) Investigators in the field have largely assumed that the addition of excess acid is an important step in the titration procedures. It should be noted that in those cases where chelation has not proceeded beyond $\bar{n} = 0.5$ the addition of acid can result in confusion rather than being helpful. This is especially the case when the dioxane is present in amounts larger than 50 volume-percent (See section 2).

(9) Structure studies are possible by these titration methods. For example, the double salt $Ni(acac)_2 \cdot Na(acac)$ is indicated to be held together by lattice forces by these methods. Enolization rate studies can also be measured with the pH meter by these methods.

Section One - Notes

(1) The chelation mechanism proposed by Stites:

Stites proposed the following chelation mechanism



on the grounds that "when a chelating agent such as acetylacetone--- etc. is added even to a very acid solution of copper salt there is a deepening of the blue color which is assumed to be due to coordination".

The following calculations show that this evidence is not sufficient to support his contention.

$$1/Ke^- = (Cu^{++}/CuKe^+)K_1; \quad \text{also } 1/Ke^- = H^+/(KeH \times K_d)$$

Therefore

$$H^+ = \frac{Cu^{++}}{CuKe^+} \cdot K_1 \cdot K_d \cdot KeH$$

$K_1 = 3.55 \times 10^9$

$K_d = 2 \times 10^{-10}$

$KoH = 8 \times 10^{-2}$

Therefore

$$H^+ = \frac{Cu^{++}}{CuKe^+} \times 5.7 \times 10^{-2}$$

for a 10 N HCl solution $\frac{Cu^{++}}{CuKe^+} = 175$; $CuKe^+$ is 4.6×10^{-5} molar

for a 1.0 N HCl solution $\frac{Cu^{++}}{CuKe^+} = 17.5$ $CuKe^+$ is 4.3×10^{-4} molar

sufficient chelation occurs in strong acid solution to color the solution.

(2) Plateau variance in one-half chelation titrations:

For the one-half chelation titrations discussed in the text (See graph 5 and tables 8) the following reactions occur. To the break in the curve;

$$Cu^{++} + KeH + OH^- \longrightarrow CuKe^+ + H_2O$$

p-62-33

Beyond this point;

$$2CuKe^{+} + 1.5\ OH^{-} + 0.5\ Cl^{-} \longrightarrow CuKe_2 + Cu(OH)_{1.5}\ Cl_{0.5}$$

A pH rise occurs proportional to the solubility of the dichelate, due to the equilibrium:

$$CuKe_2 + H^{+} \rightleftharpoons CuKe^{+} + KeH$$

Since the acetylacetone chelate compound is more soluble, it causes a greater pH rise.

(3) Maley and Mellor have failed to consider an apparent hydrogen ion concentration function (See section 2) in their chelate compound formation curve calculations. This is evident from the shape of the curves they have published. Their curves calculated from low pH data tail downward at low $\bar{n}$ values instead of approaching a horizontal line at $\bar{n} = 0.00$ asymptotically. U_{H^+} should be approximately equal to two for their data.

(4) A calculation of the solubility of $Cu(acac)_2$ at the crystallization point for the chelation titration discussed in the text. Here $\bar{n} = 1.43$ for the solution where 1.754×10^{-3} moles of copper in various forms are still in solution. It can be assumed that the first chelation is complete and therefore $(0.43/1.43) \times 1.754 \times 10^{-3} = 0.528 \times 10^{-3}$ moles of $CuKe_2$ are present and $(1.00/1.43) \times 1.754 \times 10^{-3} = 1.228$ moles $CuKe^{+}$ are present in solution. By employing the crystallization curve and the calculated K_2 curve of graph 9, the solubility of $Cu(acac)_2$ can be calculated for any pH in the same manner.

P-62-34

(6) Mathematical development of the equations used in calculating the chelate formation curves (Ref. to Calvin and Wilson).

Assume that chelation is a two-step process

$$K_1 = CuKe^+/Cu^{++} \times Ke^-$$

$$K_2 = CuKe_2/CuKe^+ \times Ke^-$$

We can calculate the successive constants from the knowledge of $\bar{n}$ the average number of ionized chelating agent molecules (Ke^-) bound to Cu^{++}.

The total bound ketone is calculated from the equations

(1) $T_{Cu^{++}} = Cu^{++} + CuKe^+ + CuKe_2$

(2) $T_{KeH} = KeH + Ke^- + CuKe^+ + 2CuKe_2$

(3) $CuKe^+ + 2Cu^{++} + Na^+ + H^+ = Cl^- + OH^- + Ke^-$

(4) $K_d = H^+ \times Ke^-/KeH$

(5) $Cl^- = A + 2T_{Cu^{++}}$ A = acid originally added.

Result: The total bound ketone

$$CuKe^+ + 2CuKe_2 = Na^+ - A + H^+ - \frac{Kw}{H} - \frac{K_d}{H}\left(T_{KeH} + A - Na^+ + H^+ + \frac{Kw}{H^+}\right)$$

$$= Na^+ - A + H^+ \text{ when } K_d \text{ is small compared to } H^+$$

$$\bar{n} = \frac{CuKe^+ + 2CuKe_2}{T_{Cu^{++}}}$$

at $\bar{n} = 0.5$ log K_1 is equal to pKe^-

as $CuKe^+ = Cu^{++}$

at $\bar{n} = 1.5$ log K_2 is equal to pKe^-

as $CuKe_2 = CuKe^+$

from $K_d = \dfrac{H^+ \times Ke^-}{KeH}$

pKe^- is equal to the log of $\dfrac{H^+}{K_d \times KeH}$

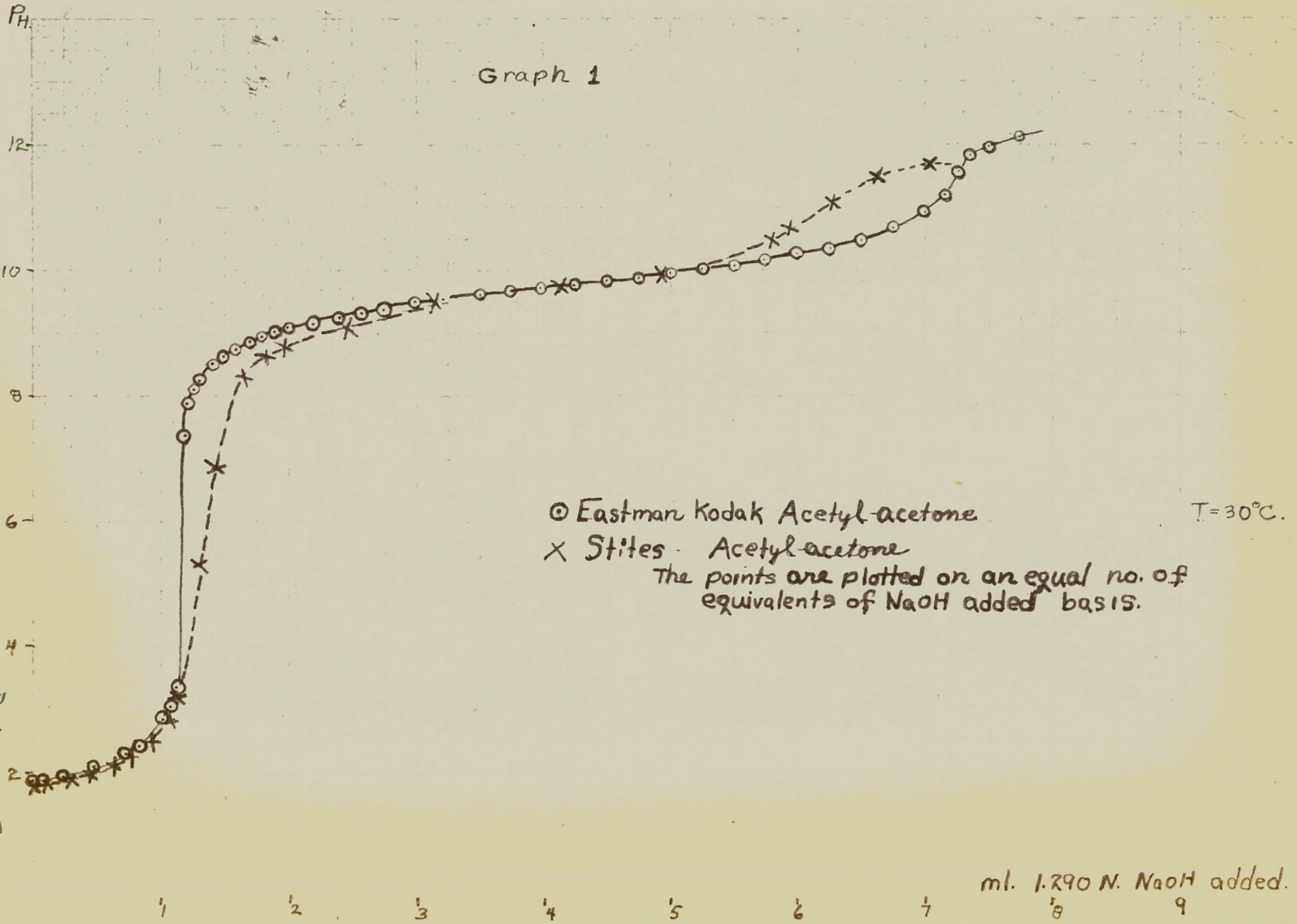
H^+ is measured by the pH meter

KeH is known by measuring the amount originally added, and K_d is taken to be the "apparent" dissociation constant of the chelating agent. This is determined from the pH value at the midpoint of the titration of the excess chelating agent in solution.

Here

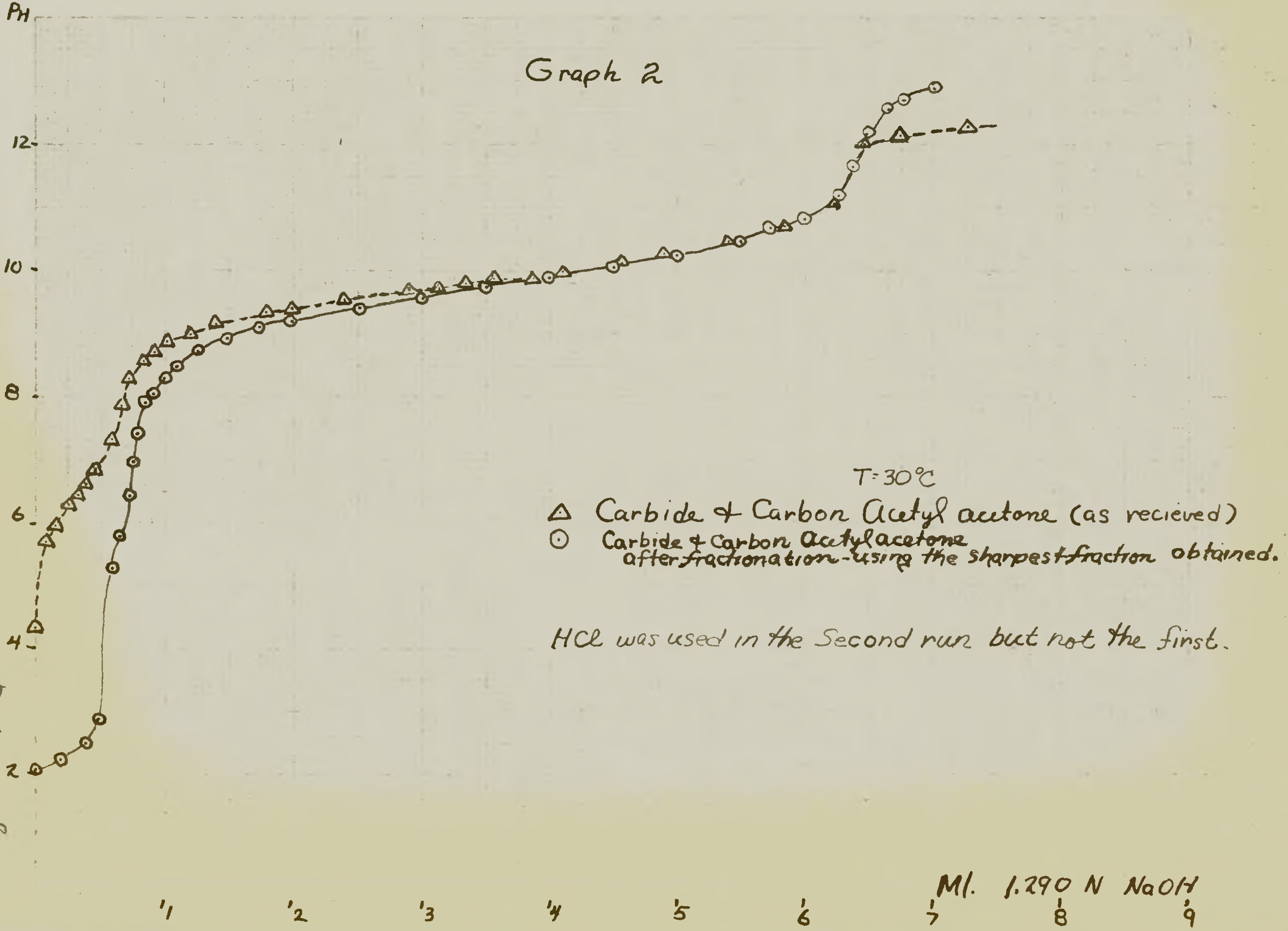
$$K_d = H^+ \times Ke^- / KeH = H^+$$

P-62-36



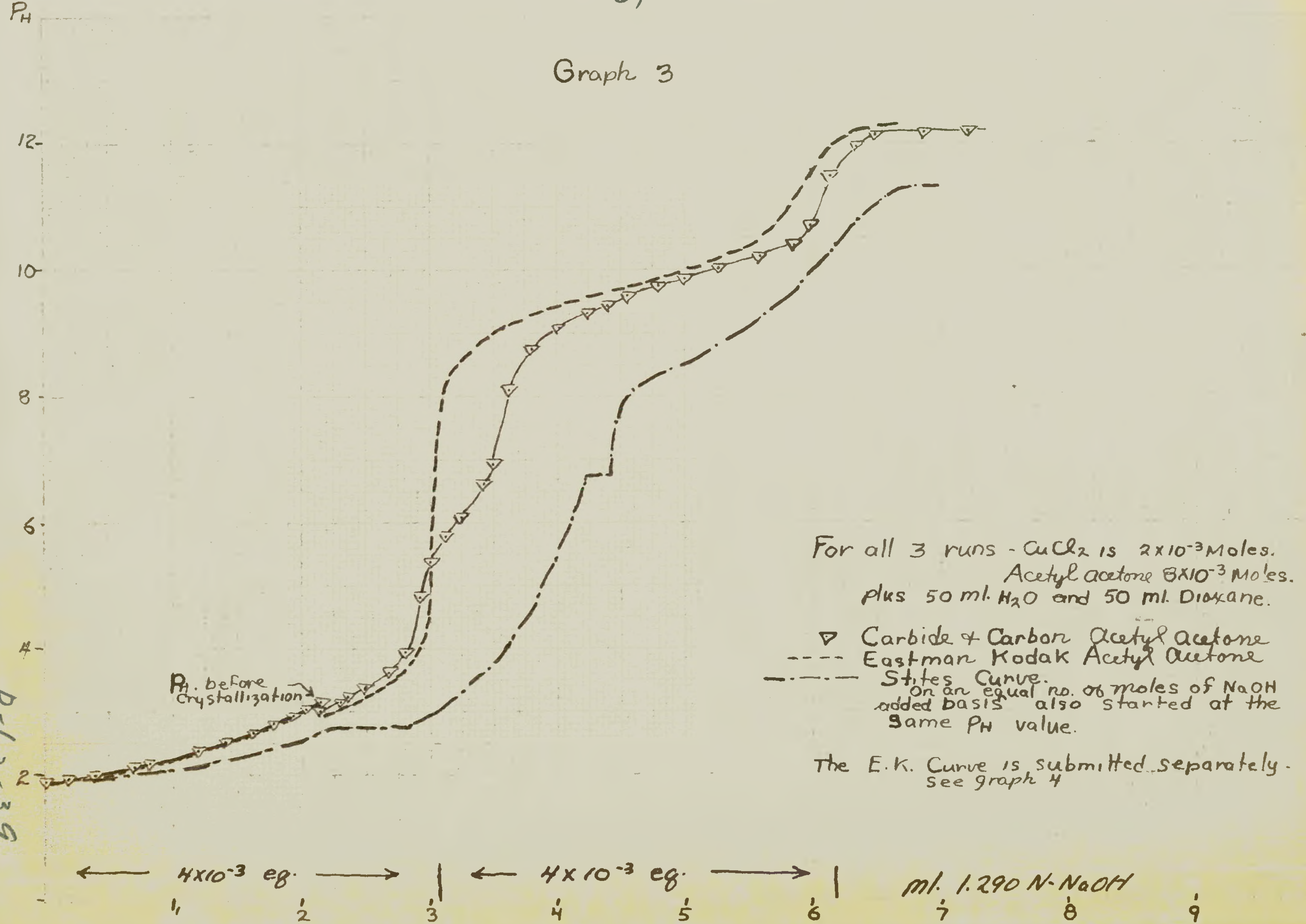
Graph 1

The points are plotted on an equal no. of equivalents of NaOH added basis.


Graph 2
PH
12
10
8
6
4
2
T=30°C
△ Carbide + Carbon Acetyl acetone (as recieved)
⊙ Carbide + Carbon Acetylacetone after fractionation - using the sharpest fraction obtained.
HCl was used in the Second run but not the first.
Ml. 1.290 N NaOH
1
2
3
4
5
6
7
8
9

