PHYSICO-CHEMICAL STUDIES ON COMPLEX ION FORMATION BETWEEN METALS AND IMIDES

Thesis Submitted for the award of
the Degree of
DOCTOR OF PHILOSOPHY

by
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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROORKEE
ROORKEE, (U. P.)
November, 1966

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Mahesh Chand Jain

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CERTIFICATE

Certified that the thesis entitled " Physico-chemical studies on complex ion formation between metals and imides", which is being submitted, by Mr. Mahesh Chand Jain, for the award of the degree of Doctor of Philosophy, in Chemistry, of the University of Roorkee, is a record of his own work, carried out under my guidance and supervision. The matter embodied in this thesis has not been submitted for the award of any other degree of any University.

This is, further, to certify that he has worked for a period of two years in this University to prepare this thesis. Malik

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GENERAL INTRODUCTION

GENERAL INTRODUCTION

Amongst the nitrogen bearing ligands those offering sites simultaneously for salt formation and co-ordination deserve special mention. Apart from their importance in biological systems, these reactions are interesting from theoretical standpoint and a few of them have yet to be investigated to add to the present state of knowledge in this field. To one such class of compounds, belong the imides, both aliphatic and aromatic, known for their tendency to give hydrolysable metal complexes difficult to be characterised. A systematic and comprehensive study of the products formed by the interaction of heavy metal ions and complexing agents containing imide groups was, therefore, considered worth undertaking. Before introducing the subject, it will not be out of place to give a brief resume of the reactions of metals with compounds closely related to imides.

Amino acids: Of these the glycinates have been most extensively investigated (1-3). The nature of the complexes has been revealed by infra red spectroscopy. It has been found that the metal-nitrogen bonds are largely covalent whereas the oxygen-metal bonds are essentially ionic (4). Trans square planar configuration exists in the zinc as well as the copper and nickel complexes, although a tetrahedral configuration is reported in some cases (5). Metal glycinates involving carboxylate bonds (6-9) and linear complexes of Ag(I) and Hg (II) formed through amino groups are also known to exist. Other amino acids besides glycine such as alanine, leucine, valine etc. also show these types of bindings (10-13). Interesting results have also been reported by Tanford (14) and Sarma (15) on cobalt-arginine and on copper-glutamic acid complexes. Green and Ang (16) have tried to explain more complicated reactions like one between chromium and alanine by introducing the concept of partial chelation and partial co-ordination in the same reaction.

With histidine and cysteine, the behaviour is far more complicated. Four possible structures have been visualised: (i) a five membered ring complex involving the carboxylate and α -amino group; (ii) a six membered ring involving the amino and the imidazole group; (iii) a seven membered ring involving the carboxylate and the imidazole groups and (iv) a structure in which all the donor groups of histidine are combined with the metal ion. The work of Edsall (17) on copper dihistidinate and the hydrogen equilibrium studies on cysteine and homocysteine carried out by Benesch (18), Schmidt (19) etc. can be put forward in support of the above contentions. Evidence for the simultaneous combination through the sulphahydryl and amino groups of cysteine has been provided in the case of Co(II) (20,21), Zn(II) and Cd(II) (22).

Complexes of cysteine with metal ions have attracted the attention of Kolthoff and Stricks (23), and a number of papers on this topic have been published in the early fifties. Their investigations on the soluble Fe(II) and Fe(III) complexes of cysteine in the high pH range (≈ 10) with the possible formulation: $FeOH\ (RS)_2^{--}$ and $Fe(RS)_3^{---}$, are most interesting.

More recently Malik and Khan (24) investigated the interaction of Cr(III) ions with glycine, lycine, leucine and aspartic acid, both spectrophotometrically and by Bjerrum's method. On the basis of spectrophotometry, they concluded: (i) for the concentration 0.04 M, leucine and lysine form complexes in the molar ratio($CrCl_3$: amino acids) 1:3 while for the concentration 0.0133 M, the ratio is 1:2 ; and for concentration 0.02 M, the ratio for lysine is 1:2 and that for leucine is 1:3 (ii) for concentrations 0.02 M and 0.0133M, aspartic acid forms a complex in the molar ratio 1:1.

The information on combining ratios as obtained by Job's method was then successfully employed to determine the stability constants of a large number of amino acids. Applying Albert's (25) procedure, the following values of stability constants in KCl medium were obtained:

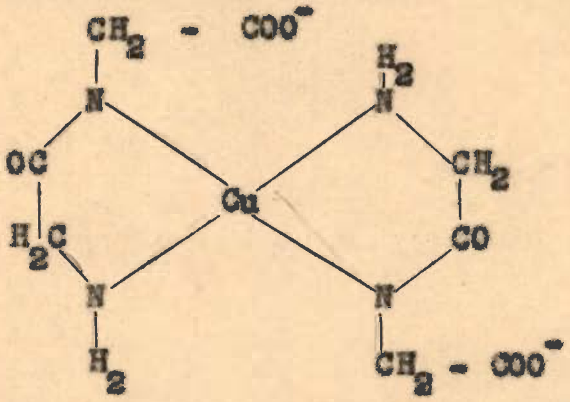
Log stability constant:

	Glycine	Valine	Leucine	Asparagine	-Alanine
I	15.30	14.60	16.3	14.0	16.2
II	18.30	17.55	18.6	16.5	18.9

	Methionine	Serine	Lysine	Arginine
I	14.60	14.0	14.7	14.1
II	17.10	17.1	17.1	17.1

Peptides: Most of the work on metal complexes of peptides cited in the literature, deals with glycyl-glycinate. Monk (26,27) gave a value of log K = 6.04 for Cu(II) glycyl-glycinate as against 8.62 for the corresponding glycinate and attributed the difference to the differing basicities of α-amino nitrogen atoms. The author found a value, log K_1 = 1.24, for calcium glycyl-glycinate which was so close to the log K_1 value for calcium acetate(1.0) that the binding of calcium to the peptide was considered to take place through carboxylate group.

Greewald(28) has mentioned the possibility of the peptide complexes undergoing ionisation in the high pH range. Dobbie and Kermack (29) have shown that the solution prepared from cuprous chloride and dipolar glycyl-glycine in the ratio 1:2 may take up four moles of alkali during the titration (pH 11). This behaviour was explained by assuming the co-ordination between Cu(II) and peptide nitrogen, resulting in the ionisation of two protons:



Monayak et al.,(30) have assigned the same structure for the complexes of glycyl-glycine and diglycyl-glycine with Co(II) and Ni(II).

<u>Proteins</u>: The literature on metal protein complexes

dealing with both qualitative and quantitative studies is so vast that it is difficult to summarise it in a few pages. However, an attempt will be made to describe a few important reactions relevant to the present studies.

Proteins offer several functional groups for combination with metals,depending on the pH of the medium. Binding of the metal with the amino group is difficult to realise even in the moderately low pH range. For example,the binding capacity of zinc at pH 7 is very small. Gurd and Goodman (31) have carried out extensive studies on the binding of zinc with serum albumin employing equilibrium technique. From these studies, they concluded that the binding of Zn(II) with albumin in the pH range 5.5 to 7.5 is almost due to sixteen imidazole groups of the histidine residues and that very little zinc is bound at more acid pH values. The significance of the imidazole group for the binding of zinc was also confirmed by Tanford(32) and Cohn (33).

Strong evidence of binding through the amino group of the protein is obtained in strongly basic medium. Mehl et al.(34,35),Klotz and Curme (36) had shown that each metal was bound to four peptide nitrogen atoms in the case of copper complexes. Iron complexes have been mainly studied with blood plasma. Competitive binding of the ferrous ions with siderophilin and β - pseudoglobulin in plasma protein (IV) were carried out by Cohn(37). On the basis of the similarity in the spectrophotometric behaviour of the iron complexes of the protein and asparaginic acid, he concluded that the metal was bound to the protein through a linkage similar to hydroxamic acid (38).

As already mentioned under amino acids, the chromium complexes of proteins present a number of difficulties due to the existence of polynuclear complexes in the aqueous solution of the metal it-self. Gustavson (39), Smythe and Schmidt (40) have provided a satisfactory reaction mechanism for the interaction of basic chromic salt with collagen. According to them, the initial reaction is an ionic interaction of cationic chromium complexes with the charged carboxyl groups of the protein, resulting in the formation of a covalent-coordinate bond. Since several chromium atoms are present in the polynuclear complex and in view of the secondary aggregation of the fixed chromium complexes by further hydrolysis, possibilities for a multipoint interaction of one chain like chromium complex with several carboxyl groups of collagen lattice exist.

The interaction of metals, especially Hg(II), with the -SH group of the protein is also worth mentioning. The mercuric ion or its mono-alkyl derivatives couple with the single sulphydryl group of serum albumin to give complexes (41,42). With albumin, a dimer is formed when one mole of Hg(II) is present for every two moles of albumin, while with higher ratio of the metal to albumin, a monomer is obtained. Silver also forms similar complexes with proteins and both the metals can, therefore, be employed to estimate the -SH groups of proteins (43,44).

Experimental evidence is available to prove that there exist relative avidities (45) of proteins for metal ions. For example, siderophilin, the metal binding component of plasma, and conalbumin show a marked affinity for both iron and copper (46,47) in comparison to other proteins. The nature of these specific sites, although not clearly understood (48), has been attributed to the = NH side chains, formed due to the displacement of H by the combining metals.

Quantitative studies on the interaction of metals with transfusion gelatin and some other proteins were recently taken up by Malik and coworkers (49-55) in order to determine the nature of binding. Employing potentiometric, polarographic, viscometric and equilibrium dialysis methods, they arrived at many interesting conclusions. Some of these are summarised below:

(i) Hydrogen equilibrium studies on transfusion gelatin carried out at different temperatures revealed the presence of 84 carboxyl, 23 amino, 4 imidazole and 48 guanidinium groups per 75 x 10^3 gms. of protein.

(ii) Polarography of cupric sulphate-transfusion gelatin mixtures revealed that copper was more strongly bound to the amino than the carboxyl group.

(iii) Polarographic and pH metric studies of the interaction of transfusion gelatin with plumbous ions gave values of 1.87 and 2.593 K.cals for the intrinsic association constant and free energy respectively.

(iv) Polarographic studies of zinc and cadmium with transfusion gelatin (employing Tanford's method) gave values of 2.778 and 2.30 respectively for the intrinsic association constants. Moreover, cadmium showed affinity to combine with the carboxylic groups only.

(v) Spectrophotometric studies on copper-transfusion gelatin mixtures in different buffers show that the binding of the metal to the protein takes place through the α -amino group of the protein.

(vi) Chromium (III) - transfusion gelatin interaction studied spectrophotometrically between pH 3.7 and 5.8 indicated the binding of the metal through the carboxyl group of the protein. Similar results were obtained with cobalt and nickel ions.

(vii) Viscometric measurements of mixtures of various proteins (transfusion gelatin, casein and haemoglobin) with metal hydrous oxides(Fe, Co, Ni, Ag, Al, Cr, Be) reveal that the metals from the hydrous oxides make themselves available for interaction with carboxylic groups of the proteins.

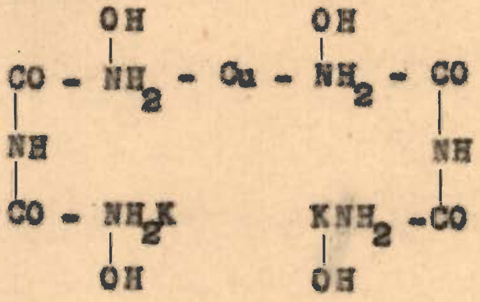
Biuret reaction:

The original concept of the biuret reaction (development of a reddish violet colour on the addition of copper sulphate to biuret in an alkaline medium) has been greatly modified and extended so as to include(i) different basic media, like barium and calcium hydroxides, magnesium oxide, sodium carbonate, ammonia, piperidine etc.;(ii) metal ions other than copper, viz., nickel and cobalt; (iii) complexing agents other than biuret, viz., amino acids, peptides, proteins, acid amides and imides.

This reaction has been excellently reviewed by Plekhan and Govrilov (56) in 1948. Korenman (57) has listed thirteen kinds of compounds, all of them aliphatic, which give this reaction. According to him, the specific grouping of atom within these compounds responsible for the biuret reaction are: $-NH.CO.\overset{|}{N}.CO.NH_2$ in biurets, $-NH\ C(:NH)\overset{|}{N}\ CO-NH_2$ in dicyanodiamidine, $>NC(:\overset{|}{N})\overset{|}{N}C(:NH)NH_2$ in biguanides, $>N\overset{|}{C}:N\overset{|}{C}(:NH)$ in N - phenyl - N′ (α-amino benzyl)-benzamidine, and $N\vdots C\overset{|}{N}\ C(:NH)NH_2$ in dicyanodiamides. These groups have in common the ability to form six membered internal complexes of the type $\overline{N-C-N-C-N-M}_n$, when M is a metal and n an integer. Still other groupings capable of this reaction, e.g., $-NH\overset{\vee}{C}-\overset{\vee}{C}-CONH_2$ in malonamides and $N\vdots C\overset{\vee\vee}{C}CONH_2$ in cyanoacetamide and its derivatives can be generalised in the form $\overline{N-C-C-C-N-M}_n$. Thus the atomic groupings, capable of giving the biuret reaction fall under two types: (i) $\overline{Z-C-X-C-N-M}_n$ of which there are twelve variations and $\overline{M_n-Z-C-X-C-N}$ of which there is one variation, X is either C or N and Z is either N or O. The number and distribution of multiple bonds within the ring is responsible for a given variation but does not effect the ability of the compound to give the biuret reaction. Moreover, the ability to undergo this reaction is not impeded by the removal, from the 6 membered ring, of an atom not directly connected with the atom.

<u>Metal complexes of biuret:</u>

The earliest studies on the biuret reaction carried out by Schiff (58,59) date back to 1896. Ley and Werner (60), Traube and Wolff (61) confirmed Schiff's work. Nickel complexes of the biuret have been reported by a number of workers (62,63). All these investigations led to the following four structures of the biuret complexes:



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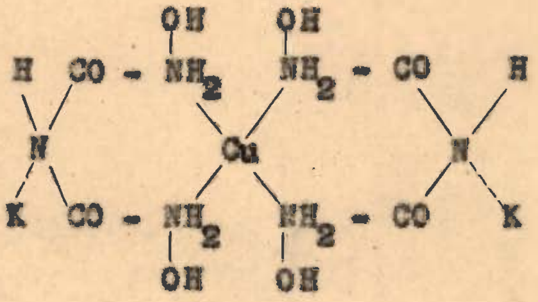

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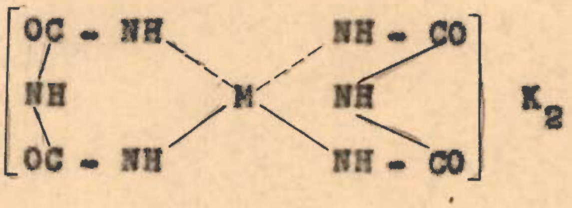

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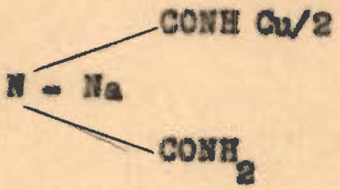
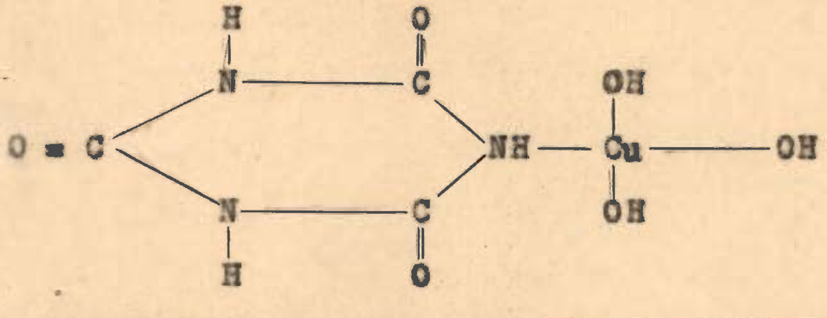


IV

Traube and his collaborators (64-67) prepared a large number of copper and nickel complexes and represented them as III above. According to them, the original biuret colour may be replaced by ammonium, sulphonium and phosphonium hydroxides as well as by ethylenediamine bases, resulting in red complex copper salts, or yellow complex nickel salts of comparable structures. More recently, Malik and Khan(68) have employed polarographic and potentiometric methods to study the copper-biuret complex in the pH range 10 to 11 and reported the formation of a 1:2 complex, $Cu(C_2H_3O_2N_3)_2^{--}$. Other metal-amino acid reactions involving biuret type of binding and: (i) biuret reaction of serine, studied polarographically and amperometrically (ii) polarographic study on the interaction of asparagine with copper, providing the following values of $E_{1/2}$s and stability constants at different pH:

pH	7.2	8.4	8.7	9.1	9.45	10.97	11.30	11.50
$E_{1/2}$	0.25	0.29	0.315	0.33	0.34	0.345	0.355	0.365
pK	11.06	12.76	13.59	13.58	13.88	14.1	12.5	12.9

and (iii) polarography of the biuret reaction of cyanuric acid established the formation of a complex involving combination with one molecule of cyanuric acid and three hydroxyl groups as indicated below:



<u>Biuret reaction of amino acidamides</u>: Metal-amino acid-amide complexes have been reported by Rising and Yang(69). The amino acid-amides gave purple colouration with copper in the absence of alkali. This behaviour was considered to be because of their ready enolisation, the cupric ion being

co-ordinated with four nitrogen atoms of two molecules of acid-amides. The analysis confirms the loss of one hydrogen atom by each molecule of the acid-amide as in the case of glycine and alanine. By treatment of the amino acid-amides with copper acetate, the following compounds were prepared; cupric dl leucinamide $Cu\ [Me_2\ CH.CH_2.CH\ (NH_2)\ CONH]_2$, cupric - 1 asparagine $Cu\ [HO_2.C.CH\ (NH_2)\ CONH]_2$, cupric-glycinamide $Cu[(CH_2)\ (NH_2)\ CONH]_2.H_2O$. and cupric d-alaninamide $Cu[(Me\ CH\ (NH_2)\ CONH]_2$. The view-point that four basic nitrogen atoms are essential for the biuret reaction, either 2 or 4 hydrogen atoms being split off at the same time, is confirmed by the above restults.