P.62-38

Graph 3

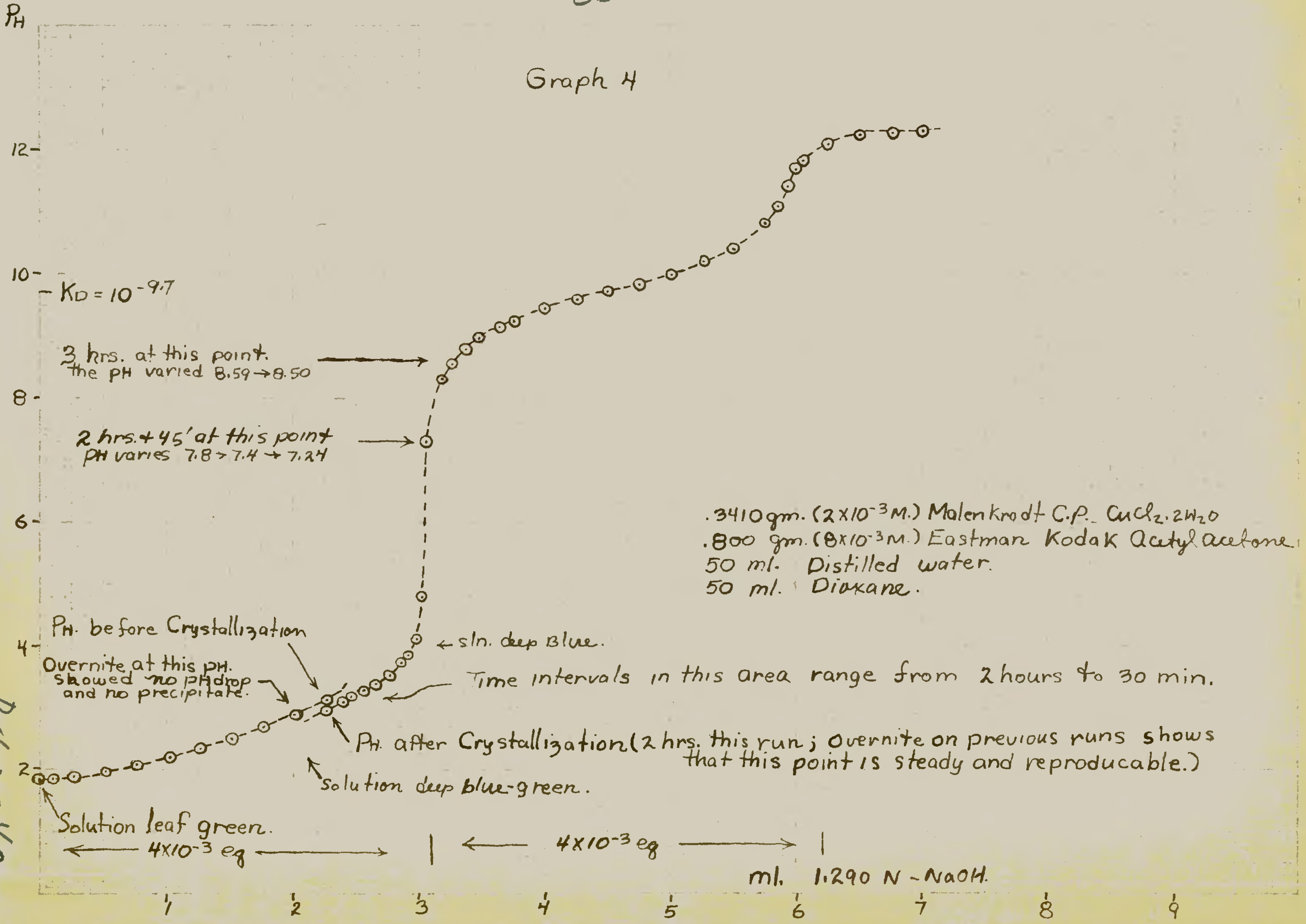


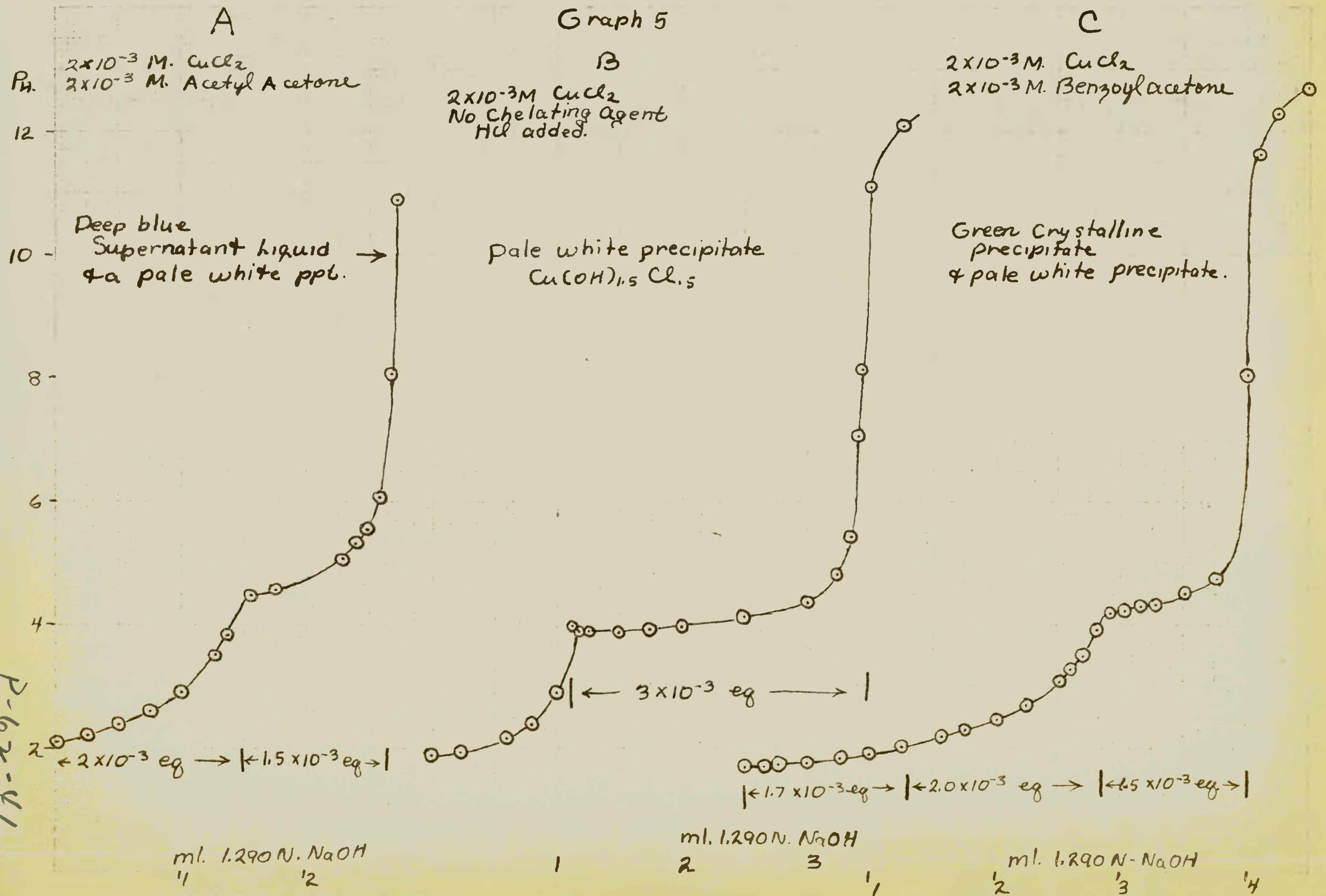
For all 3 runs - $CuCl_2$ is 2×10^{-3} Moles.
Acetyl acetone 8×10^{-3} Moles.
plus 50 ml. H_2O and 50 ml. Dioxane.

▽ Carbide + Carbon Acetyl acetone
- - - Eastman Kodak Acetyl acetone
—·—·— Stites Curve.
On an equal no. of moles of NaOH added basis also started at the same PH value.

The E.K. Curve is submitted separately.
See graph 4

6-22-39

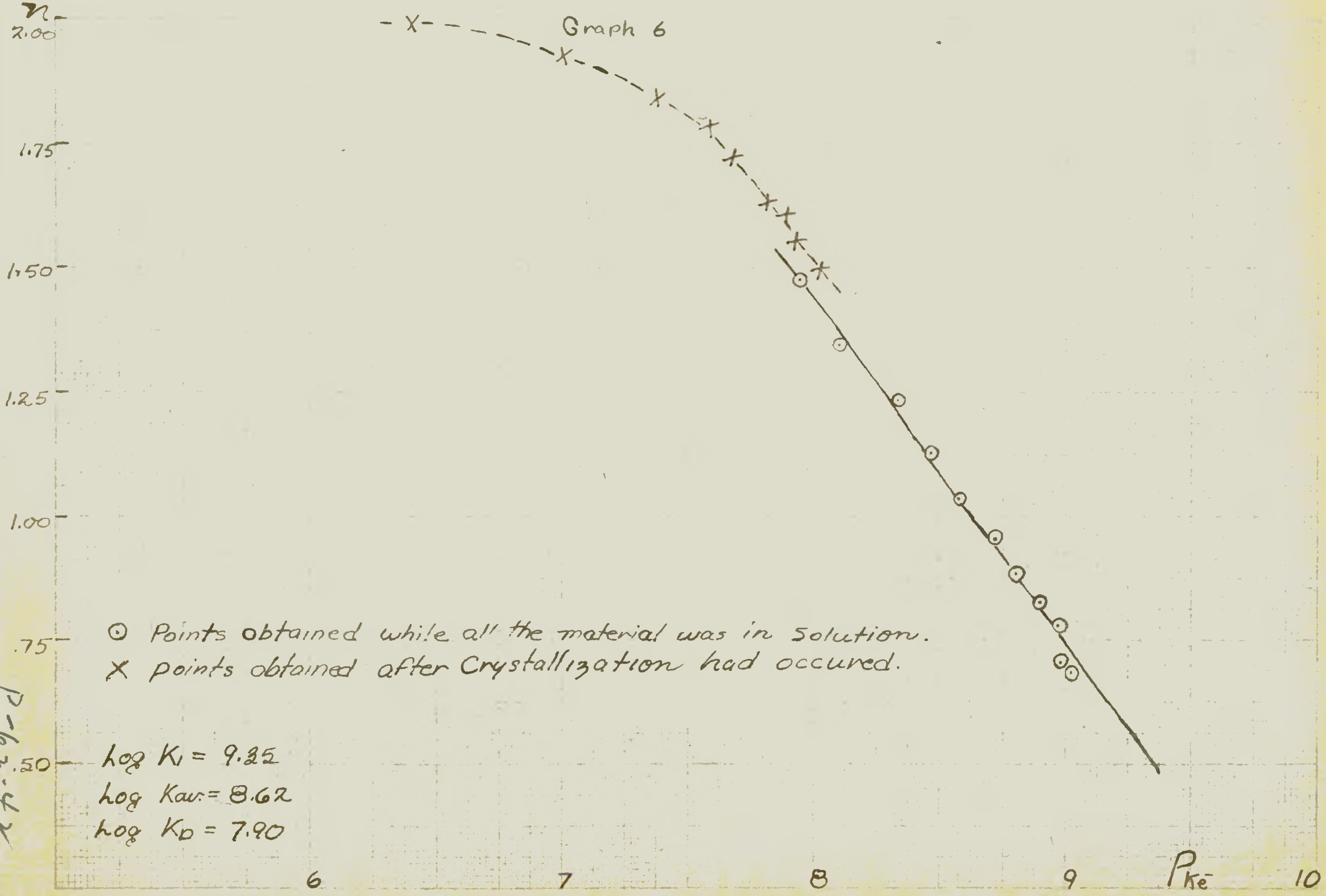

PH
Graph 4
12
10
8
6
4
2
- KD = 10^-9.7
3 hrs. at this point.
the pH varied 8.59 → 8.50
2 hrs. + 45' at this point
PH varies 7.8 > 7.4 → 7.24
.3410 gm. (2x10^-3 M.) Malenkrodt C.P. CuCl2·2H2O
.800 gm. (8x10^-3 M.) Eastman Kodak Acetylacetone
50 ml. Distilled water.
50 ml. Dioxane.
PH. before Crystallization
← sln. deep Blue.
Overnite at this pH. showed no pH drop and no precipitate.
Time intervals in this area range from 2 hours to 30 min.
PH. after Crystallization (2 hrs. this run; overnite on previous runs shows that this point is steady and reproducable.)
Solution deep blue-green.
Solution leaf green.
← 4x10^-3 eq →
← 4x10^-3 eq →
ml. 1.290 N - NaOH.
1
2
3
4
5
6
7
8
9



Graph 5

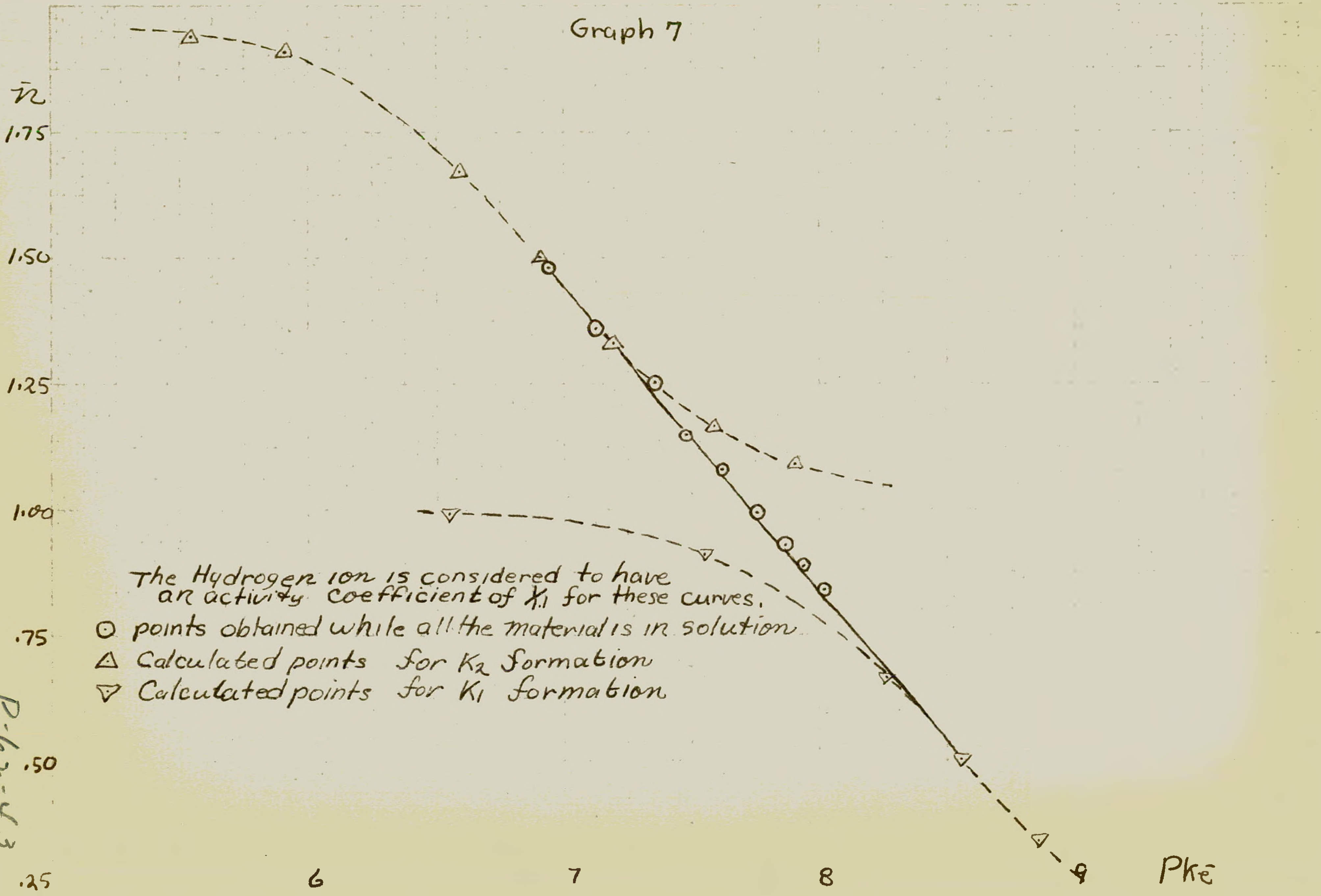
A
2×10^{-3} M. $CuCl_2$
2×10^{-3} M. Acetyl Acetone
PH.
12
10
8
6
4
2
Deep blue Supernatant Liquid & a pale white ppt. →
← 2×10^{-3} eq → |← 1.5 x 10^{-3} eq →|
ml. 1.290 N. NaOH
1
2
B
2×10^{-3}M $CuCl_2$
No Chelating Agent
HCl added.
pale white precipitate
$Cu(OH)_{1.5}Cl_{.5}$
|← 3×10^{-3} eq → |
ml. 1.290 N. NaOH
1
2
3
C
2×10^{-3}M. $CuCl_2$
2×10^{-3}M. Benzoylacetone
Green Crystalline precipitate & pale white precipitate.
|← 1.7 x 10^{-3} eq →|← 2.0 x 10^{-3} eq →|← 1.5 x 10^{-3} eq →|
ml. 1.290 N - NaOH
1
2
3
4

Graph 6



$\log K_1 = 9.25$
$\log K_{av.} = 8.62$
$\log K_D = 7.90$

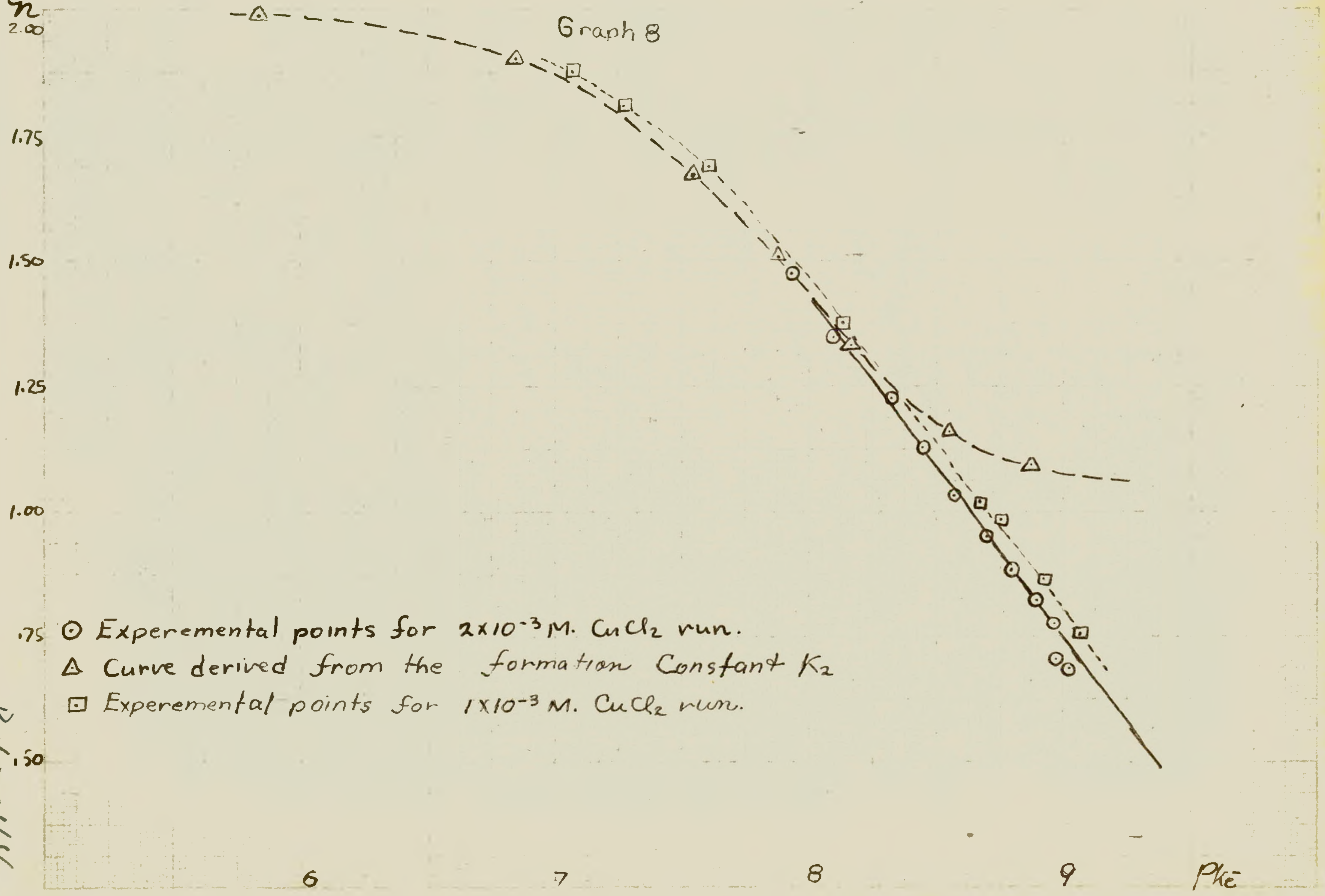
P-6-2.47



Graph 7

The Hydrogen ion is considered to have an activity coefficient of K_1 for these curves.

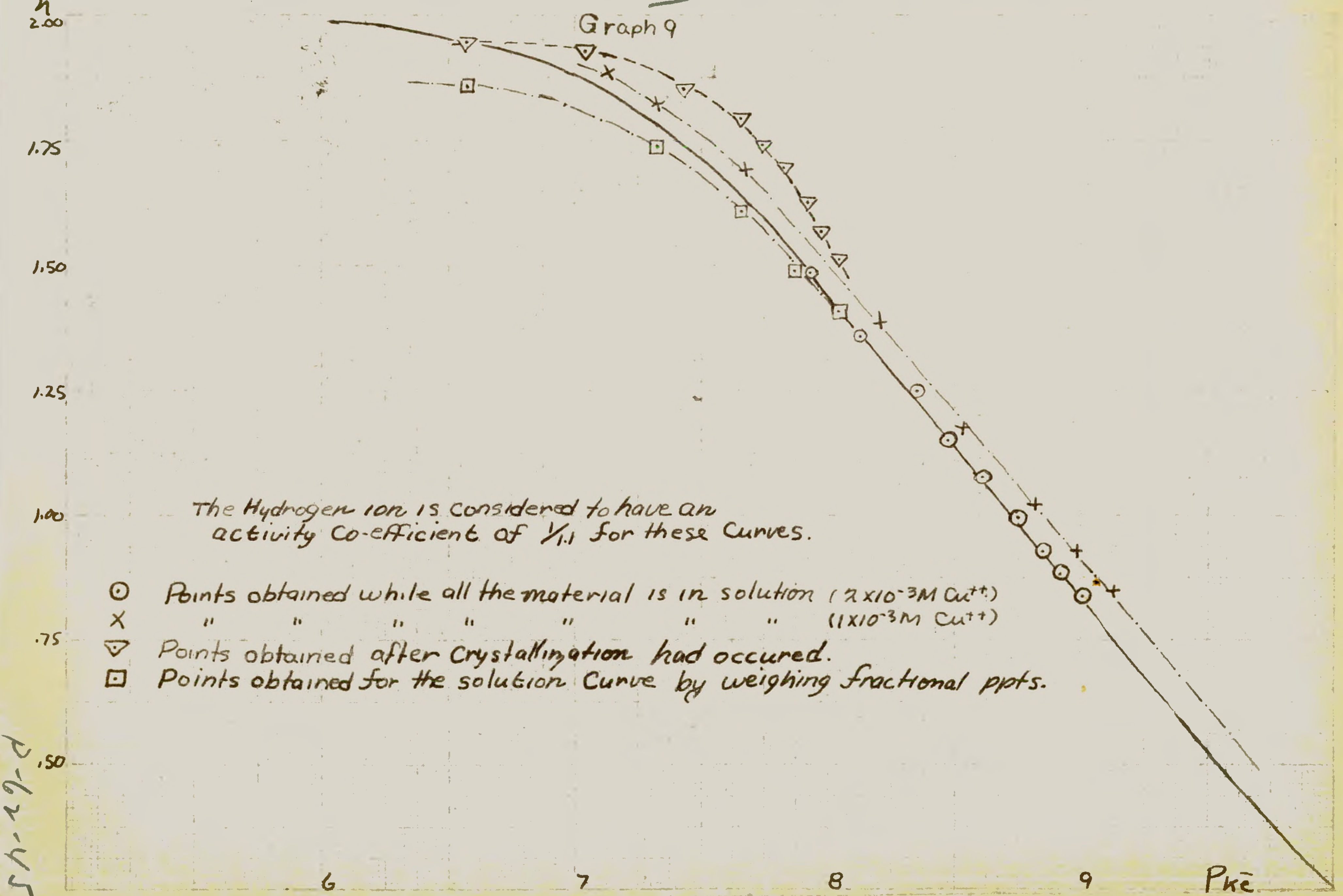
P.62-63



Graph 8

$\bar{n}$
2.00
1.75
1.50
1.25
1.00
.75
.50
6
7
8
9
Pke
⊙ Experemental points for 2x10⁻³ M. CuCl₂ run.
△ Curve derived from the formation Constant K₂
⊡ Experemental points for 1X10⁻³ M. CuCl₂ run.