Biuret reaction of diacid amides: Acid-amides are also well known for giving biuret reaction. Rising and coworkers (70) studied the reaction of diacid amides with copper in the presence of alkali and showed that there must be two hydrogen atoms in each molecule of the amide for salt formation and one or more amino nitrogen atoms for complex ion formation. They also observed that an increase in the number of carbon or nitrogen atoms separating the amide groups (separation factor), also weakens the strength of the amides as acids so that salt formation is ultimately hindered. Thus biuret oxamide and malonamide readily show this reaction. Mono and symmetrical dialkyl oxamides give the reaction, while unsymmetrical and trialkyl oxamides do not give.

Malik and coworkers (71) studied polarographically the biuret reaction of malonamide with copper and reported that the complex is reducible reversibly at the dropping mercury electrode with one electron transfer. The polarographic data gave evidence that two molecules of the amide took part in the complex formation with one atom of copper. On this basis, the structural formula of the complex was given as:

Metal-imide complexes:

Comparatively little attention has been paid to study the metal imide complexes on account of their hydrolysable nature. The few investigations reported in the existing literature deal with the isolation of the complexes, their chemical analysis and measurements of magnetic susceptibilities. Nothing has been reported on the use of physico-chemical methods for the elucidation of the structure and stability of these complexes. A brief account of the work already done on metal imide complexes is given below:

Mary M. Rising (72) prepared Ba Cu succinimide complex(Ba Cu $C_{16}H_{16}N_4O_8$) which was brownish red in colour. The theory and facts of the biuret reaction so far developed are in agreement with the character of these salts. Hexa hydrate copper succinimide complex ($Cu (N C_4O_2H_4). 6H_2O$) (73) was prepared by the action of metallic copper with mercuric acetate and a paste of mercuric succinimide. The structure was confirmed by chemical analysis. Some gold complexes of succinimide have also been reported (74). Seshadri and Rao (75) isolated 1:2 mercury complexes of succinimide and phthalimide with ethyl alcohol.

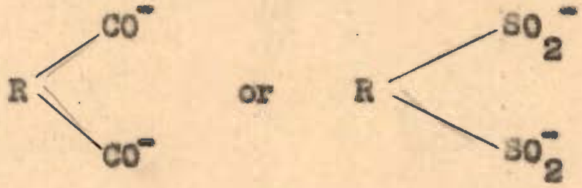
Livio Cambi (76) reported the magnetic properties of potassium salt of nickel complexes of succinimide, substituted succinimide and phthalimide;potassium salts of palladium complexes of succinimide and phthalimide and methyl and ethyl amine salts of nickel complexes of phthalimide and tetra methyl succinimide. The magnetic susceptibility of the most symmetrical complexes were ≈ 0. In the remaining complexes,there appeared a residual para magnetism although according to the theory of Pauling they should be dimagnetic. Magneto-chemical studies on the copper,nickel and cobalt complexes derived from imides have also been reported in the literature.

Aim of the present studies:

While planning investigations on the metal-imide interaction,the following aspects of the problem were kept in view: (i) selection of the ligands based on the classification of imides;(ii) employment of different physico-chemical methods which were likely to give reproducible data both in the aqueous and non-aqueous media;(iii) selecting reactions,based on biuret and non-biuret reaction mechanism.

(I) Selection of ligands:- The choice of the different imides employed in the present work was based on their classification.

The best known acid-imides are cyclic derivatives of ammonia, having the formulae R= NH in which R is usually a bivalent acyl radical:



The acid-imides may be derived from acid anhydrides by replacing oxygen with an imino group. The unsubstituted (three membered ring) oxalimide is unknown. Attempts for preparing it resulted in the formation of tetra oxopiperazine (NH -CO -CO - NH - CO - CO). Similarly in the case of malonimide(four membered ring) only its derivatives have been prepared. Five or six membered ring imides are prepared easily.

Other imides such as diacyl ammonias which also contain CO-NH-CO-radical(usually called diacyl or secondary amides) the cyclic imides of the olefinic dicarboxylic acids, sulpho derivatives of imides such as lauryl sulpho succinimide, sulphonamides of dicarboximides, for example phthalimide -4 sulphonamide and the bis-dimethyl sulphonamide of 2:3 naphthalene dicarboximide, and aryl derivatives of hetro cyclic imides are not useful from the view-point of complex ion formation, but are of industrial importance and are used in the preparation of resins, emulsifiers and medicines etc. (77-80).

Out of these the following imides were selected for metal interaction: succinimide and phthalimide(typical five membered aliphatic and aromatic ring imides), glutarimide(with a six membered ring) and saccharin (containing SO_2 in place of CO).

II. In view of the hydrolytic nature of some of these complexes and the different modes of interaction in the aqueous and non-aqueous media, investigations were carried out both in water and methanol.

Both spectrophotometric and electrochemical techniques could successfully be employed in polar organic solvents. The pH metric method, however, could be employed in aqueous and in 50% water-methanolic mixtures only. Although the suitability of pH metric measurements in non-aqueous medium has not been extensively investigated, there is no overriding reason why acidity scale analogous with the pH scale should not be set up for any solvent.

III. The following aspects of the problem were considered worth investigating:

1. Nickel complexes of succinimide, phthalimide and glutarimide involving biuret as well as non biuret reaction mechanisms in aqueous and non-aqueous media.
2. Insoluble copper complexes of succinimide, phthalimide and glutarimide involving biuret reaction mechanism in methanolic medium.
3. Soluble copper complexes of succinimide(aqueous medium) and of saccharin(methanolic medium)involving non biuret reaction mechanism.
4. Cobalt(II) complexes of succinimide and phthalimide in purely methanolic medium involving a non-biuret reaction mechanism.

****

CHAPTER I.

Nickel-succinimide complexes(biuret and non biuret reaction mechanisms).

INTRODUCTION

Comparatively little work has been done to investigate imide complexes of nickel. Livio Cambi(1) had reported the magnetic properties of two such complexes: a green one and the other yellow in colour. Evidence for the existence of potassium salt of nickel succinimide was given by Mann and Watson (2) on the basis of chemical analysis. The latter author's also reported the decomposition action of water on these complexes. These forsaken studies were neither comprehensive nor systematic as to give a clear indication of the nature and composition of the complexes formed. It was, therefore, considered worthwhile to investigate them by instrumental and non-instrumental methods of analysis and to elucidate their structure by infra-red spectroscopy.

Preliminary investigations carried out in aqueous and methanolic media brought to light the following interesting facts. In purely methanolic medium nickel chloride with excess of succinimide gives a yellow coloured soluble complex in the higher pH range (pH $>$ 9). The product thus obtained got decomposed in presence of moisture as well as in excess of nickel chloride. In the former nickel hydroxide got precipitated while in the latter a soluble product green in colour was obtained.

Under similar conditions the behaviour was slightly different in the aqueous medium. The complex obtained in presence of excess of succinimide was green in colour while in excess of metal ion precipitation of the hydroxide took place. It looked as if excess of succinimide was checking the decomposition of the complex by water.

The yellow and the green complexes appeared to be formed by different mechanisms. The combining ratio of the reactants was found by spectrophotometric, conductometric and pH metric methods in the case of the yellow complex. The green complex (formed in the higher proportions of nickel ions) could only be studied spectrophotometrically since the conductometric method failed to give sharp inflexion points and the Bjerrum's (3) method was not employed due to the limited concentration range of succinimide in which the complex could be studied.

The complex in the aqueous medium could be studied by Bjerrum's method, employing the procedure of Calvin and Melchoir (4), due to the precipitation of nickel hydroxide in mixtures containing higher proportion of nickel.

The yellow complex was subjected to chemical analysis and infra-red spectroscopy. Any attempt to crystallise the green complex was met with failure since nickel hydroxide was invariably co-precipitated.

EXPERIMENTAL

Succinimide solution: Succinimide was prepared by the action of ammonia on succinic acid and distilling the subsequent product ammonium succinate(5).

Details of the procedure: In a 500 ml. distilling flask fitted with an air condenser about 40 cms. long and 1 cm. in diameter, 108 gms. of succinic acid was placed and added slowly with cooling and shaking 140 ml. of concentrated ammonium hydroxide solution(sp.gr. 0.88). Most of the acid got dissolved forming a clear solution: inserted a thermometer into the mouth of the flask. Attached a 250 ml. conical flask to the lower end of the air condenser and supported it in a large funnel so that it may be water cooled. The reaction mixture was gently heated with a free flame, the temperature soon raised to 100°C .and remained at this point until about 100 ml. of water was distilled over. Then with evolution of ammonia the temperature first lowered slightly and then again rose to 275°C.. The receiver was changed and succinimide collected at 275° to 290° (largely 285° - 290°C.). The distillation was stopped when the tarry matter began to decompose with yellow fumes. Crude succinimide was recrystallised from alcohol(1 ml. per gm. of the solid) and cooled the solution to 0°C. for some hours. Crystals of succinimide were filtered at pump and washed with 15 ml. of ice cold alcohol. The pure succinimide crystals were dried at about 90°C..

Solution of succinimide was prepared by direct weighing of the pure product and dissolving it in the requisite volume of methyl alcohol.

Nickel chloride solution: Stock solution of nickel chloride was prepared by dissolving the green(B.D.H.) crystals in doubly distilled methyl alcohol (B.D.H.) and its strength was determined gravimetrically as nickel dimethyl-glyoxime. The strength of the stock solution was found to be 0.2994 M. Solutions of desired strength were obtained by diluting the stock solution with doubly distilled methyl alcohol.

Potassium hydroxide solution: Potassium hydroxide (B.D.H.) A.R. was washed by methyl alcohol three to four times in order to ensure the removal of carbonate, if any, and then dissolved in methyl alcohol to obtain the stock solution. 5 ml. of the stock solution were then made upto 100 ml. in a measuring flask and the strength was determined volumetrically by titrating against 0.1 N oxalic acid solution. The strength of stock solution was found to be 4.202 M. Methanolic solutions of potassium hydroxide of desired strength were prepared by diluting the requisite volume of stock solution and the strength was further checked by titrating against standard oxalic acid solution.

Aqueous solutions: These were prepared as above by dissolving the respective reagents in double distilled water.

Spectrophotometry of the complexes.

Spectrophotometry in the visible region occupies a unique position amongst the various physical methods employed for studying the complex ion formation. The special feature of this method is that it allows the study of complexes which are not stable enough to permit their isolation. Job (6) has developed a very useful method for this type of studies. The method goes by the name of "the method of continued variation" which is of great fundamental importance in the realm of physical and inorganic chemistry. This method may be extended to other physical properties like conductivity, molar heat content, refractivity etc., and makes use of any measurable additive property of two species in solution so long as the property has different values for one another. Any complex formed by the interaction of two components would give a value for the same property which is different from the weighted mean of the values for separate components.

The application of this method may be examplified by the simplest equilibrium of the type $A + nB \rightleftharpoons AB_n$, where A represents a metal ion, B a co-ordinating group and AB_n a complex ion. Solutionswith different mole fractions of the component are prepared but the total sum of the moles of both the components is kept constant. The absorption of a monochramatic light by these solutions is measured and a graph of absorption against mole-fraction of one of the components is plotted. If a complex is being formed the plot deviates from linearity, the deviation being maximum at the mole fraction corresponding to the composition of the complex whereas a straight line points towards no interaction. When the deviation is plotted against mole fraction, the maximum point gives the desired composition. This conclusion may be verified by repeating the process at other wavelengths since according to Job the position of maximum is independent of wavelength.

The method of continued variation, which as Job himself has pointed out, is only applicable to the systems where the possibility of formation of only one complex exists and is not generally useful when more than one complexes are formed,has been extended by VosBurgh and Cooper (7) for systems involving more than one complexes. They have shown that the results are independent of the wavelength of light used only when a single complex is formed, while in a system with more than one compounds wavelength plays an important role and a careful selection of wavelengths should be made while studying complex ion formation. These authors have studied the complexes of Ni(II) with O-phenanthroline and ethylene diamine(1:1,1:2 and 1:3) and copper ammonia complexes(ratio Cu^{++} : NH$_3$ as 1:2 and 1:4) and thus confirmed the validity of their method. The method was further extended by VosBurgh and coworkers (loc.cit.) to the study of ferric-thiocyanate, ferrous-o-phenanthroline and copper glycine systems yeilding satisfactory results. Besides,this method gave results of far reaching importance,for example,VosBurgh reported for the first time, a co-ordination number of six for nickel-ethylene diamine complexes and existence of ions like $(Ni - en)^{++}$, $(Ni - en_2)^{++}$ and $(Ni - en_3)^{++}$. Haendler (8) got similar results while investigating diethylene traiamine complexes of copper.

Before performing the actual experiments on the composition of nickel-succinimide complexes by the spectrophotometric methods, absorption experiments were performed with nickel chloride solutions as well as the complex at different wave lengths in order to select suitable wavelength to work with. Furthermore, the VosBurgh Cooper's method was employed in order to determine the number of complexes formed. Nickel chloride and succinimide (prepared in equivalent amount of KOH), both of strength 5×10^{-2}M were mixed in the ratios of nickel to succinimide as 1:8, 1:6, 1:4, 1:2, 1:1 and 2:1 by mixing the 1.35, 1.7, 2.4, 4.0, 6.0 and 8.0 ml. of nickel chloride solution to 10.65, 10.3, 9.6, 8.0, 6.0 and 4.0 ml. of succinimide solution.

Optical density measurements were carried out with a Bausch and Lomb 'Spectronic 20' after allowing a sufficient warming up period for the instrument. Measurements above 650 mu were made after changing to the red filter.

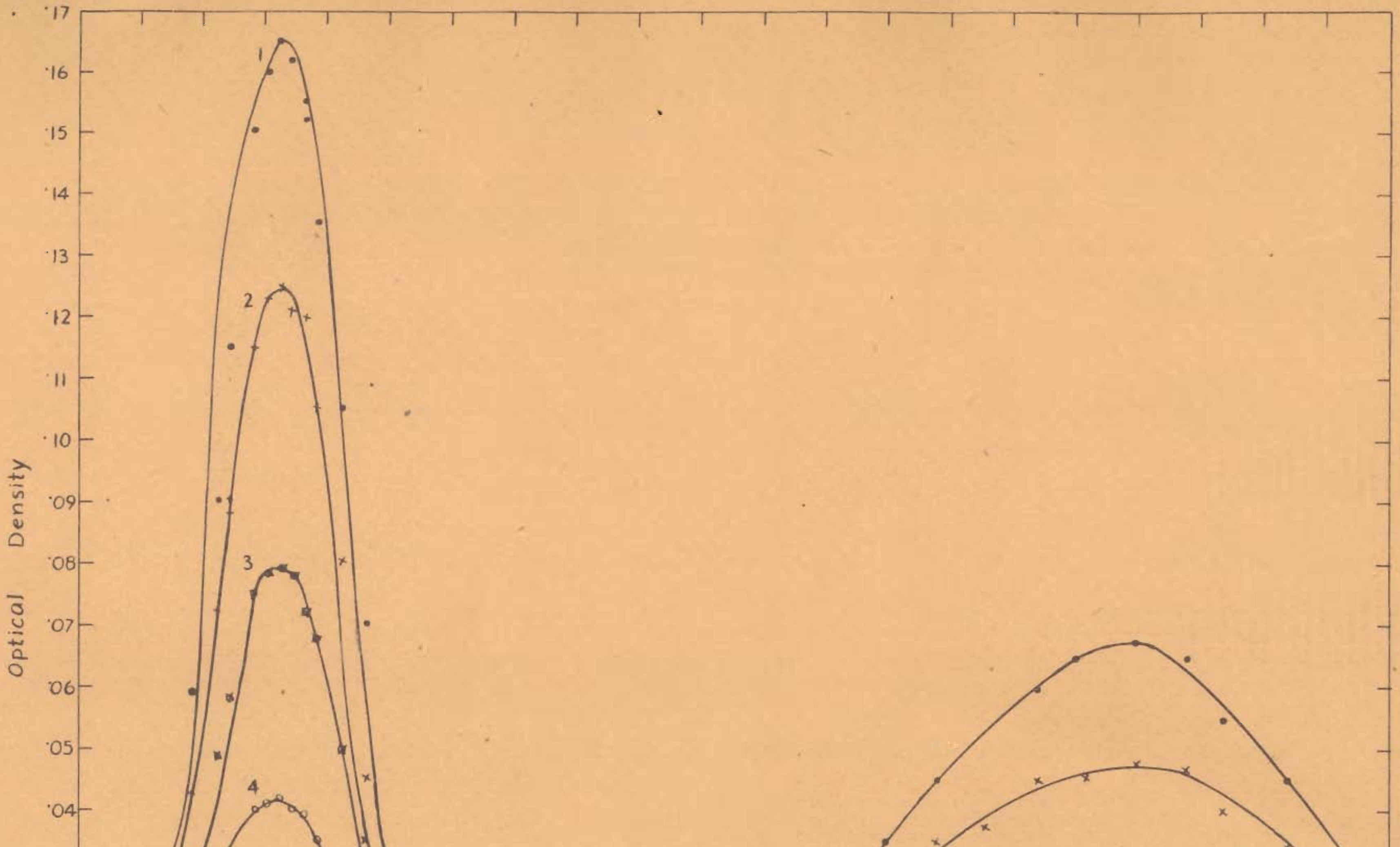
TABLE NO. 1

Optical density of nickel chloride solution.