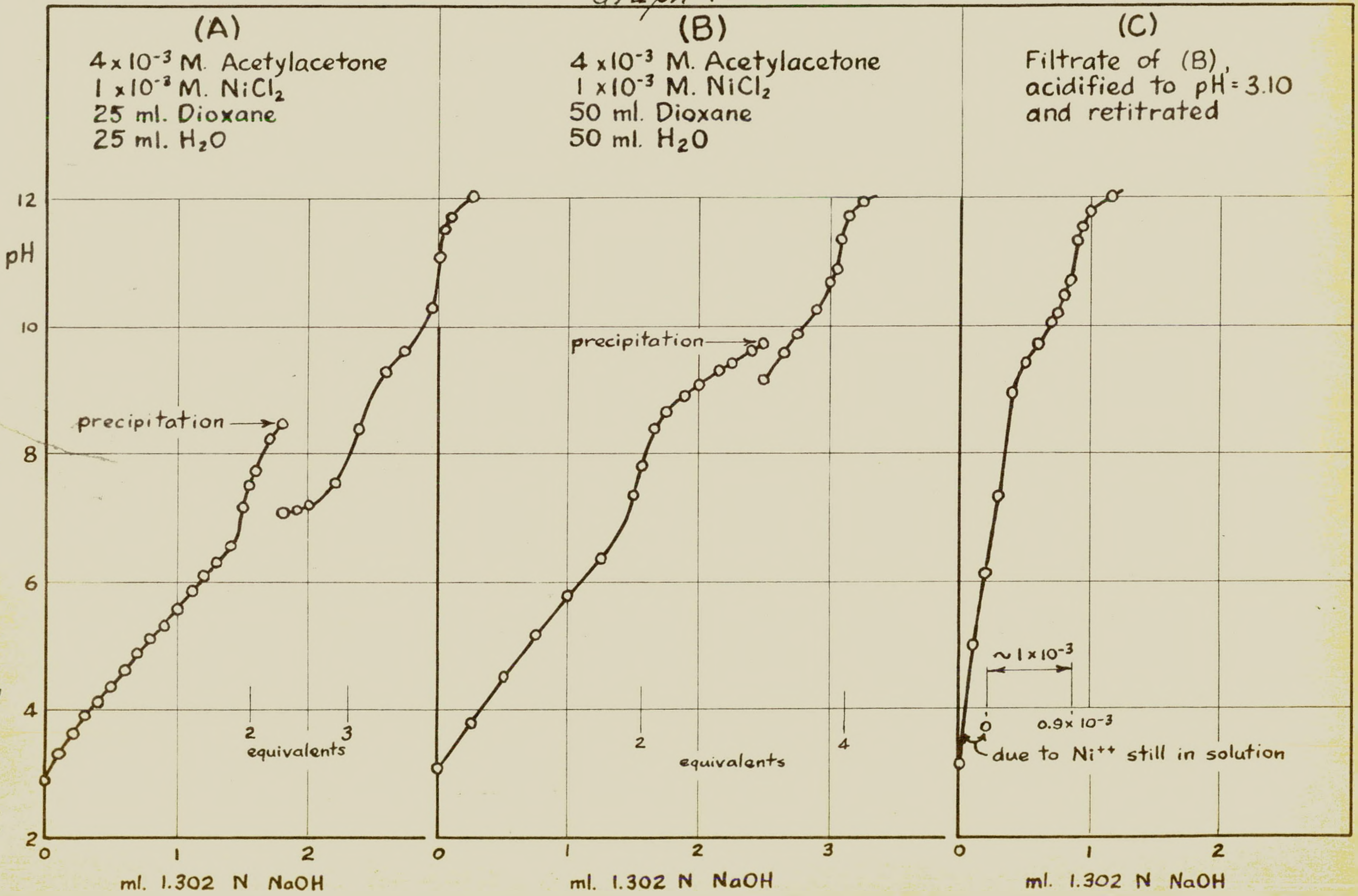
Graph 9



The Hydrogen ion is considered to have an activity Co-efficient of 1/1.1 for these Curves.

D-29-45

Graph 10



D-6x-46

Section Two

An Empirical Method For The Determination of Hydrogen Ion Concentration in Water-dioxane Solutions

General:

Calvin and Wilson[1] recommended the use of a solvent solution consisting of 50 volume-percent dioxane and 50 volume-percent water. They had found, upon exploring this medium that the glass electrode vs. the saturated calomel electrode gave approximately the correct pH readings. Their observations have been substantiated in these experiments. However, inasmuch as many of the *beta*-diketones under consideration are not soluble in a 50-50 water-dioxane mixture it has been found necessary to increase the proportion of dioxane. For purposes of convenience the new dioxane-water ratio of 75 volume-percent dioxane to 25 volume-percent water was selected.

The performance of the glass electrode vs. the saturated calomel electrode was checked for the new ratio of dioxane to water. The results indicated that corrections to the readings indicated by the pH meter were necessary. The following discussion will concern the derivation of these corrections. Note that references to the pH readings as measured by the glass electrode will be taken to mean the pH reading indicated on the dial of the pH meter when a pH measurement is made on the given solution and nothing more.

In the following discussion a series of experiments followed by the conclusions that may be drawn from them will be described.

Experiment A (See graph 11A and table 1B)-

The pH readings of a series of solutions, all of which were 0.022 molar in HCl but varied in the ratio of dioxane to water from zero to [illegible] volume-percent dioxane were measured. The activity of the

P-62-47

hydrogen ions present in each solution, as indicated by the pH meter, was divided by the known acid strength to derive a series of values which will be called the hydrogen-ion function and given the symbol U_{H^+}.

The U_{H^+} values so derived are values greater than one for solutions containing less than 45 volume-percent of water. The main curve shown on graph 11A indicates the values of U_{H^+} only for that set of conditions under which these values were found. The short line above the main curve approximates the U_{H^+} values that were found for solutions that contained the same water-dioxane ratios and were of an ionic strength comparable to that occurring in the chelation titrations discussed in section three. The line below the main curve was obtained for the same acid concentration as the main curve but in this case the solutions were also 0.01 molar in $BaCl_2$.

Experiment B (See table 3B and graph 11C)-

The pH values of a series of water-dioxane solutions, all of which contained 28 volume-percent water but varying amounts of electrolyte (all monovalent ions), were measured. The electrolyte for curve B was entirely HCl while that for curve A was 11.3 mole percent HCl and 88.7 mole percent NaCl.

Curve B shows that U_{H^+} is a function of the concentration of the HCl present for a given dioxane-water ratio.

Curve A extends the observation drawn from curve B to show that U_{H^+} is a function of ionic strength and also that for a solution in which the ionic strength is larger than 0.02 and where the hydrogen ion accounts for a relatively small part of the total ionic strength that U_{H^+} is nearly constant.

P-62-48

Experiment C (See graph 11B and table 2B)-

To check the last observation of experiment B and to determine U_{H^+} for the chelation titrations of section 3, the pH values of a series of solutions containing 75 volume-percent of dioxane and having a constant ionic strength were measured. The ionic strengths of the solutions were the same as those which exist at $\bar{n} = 0.5$ for the chelation titrations in section 3; but the ratio of hydrogen-ion concentration to sodium-ion concentration was varied. The results show that for these solutions U_H^+ is nearly constant and equal to approximately 2.7 on the average.

It was found that the U_{H^+} value of 2.7 could be used throughout the course of the chelation titrations listed in section 3 for the following reasons:

(a) The value of U_{H^+} tends to decrease as the titration proceeds due to the diluting effect of the water added in the process of adding base.

(b) The value of U_{H^+} tends to increase as more base is added due to the conversion of M^{++} ions to MKe^+ ions. The divalent ions have a greater depressing effect on U_{H^+} than monovalent ions.

(c) These two tendencies are nearly equal and in opposite directions.

The explorations of the water-dioxane solutions so far conducted are comparable to a calibration of the pH measuring device employed against a pH measuring cell containing no liquid junctions:

i.e., $Pt/H_2 \quad HCl \quad AgCl/Ag$

Inasmuch as the HCl concentration is a known value in every case for the calibration procedure, we can safely deduce the pH measurements taken in other solutions of comparable ionic strength and the same

P-62-49

water-dioxane ratio within the limitations above described will lead to satisfactory estimations of the number of protons in solution. Also, when the conditions surrounding a given titration are properly calibrated under the same conditions, it is expected that activity coefficients will cancel out. Harned and Fallon[10] have published data concerning the dissociation constant of acetic acid in 82 volume-percent dioxane. Their curves indicate that at an ionic strength of 0.02 the measured dissociation constant for acetic acid is no more than 0.03 pK_d units lower than the extrapolated pK_d value for zero concentration. This should be sufficient to show that any peculiar effects such as might be ascribed to triple ion formation, etc. will not appreciably affect the results obtained at these concentrations.

Experiment D (See table 4B)

The explorations of the water-dioxane solutions so far carried out have been limited to acid solutions. The calibration of the pH readings of solutions of known acid strength becomes impossible for high pH values. Therefore, to ascertain whether the U_{H^+} values found in acidic solutions are applicable to the pH readings measured at higher pH values, buffer solutions of several <u>beta</u>-diketones were prepared. Their pH values were measured both by the glass electrode vs. the saturated calomel electrode and the cell;

Pt/H_2 (1at.), Ke^- (0.01), KeH (0.01), Cl^- (0.01), AgCl/Ag

by the methods of Harned and Thomas,[11] and Harned and Kazanjian[12] (See table 4B). The results indicate that the pH value measured by using the glass electrode plus the correction for U_{H^+} gives approximately the same pH value as those which were calculated from the

p-6-2-50

measurements made in the above cell for intermediate pH values. The corrected glass electrode pH values are low by about 0.2 pH units when the Beckman type E glass electrode is employed and low by about 0.4 pH units when the Beckman plain glass electrode is employed for pH values determined in the neighborhood of pH = 11.

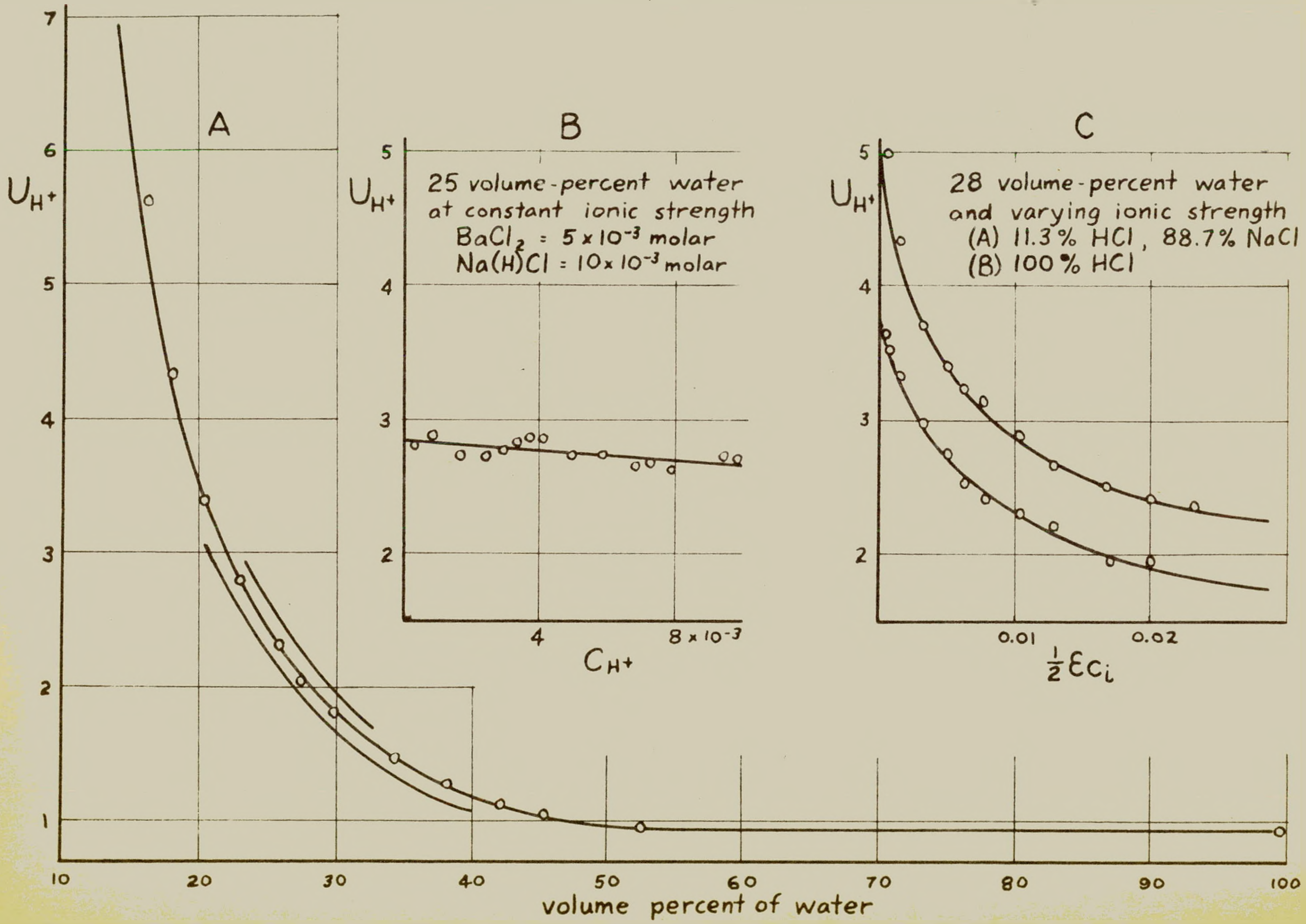
Experiment B (See table 5B and graphs 12B and 12C)

It may be observed here that the Beckman type E glass electrode and the Beckman plain glass electrode give the same pH readings up to a pH of about 10 according to the experimental data listed in table 5B and plotted in graphs 12B and 12C. Beyond a pH of ten very large deviations are found between the two electrodes as shown by graph 12C. The Beckman type E electrode reads the more correctly of the two.

It should be noted at this point that pH values that are off scale to the ordinary pH meter are easily obtainable in these solutions inasmuch as Kw, the dissociation constant for water, is of the order of 10^{-18} in a 75 volume-percent dioxane solution.

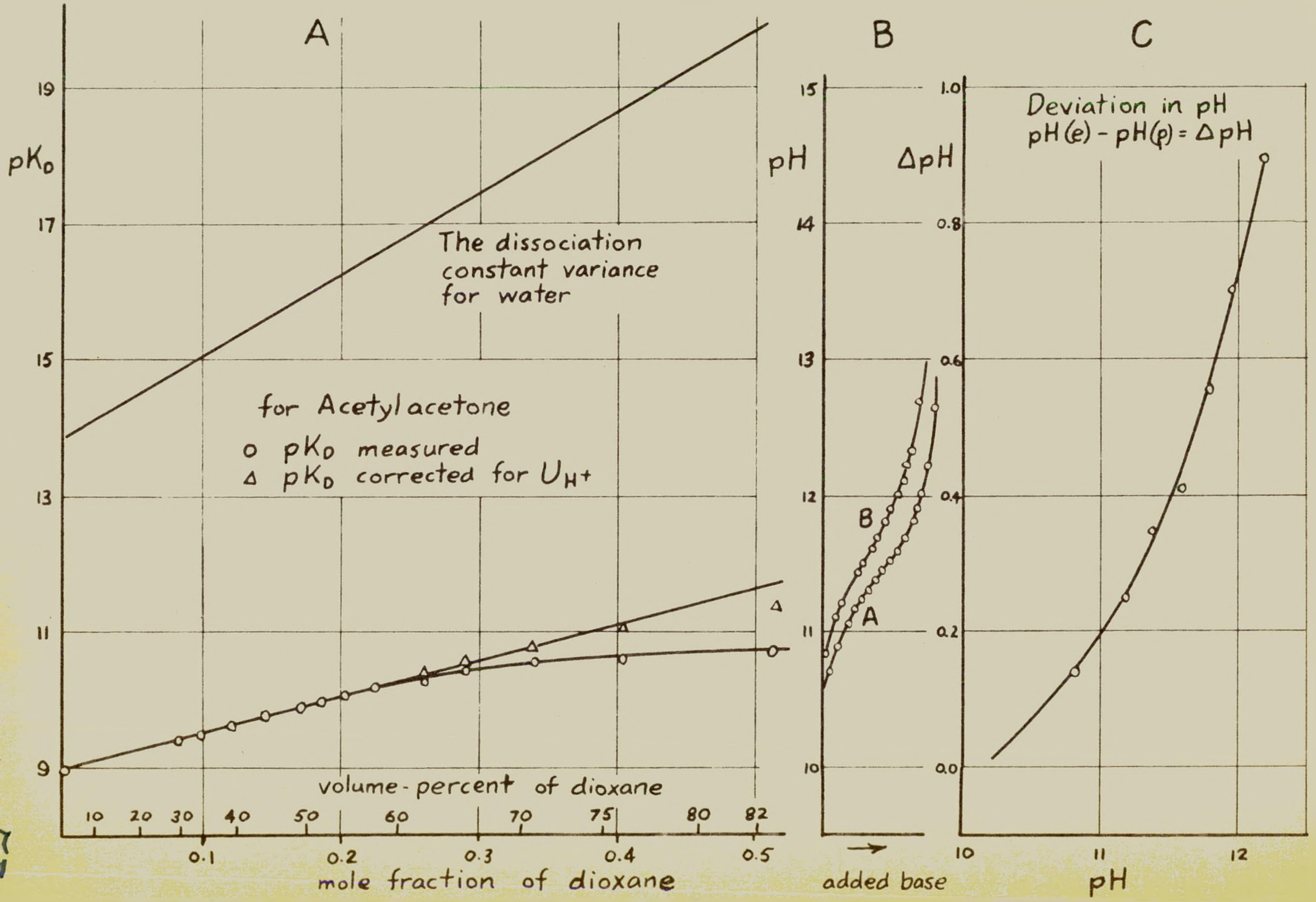
P-62-51

Graph 11



P-62-51

Graph 12



P-62-53

The Dissociation Constants of *Beta*-diketones

General:

The dissociation constants taken into consideration here are the "apparent" dissociation constants for the chelating agents, and therefore shall be defined as the product of the hydrogen ion concentration (H^+) times the concentration of ionized chelating agent (Ke^-) divided by the sum of the concentrations of the keto and enol forms of the molecular chelating agent present as such in the solution. The following relationship between the "apparent" dissociation constant and the enol form dissociation constant is easily derived.

$$K(\text{enol}) = K \text{ apparent} \quad \left(1 + \frac{\text{keto}}{\text{enol}}\right)$$

Since information concerning the keto-enol equilibrium of the chelating agents under consideration is not available for the conditions existing in these titrations no attempt will be made to take cognizance of their interrelationship.

The dissociation constant K_d (equal to the "apparent" dissociation constant) will be considered as a measure of the tendency for the combined forms of the chelating agent to ionize.

The dissociation constants which have been determined for the several *beta*-diketones under consideration are variable with the water-dioxane ratio and ionic strength of the solution in which they are measured.

P-6r-54

Variation with Water-dioxane Ratio

Harned and Owen[13] point out that the pK_d values for water, acetic acid, and several other substances increase almost linearly with the mole fraction of dioxane present in the solution. Quite possibly this same relation can be carried over to beta-diketones. A graph of the pH values measured in a series of acetylacetone buffers which varied only in their water-dioxane ratio gives fairly satisfactory results for this type of plot when the U_{H^+} corrections are applied. (See graph 12A and table 1C)

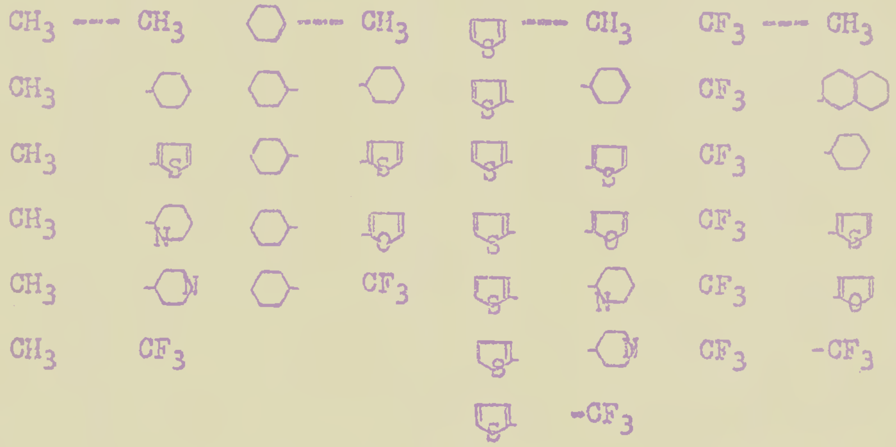
Variation with Ionic Strength

The order in which the beta-diketones may be placed in regards to increasing values of K_d is dependent upon the ionic strength of the solution in which the measurements are made. This is illustrated for the case of dibenzoylmethane and acetylacetone in graph 13 and tables 2C, 3C, and 4C. For solutions of low ionic strength, dibenzoylmethane has a higher pK_d value (smaller dissociation constant) than acetylacetone; but upon increasing the ionic strength (adding $BaCl_2$ in this case) the order is reversed. Other reversals are shown in table 7C. Graph 13 also shows that the presence of a given number of equivalents of a divalent metal salt depresses the pK_d values much more than the same number of equivalents of a monovalent metal salt.