Wave length	O.D. of methanolic solutions of concentration.				
mu	.02M	.0133M	.01M	.005M	.0025M
325	.019	.0125	.01	.01	.01
350	.022	.017	.013	.012	.01
370	.059	.0425	.029	.020	.017
380	.09	.072	.049	.03	.02
385	.115	.088	.058	.032	.021
395	.15	.115	.075	.04	.025
400	.16	.123	.078	.041	.025
405	.165	.125	.079	.042	.026
410	.162	.121	.078	.04	.025
415	.155	.12	.072	.039	.021
420	.135	.105	.068	.035	.02
430	.105	.08	.05	.025	.018
440	.07	.045	.035	.02	.014
460	.03	.021	.015	.011	.01
480	.015	.012	.009	.006	.005
500	.009	.007	.004	.004	.004
525	.005	.004	.004	.003	.003
550	.005	.005	.003	.002	.002
575	.005	.005	.002	.001	.001
600	.01	.009	.005	.005	.005
625	.02	.015	.012	.01	.009
650	.035	.025	.02	.011	.009
670	.045	.035	.0275	.0125	.009
690	.05	.0375	.028	.015	.01
710	.06	.045	.029	.015	.011
730	.065	.045	.03	.018	.02
750	.0675	.0475	.031	.019	.012
770	.065	.0475	.03	.02	.018
790	.055	.04	.029	.014	.01
810	.045	.034	.02	.011	.008
850	.025	.018	.0125	.008	.005

Fig.1

Two peaks were obtained for nickel chloride one at 405 mu and the other at 750 mu.



O. D. CURVES OF $NiCl_2$

FIG · I

Selection of wave lengths.

TABLE NO. 2.

Absorbance of nickel chloride-succinimide mixtures, mixed according to VosBurgh Cooper's method.

Concentration of nickel chloride = 5.0 x10^{-2} M

Concentration of succinimide = 5.0 x10^{-2} M

Wave length. mu	Ratio of nickel chloride to succinimide. 2:1	1:1	1:2	1:4	1:6	1:8
350	0.055	0.06	0.078	0.08	0.062	0.062
370	0.135	0.143	0.165	0.142	0.101	0.081
390	0.27	0.243	0.221	0.193	0.145	0.117
395	0.295	0.247	0.219	0.197	0.151	0.12
400	0.300	0.245	0.207	0.202	0.154	0.122
405	0.300	0.233	0.193	0.202	0.160	0.127
410	0.285	0.213	0.176	0.20	0.159	0.128
420	0.230	0.165	0.13	0.186	0.15	0.125
430	0.17	0.115	0.078	0.168	0.14	0.12
435	0.142	0.09	0.06	0.16	0.129	0.115
440	0.115	0.07	0.045	0.145	0.125	0.108
445	0.09	0.06	0.037	0.14	0.116	0.10
450	0.074	0.048	0.029	0.128	0.11	0.098
470	0.035	0.026	0.018	0.10	0.088	0.077
500	0.015	0.014	0.009	0.065	0.049	0.042
525	0.01	0.01	0.009	0.03	0.025	0.02
550	0.011	0.013	0.013	0.02	0.017	0.013
575	0.019	0.022	0.025	0.028	0.02	0.015
600	0.032	0.042	0.065	0.042	0.03	0.021
625	0.065	0.072	0.09	0.06	0.043	0.03
650	0.095	0.100	0.11	0.068	0.049	0.03
675	0.100	0.098	0.10	0.063	0.043	0.028
700	0.09	0.095	0.10	0.052	0.035	0.022
725	0.07	0.078	0.085	0.035	0.023	0.018
750	0.043	0.054	0.065	0.02	0.013	0.008

Fig.2.

Optical density measurements carried out in the visible region from 325 to 850 mu show two maxima for nickel chloride in methanolic solution at 405 mu and 750 mu. From the O.D. values of various mixtures (Table No.2) at different wave lengths gave two maxima shifted (also see below) from the nickel chloride solution, at 395 mu and 660 mu (Fig.2).

The absorbance curves depicted in Fig.2,needed a certain degree of elaboration since they were slightly different from the usual VosBurgh-Cooper's curves. These curves not only provided the necessary information for the number of complexes formed and the suitable wavelengths to work with but helped immensly in fore-seeing the nature of the complexes formed. From the curves it would be seen that the mixtures with higher proportions of succinimide showed appreciable absorption in the range 430 to 480 mu,while mixtures having lower proportions of succinimide showed very little absorption in the above wavelength region. Hence the stoichiometry of the yellow complex could best be carried out in this wavelength region and the difficulty met with in working at two wavelengths, viz.,405 mu (nickel chloride) and 395 mu (complex) very close together could be dispensed with(the absorption of nickel chloride in the wavelength region 430 to 480 mu was negligible).

The above difficulty was not,however, encountered for the second complex, since the two wavelengths corresponding to the second maxima were quite far apart.

Composition of the yellow complex:

For determining the composition of yellow coloured nickel succinimide complex by Job's method of continued variation, the following sets of mixtures were prepared. Succinimide solution used in all these studies was prepared in equivalent amount of potassium hydroxide.

Set I. 0.5,1.0,1.5,2.0,2.5 ..... 9.5 ml. of nickel-chloride mixed with 9.5,9.0,8.5,8.0,7.5 ..... 0.5 ml. of succinimide. The concentration of both the reactants being 0.1 M.

Set II. 0.5,1.0,1.5,2.0 ..... 11.5 ml. of nickel chloride mixed with 11.5,11.0,10.5,10.0 ..... 0.5 ml. of succinimide. Concentration of the reactants being 0.0667 M.

Set III. Concentration of the reactants 0.05 M; mixed as under Set II.

O.D. measurements were carried out at wavelengths 440 mu,450 mu and 460 mu, curves were plotted in the difference of O.D. of the mixtures and nickel chloride against the ratio $(Ni)^{++}/(Ni)^{++}+(Succ)$. The results are given in the following tables.

Set I.

TABLE NO. 3.

Wave length 440 mu.

Vol. of $NiCl_2$	Vol. of succinimide.	O.D. mixt.	$NiCl_2$ O.D.	Difference
0.5	9.5	0.115	0.025	0.081
1.0	9.0	0.22	0.046	0.174
1.5	8.5	0.287	0.067	0.22
2.0	8.0	0.40	0.077	0.323
2.3	7.7	0.385	0.098	0.287
2.6	7.4	0.375	0.113	0.262
3.0	7.0	0.225	0.125	0.10
3.5	6.5	0.10	0.145	-0.045
4.0	6.0	0.102	0.16	-0.058

(Fig.3,curve 1)

TABLE NO. 4.

Wave length 450 mu.

Vol. of $NiCl_2$	Vol. of succinimide.	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	9.5	0.10	0.019	0.081
1.0	9.0	0.202	0.03	0.172
1.5	8.5	0.265	0.045	0.22
2.0	8.0	0.365	0.055	0.31
2.3	7.7	0.35	0.062	0.288
2.6	7.4	0.317	0.077	0.240
3.0	7.0	0.195	0.08	0.115
3.5	6.5	0.070	0.100	-0.030
4.0	6.0	0.068	0.107	-0.039

(Fig. 4, Curve 1).

TABLE NO. 5.

Wave length 460 mu.

Vol. of $NiCl_2$	Vol. of succinimide.	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	9.5	0.092	0.012	0.08
1.0	9.0	0.183	0.022	0.161
1.5	8.5	0.269	0.029	0.24
2.0	8.0	0.335	0.038	0.297
2.3	7.7	0.32	0.04	0.28
2.6	7.4	0.30	0.05	0.25
3.0	7.0	0.170	0.055	0.115
3.5	6.5	0.048	0.07	-0.022
4.0	6.0	0.05	0.07	-0.020

(Fig. 5, Curve 1).

JOB'S METHOD

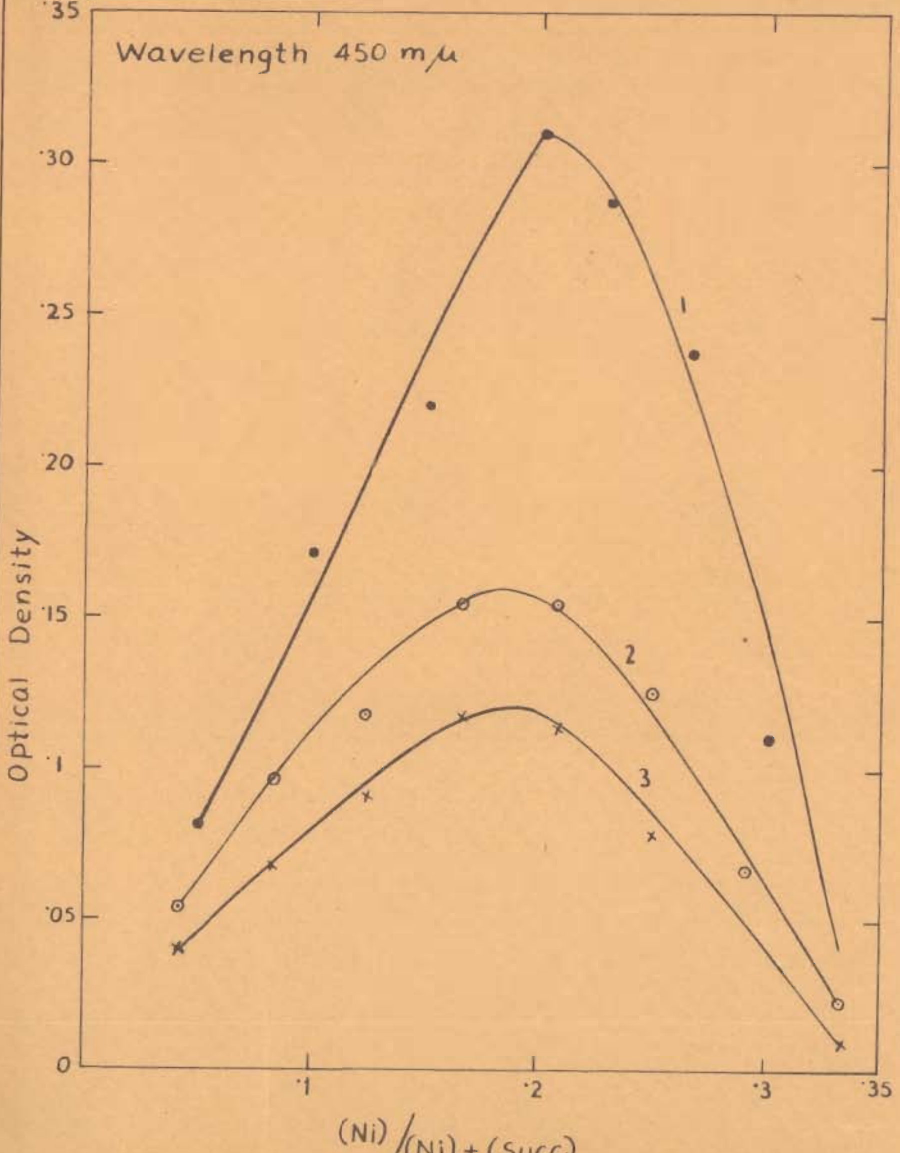


FIG. 4

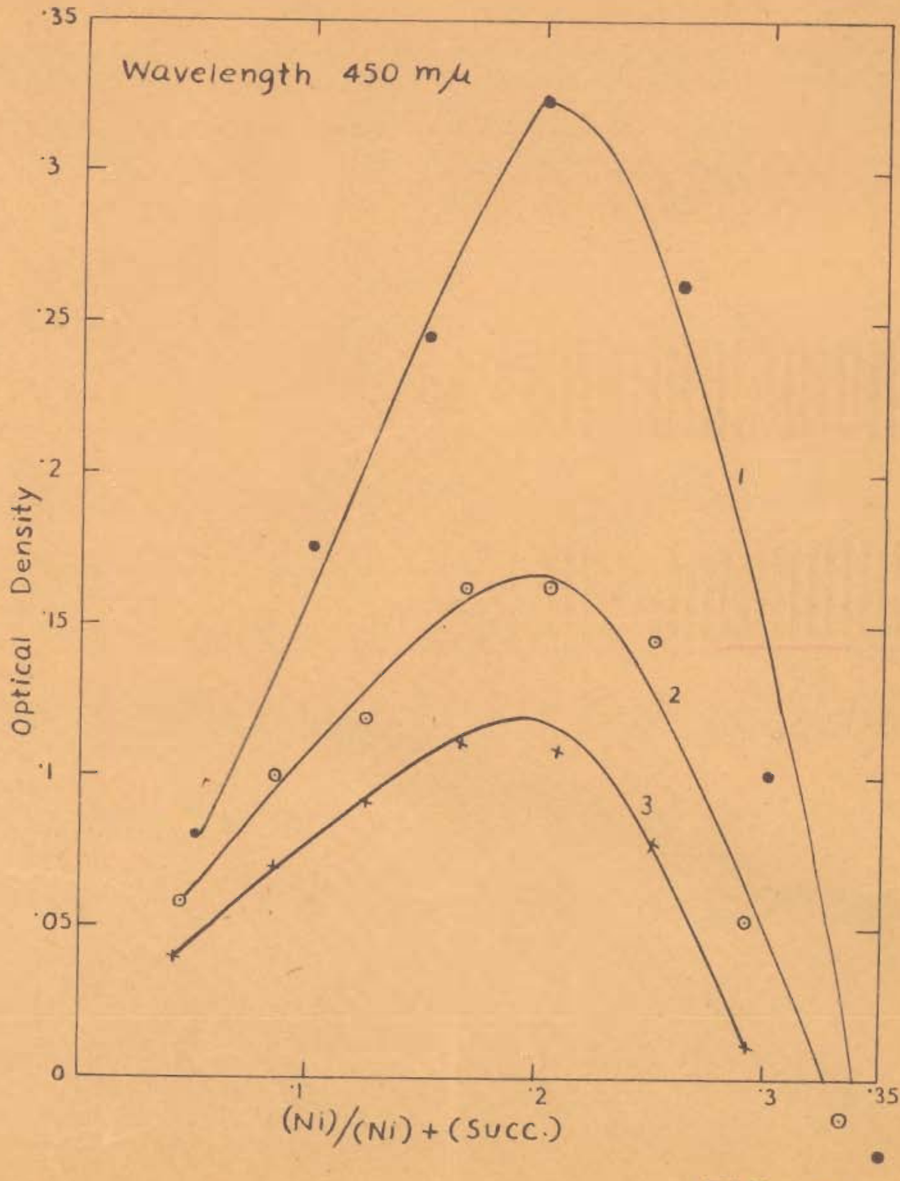


FIG · 3

Set II.

TABLE NO. 6.

Wave length 440 mu.

Vol. of $NiCl_2$.	Vol. of succinimide.	O. D. mixt.	O. D. $NiCl_2$.	Difference.
0.5	11.5	0.072	0.014	0.058
1.0	11.0	0.125	0.025	0.10
1.5	10.5	0.157	0.038	0.119
2.0	10.0	0.21	0.048	0.162
2.5	9.5	0.22	0.058	0.162
3.0	9.0	0.213	0.067	0.146
3.5	8.5	0.12	0.067	0.053
4.0	8.0	0.073	0.092	-0.019
5.0	7.0	0.077	0.115	-0.038
7.0	5.0	0.129	0.165	-0.036

(Fig.3, Curve 2).

TABLE NO.7.

Wave length 450 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	11.5	0.064	0.01	0.054
1.0	11.0	0.115	0.019	0.096
1.5	10.5	0.143	0.024	0.119
2.0	10.0	0.189	0.034	0.155
2.5	9.5	0.195	0.04	0.155
3.0	9.0	0.168	0.043	0.125
3.5	8.5	0.110	0.045	0.065
4.0	8.0	0.087	0.062	-0.025
5.0	7.0	0.05	0.076	-0.026
7.0	5.0	0.079	0.098	-0.019

(Fig.4, Curve 2).

TABLE NO. 8.

Wave length 460 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	11.5	0.055	0.009	0.046
1.0	11.0	0.101	0.013	0.088
1.5	10.5	0.127	0.015	0.112
2.0	10.0	0.167	0.023	0.144
2.5	9.5	0.180	0.025	0.155
3.0	9.0	0.155	0.025	0.13
3.5	8.5	0.095	0.035	0.06
4.0	8.0	0.037	0.043	-0.006
5.0	7.0	0.037	0.05	-0.013
7.0	5.0	0.055	0.06	-0.004

(Fig. 5, Curve 2).

Set III.

TABLE No. 9.

Wave length 440 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	11.5	0.048	0.009	0.039
1.0	11.0	0.088	0.02	0.068
1.5	10.5	0.117	0.025	0.092
2.0	10.0	0.141	0.03	0.111
2.5	9.5	0.145	0.035	0.110
3.0	9.0	0.121	0.042	0.079
4.0	8.0	0.07	0.058	0.009
5.0	7.0	0.061	0.075	-0.014
6.0	6.0	0.075	0.086	-0.011
6.5	5.5	0.098	0.097	-0.001

(Fig. 3, Curve 3).

TABLE NO.10.