The Variation of the Dissociation Constants of the Beta-diketones with the End Groups of the Molecules

The pK_d values of the beta-diketones are tabulated in table 5C for the case where the ionic strength of the solution is comparable to that existing at $\bar{n} = 0.5$ for the copper chelation titrations described in section 4. (See graph 14 and table 6C for the titration data). The pK_d values for several dissimilar conditions are listed in table 7B.

For the $\bar{n} = 0.5$ case the following series of end group influences are evident.



For this one set of conditions then, the order of end group influence in causing increasing values, of pK_d (influence increases to the left) is as follows.

This order does not necessarily hold for a different ionic strength of solution. Note the order reversals in table 4B. In this table the following reversals of values tabulated in table A have occurred.

Table A

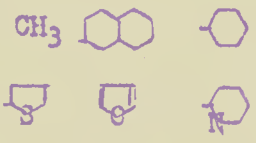
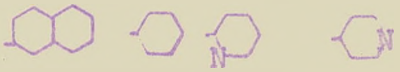


Table B

There have also been some reversals by molecules which have no end groups in common. But these cannot readily be compared.

If the end groups are considered as <u>two</u> series, the relative order of the end groups is preserved.

Series (i) CH_3  CF_3

Series (ii) 

The order found for the above series follows the general rule that the greater the capacity of the end groups to function as electron sources, the smaller the degree of dissociation of the molecule will be.

For series (i): The triple bond is known to be able to function as a good electron source. In this series the methyl group $H_3 \equiv C$- acts similarly to a triple bond. Sulfur is known to be multivalent, and therefore the thiophene group can easily enter into resonance structures that contain triply bonded sulfur. The more readily a structure can assume resonance forms, the better it can function as an electron sink or source. Oxygen has a smaller atomic radius than sulfur and therefore holds the electrons under its influence more securely than does sulfur. Therefore, the furane ring will not tend to give up electrons as freely as the thiophene ring does and hence cannot function as well as an electron source. The trifluro group, $-CF_3$, has a strong tendency to attract electrons and therefore cannot be considered to be able to function as an electron source.

For series (ii), the same pattern applies. The larger the number of resonance forms and the greater the freedom with which an end group can assume them, the more readily that group can function as an electron source.

P-62-57

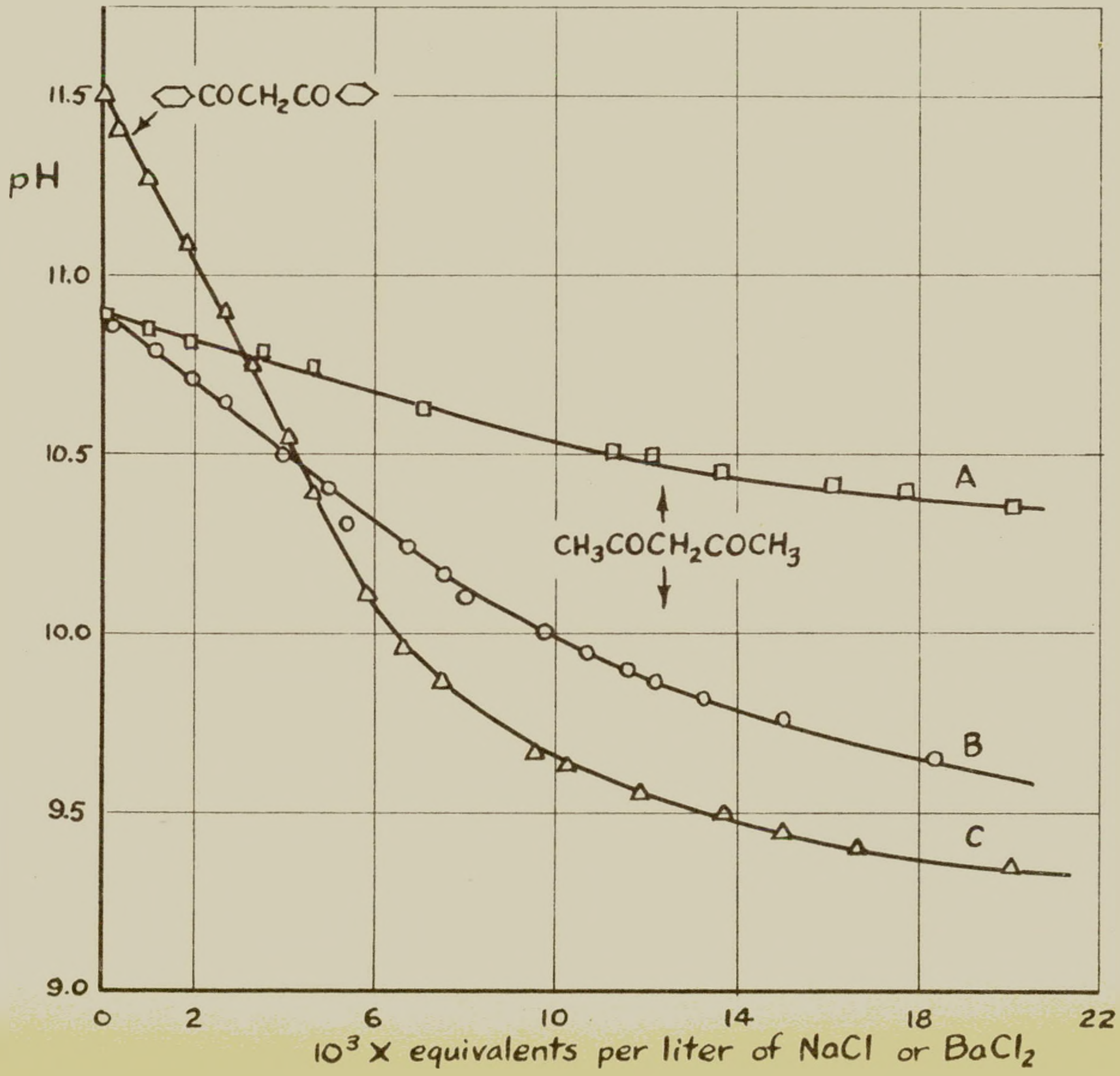
It would appear that series (ii), consisting of six membered rings, is affected to a greater degree by a change in ionic strength of the solution than are the members or series (i); this may be related to a keto-enol equilibrium difference for the two series.

Enolization rates:

It was observed in titrating the diketones that those molecules containing the $-CF_3$ (electron attracting) group were very slow in reacting with NaOH under the same conditions that the remaining diketones came to equilibrium quickly. This can be attributed to a low tendency for those molecules containing the $-CF_3$ group to enolize.

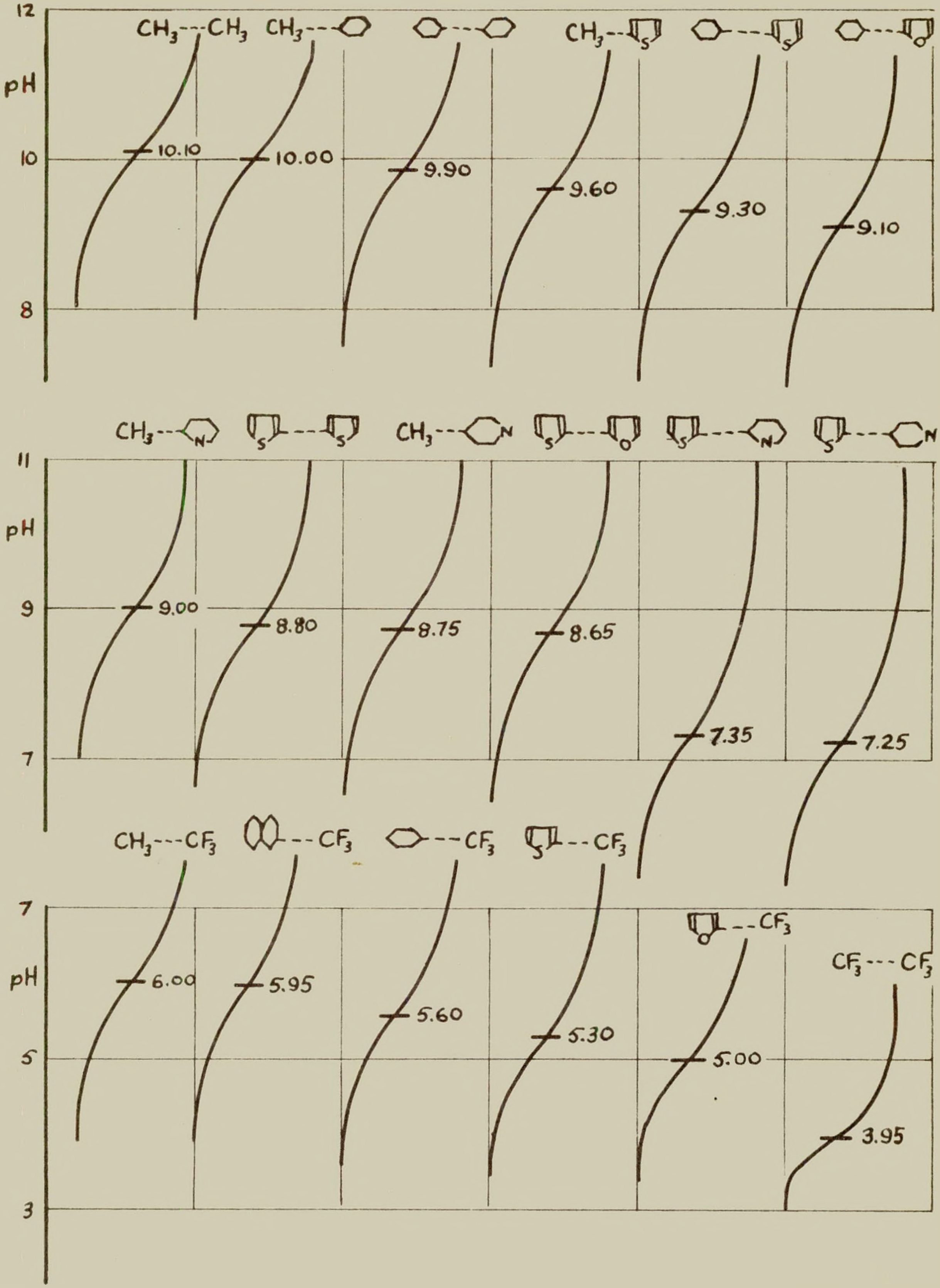
P-62-58

Graph 13


pH
11.5
11.0
10.5
10.0
9.5
9.0
0
2
6
10
14
18
22
10³ x equivalents per liter of NaCl or BaCl₂
⬡COCH₂CO⬡
CH₃COCH₂COCH₃
A
B
C

Graph 14

$\bar{n} = 0.5$ chelating agent titrations



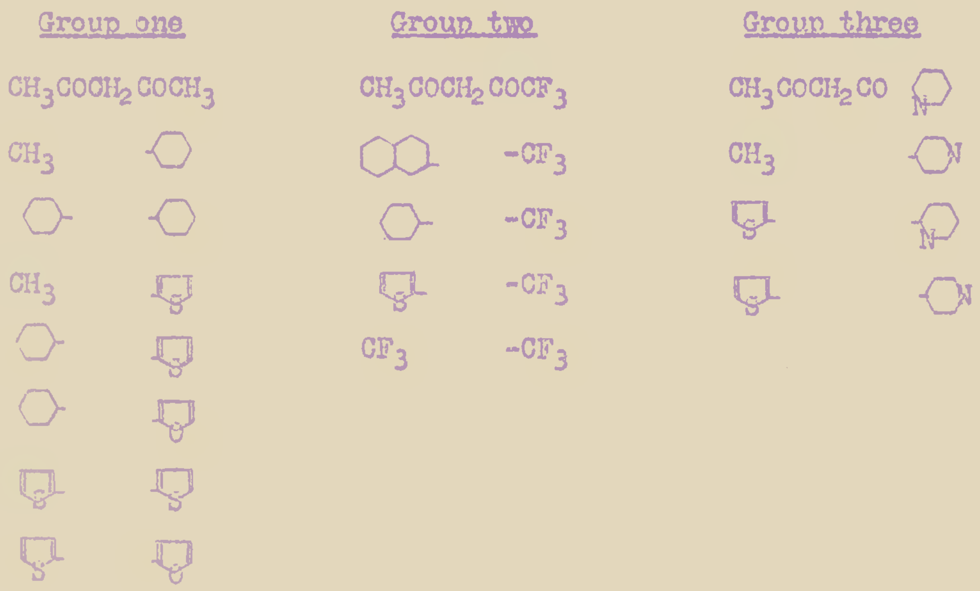
P-6r-60

Section 4

Beta-diketone Chelation Titrations with Copper

General:

The beta-diketones so far studied fall naturally into three groups in regards to their reactions under the conditions employed in these chelation titrations.



Group one:

These molecules have relatively large pK_d values and are quite stable towards acid or base in regards to hydrolysis. The di-ring-substituted molecules are generally insoluble in a 50-50 volume-percent water-dioxane solution. For this reason a 75 volume-percent dioxane solution was employed to study them.

Group two:

These molecules have relatively small pK_d values and are unstable in the presence of acid or base. The compounds hydrolize readily in the presence of 0.01 molar HCl, and therefore, special methods have been employed to gather information concerning them. These molecules are soluble in a 50-50 volume-percent water-dioxane solution but the copper chelate compounds formed by the ones containing six-membered rings are not soluble to any appreciable extent in this solution. Therefore, it was also necessary to study this group in a 75 volume-percent dioxane solution.

Group three:

The pyridyl compounds complicate the calculations and measurements necessary to determine their chelate compound formation constants inasmuch as the ring nitrogen picks up protons from solution. Study of the chelation characteristics of these compounds with the copper ion were not carried out due to an insufficiency in the quantities available of the diketones. The chelating abilities of these compounds along with those of group two can more advantageously be studied in the presence of the nickel ion. It is expected that the difficulties encountered in using copper as the metal ion for the chelation studies will be largely avoided for the following reason: the nickel ion has a much smaller chelating tendency than the copper ion and therefore will not combine as strongly with the above chelating agents. Chelation is nearly proportional to the amount of base added when the nickel ion is used. Also the pH is much higher during the chelation titrations. This should arrest hydrolysis in the case of the trifluro compounds and remove the difficulties encountered in calculating the chelate compound formation constants for the pyridyl compound.

P-62-62

Experimental Procedure

Group one:

The chelation titrations for this group were carried out as follows:

Mixtures of 75 ml. of dioxane, 25 ml. of H_2O, 1 x 10^{-3} moles (0.1705 gms.) of $CuCl_2 \cdot 2H_2O$ and 4 x 10^{-3} moles of chelating agent (KeH) were titrated with a 1.302 N solution of NaOH. A smooth titration curve was obtained in all cases except for that of dibenzoyl methane in which a pH drop coinciding with precipitation occurred. The graphs, titration data, and calculations for these curves are included in appendix D.

Group two:

The fact that the trifluro-beta-diketones hydrolize readily in small concentrations of acid or base can lead to erroneous conclusions as to the number of chelating groups associating themselves with a single metal ion inasmuch as CF_3COOH, one of the products of hydrolysis, is a strong acid and therefore is titrated over the same portion of the pH titration curve that ordinarily is considered to measure the extent of the chelation that has occurred. (See graph 15A). Notice that approximately three equivalents of protons were titrated before the rise in pH to the titration level of the excess chelating agent present. The broken curve outlines approximately the pH values that would have been read if hydrolysis had not occurred. It should also be noted that the copper dichelate formed at the lower level of the titration curve is hydrolized at an approximate pH of 10. The equivalents of base required to titrate this plateau shows that only 2 chelating groups coordinated per atom of copper and not three as

p-62-63

might be inferred from the stochiometry of the lower part of the curve. Sufficient acid to cause a fairly rapid hydrolysis of the chelating agents to occur is automatically produced in solution as soon as the diketones of this group and the copper ion are combined. In these cases approximately one-half of the total chelation occurs on mixing; this results in a 0.01 N HCl solution being produced.

It should be noted at this point that the trifluro-*beta*-diketones react with divalent copper ions much more rapidly than with sodium hydroxide. When a copper chloride solution is added to a trifluro-*beta*-diketone solution equilibrium, excluding hydrolysis, is obtained quickly. But when NaOH is added instead it generally takes a considerable length of time for the pH meter to indicate a final equilibrium. Hydrolysis does not occur in the last mentioned case since the trifluro-*beta*-diketones titrate close to a neutral pH. These observations tend to indicate that metal ions may combine with *beta*-diketones which are in the keto as well as enol form.

To avoid the effects of hydrolysis, the following (less exact) method for obtaining chelation data was employed: Mixtures of 75 ml. of dioxane and 4 x 10^{-3} moles of chelating agent were combined in the four-necked flask and the stirring motor started. The pH meter electrodes were then placed into the solution. To this was then added 25 ml. of a solution containing either (A) 25 ml. of H_2O and 1 x 10^{-3} moles of copper chloride; or (B) 23 ml. of H_2O, 2 ml. of 1.142 N HCl and 1 x 10^{-3} moles of copper chloride. The first "semi steady" pH reading was recorded. The value recorded was indicated by the pH meter within a few seconds after mixing and was the lowest pH value indicated by the meter. It was observed that the pH of the solution rose slowly to a value 0.1 to 0.2 pH units higher than the recorded value. The

P-62-64

reasons that the first "semi-steady" pH readings were chosen as the best values to employ in calculating the formation constants for these chelate compounds are as follows:

(a) To 75 ml. of dioxane contained in the titration apparatus was added a mixture of 23 ml. of H_2O and 2 ml. of 1.142 N NaOH. Result: The pH came to a steady value very quickly thus showing that stirring equilibrium is rapid, and that the electrodes respond quickly.

(b) To 75 ml. of dioxane and 4×10^{-3} moles of trifluroacetylacetone in the titration apparatus was added a mixture of 23 ml. of H_2O and 2 ml. of 1.142 N NaOH. Again the pH came to a steady value very quickly.

(c) If the copper ion only chelated with the enol form of the beta-diketone the slow conversion of the keto form to the enol form could only result in a larger hydrogen ion concentration and therefore a pH drop.

(d) Any slowness in mixing or chelating processes in general for these beta-diketones can only result in the pH decreasing.

The above facts rule out any explanation other than hydrolysis. Consider the following: The ionized chelating agent molecule Ke^- for these compounds has an almost equal attraction for H^+ and Cu^{++}.

$$CuKe^+ + H^+ \rightleftharpoons Cu^{++} + KeH$$

As KeH is removed from the solution by hydrolysis the above equilibrium shifts to the right causing a pH rise. The extent of this rise is limited by the dissociation of the acid produced in hydrolyzing the chelating agent.

It is believed that the pH values thus found will lead to approximately correct points on the calculated formation curve of the

P-62-65

copper dichelates.

The case for hexafluroacetylacetone was approached in the same manner as for the first group. Hexafluroacetylacetone does not chelate with copper ion readily and apparently is not as subject to hydrolysis as the trifluro compounds. (See graph 15B). The chelation titration for this compound (table 3D) required a considerable amount of time. This is related to the slowness of enolization of the trifluro and hexafluro compounds. For the trifluro compounds chelation was much faster than enolization, but for the hexafluro compound chelation appears to be a consequence of enolization and therefire is a much slower process. The calculation of the chelate compound formation constants for this compound must take in account the large value of K_d. The long formula developed in note 6 of section one is used to find $\bar{n}$ in this case. It should be noted (See graph 17 and table 4D) that chelation does not go beyond the first step before hydrolysis of the chelate compound begins.

P-62-66

Calculation of the Chelate Compound Formation Constants

In section three it was shown that the presence of divalent ions in solution depressed the pK_d value of a beta-diketone much more than the same number of equivalents of a monovalent ion. This of course results in an increase in the pK_d value of a chelating agent during a chelation titration up to the point ($\bar{n} = 1.0$) where all the divalent metal ions in a solution have been converted into monovalent (monochelated) ions. Beyond this point, dilution effects (increase in H_2O) will cause pK_d to decrease.

To avoid considering a varying K_d value in the chelate compound formation constants calculations, the calculations have been arranged to determine the difference in the tendency for the ionized chelating agent molecule Ke^- to combine with the copper ion and a proton. It has been assumed that the values so found will be nearly independent of the fluctuations in K_d. The same K_d value is then employed to determine the several formation constants. The K_d values employed in these calculations have been measured under the conditions of solvent composition and ionic strength which typically exist at the midpoint of the first chelation. That is to say where $\bar{n} = 0.5$ (See section 2, experiment C).

This series of K_d values is the most applicable for comparing the K_d values of the chelating agents with the first formation constants of the metal chelates. (See graph 18 and table 7D).

The ($\bar{n} = 0.5$) K_d values employed are "apparent" K_d values and are not strictly comparable as enol form K_d values would be, but they provide a satisfactory measurement of the average tendency for the

P. 62-67

chelating agent to give up a proton.

The calculation methods employed in this section will be a modification of those employed in section one. See note 6 of section one for the mathematical development.

Specifically:

$$\bar{n} = (Na^+ + H^+ - A)/T_{Cu^{++}}$$

Where:

$\bar{n}$ equals the average number of chelating agent molecules chelated with Cu^{++}.

Na^+ equals a constant factor times the number of equivalents of base that have been added.

H^+ equals the same factor times the number of equivalents of hydrogen ion present.

A equals the same factor times the number of equivalents of acid (if any) originally added.

$T_{Cu^{++}}$ equals the same factor times the number of moles of copper present in all forms.

Note that the factors cancel

at $\bar{n} = 0.5$

the formation constant $K_1 = (CuKe^+)/(Cu^{++})(Ke^-) = 1/Ke^-$

and at $\bar{n} = 1.5$

the formation constant $K_2 = (CuKe_2)/(CuKe^+)(Ke^-) = 1/Ke^-$

Therefore at

$\bar{n} = 0.5$ $\log K_1 = pKe^-$

and at $\bar{n} = 1.5$ $\log K_2 = pKe^-$

pKe^- is calculated from the previously determined dissociation constant and the ratio of the hydrogen ion concentration to the concentration of the chelating agent present.

p-62-68

$\log (H^+)/(KeH) \qquad pK_d = pKe^-$

at $\bar{n} = 0.5$ and $\bar{n} = 1.5$ log $(H^+)/(KeH)$ is equal to the log of the formation constant sought minus pK_d, or represents the difference in the tendencies of Ke^-, the ionized chelating agent molecule, to associate with a copper ion and a proton. These values are tabulated in table 7D.

The values for $\bar{n}$ and log H^+/KeH are solved for and graphed (see graph 17). The values for log H^+/KeH at $\bar{n} = 0.5$, $n = 1.0$, and $\bar{n} = 1.5$ are then determined from the graph and added to the value of pK_d to give log K_1, log K (av.), and log K_2.

Conclusions:

(1) It may be stated that in a general way the formation constants for the copper chelates have a fixed relationship to their respective chelating agent dissociation constants that is independent of the solvent medium. Referring to graph 18 the points for pK_d vs. log K will all fall approximately on the same line regardless of the water-dioxane ratio. The formation constants for different copper chelates which have been measured in different water-dioxane ratios may be compared provided the dissociation constant for each chelating agent is known for one solution.

(2) The order of increasing K's for the copper chelates is the same as the order of increasing pK_d for the chelating agents when the latter are measured under the same conditions as those that were present during the chelation titrations. The above is a tentative statement.

(3) The log H^+/KeH values plotted on graph 17 show that the larger a pK_d value a chelating agent has the greater is its combining perfer-

p.62-69

ence for a proton over the copper ion. Both tendencies, however, are increased. Hexafluroacetone is an exception.

(4) A plot of the first formation constant and the average formation constant of the copper chelate compounds considered in this thesis versus pK_d show the following relationships.

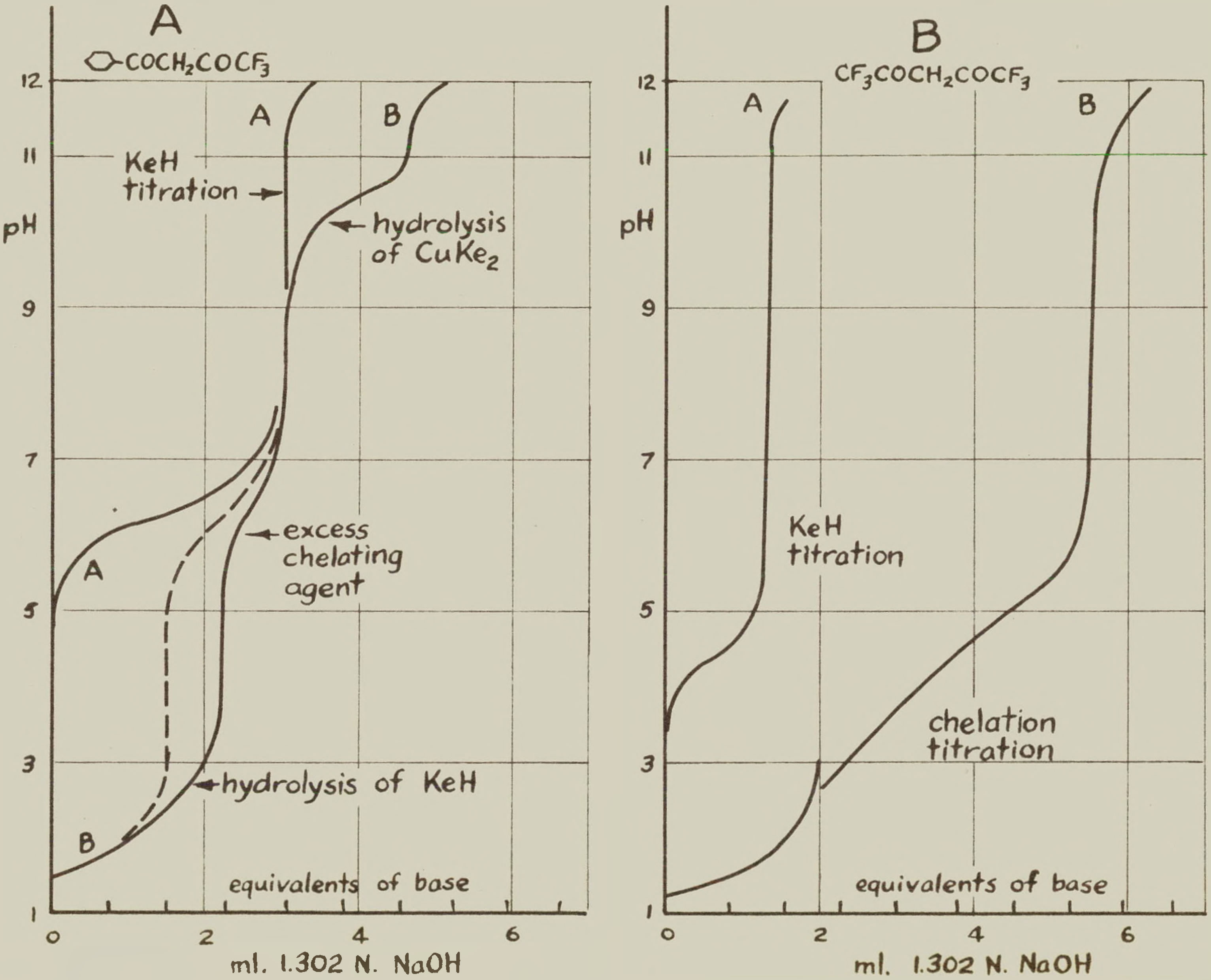
(a) The plot pK_d vs. log K (av) is a straight line. This indicates that the average chelating tendencies of the <u>beta</u>-diketones that have been considered are proportional to their formation constants.

(b) The plot pK_d vs. log K_1 is a curved line showing that as the pK_d value for a <u>beta</u>-diketone increases, pK_d/log K_1 increases. The change in the ratio is small for high pK_d values.

(5) A large initial chelation is an indication that the tendency for an ionized chelating agent molecule to coordinate a metal ion and to associate with a proton are nearly equal. This does not indicate that the chelating tendency is large in an absolute sense. This is general for the trifluro-<u>beta</u>-diketones.

The generalities that have been pointed out are derived from information that has been gathered so far and are not represented to be conclusive. Further work will substantiate or alter them as they are now given. Conclusions that may be drawn concerning matters that are more specific in nature have been made throughout this thesis in the sections with which they are concerned.

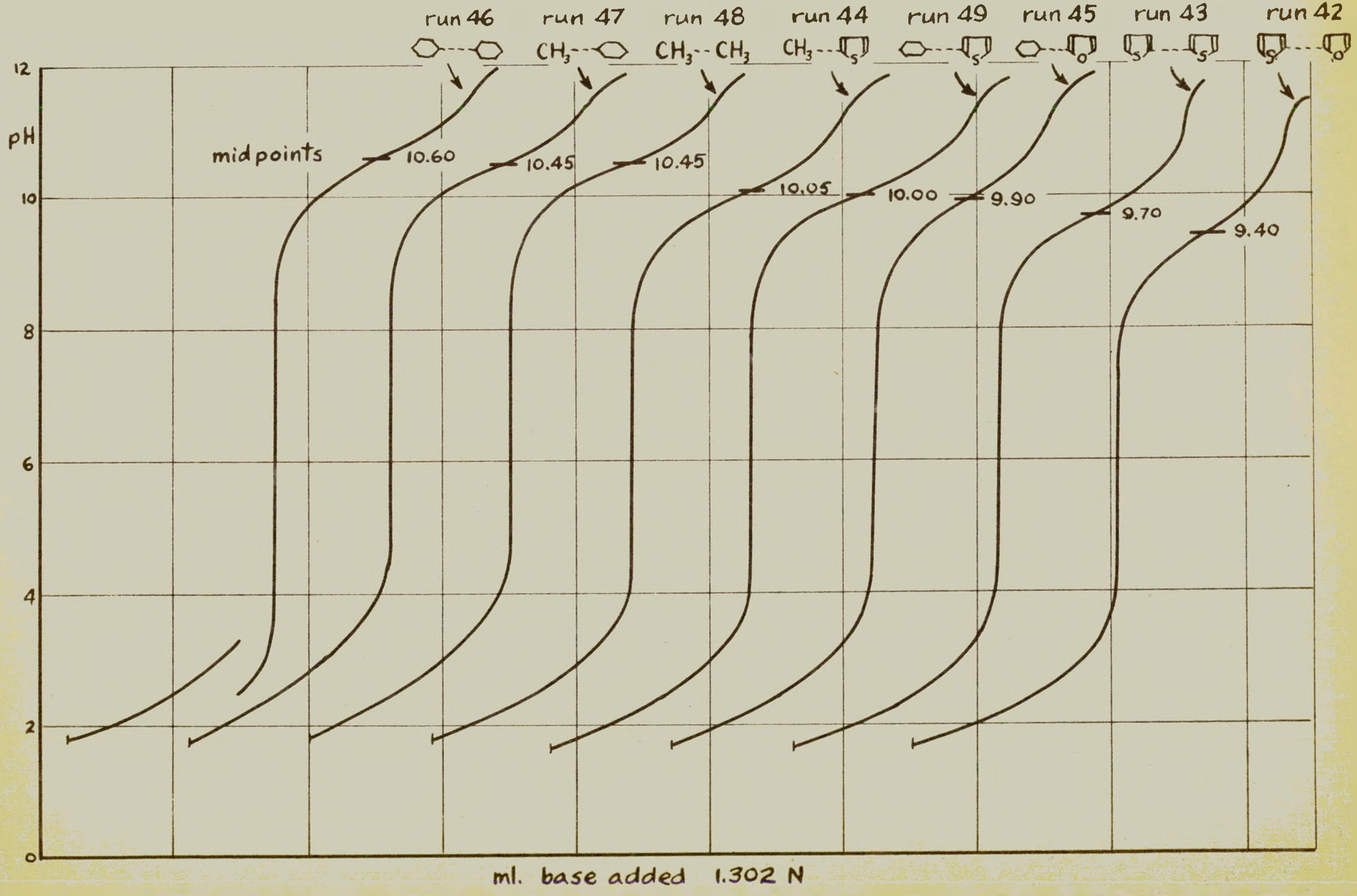
Graph 15



p-62.71

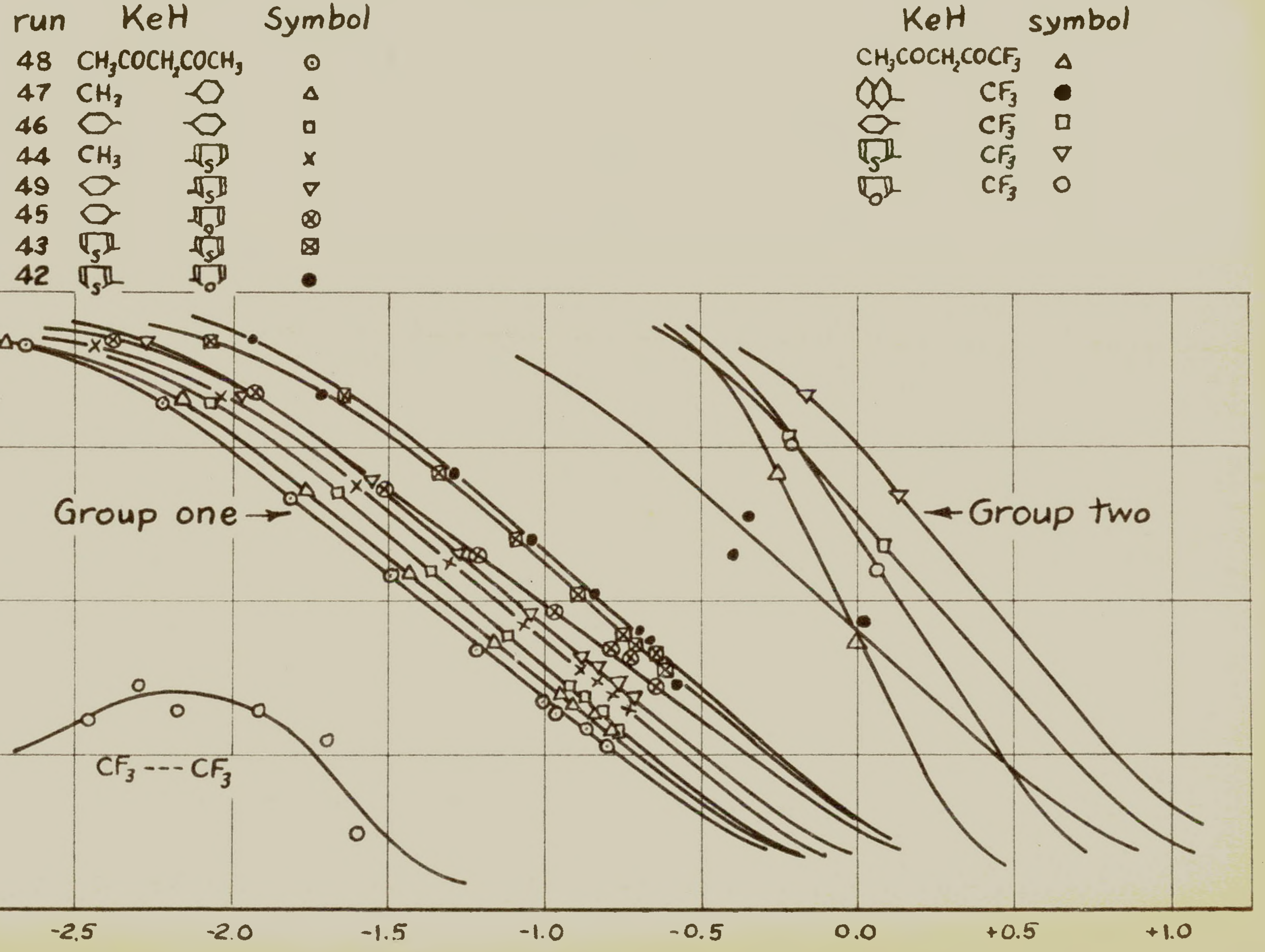
Graph 16

Group one chelation titrations

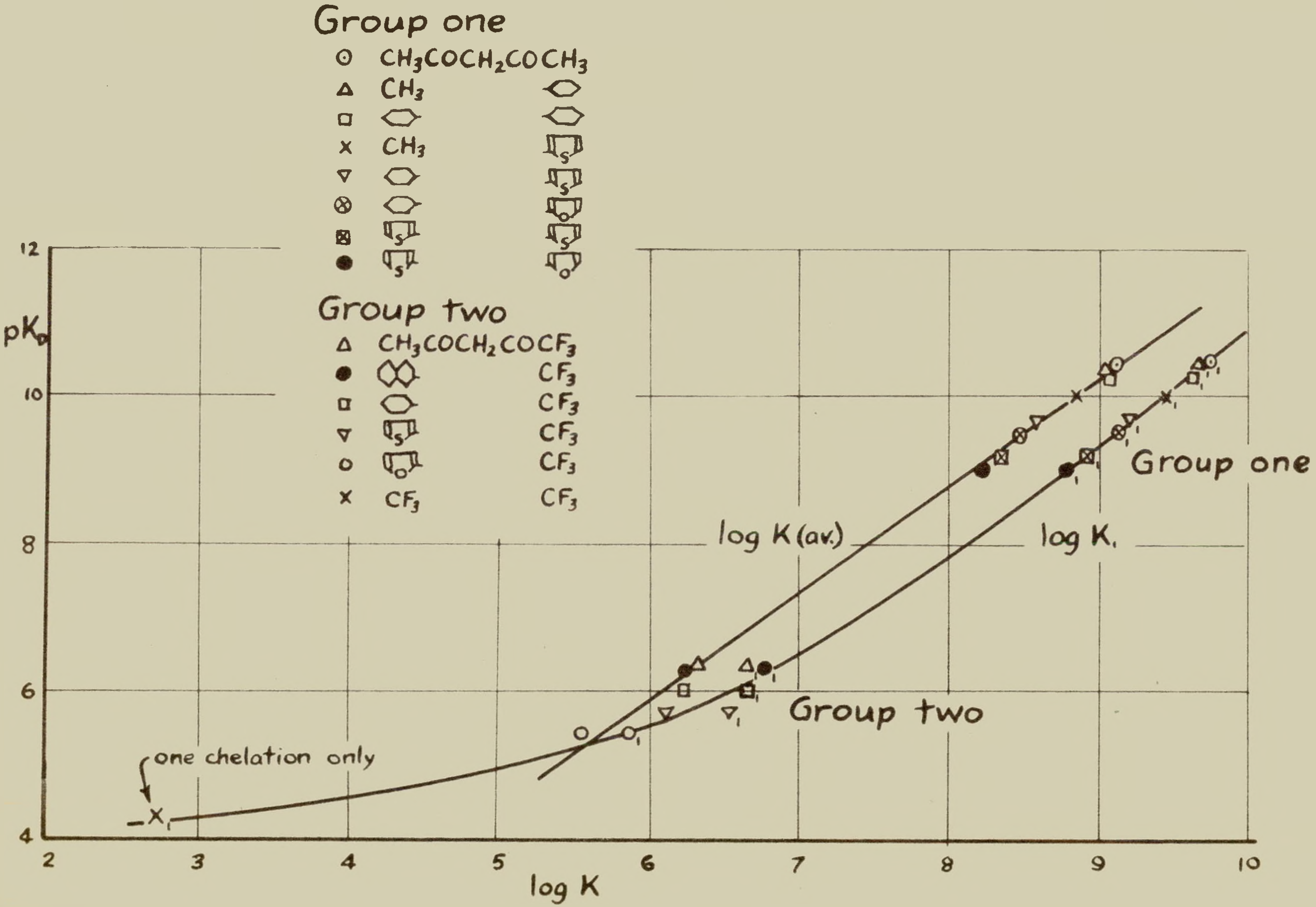


p. 62-72

Graph 17


run
KeH
Symbol
48
CH3COCH2COCH3
⊙
47
CH3
△
46
□
44
CH3
×
49
▽
45
⊗
43
⊠
42
●
KeH
symbol
CH3COCH2COCF3
△
CF3
●
CF3
□
CF3
▽
CF3
○
n̄
1.5
1.0
0.5
Group one
Group two
CF3 --- CF3
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
+0.5
+1.0

Graph 18


Group one
CH3COCH2COCH3
CH3
CH3
Group two
CH3COCH2COCF3
CF3
CF3
CF3
CF3
CF3
CF3
pKD
12
10
8
6
4
2
3
4
5
6
7
8
9
10
log K
log K (av.)
log K1
Group one
Group two
one chelation only

Summary

(1) The methods previously employed in titrating water-dioxane solutions have been examined and extended to solutions containing more than fifty volume-percent dioxane.

(2) The existence of compounds of the type $MKe_2 \cdot NaKe$ has been demonstrated.

(3) The chelating tendencies of several beta-diketones with copper have been determined and correllated with their respective dissociation constants.

(4) The influence of the end groups of beta-diketones have been demonstrated.