Wave length 450 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	11.5	0.045	0.006	0.039
1.0	11.0	0.081	0.012	0.069
1.5	10.5	0.103	0.012	0.091
2.0	10.0	0.132	0.015	0.117
2.5	9.5	0.130	0.016	0.114
3.0	9.0	0.105	0.027	0.078
3.5	8.5	0.05	0.04	0.01
4.0	8.0	0.043	0.05	-0.007
6.0	6.0	0.051	0.058	-0.007

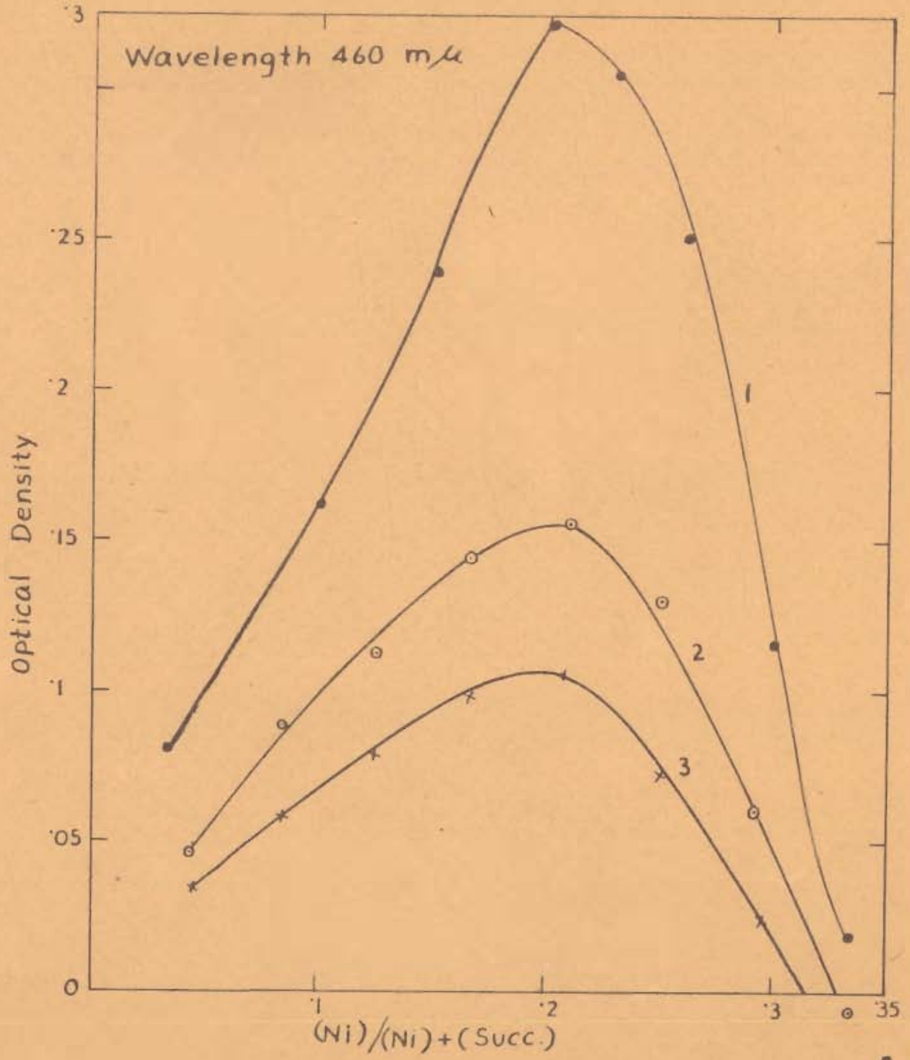
(Fig. 4, Curve 3).

TABLE NO. 11.

Wave length 460 mu.

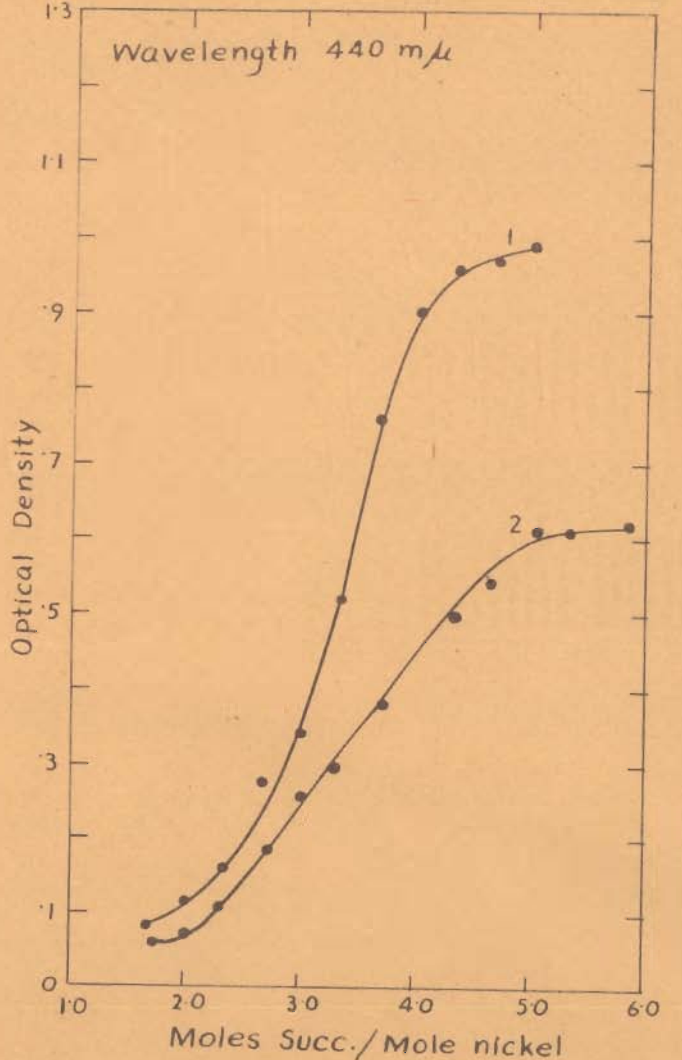
Vol. of $NiCl_2$	Vol. of succinimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	11.5	0.035	0.002	0.033
1.0	11.0	0.068	0.010	0.058
1.5	10.5	0.086	0.008	0.078
2.0	10.0	0.108	0.010	0.098
2.5	9.5	0.120	0.015	0.105
3.0	9.0	0.085	0.012	0.073
3.5	8.5	0.044	0.019	0.025
4.0	8.0	0.027	0.032	-0.005
6.0	6.0	0.03	0.034	-0.004

(Fig. 5, Curve 3).



JOB'S METHOD

FIG· 5



MOLE RATIO METHOD

FIG· 6

Mono-variation method: The method was developed by Yoe and Jones (9) and was termed the mole ratio method. A series of solutions of increasing ratios of the metal to the reagent or vice-versa are prepared and the absorbance of the mixtures is measured. The plots of O.D. against molar ratio give inflexion corresponding to complex ion formation. When both the reactantsare colourless,the curve rises from the origin as a straight line and breaks sharply to a constant absorbance at the molar ratio of the components in the complex. However,for complexes that undergo dissociation in solution,a continuous curve which becomes approximately paralell to the molar ratio axis is obtained,only when an excess of the variable component is added.

Some-times it is found that the results obtained by extrapolation of this curve are uncertain. It is observed that in many cases such a curve may be made to break sharply at the correct molar ratio, if the ionic strength of the solution is adjusted to a suitable value by addition of an indifferent electrolyte(this is however difficult to achieve in non-aqueous medium). Thus in such cases also, it is possible, to get information about the composition of the complex by this method. Recently Mayer and Ayres(10) deduced the stoichiometry of complexes in solution for situation in which several complexes exist under a given set of conditions from the mole ratio method.

Experiments for the mole ratio method (keeping constant amount of nickel chloride and varying the concentration of succinimide) were performed at two different concentrations of nickel chloride(0.03 M and 0.02 M). The O.D. measurements were carried out at 440,450 and 460 mu. The results are given below:

TABLE NO.12.

Absorption values for mole ratio method.

Concentration of nickel chloride = 0.02 M(in 10 ml.).

Concentration of succinimide = 0.2 M

Total volume 10 ml.in each.

Vol.of $NiCl_2$	Vol.of succinimide	440 mu	450 mu	460 mu
4.0	1.0	0.055	0.035	0.027
4.0	1.7	0.06	0.043	0.03
4.0	2.0	0.073	0.051	0.042
4.0	2.3	0.108	0.085	0.069
4.0	2.7	0.185	0.16	0.14
4.0	3.0	0.255	0.222	0.195
4.0	3.3	0.295	0.26	0.23
4.0	3.7	0.38	0.335	0.305
4.0	4.0	0.50	0.47	0.425
4.0	4.3	0.54	0.50	0.46
4.0	4.7	0.61	0.55	0.50
4.0	5.0	0.61	0.55	0.52
4.0	5.5	0.62	0.56	0.53

Fig.6,Curve 2. Fig.7,Curve 2. Fig.8,Curve 2.

TABLE NO.13.

Absorption values for mole ratio method.

Concentration of nickel chloride =0.03M (in 10 ml.).