P-62-75

APPENDIX A

P-62-76

Table 1 A

Titration Data for Graph 4

50 ml. distilled H_2O
50 ml. dioxane
0.800 gms. Eastman Kodak acetylacetone 8 x 10^{-3}
0.3410 gms. Malenkrodt C.P. $CuCl_2 \cdot 2H_2O$ (2 x 10^{-3} mole)

The resulting pH for this mixture is 1.87

Time	Burette	Ml	pH	
4:28 p.m.	0.00	0.00	1.87	solution
4:32	0.05		1.88	green
	0.11		1.90	
4:37	0.27		1.92	
	0.50		2.00	
4:40	0.75		2.10	
	1.00		2.21	
	1.25		2.35	
	1.50		2.50	
	1.75		2.65	solution
5:00 p.m.	2.00	2.00	2.87	deep blue-green
8:15 p.m.			2.89	
overnite				
7:30 a.m.			2.89	no ppt.
				has formed
7:45 a.m.	2.25	2.00	2.89	0.25 ml. base
				drained off from
	250	2.25	3.11	burette
9:45 a.m.			3.00	the ppt. is now down
9:50	2.61	2.36	3.11	
11.45			3.09	
"	2.70	2.45	3.19	
12:30			3.15	
"	2.80	2.55	3.27	
1:10			3.25	
"	2.90	2.65	3.39	
1:55			3.37	
"	3.00	2.75	3.50	
2.30			3.50	
"	3.10	2.85	3.76	
2:40			3.71	
"	3.14	2.89	3.81	
2:55	3.20	2.95	4.10	
3:05			4.09	
3:10	3.25	3.00	4.78	
3.40			4.77	
3.43	3.30	3.05	7.30	
6:45	3.30	3.05	7.24	
"	3.40	3.15	8.29	
7:00	3.49	3.24	8.59	

P-6r-77

Table 1 A (continued)

Titration data for graph 4 (continued)

Time	Burette	Ml	pH
10:10	3.60	3.35	8.73
	3.70	3.45	8.90
	3.86	3.61	9.08
	3.98	3.73	9.17
	4.25	4.00	9.40
	4.50	4.25	9.55
	4.75	4.50	9.69
	5.00	4.75	9.81
	5.25	5.00	9.99
	5.50	5.25	10.15
	5.75	5.50	10.37
	6.00	5.75	10.72
	6.11	5.86	11.02
	6.20	5.99	11.36
	6.25	6.00	11.68
	6.30	6.05	11.78
	6.50	6.25	12.08
	6.75	6.50	12.21
	7.00	6.75	12.26
	7.25	7.00	12.29

Table 2 A

Data for the Chelate Formation Curve of Graph 7

2×10^{-3} M $CuCl_2$; 8×10^{-3} M acetylacetone

A	V	pH	$[H^+]$	H^+	$\bar{n}$	$\bar{n}'$	pKe^-	pKe'^-
0.00	101.	1.87	0.0135		0.683		9.010	
0.11	101.1	1.90	0.0126		0.710		8.985	
0.27	101.3	1.92	0.0120	0.0132	0.785	0.844	8.974	9.015
0.50	101.5	2.00	0.0100	0.0110	0.832	0.884	8.902	8.945
0.75	101.7	2.10	0.00794	0.00873	0.884	0.925	8.811	8.853
1.00	102.0	2.21	0.00616	0.00678	0.960	0.990	8.713	8.755
1.25	102.2	2.35	0.00449	0.0049	1.034	1.057	8.581	8.623
1.50	102.5	2.50	0.00310	0.00348	1.132	1.150	8.450	8.479
1.75	102.7	2.65	0.00224	0.00246	1.241	1.255	8.317	8.361
2.00	103.0	2.89	0.00128	0.00141	1.350	1.36	8.092	8.133
2.25	103.2	3.11	0.000775	0.000853	1.485	1.495	7.898	7.96
2.25	103.2	3.00	0.00100	0.00110	1.500	1.51	8.012	8.04
2.36	103.4	3.09	0.00081	0.00089	1.56	1.57	7.918	7.958
2.45	103.4	3.15	0.00071	0.00078	1.62	1.625	7.880	7.923
2.55	103.5	3.25	0.00053	0.00062	1.68		7.792	7.832
2.65	103.6	3.37	0.00043	0.00047	1.73		7.681	7.725
2.75	103.7	3.50	0.00032	0.00035	1.79		7.579	7.626
2.85	103.8	3.71	0.00019	0.00021	1.845		7.380	7.415
2.95	103.9	4.10	0.00008		1.92		7.000	7.04
3.00	104.0	4.77	0.00002		1.94		6.397	6.598
3.05	104.0	7.40	4×10^{-8}		1.95			

A = ml. 1.290 N base added

V = volume of solution

$[H^+]$ = hydrogen ion activity as indicated by the pH meter

H^+ = hydrogen ion concentration, assuming $U_H{}^+ = 1/1.1$

$\bar{n} = \bar{n}$ (using conc. = activity) $\bar{n} = \dfrac{\frac{A}{V} \times 1.290\ [H^+]}{2/V}$

$\bar{n}' = \bar{n}$ using conc. = activity x 1/1.1 $\bar{n} = \dfrac{\frac{A}{B} \times 1.290\ H^+}{2/V}$

$$pKe^- = \log \frac{[H^+]}{K_d \times 8/V}$$

$$pKe'^- = \log \frac{H^+}{K_d \times 8/V}$$

Table 3 A

Titration Data for the

1×10^{-3} M $CuCl_2$ and

4×10^{-3} M acetylacetone run (See graph 8)

No precipitation occurred on this run

Ml	pH
0.00	2.12
0.1	2.17
0.25	2.27
0.35	2.35
0.50	2.48
0.60	2.57
0.77	2.78
0.90	2.92
1.00	3.11
1.09	3.28
1.21	3.52
1.30	3.71
1.40	4.10
1.45	4.28
1.50	5.20
1.55	7.82
1.60	8.60
1.70	9.03
1.80	9.19
1.90	9.39
2.00	9.50
2.25	9.78
2.50	10.02
2.75	10.33
2.90	10.60
3.00	10.95
3.07	11.10
3.11	11.48
3.25	11.92
3.35	12.02

P-62-80

Table 4 A

Data for the 1×10^{-3} M $CuCl_2$ and 4×10^{-3} M acetylacetone Chelate Compound Formation Curve (graph 7)

Ml NaOH added	Vol.of Sln.	pH	* H^+	$\bar{n}$	$1/Ke^-$		pKe^-
0.00	101	2.12	8.33×10^{-3}	0.843	1.30	$\times 10^{-9}$	9.113
0.25	101.2	2.27	5.90×10^{-3}	0.920	0.955	"	8.979
0.50	101.5	2.48	3.63×10^{-3}	1.012	0.632	"	8.800
0.77	101.7	2.78	1.83×10^{-3}	1.180	0.307	"	8.486
1.00	102.0	3.11	8.51×10^{-4}	1.380	0.165	"	8.216
1.30	102.3	3.71	2.15×10^{-4}	1.698	0.0480	"	7.681
1.40	102.4	4.10	8.7×10^{-5}	1.810	0.0204	"	7.309
1.45	102.4	4.29	5.6×10^{-5}	1.879	0.0135	"	7.130
1.50	102.5	5.20	1.7×10^{-6}	1.939	3.71	$\times 10^{-3}$	7.611

* These values assume $U_{H^+} = 1/1.1$

Table 5 A

Values for K_2 curve found using $1/Ke = \frac{CuKe^+}{CuKe_2} \cdot K_2$

where K_2 is taken from graph 7;

$\frac{CuKe^+}{CuKe_2}$	$\bar{n}$	$\log \frac{CuKe^+}{CuKe_2}$	$\log K_2$	pKe^-
0.01	$\frac{201}{101} = 1.99$	-2	7.90	5.90
0.10	$\frac{21}{11} = 1.91$	-1	7.90	6.90
0.50	$\frac{5}{3} = 1.67$	-.3	7.90	7.60
1.00	$\frac{3}{2} = 1.50$	-0	7.90	7.90
2.00	$\frac{4}{3} = 1.33$	.3	7.90	8.20
5.00	$\frac{7}{6} = 1.17$	.7	7.90	8.60
10.00	$\frac{12}{11} = 1.09$	1.0	7.90	8.90

P-62-81

Table 5 A (continued)

Values for K_1 curve found using $\frac{1}{Ke^-} = \frac{Cu^{++}}{CuKe^+} \cdot K_1$

$\frac{Cu^{++}}{CuKe^+}$	$\bar{n}$	$\log \frac{Cu^{++}}{CuKe^+}$	$\log K_1$	pKe^-
0.01	$\frac{100}{101} = .99$	-2	9.55	7.55
0.1	$\frac{10}{11} = .91$	-1	9.55	8.55
0.5	$\frac{2}{3} = .67$	-.3	9.55	9.25
1.0	$\frac{1}{2} = .50$	0	9.55	9.55
2.0	$\frac{1}{3} = .33$	.3	9.55	9.85
5.0	$\frac{1}{6} = .167$	.7	9.55	10.25
10.0	$\frac{1}{11} = .091$	1.0	9.55	10.55

Table 6 A
(refer graph 7)

Precipitation curve using $U_{H^+} = 1/1.1$

Ml	NaOH	Amount pptd.	Total ppt.	Moles
(1)	2.25	0.0890 gms.	0.0890 gms.	0.34×10^{-3}
(2)	2.50	0.0744 gms.	0.1634 gms.	0.63×10^{-3}
(3)	2.75	0.0775 gms.	0.2409 gms.	0.92×10^{-3}
(4)	2.90	0.0461 gms.	0.2870 gms.	1.097×10^{-3}
(5)	3.00	0.0153 gms.	0.3023 gms.	1.16×10^{-3}

$\bar{n}$ values on the crystallization curve

(1) 1.51 (2) 1.65 (3) 1.79 (4) 1.88 (5) 1.94

Substituting into $\dfrac{T_{Ke^-} \ -2a}{T_{Cu^{++}} -a} = \bar{n}$

$$(1)\quad \frac{1.51 \times 2 \times 10^{-3} - .34 \times 10^{-3} \times 2}{a \times 10^{-3} - 0.34 \times 10^{-3}} = \frac{2.34}{1.66} = 1.41$$

$$(2)\quad \frac{1.65 \times 2 \times 10^{-3} - .63 \times 2 \times 10^{-3}}{2 \times 10^{-3} - 0.63 \times 10^{-3}} = \frac{2.04}{1.37} = 1.49$$

$$(3)\quad \frac{1.79 \times 2 \times 10^{-3} - .92 \times 2 \times 10^{-3}}{2 \times 10^{-3} - 0.92 \times 10^{-3}} = \frac{1.74}{1.08} = 1.61$$

$$(4)\quad \frac{1.88 \times 2 \times 10^{-3} - 1.097 \times 2 \times 10^{-3}}{2 \times 10^{-3} - 1.097 \times 10^{-3}} = \frac{1.57}{.903} = 1.74$$

$$(5)\quad \frac{1.94 \times 2 \times 10^{-3} - 1.16 \times 2 \times 10^{-3}}{2 \times 10^{-3} - 1.16 \times 10^{-3}} = \frac{1.56}{.84} = 1.86$$

	Crystal Curve $\bar{n}$	Sln. Curve $\bar{n}$	pKe^-
(1)	1.51	1.41	8.04
(2)	1.65	1.49	7.86
(3)	1.79	1.61	7.63
(4)	1.88	1.74	7.32
(5)	1.94	1.86	6.58

P-62-83

Table 7 A.

$Ni(acac)_2$ Titrations

(A) 25 ml. dioxane, 25 ml. H_2O, 2 ml. 0.500 molar $NiCl_2$ solution and 4 x 10^{-3} moles of acetylacetone, titrated with 1.302 N NaOH

Burette	pH	Burette	pH	Burette	pH	Burette	pH
0.00	2.88	0.80	5.11	1.55	7.52	2.40	8.40
0.10	3.35	0.90	5.30	1.60	7.70	2.60	9.28
0.20	3.65	1.00	5.60	1.70	8.21	2.75	9.60
0.30	3.92	1.11	5.88	1.80	8.50	2.95	10.30
0.40	4.12	1.21	6.10	drop to	7.05	3.00	11.05
0.50	4.38	1.30	6.30	1.90	7.10	3.05	11.50
0.60	4.62	1.40	6.57	2.00	7.20	3.10	11.70
0.70	4.87	1.50	7.18	2.20	7.55	3.26	12.00

(B) 50 ml. dioxane, 50 ml. H_2O, 2 ml. 0.500 molar $NiCl_2$ solution and 4 x 10^{-3} moles of acetylacetone, titrated with 1.302 N NaOH

Burette	pH	Burette	pH	Burette	pH	Burette	pH
0.00	3.10	1.50	7.35	2.15	9.27	2.75	9.86
0.25	3.89	1.55	7.80	2.25	9.40	2.91	10.26
0.50	4.50	1.65	8.20	2.40	9.60	3.00	10.65
0.75	5.18	1.75	8.65	2.50	9.71	3.05	10.85
1.00	5.78	1.90	8.90	drop to	9.15	3.10	11.35
1.25	6.35	2.00	9.05	2.65	9.57	3.15	11.72
						3.25	11.91

(C) Titration of filtrate from (B) after acidification to pH = 3.1

Burette	pH	Burette	pH	Burette	pH
0.00	3.10	0.70	10.05	1.00	11.80
0.10	4.98	0.75	10.15	1.13	12.00
0.20	6.12	0.80	10.47		
0.30	7.30	0.85	10.70		
0.40	8.94	0.90	11.35		
0.50	9.40	0.95	11.35		
0.60	9.71				

Table 8 A

One-half Chelation Titrations

Solution A: 2 x 10^{-3} M $CuCl_2$, 2 x 10^{-3} acetylacetone 50 ml. dioxane and 50 ml. H_2O titrated with 1.290 N NaOH

Burette	pH	Burette	pH
0.00	2.08	1.74	4.52
0.25	2.20	2.25	5.03
0.50	2.39	2.35	5.27
0.75	2.59	2.45	5.50
1.00	2.90	2.55	6.03
1.25	3.49	2.65	8.03
1.35	3.81	2.70	10.9
1.55	4.42		

Solution B: 2 x 10^{-3} M $CuCl_2$, 50 ml. dioxane, 50 ml. H_2O & HCl titrated with 1.302 N NaOH

Burette	pH	Burette	pH	Burette	pH
0.00	1.86	1.20	3.88	3.25	4.80
0.25	1.92	1.25	3.87	3.35	5.42
0.60	2.17	1.50	3.89	3.40	7.30
0.80	2.39	1.75	3.92	3.42	8.17
1.00	2.88	2.00	3.96	3.50	11.5
1.05	3.07	2.50	4.12	3.75	12.13
1.15	3.95	3.00	4.38		

Solution C: 2 x 10^{-3} M $CuCl_2$, 2 x 10^{-3} M benzoylacetone, 50 ml. dioxane & 50 ml. H_2O: - titrated with 1.290 N NaOH

Burette	pH	Burette	pH	Burette	pH
0.00	1.67	1.75	2.30	3.05	4.23
0.05	1.68	2.00	2.47	3.15	4.30
0.15	1.69	2.25	2.71	3.25	4.33
0.25	1.71	2.50	3.07	3.50	4.51
0.50	1.78	2.60	3.29	3.75	4.76
0.75	1.86	2.70	3.48	4.00	8.10
1.00	1.91	2.80	3.98	4.10	11.40
1.25	2.01	2.90	4.20	4.25	12.36
1.55	2.19	3.00	4.21		

P-62-85

APPENDIX B

Table 1 B
(See graph 11 A)

Solution (A) 49 ml. dioxane
2 ml. H_2O
1 ml. 1.142 N HCl

Solution (B) 51 ml. H_2O
1 ml. 1.142 N HCl pH = 1.70

Solution	pH	H^+	Vol % dioxane	UH^+
(A)			94.4	
4 ml. B	0.72	0.190	87.5	8.66
2	0.90	0.126	84.5	5.75
2	1.02	0.0955	81.9	4.36
2	1.12	0.0758	79.1	3.41
2	1.21	0.0616	76.8	2.81
2	1.28	0.0521	73.3	2.38
2	1.34	0.0457	72.2	2.08
2	1.40	0.0398	70.0	1.82
5	1.49	0.0324	65.4	1.48
5	1.53	0.0295	61.4	1.35
5	1.60	0.0251	57.6	1.15
5	1.63	0.0234	54.4	1.07
all.	1.69	0.0204	47.1	0.93
B	1.70	0.0200	00.0	

Table 2 B
(See graph 11 B)

Solution (A)		(B)	
	75 ml. dioxane		75 ml. dioxane
	25 ml. H_2O		25 ml. H_2O
	5×10^{-4} mole $BaCl_2$		5×10^{-4} mole $BaCl_2$
	1×10^{-3} mole NaCl		1×10^{-3} mole HCl

Solution	pH	moles H^+ x 10^3	V	$H^+ \times 10^3$	$[H^+] \times 10^3$	U_{H^+}
Sol. (A)	6.67					
& 2 ml. (B)	3.26	0.020	102	0.196	0.550	2.81
2	2.96	0.040	104	0.385	1.095	2.85
2	2.79	0.060	106	0.566	1.62	2.87
2	2.67	0.080	108	0.742	2.14	2.88
2	2.58	0.100	110	0.910	2.63	2.89
5	2.42	0.150	115	1.305	3.80	2.91
5	2.33	0.200	120	1.670	4.58	2.75
10	2.20	0.300	130	2.31	6.30	2.73
10	2.10	0.400	140	2.86	7.92	2.77
10	2.03	0.500	150	3.33	9.32	2.80
10	1.98	0.600	160	3.75	10.50	2.80
10	1.93	0.700	170	4.12	11.75	2.84

This last solution becomes solution (C)

Solution						
(B)	1.57	0.300	30	10.00	27.0	2.70
5 ml. (C)	1.60	0.321	35	9.20	25.0	2.72
10	1.68	0.362	45	8.04	20.9	2.60
10	1.71	0.403	55	7.34	19.5	2.66
10	1.75	0.444	65	6.83	17.0	2.62
10	1.77	0.485	75	6.47	17.0	2.63
25	1.80	0.588	100	5.88	15.8	2.70
50	1.84	0.796	150	5.31	14.4	2.72
all.	1.87	1.000	200	5.00	13.5	2.70

P-62-88

Tables 3B
(See graph 11 C)

Solution A: 150 ml. dioxane and 50 ml. H_2O

Solution B: 48 ml. of soln. (A) & 2 ml. 1.142 N HCl

Solution C: 48 ml. of soln. (A) & 2 ml. H_2O

Solution D: 48 ml. of soln. (A) & 2 ml. H_2O

Solution E: 48 ml. of soln. & 2 ml. 0.1160 N HCl & 2.052×10^{-3} M NaCl

Curve (B)

Solution	Vol.	Moles H^+ x 10^2	H^+	pH	$[H^+]$	1/2 Eci x 10^2	U_{H^+}
(C) 1 ml.							
(B)	51	0.00456	0.000895	2.49	0.00323	0.0895	3.61
1 ml. (B)	52	0.00912	0.001755	2.23	0.00589	0.175	3.35
2	54	0.0182	0.00338	2.00	0.0100	0.338	2.96
2	56	0.0274	0.00489	1.87	0.0135	0.489	2.76
2	58	0.0365	0.00630	1.80	0.0158	0.630	2.51
2	60	0.0456	0.00760	1.74	0.0182	0.760	2.40
5	65	0.0684	0.01050	1.61	0.0245	1.050	2.33
5	70	0.0912	0.01305	1.53	0.0292	1.305	2.23
10	80	0.1368	0.01710	1.48	0.0331	1.710	1.93
10	90	0.1824	0.0203	1.40	0.0397	2.03	1.96
(B)	50	0.2284	0.04580	1.17	0.0675	4.58	1.48

Curve (A)

Solution							
(D) 1 ml.							
(E)	51	0.000465	0.0000912	3.34	0.000456	0.0895	5.00
1 ml.	52	0.000930	0.000179	3.11	0.000776	0.175	4.34
2	54	0.001860	0.000345	2.89	0.001285	0.338	3.73
2	56	0.00279	0.000500	2.77	0.00170	0.489	3.40
2	58	0.00372	0.000641	2.68	0.00209	0.630	3.26
2	60	0.00465	0.000775	2.61	0.00245	0.760	3.16
5	65	0.00698	0.001070	2.51	0.00309	1.050	2.89
5	70	0.00930	0.001330	2.45	0.00355	1.305	2.67
10	80	0.01395	0.001745	2.36	0.00437	1.710	2.50
10	90	0.01861	0.00207	2.30	0.00503	2.03	2.43
all.	100	0.0232	0.00232	2.26	0.00550	2.29	2.37
E	50	0.0232	0.00465	2.09	0.0081	4.58	1.74

p-62-89

Table 4 B

Preface:

Solution (X): A solution consisting of 5×10^{-3} moles of NaCl dissolved in 125 ml. H_2O and 375 ml. dioxane. Divide solution (X) into 5 portions of 99 ml. each — these will be called solutions A, B, C, D, and E.

To solution A add 1 ml. of 0.1160 N HCl; here $H^+ = 1.160 \times 10^{-3}$ molar and $Cl^- = 0.01116$ molar.

To solution B add 2×10^{-3} moles of acetylacetone and .77 ml. of 1.302 1.302 N NaOH.

To solution C add 2×10^{-3} moles of benzoylacetone and .77 ml. of 1.302 N NaOH.

To solution D add 2×10^{-3} moles of triflureacetylacetone and .77 ml. of 1.302 N NaOH.

To solution E add 2×10^{-3} moles of thenoyltrifluroacetone and .77 ml. ml. of 1.302 N NaOH

The pH of each solution was measured both with a plain glass electrode and a Beckman type E glass electrode vs. a saturated calomel electrode. Potential measurements were also made on each solution by means of a hydrogen electrode and a silver-silver chloride electrode. Some difficulty was experienced in obtaining accurate readings with the hydrogen electrode therefore each solution was checked with two hydrogen electrodes and two silver-silver chloride electrodes.

The silver chloride electrodes were prepared by depositing Ag upon a no. 20 platinum wire from a $KAg(CN)_2$ solution for 7 hours with a current of one milliampere per electrode. They were then employed as anodes while electrolyzing a 0.75 N HCl solution for one hour at

P-62-90

a current of one milliampere per electrode.

For solution A: The Nernst equation is applied to determine E_0', (the E_0 for the cell employed in the given solution).

$$E = E_0' - 0.060 \log C_{H^+} - 0.060 \log C_{Cl^-}$$

The activity coefficients are considered to be unity for these calculations.

Since E_0' has been determined from solution (A), the rearranged Nernst equation

$$1/0.0600\ (E - E_0')\ \ \log C_{Cl^-} = pH$$

may be employed to determine pK_d in the remaining solutions.

Table 4 B

Solution	Added Constituent	pH(e)	pH(p)	Hydrogen electrode volts	
				E (1)	E (2)
(A)	HCl	2.52	2.52	0.360	0.360
(B)	$CH_3COCH_2COCH_3$	10.45	10.27	0.860	0.865
(C)	 $COCH_2COCH_3$	10.50	10.27	0.862	0.860
(D)	$CH_3COCH_2COCF_3$	6.66	6.66	0.618	0.615
(E)	 $COCH_2COCF_3$	6.50	6.50	0.620	0.620

From (A)

$$E = E_0' - 0.060 \log C_{H^+} - 0.060 \log C_{Cl^-}$$

$$.1360 = E_0' + 0.176 \qquad + 0.117 \qquad E_0' = 0.077 \text{ m.v.}$$

also from solution (A)

$U_{H^+} = 2.6$ therefore the correction 0.41 should be added to all pH values.

The concentration of (Cl^-) is 0.01 for the remaining solutions hence for each case,

$$1/0.0600\ \ (E - 0.077) - 2 = pH$$

p.62-91

Solution	pH (H_2)	pH (e)	pH (p)	(e)	(p)
B	11.1	10.86	10.68	-.25	-.42
C	11.1	10.91	10.68	-.19	-.42
D	7.0	7.07	7.07	+.07	+.07
E	7.05	6.91	6.91	-.14	-.14

pH (H_2) measured by the hydrogen electrode vs. AgCl; Ag electrode

pH (e) measured by the Beckman type E glass electrode

pH (p) measured by the Beckman plain glass electrode .

(e) pH (H_2) - pH(e)

(p) pH (H_2) - pH(p)

Table 5 B
(See graph 12 B & 12 C)

Two identical solutions (A) & (B) each containing 75 ml. dioxane, 25 ml. H_2O and 1×10^{-3} moles of dibenzoylmethane were titrated with 1.302 N NaOH. The pH measurements were made with a Beckman plain glass electrode for solution A and a Beckman type E glass electrode for solution B.

Solution (A)			Solution (B)	
Burette	pH	(E-P)	Burette	pH
0.00	6.70		0.00	6.80
0.05	10.70	0.14	0.05	10.84
0.11	10.90		0.10	11.14
0.18	11.10		0.15	11.20
0.25	11.19	0.26	0.25	11.45
0.30	11.22	0.28	0.30	11.50
0.35	11.31	0.30	0.35	11.61
0.41	11.40		0.40	11.68
0.45	11.45	0.35	0.45	11.80
0.50	11.52	0.37	0.50	11.89
0.55	11.59	0.41	0.55	12.00
0.60	11.71		0.61	12.20
0.66	11.80		0.65	12.33
0.70	12.00	0.70	0.70	12.70
0.75	12.21	0.87	0.75	13.08
0.77	12.49		0.77	off scale
0.80	12.65			
0.85	12.70			

The two titrations are plotted in graph 12 B and their difference is plotted in graph 12 C.

APPENDIX C

Table 1 C

(See graph 12 A)

Solution A	Solution B
50 ml. dioxane	118 ml. H_2O
9 ml. H_2O	3.1 ml. 1.302 N NaOH
1.55 ml. 1.302 N NaOH	8 x 10^{-3} mole acetylacetone
4 x 10^{-3} mole acetylacetone	

Solution	Volume-percent of dioxane	pH	estimated $\log U_{H^+}$	estimated total
(A)	82.7	10.67	0.72	11.4
5 ml (B)	76.3	10.58	0.48	11.1
5	70.9	10.50	0.32	10.8
5	66.2	10.40	0.23	10.6
5	62.0	10.25	0.14	10.4
5	58.5	10.14	0.08	10.2
5	55.3	10.04	0.04	10.1
5	52.3	9.95		9.95
5	49.8	9.87		9.87
10	45.1	9.74		9.74
15	40.0	9.60		9.60
20	34.0	9.48		9.48
20	30.2	9.37		9.37
solution B	100.0	8.95		8.95

measurements were made with a plain glass electrode

Table 2 C

(See graph 13)

Curve (A)

Solution A	Solution B
75 ml. dioxane	75 ml. dioxane
25 ml. H_2O	25 ml. H_2O
1×10^{-3} M acetylacetone	1×10^{-3} M acetylacetone
0.36 ml. 1.302 N NaOH	0.36 ml. 1.302 N NaOH
	2×10^{-3} M NaCl

Solution	pH	concentration of NaCl
A	10.88	0.00
5 ml (B)	10.85	(5/105) x .02 = 0.000953
5 ml	10.82	(10/110) " = 0.00182
10	10.78	(20/120) " = 0.00332
10	10.76	(30/130) " = 0.00462
25	10.70	(55/155) " = 0.00710

This mixture is solution (C)

45 ml solution (B)		0.02
	10.35	
10 ml (C)	10.40	(45 x .02 0.0071 x 10)/55 = 0.0177
10	10.42	(" " x 20)/65 = 0.0161
25	10.48	(" " x 45)/90 = 0.0136
25	10.50	(" " x 70)/115 = 0.0121
25	10.51	(" " x 95)/140 = 0.0112

P-62-96

Table 3 C
(See graph 13)

Curve (B)

Solution A	Solution B
75 ml. dioxane	75 ml. dioxane
25 ml. H_2O	25 ml. H_2O
1 x 10^{-3} M acetylacetone	1 x 10^{-3} M acetylacetone
0.36 ml. 1.302 N NaOH	0.36 ml. 1.302 N NaOH
	0.000917 M $BaCl_2$

Solution	pH	Normality of $BaCl_2$
(A)	10.89	0.00
(A) 1 ml. B	10.88	(1/101) x 0.000917 x 2 = 0.000183
1	10.86	(2/102) " = 0.000367
5	10.79	(7/107) " = 0.00120
5	10.71	(12/112) " = 0.00196
5	10.64	(17/117) " = 0.00266
10	10.50	(27/127) " = 0.00339
10	10.40	(37/137) " = 0.00495
10	10.30	(47/147) " = 0.00537
10	10.23	(57/157) " = 0.00665
10	10.17	(67/167) " = 0.00734
10	10.11	(77/177) " = 0.00798

This now is solution (C)

20 ml. sln.(B)	9.65	0.01834 = 0.01834
10 ml. (C)	9.76	(0.01834 x 20 0.00798 x 10)/ 30 = 0.01495
10	9.82	(" " " x 20)/ 40 = 0.0132
10	9.87	(" " " x 30)/ 50 = 0.0122
10	9.90	(" " " x 40)/ 60 = 0.0115
20	9.94	(" " " x 60)/ 80 = 0.0106
40	10.00	(" " " x 100)/120 = 0.00972

P-62-97

Table 4 C
(See graph 13)

Curve (C)

Solution A	Solution B
75 ml. dioxane	75 ml. dioxane
25 ml. H_2O	25 ml. H_2O
1 x 10^{-3} M dibenzoylmethane	1 x 10^{-3} M dibenzoylmethane
0.36 ml. 1.302 N NaOH	0.36 ml. 1.302 N NaOH
	1 x 10^{-3} M $BaCl_2$

Solution	pH	$BaCl_2$ (Normality)			
(A)	11.50	0.000			
(A) 2 ml.					
(B)	11.42	(2/102)	x 0.02	=	0.000392
3	11.27	(5/105)	"	=	0.000995
5	11.08	(10/110)	"	=	0.001815
5	11.90	(15/115)	"	=	0.00261
5	10.73	(20/120)	"	=	0.00334
5	10.55	(25/125)	"	=	0.00400
5	10.38	(30/130)	"	=	0.00463
10	10.10	(40/140)	"	=	0.00572
10	9.97	(50/150)	"	=	0.00666
10	9.86	(60/160)	"	=	0.00750

This now is solution C

30 ml.(B)	9.34	0.020			= 0.020
10 ml.(C)	9.41	(0.01 x 30	0.00375	x 10)/ 40	= 0.0166
10	9.46	("	"	x 20)/ 50	= 0.0150
10	9.50	("	"	x 30)/ 60	= 0.0137
25	9.57	("	"	x 5.5)/ 85	= 0.0119
50	9.63	("	"	x 10.5)/135	= 0.0103
50	9.68	("	"	x 15.5)/185	= 0.00952

P-62-98

Table 5 C

n = 0.5 Chelating agent titrations

The solutions titrated:

75 ml. dioxane

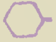
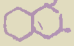
25 ml. H_2O

5×10^{-4} moles $BaCl_2$

5×10^{-4} moles NaCl

1×10^{-3} moles KeH

The solutions were titrated with 1.302 N NaOH. The value for the stochiometric midpoints are recorded.

Chelating group			measured pH	corrected for U_{H^+}
1	$CH_3COCH_2COCH_3$		10.10	10.50
2	CH_3		10.00	10.40
3			9.90	10.30
4	CH_3		9.60	10.00
5			9.30	9.70
6			9.10	9.50
7	CH_3		9.00	9.40
8			8.80	9.20
9	CH_3		8.75	9.15
10			8.65	9.05
11			8.35	8.75
12			8.25	8.65
13	CH_3	CF_3	6.00	6.40
14		CF_3	5.95	6.35
15		CF_3	5.60	6.00
16		CF_3	5.30	5.70
17		CF_3	5.00	5.40
18	CF_3	CF_3	3.95	4.35

$U_{H^+} = 2.7$ U_{H^+} correction = 0.41

The figures are rounded off to the nearest 0.05 pH units. The tabulated pH values are equal to the pK_d values for the <u>beta</u>-diketones.

See graph 4 and tables 7 B for the titration data.

Tables 6 C

(See graph 14)

$(\bar{n} = 0.5)$ Chelate compound titrations using the plain glass electrode

CH_3 ---	CH_3	CH_3 ---		 ---		CH_3 ---	
Burette	pH	Burette	pH	Burette	pH	Burette	pH
0.00	6.08	0.00	6.12	0.00	5.39	0.00	5.90
0.05	8.41	0.05	8.42	0.05	8.30	0.05	8.00
0.10	9.05	0.10	8.96	0.10	8.85	0.10	8.53
0.15	9.22	0.15	9.18	0.15	9.11	0.15	8.79
0.25	9.67	0.26	9.60	0.25	9.43	0.25	9.13
0.30	9.81	0.31	9.71	0.30	9.60	0.30	9.29
0.36	9.99	0.36	9.90	0.35	9.75	0.35	9.45
0.40	10.09	0.40	10.01	0.40	9.90	0.40	9.60
0.50	10.33	0.50	10.30	0.50	10.17	0.45	9.72
0.60	10.57	0.60	10.50	0.60	10.50	0.51	9.90
0.65	10.68	0.70	10.84	0.70	11.00	0.60	10.19
0.70	10.83	0.75	11.15	0.76	11.28	0.70	10.60
0.75	10.99	0.80	11.58	0.80	12.20	0.75	10.95
0.80	11.28					0.79	11.27
0.83	11.50					0.81	11.80

 ---		 ---		CH_3---		 ---	
Burette	pH	Burette	pH	Burette	pH	Burette	pH
0.00	5.75	0.00	4.85	0.00	5.28	0.00	5.27
0.05	8.00	0.05	7.67	0.05	7.80	0.05	7.42
0.10	8.31	0.10	8.10	0.10	8.14	0.10	7.81
0.15	8.55	0.15	8.40	0.16	8.40	0.15	8.05
0.25	8.92	0.25	8.77	0.25	8.67	0.25	8.40
0.30	9.10	0.30	8.91	0.30	8.80	0.30	8.55
0.35	9.22	0.35	9.08	0.35	8.95	0.35	8.71
0.40	9.32	0.40	9.24	0.40	9.10	0.41	8.88
0.45	9.52	0.45	9.42	0.50	9.45	0.46	9.03
0.50	9.64	0.53	9.68	0.60	9.87	0.50	9.19
0.60	10.02	0.60	9.97	0.70	10.51	0.60	9.58
0.70	10.37	0.65	10.21	0.73	10.97	0.70	10.14
0.75	10.80	0.70	10.70	0.75	12.08	0.75	11.00
0.78	11.80	0.75	11.81				
0.80	12.10	0.77	12.22				

Table 6 C (continued)

Burette	pH
0.00	5.35
0.05	7.20
0.10	7.78
0.15	8.03
0.26	8.38
0.31	8.50
0.35	8.59
0.40	8.78
0.45	8.90
0.49	9.00
0.60	9.34
0.71	9.78
0.75	10.11
0.78	10.70
0.80	11.80

Burette	pH
0.00	5.00
0.05	7.22
0.10	7.61
0.15	7.89
0.25	8.24
0.30	8.41
0.35	8.58
0.40	8.71
0.45	8.90
0.50	9.04
0.60	9.48
0.70	10.60
0.75	12.10

a ppt. drop to 10.50
occurred at 10.60

Tables 6 C (continued)

 --- 

Burette	pH
0.00	5.70
0.05	7.28
0.10	7.52
0.15	7.71
0.25	8.00
0.30	8.10
0.35	8.26
0.41	8.42
0.46	8.57
0.50	8.70
0.60	9.20
0.70	9.85
0.75	10.38
0.78	11.78

 --- 

Burette	pH
0.00	5.87
0.05	6.80
0.10	7.32
0.15	7.55
0.25	7.86
0.30	8.05
0.36	8.17
0.41	8.34
0.45	8.45
0.50	8.62
0.60	8.97
0.70	9.54
0.75	10.40
0.78	11.80

CH_3 --- CF_3

Burette	pH
0.00	3.72
0.05	4.55
0.10	5.14
0.15	5.40
0.25	5.69
0.30	5.85
0.35	6.00
0.42	6.15
0.50	6.40
0.60	6.75
0.70	7.48
0.72	8.50
0.77	12.10

 --- CF_3

Burette	pH
0.00	3.77
0.05	4.58
0.10	5.00
0.15	5.33
0.30	5.83
0.35	5.95
0.40	6.02
0.50	6.17
0.60	6.80
0.70	9.00
0.75	12.50

 --- CF_3

Burette	pH
0.00	3.50
0.05	4.30
0.10	4.60
0.15	4.95
0.25	5.32
0.35	5.55
0.40	5.69
0.50	5.90
0.60	6.24
0.70	6.70
0.75	7.40
0.80	12.00

 --- CF_3

Burette	pH
0.00	3.35
0.06	4.35
0.10	4.65
0.15	4.78
0.25	5.00
0.35	5.20
0.40	5.37
0.50	5.60
0.60	5.88
0.70	6.30
0.75	6.90
0.78	8.30

 --- CF_3

Burette	pH
0.00	3.57
0.05	3.90
0.10	4.24
0.15	4.45
0.25	4.70
0.35	4.95
0.40	5.10
0.50	5.36
0.60	5.70
0.70	6.40
0.76	8.25

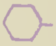
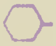
CF_3 --- CF_3

Burette	pH
0.00	3.20
0.05	3.50
0.15	3.68
0.25	3.80
0.38	3.94
0.55	4.22
0.72	4.75
0.75	8.00

P-62-102

Table 7 C

pK_d values measured under other conditions than $\bar{n} = 0.5$ values.

Chelating Groups		$1/2Ec_i$	measured pH	pH corrected for U_H	Volume-percent dioxane	Refer to chelation titration
 COCH$_2$CO		0.030	10.60	11.00	73.5	46
	CH$_3$	0.030	10.45	10.85	73.5	47
CH$_3$	CH$_3$	0.030	10.45	10.85	73.5	48
CH$_3$		0.021	10.10	10.55	73.8	
CH$_3$		0.030	10.05	10.45	73.5	44
		0.030	10.00	10.40	73.5	49
		0.030	9.90	10.30	73.5	45
		0.021	9.85	10.25	73.8	
		0.030	9.70	10.10	73.5	43
		0.030	9.40	9.80	73.5	42
CH$_3$		0.021	9.15	9.60	73.8	
		0.021	9.15	9.60	73.8	
	CF$_3$	0.020	6.75	7.20	73.8	
CH$_3$	CF$_3$	0.020	6.65	7.10	73.8	
	CF$_3$	0.020	6.35	6.80	73.8	
	CF$_3$	0.010	6.25	6.75	74.5	
	CF$_3$	0.020	5.80	6.25	73.8	
CF$_3$	CF$_3$	0.010	4.40	4.90	74.5	

The ions present at the point of determining pK_d are all monovalent for these measurements

U_{H^+} for $1/2\ Ec_i$ = 0.030 is 2.6 U_{H^+} correction = + 0.40
= 0.020 is 2.9 " = + 0.45
= 0.010 is 3.2 " = + 0.50

The pH measurements recorded above for the trifluro and pyridyl compounds were made at the point where $Ke^- = KeH$ for the chelating agent titrations. There was no extra electrolyte added when the trifluro compounds were titrated, but 1.1×10^{-3} moles of HCl was added when the pyridyl compounds were titrated.

P-62-103

APPENDIX D

P-62-104

Table 1 D

Trifluro Compound Hydrolysis

Solution: Curve A

75 ml. dioxane, 25 ml. H_2O, 4 x 10^{-3} moles of benzoyltrifluroacetone.

Solution: Curve B

75 ml. dioxane, 25 ml. H_2O, 4 x 10^{-3} moles of benzoyltrifluroacetone and 1 x 10^{-3} moles of copper chloride.

Both solutions were titrated with 1.302 N NaOH

Curve A		Curve B		
Burette	pH	Burette	pH	
0.00	4.60	0.00	1.54	solution leaf green
0.05	5.40	0.10	1.59	
0.17	5.75	0.25	1.65	
0.25	5.80	0.50	1.78	
0.50	5.98	0.75	1.93	
0.75	6.10	1.05	2.09	
1.00	6.15	1.50	2.40	
1.50	6.33	2.00	3.10	
2.00	6.58	2.25	5.50	5.26 ppt. coming down light green in color
2.50	6.91	2.35	5.80	
2.75	7.20	2.52	6.30	
2.80	7.34	2.75	6.76	
2.87	7.48	2.85	7.11	
3.00	8.10	3.00	8.10	
3.05	9.70	3.10	9.30	
3.26	11.95	3.20	9.79	
3.35	12.01	3.30	10.10	
		3.50	10.28	ppt. dissolving; the solution is becoming clearer and more blue; $Cu(OH)_2$ forming.
		3.75	10.41	
		4.00	10.54	
		4.50	10.74	
		4.75	11.67	sln. deep brown in color; hydrous copper oxide forming
		5.00	11.97	
		5.10	12.00	

As a general rule the trifluro-<u>beta</u>-diketone copper chelate hydrolyze around a pH of 10.

P-62-105

Table 2 D

The formation constant calculations for the trifluro-<u>beta</u>-diketones.

R = The end group other than $-CF_3$

Group A:

25 ml. H_2O and 1×10^{-3} M $CuCl_2$ added to 75 ml. dioxane and 4×10^{-3} moles of chelating agent.

Group B:

23 ml. H_2O, 2 ml. 1.142 N HCl, and 1×10^{-3} M $CuCl_2$ added to 75 ml. dioxane and 4×10^{-3} moles of chelating agent.

Group B - $U_{H^+} = 2.35$

R	pH	H^+	A	$\bar{n}$	KeH	log H^+/KeH
	1.12	0.0321	0.0228	0.93	0.0307	0.018
	1.13	0.0315	0.0228	0.87	0.0313	0.000
CH_3	1.13	0.0315	0.0228	0.87	0.0313	0.000
	1.09	0.0345	0.0228	1.17	0.0283	0.086
	1.07	0.0362	0.0228	1.34	0.0266	0.133
	1.10	0.0338	0.0228	1.10	0.0290	0.064

Group A - $U_H = 2.7$

R	pH	H^+	$\bar{n}$	KeH	log H^+/KeH
	1.48	0.0123	1.23	0.0278	- 0.355
	1.51	0.0115	1.15	0.0286	- 0.397
CH_3	1.42	0.0141	1.41	0.0259	- 0.264
	1.39	0.0151	1.51	0.0249	- 0.218
	1.35	0.0165	1.65	0.0235	- 0.152
	1.39	0.0151	1.51	0.0249	- 0.216

Table 3 D

Hexafluroacetone

Solution:

Curve A: 75 ml. dioxane, 25 ml. H_2O, 1.7 x 10^{-3} mole hexafluroacetone.

Curve B: 75 ml. dioxane, 23 ml. H_2O, 2 ml. 1.142 N HCl, 1 x 10^{-3} mole $CuCl_2$ and 3.4 x 10^{-3} mole hexafluroacetone.

Titrate with 1.302 N NaOH

See graph 5 B

Curve A		Curve B		Curve B (cont.)	
Burette	pH	Burette	pH	Burette	pH
0.00	3.42	0.00	1.27	3.00	3.70
0.05	3.82	0.25	1.32	3.25	3.95
0.10	3.98	0.50	1.39	3.50	4.20
0.20	4.10	0.75	1.49	3.75	4.41
0.30	4.20	1.00	1.59	4.00	4.65
0.50	4.34	1.25	1.73	4.25	4.82
0.75	4.50	1.50	1.92	4.50	5.11
1.00	4.78	1.75	2.24	4.75	5.25
1.25	5.65	2.00	2.98 2.73	5.00	5.45
1.40	11.55	2.25	2.87 drop	5.51	8.70
1.50	11.74	2.50	3.21	5.75	11.20
		2.75	3.49	6.00	11.70

Table 4 D

Chelate compound formation data using $U_H = 2.3$ log. $K_d = 4.35$ and $\bar{n} = [Na^+ - A{+}H^+ - \frac{Kw}{H^+} - \frac{K_d}{H^+}(T_{KeH^+} A - Na^+ - H^+ + \frac{Kw}{H^+}]/T_{Cu^{++}}$

The KeH values above pH 3 were determined from $T_{KeH} - Na^+ + A \cong KeH$

P-62-107

Table 4 D (continued)

ml Base	V	Na^+	A	pH	H^+	Kd/H^+
2.00	101	0.0258	0.0226	2.73	0.00081	0.0553
2.25	101	0.0294	0.0226	2.87	0.00059	0.0765
2.50	101.5	0.0321	0.0225	3.21	0.00029	0.156
2.75	101.7	0.0350	0.0224	3.59	0.00014	0.319
3.00	102	0.0383	0.0224	3.70	0.000087	0.515
3.25	102	0.0415	0.0224	3.95	0.0000487	0.920

$T_{Cu^{++}}$	$\bar{n}$	KeH	H^+/KeH	log H^+/KeH
0.0099	0.23	0.0314	0.0258	- 1.59
0.0099	0.54	0.0283	0.0209	- 1.68
0.0098	0.63	0.0239	0.0121	- 1.92
0.0098	0.63	0.0207	0.0068	- 2.17
0.0097	0.72	0.0174	0.0050	- 2.30
0.0097	0.61	0.0142	0.0034	- 2.46

Hexafluroacetone Titrations Description

(See table 3 D and graph 5 B)

Curve A:

This compound has the largest K_d value of the flourine <u>beta</u>-diketones studied. In spite of this it is one of the slowest to react with NaOH.

It requires over three hours to titrate 2 x 10^{-3} moles of the material by itself with 1.302 N NaOH.

Upon adding base to the solution the pH rises immediately to 7 then falls, after a few seconds, quickly at first, then progressively less rapidly toward an equilibrium value. The solution of this compound stays at high pH values much longer then the other solutions titrated, before dropping occurs.

Curve B: The chelation titration-

There is no apparent chelation at the start of this run. The color of the initial solution is that which would be expected for copper chloride alone.

The additions of 1.302 N NaOH over the first 1.75 ml. of the titration resulted in the quick establishment of equilibrium, almost instantaneous. This part of the titration is principally an acid-base reaction. Upon adding the ml. = 2.00 addition of base pH dropping occurred. The solution required better than two hours to come to equilibrium. The next addition was given overnite to come to equilibrium and the following ones approximately two hours apiece. These long period intervals were characterized by the following cycle:

1. Base is added.

2. $Cu(OH)_2$ precipitates in highly dispersed form.

3. The pH meter indicates a very slowly dropping pH as long as the precipitate is present, but as the solution clears the pH reading drops more rapidly.

4. The solution, after clearing, has changed from the former copper blue color to a green tint.

5. Equilibrium is established in about an additional 15 minutes. Beyond the ml. = 3.5 base addition, the solution no longer becomes completely clear.

The precipitate at all points appears to be a mixture of the chelate and hydroxide.

The chelation curve is continuous with the chelating agent titration curve and the copper chelate hydrolysis curve.

At ml. 4.5 the precipitate becomes more blue in color showing definite increase in hydrolysis.

Beyond ml. NaOH = 3.5 hydrolysis is evidently prevalent along with the titration of the excess ketone.

The titration was continued up to a pH of 11.9. Upon adding the ml. = 5.75 addition of base the pH rose to 11.5 falling to 11.2 overnite. Even at the pH of 11.9 there was no decomposition to the hydrous oxide of copper as has occurred in other cases. The cloudy precipitate still maintains a blue-green tinge showing that a tendency toward chelation still persists.

P.62-100

Table 5 D

Titrations - group one

(See graph 6)

Run 42 - 2-thenoyl-2-furoylmethane

Burette	pH	Burette	pH
0.00	1.69	1.60	8.30
0.12	1.74	1.75	8.79
0.20	1.79	2.00	9.20
0.25	1.82	2.25	9.51
0.50	2.00	2.50	9.80
0.75	2.24	2.75	10.50
1.00	2.53	2.85	11.25
1.25	2.99	2.90	11.50
1.40	3.49	3.02	11.61
1.50	5.62		
1.55	7.88		

$T_{KeH} = 3.65 \times 10^{-3}$ mole

Run 43 - di-2-thenoylmethane

Burette	pH	Burette	pH
0.00	1.69	1.60	8.50
0.10	1.72	1.70	8.90
0.20	1.79	1.80	9.13
0.25	1.82	2.00	9.40
0.50	2.00	2.25	9.69
0.75	2.21	2.50	9.97
1.00	2.50	2.75	10.30
1.25	2.88	2.85	10.52
1.40	3.33	2.95	10.99
1.50	4.29	3.00	11.43
1.55	7.69	3.10	11.72
		3.25	11.86

$T_{KeH} = 3.90 \times 10^{-3}$ mole

Run 44 - 2-thenoylacetone

Burette	pH	Burette	pH
0.00	1.77	1.75	9.33
0.10	1.83	2.00	9.75
0.20	1.89	2.25	10.00
0.26	1.95	2.50	10.23
0.50	2.15	2.75	10.50
0.75	2.41	2.90	10.72
1.00	2.75	3.00	10.95
1.25	3.25	3.10	11.22
1.40	3.68	3.20	11.60
1.50	4.04	3.50	11.80
1.55	8.55		
1.60	8.83		

Run 45 - benzoyl-2-furoylmethane

Burette	pH	Burette	pH
0.00	1.72	1.75	9.20
0.20	1.82	2.02	9.67
0.26	1.88	2.25	9.95
0.50	2.09	2.50	10.25
0.75	2.37	2.75	10.72
1.00	2.70	2.85	11.11
1.26	3.19	2.95	11.60
1.40	3.68	3.00	11.65
1.50	4.41	3.25	11.83
1.57	8.10		
1.70	8.79		

$T_{KeH} = 3.78 \times 10^{-3}$ mole

Table 5 D (continued)

Titration - group one

Run 46 - dibenzoylmethane

Burette	pH	Burette	pH
0.00	1.80	1.60	9.27
0.10	1.86	1.70	9.77
0.20	1.93	1.75	9.84
0.25	1.98	2.00	10.29
0.50	2.20	2.25	10.50
0.75	2.48	2.50	10.73
1.00	2.81	2.75	11.00
1.27	3.27	3.00	11.60
1.40	2.79	3.15	11.92
1.50	3.39	3.25	12.00
1.55	4.88		

ppt. formed at ml. = 1.27
pH dropped to 2.50

Run 47 - benzoylacetone

Burette	pH	Burette	pH
0.00	1.81	1.60	9.47
0.10	1.87	1.75	9.83
0.20	1.97	2.00	10.17
0.25	2.00	2.25	10.40
0.50	2.25	2.50	10.59
0.75	2.56	2.75	10.83
1.00	2.92	2.88	11.10
1.25	3.42	3.00	11.27
1.40	3.97	3.10	11.60
1.50	8.53	3.20	11.76
1.55	9.04	3.35	11.83

Run 48 acetylacetone

Burette	pH	Burette	pH
0.00	1.83	1.61	9.29
0.10	1.90	1.75	9.83
0.20	2.00	2.00	10.16
0.25	2.04	2.25	10.37
0.50	2.29	2.50	10.57
0.75	2.59	2.75	10.81
1.00	2.95	3.01	11.27
1.25	3.42	3.10	11.65
1.40	3.90	3.20	11.79
1.50	5.43		
1.55	9.10		

Run 49 - benzoyl-2-thenoylmethane

Burette	pH	Burette	pH
0.00	1.74	1.60	9.03
0.10	1.79	1.75	9.48
0.20	1.87	2.00	9.78
0.25	1.90	2.25	9.98
0.50	2.11	2.50	10.18
0.75	2.38	2.75	10.42
1.00	2.67	3.00	10.71
1.25	3.13	3.10	10.97
1.40	3.49	3.20	11.31
1.50	4.30	3.25	11.47
1.55	8.60		

$T_{KOH} = 4.18 \times 10^{-3}$ mole

R-62-112

Table 6 D

Group one chelate compound formation constants calculations

For these runs $U_{H^+} = 2.70$

Run 42 - 2-thenoyl-2-furoylmethane

ml. Base	V	Na^+	pH	H^+	$T_{Cu^{++}}$	$\bar{n}$
0.00	100.0	0.000	1.69	0.00755	0.0100	0.755
0.20	100.2	0.00260	1.79	0.00600	0.00998	0.862
0.25	100.2	0.00325	1.82	0.00559	0.00998	0.886
0.50	100.5	0.00648	2.00	0.00370	0.00996	1.02
0.75	100.7	0.00970	2.23	0.00215	0.00994	1.19
1.00	101.0	0.01290	2.53	0.00109	0.00990	1.41
1.25	101.2	0.01608	2.99	0.00038	0.00988	1.66
1.40	101.4	0.01800	3.49	0.00020	0.00986	1.85

T_{KeH}	KeH	log H^+/KeH
0.0365	0.0290	- 0.584
0.0364	0.0278	- 0.665
0.0364	0.0276	- 0.694
0.0363	0.0261	- 0.848
0.0362	0.0244	- 1.052
0.0361	0.0221	- 1.305
0.0360	0.0195	- 1.713
0.0360	0.0178	- 1.950

Run 43 - di-2-thenoylmethane

ml. Base	V	Na^+	pH	H^+	$T_{Cu^{++}}$	$\bar{n}$
0.00	100.0	0.000	1.69	0.00756	0.01000	0.756
0.10	100.1	0.00130	1.72	0.00705	0.00999	0.836
0.20	100.2	0.00260	1.79	0.00600	0.00998	0.862
0.25	100.2	0.00325	1.82	0.00560	0.00998	0.887
0.50	100.5	0.00648	2.00	0.00370	0.00996	1.02
0.75	100.7	0.00970	2.21	0.00228	0.00994	1.20
1.00	101.0	0.001290	2.50	0.00117	0.00990	1.42
1.25	101.2	0.01608	2.88	0.00049	0.00988	1.67
1.40	101.4	0.01800	3.33	0.00017	0.00987	1.84

T_{KeH}	KeH	log H^+/KeH
0.0390	0.0314	- 0.619
0.0390	0.0306	- 0.647
0.0389	0.0303	- 0.703
0.0389	0.0301	- 0.738
0.0388	0.0286	- 0.888
0.0387	0.0267	- 1.067
0.0386	0.0245	- 1.319
0.0385	0.0219	- 1.649
0.0385	0.0203	- 2.069

Table 6 D (continued)

Run 44 - 2-thenoylacetone

ml. Base	V	Na^+	pH	H^+	$T_{Cu^{++}}$	$\bar{n}$
0.00	100.0	0.000	1.77	0.00630	0.01000	0.63
0.10	100.1	0.00130	1.83	0.00550	0.00999	0.68
0.20	100.2	0.00260	1.89	0.00480	0.00998	0.74
0.26	100.2	0.00338	1.95	0.00415	0.00998	0.75
0.50	100.5	0.00648	2.15	0.00263	0.00996	0.91
0.75	100.7	0.00970	2.41	0.00147	0.00994	1.13
1.00	101.0	0.01290	2.75	0.000646	0.00991	1.38
1.25	101.2	0.01608	3.25	0.000207	0.00988	1.65
1.40	101.4	0.01800	3.67	0.000078	0.00987	1.82

T_{KeH}	KeH	log H^+/KeH
0.0400	0.0337	- 0.728
0.0400	0.0332	- 0.779
0.0399	0.0325	- 0.832
0.0399	0.0324	- 0.892
0.0398	0.0307	- 1.066
0.0397	0.0285	- 1.284
0.0396	0.0261	- 1.604
0.0395	0.0232	- 2.049
0.0395	0.0214	- 2.438

Run 45 - benzoyl-2-furoylmethane

ml. Base	V	Na^+	pH	H^+	$T_{Cu^{++}}$	$\bar{n}$
0.00	100.0	0.000	1.72	0.00702	0.0100	0.70
0.20	100.2	0.00260	1.82	0.00560	0.00998	0.82
0.26	100.3	0.00338	1.88	0.00489	0.00997	0.82
0.50	100.5	0.00648	2.09	0.00300	0.00996	0.95
0.75	100.7	0.00970	2.37	0.00158	0.00994	1.13
1.01	101.0	0.01300	2.73	0.00069	0.00990	1.32
1.26	101.3	0.01620	3.19	0.00024	0.00988	1.66
1.40	101.4	0.01800	3.68	0.00078	0.00987	1.83

T_{KeH}	KeH	log H^+/KeH
0.0378	0.0308	- 0.642
0.0377	0.0295	- 0.721
0.0377	0.0294	- 0.779
0.0376	0.0281	- 0.970
0.0375	0.0262	- 1.22
0.0374	0.0237	- 1.54
0.0373	0.0209	- 1.94
0.0373	0.0192	- 2.39

Table 6 D (continued)

Run 46 - dibenzoylmethane

ml. Base	V	Na^+	pH	H^+	$T_{Cu^{++}}$	$\bar{n}$
0.00	100.0	0.000	1.80	0.00584	0.01000	0.584
0.10	100.1	0.00130	1.86	0.00511	0.00999	0.642
0.20	100.2	0.00260	1.93	0.00435	0.00998	0.697
0.25	100.2	0.00325	1.98	0.00388	0.00997	0.715
0.50	100.5	0.00648	2.20	0.00234	0.00996	0.886
0.75	100.7	0.00970	2.48	0.00122	0.00994	1.10
1.00	101.0	0.01290	2.81	0.00057	0.00991	1.35
1.25	101.2	0.01620	3.27	0.00020	0.00988	1.66

T_{KeH}	KeH	log H^+/KeH
0.0400	0.0342	- 0.767
0.0400	0.0336	- 0.814
0.0399	0.0330	- 0.879
0.0399	0.0328	- 0.924
0.0398	0.0310	- 1.12
0.0397	0.0288	- 1.37
0.0396	0.0261	- 1.66
0.0395	0.0231	- 2.06

Run 47 - benzoylacetone

ml. Base	V	Na^+	pH	H^+	$T_{Cu^{++}}$	$\bar{n}$
0.00	100.0	0.000	1.81	0.00574	0.01000	0.574
0.10	100.1	0.00130	1.87	0.00500	0.00999	0.631
0.20	100.2	0.00260	1.97	0.00396	0.00998	0.657
0.25	100.2	0.00325	2.00	0.00372	0.00997	0.699
0.50	100.5	0.00648	2.25	0.00208	0.00996	0.858
0.75	100.7	0.00970	2.56	0.00102	0.00995	1.08
1.00	101.0	0.01290	2.92	0.00045	0.00991	1.35
1.25	101.2	0.01608	3.42	0.00014	0.00988	1.65
1.40	101.4	0.01800	3.97	0.00004	0.00987	1.83

T_{KeH}	KeH	log H^+/KeH
0.0400	0.0343	- 0.776
0.0400	0.0337	- 0.829
0.0399	0.0333	- 0.924
0.0399	0.0329	- 0.946
0.0398	0.0312	- 1.18
0.0397	0.0290	- 1.45
0.0396	0.0263	- 1.77
0.0395	0.0233	- 2.22
0.0395	0.0215	- 2.73

P-62-115

Table 6 D (continued)

Run 48 - acetylacetone

ml. Base	V	Na^+	pH	H^+	$T_{Cu^{++}}$	$\bar{n}$
0.00	100.0	0.000	1.83	0.00545	0.00100	0.545
0.10	100.1	0.00130	1.90	0.00466	0.00999	0.597
0.20	100.2	0.00260	2.00	0.00370	0.00998	0.632
0.25	100.2	0.00325	2.04	0.00336	0.00998	0.663
0.50	100.5	0.00648	2.29	0.00190	0.00995	0.840
0.75	100.7	0.00970	2.59	0.00095	0.00992	1.07
1.00	101.0	0.01290	2.95	0.00042	0.00990	1.34
1.25	101.2	0.01608	3.42	0.00014	0.00988	1.64
1.40	101.4	0.01800	3.90	0.00005	0.00987	1.83

T_{KeH}	KeH	log H^+/KeH
0.0400	0.0345	- 0.800
0.0400	0.0340	- 0.862
0.0399	0.0336	- 0.958
0.0399	0.0333	- 0.995
0.0398	0.0314	- 1.22
0.0397	0.0290	- 1.49
0.0396	0.0263	- 1.80
0.0395	0.0233	- 2.21
0.0395	0.0215	- 2.67

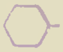
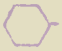
Run 49 - benzoyl-2-thenoylmethane

ml. Base	V	Na^+	pH	H^+	$T_{Cu^{++}}$	$\bar{n}$
0.00	100.0	0.000	1.74	0.00675	0.00100	0.675
0.10	100.1	0.00130	1.79	0.00600	0.00999	0.731
0.20	100.2	0.00260	1.87	0.00500	0.00998	0.762
0.25	100.2	0.00325	1.90	0.00470	0.00998	0.797
0.50	100.5	0.00648	2.11	0.00288	0.00995	0.938
0.75	100.7	0.00970	2.38	0.00154	0.00992	1.13
1.00	101.0	0.01290	2.67	0.00080	0.00990	1.38
1.25	101.2	0.01608	3.13	0.00028	0.00988	1.66
1.40	101.4	0.01800	3.49	0.00012	0.00987	1.84

T_{KeH}	KeH	log H^+/KeH
0.0418	0.0350	- 0.716
0.0418	0.0345	- 0.759
0.0417	0.0341	- 0.833
0.0417	0-0338	- 0.856
0.0416	0.0322	- 1.05
0.0415	0.0303	- 1.29
0.0414	0.0277	- 1.54
0.0413	0.0249	- 1.96
0.0413	0.0232	- 2.29

Table 7 D

$CuKe_2$ Formation Constants

Chelating agent		pK_d	C_1	C_{av}	C_2	log K_1	logK_{av}	log K_2
$CH_3COCH_2COCH_3$		10.50	-0.77	-1.40	-2.04	9.73	9.10	8.46
CH_3		10.40	-0.71	-1.34	-1.97	9.68	9.06	8.43
		10.30	-0.67	-1.25	-1.85	9.63	9.05	8.45
CH_3		10.00	-0.57	-1.16	-1.76	9.43	8.84	8.24
		9.70	-0.52	-1.11	-1.71	9.18	8.59	7.99
		9.50	-0.36	-1.02	-1.70	9.14	8.48	7.80
CH_3		9.40						
		9.20	-0.30	-0.86	-1.45	8.90	8.34	7.75
CH_3		9.15						
		9.05	-0.27	-0.84	-1.40	8.78	8.21	7.65
		8.75						
		8.65						
CH_3	CF_3	6.40	0.19	-0.06	-0.26	6.59	6.34	6.14
	CF_3	6.35	0.43	-0.10	-0.65	6.78	6.25	5.70
	CF_3	6.00	0.65	0.23	-0.20	6.65	6.23	5.80
	CF_3	5.70	0.85	0.42	0.00	6.55	6.12	5.70
	CF_3	5.40	0.46	0.18	-0.20	5.86	5.58	5.20
CF_3	CF_3	4.35	-1.65			2.70		

P-62-117

REFERENCES

(1) Calvin, M., and Wilson, K. W.: J. Am. Chem. Soc. 67, 2003 (1945).

(2) Maley, L. E., and Mellor, D. P.: Australian Journal of Scientific Research. Series A, Physical Sciences, Vol.2, No.1, 92-110 (1949).

(3) Calvin, M., and Melchior, N.: J. Am. Chem. Soc. 70, 3270 (1948).

(4) Stites, J. G., Jr.: Dissertation, Michigan State College (1949).

(5) Brilliantes, R. P.: Thesis, Michigan State College (1950).

(6) Bjerrum, J.: "Metal Ammine Formation in Aqueous Solutions." P. Haase and Son, Copenhagen (1941).

(7) Lange's Handbook of Chemistry, Sixth Edition.

(8) Sidgwick, N. V.: "The Chemical Elements and Their Compounds." Oxford Press, London (1949).

(9) Näsänen and Tamminen: J. Am. Chem. Soc. 71, 2168 (1949).

(10) Harned, H. S., and Fallon, L. D.: J. Am. Chem. Soc. 61, 2377 (1939).

(11) Harned, H. S., and Thomas, H. C.: J. Am. Chem. Soc. 57, 1666 (1935).

(12) Harned, H. S., and Kazanjian, G. L.: J. Am. Chem. Soc. 58, 1912 (1936).

(13) Harned, H. S., and Owen, B. B.: "The Physical Chemistry of Electroytic Solutions." Sec. Ed., p. 509, Reinhold Publishing Corp., New York (1949).

(14) Reid, J. C., and Calvin, M.: Atomic Energy Report MDDC, 1405 (1947).

(15) Snavely, F. A., and Fernelius, W. C.: Report: The Penn State College Contract No. AT(30-1) 604.

P-62-118