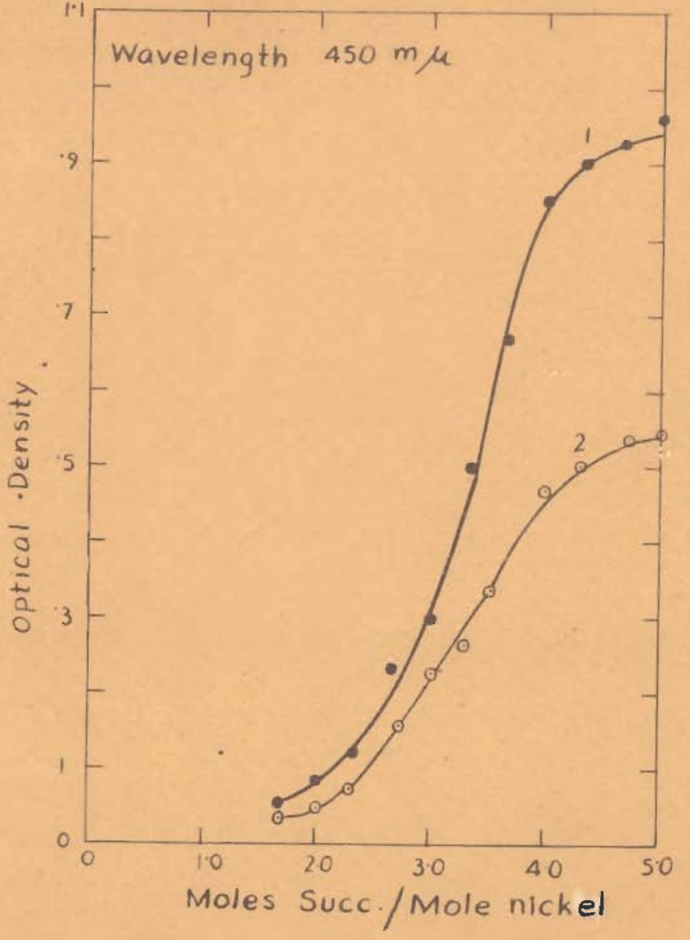
Concentration of succinimide =0.2 M

Total volume made up =10.0 ml.

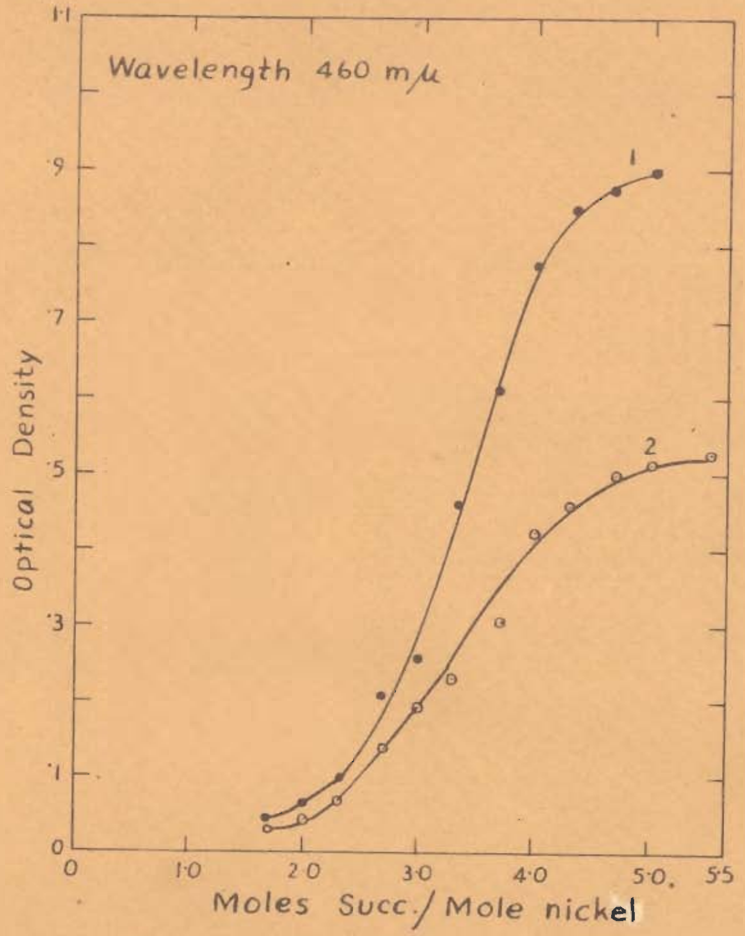
Vol. of $NiCl_2$	Vol. of succinimide	440 mu	450 mu	460 mu
3.0	2.5	0.082	0.055	0.04
3.0	3.0	0.113	0.085	0.065
3.0	3.5	0.16	0.12	0.10
3.0	4.0	0.275	0.235	0.205
3.0	4.5	0.34	0.30	0.26
3.0	5.0	0.52	0.50	0.46
3.0	5.5	0.76	0.67	0.61
3.0	6.0	0.90	0.85	0.775
3.0	6.5	0.96	0.90	0.85
3.0	7.0	0.97	0.93	0.875
3.0	7.5	1.00	0.96	0.90
		Fig.6, Curve 1.	Fig.7, Curve 1.	Fig.8, Curve 1.

Composition of green complex: The solutions of the reactants were mixed according to the method as described under Job's method of continued variation for the yellow complex. Optical density was measured at three different concentrations (1×10^{-1} M, 7.7×10^{-2} M and 5.88×10^{-2} M), for sets I, II and III respectively, at wavelengths 630 mu, 650 mu and 670 mu, for each set. The curves were plotted in the O.D. difference of mixture and metal ion against the ratio $(Ni)^{++}/(Ni)^{++} + (Succ)$. The results are given in the following tables:

MOLE- RATIO METHOD



FIG· 7



FIG· 8

Set I.

TABLE NO.14.

Wave length 630 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	9.5	0.024	0.005	0.019
1.0	9.0	0.058	0.019	0.039
1.5	8.5	0.093	0.020	0.073
2.0	8.0	0.130	0.024	0.106
2.6	7.4	0.176	0.030	0.146
3.0	7.0	0.216	0.040	0.176
3.5	6.5	0.200	0.050	0.150
4.0	6.0	0.195	0.055	0.140
5.0	5.0	0.165	0.061	0.104
6.0	4.0	0.150	0.075	0.075
7.0	3.0	0.139	0.090	0.049
8.0	2.0	0.135	0.110	0.025

Fig.9, Curve 1.

TABLE NO.15.

Wave length 650 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	9.5	0.026	0.008	0.018
1.0	9.0	0.065	0.027	0.038
1.5	8.5	0.100	0.028	0.072
2.0	8.0	0.140	0.036	0.104
2.6	7.4	0.200	0.050	0.150
3.0	7.0	0.225	0.060	0.165
3.5	6.5	0.227	0.075	0.152
4.0	6.0	0.212	0.078	0.134
5.0	5.0	0.200	0.100	0.100
6.0	4.0	0.190	0.117	0.073
7.0	3.0	0.185	0.144	0.041
8.0	2.0	0.185	0.170	0.015

Fig.10, Curve 1.

TABLE NO.16.

Wave length 670 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	9.5	0.025	0.011	0.014
1.0	9.0	0.062	0.027	0.035
1.5	8.5	0.08	0.035	0.045
2.0	8.0	0.120	0.050	0.070
2.3	7.7	0.148	0.062	0.086
2.6	7.4	0.175	0.068	0.107
3.0	7.0	0.220	0.078	0.142
3.5	6.5	0.234	0.095	0.139
4.0	6.0	0.226	0.100	0.126
5.0	5.0	0.227	0.130	0.097
6.0	4.0	0.230	0.160	0.070
7.0	3.0	0.235	0.186	0.049
8.0	2.0	0.245	0.220	0.025

Fig.11, Curve 1.

TABLE NO. 17.

Set II.

Wave length 630 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O. D. mixt.	O. D. $NiCl_2$	Difference
1.0	9.0	0.030	0.013	0.017
1.5	8.5	0.047	0.016	0.031
2.0	8.0	0.075	0.019	0.056
2.5	7.5	0.102	0.024	0.078
3.0	7.0	0.150	0.025	0.125
3.5	6.5	0.146	0.030	0.116
4.0	6.0	0.133	0.037	0.096
5.0	5.0	0.114	0.050	0.064
6.0	4.0	0.104	0.055	0.049
7.0	3.0	0.098	0.067	0.031

Fig.9, Curve 2.

TABLE NO.18.

Wave length 650 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O. D. mixt.	O. D. $NiCl_2$	Difference
1.0	9.0	0.035	0.020	0.015
1.5	8.5	0.058	0.026	0.032
2.0	8.0	0.090	0.030	0.060
2.5	7.5	0.138	0.038	0.100
3.0	7.0	0.164	0.040	0.124
3.5	6.5	0.168	0.049	0.119
4.0	6.0	0.162	0.060	0.102
5.0	5.0	0.145	0.074	0.071
6.0	4.0	0.143	0.087	0.056
7.0	3.0	0.141	0.105	0.036

Fig. 10, Curve 2.

TABLE NO.19.

Wave length 670 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O. D. mixt.	O. D. $NiCl_2$	Difference
1.0	9.0	0.032	0.020	0.012
1.5	8.5	0.050	0.030	0.020
2.0	8.0	0.078	0.035	0.043
2.5	7.5	0.106	0.047	0.059
3.0	7.0	0.153	0.052	0.101
3.5	6.5	0.165	0.060	0.105
4.0	6.0	0.163	0.075	0.088
5.0	5.0	0.159	0.100	0.059
6.0	4.0	0.165	0.122	0.043
7.0	3.0	0.170	0.135	0.035

Fig. 11, Curve 2.

Set III.

TABLE NO.20.

Wave length 630 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O.D. mixt.	O.D. $NiCl_2$	Difference
1.0	9.0	0.030	0.015	0.015
2.0	8.0	0.055	0.018	0.037
2.5	7.5	0.085	0.025	0.060
3.0	7.0	0.125	0.030	0.095
3.5	6.5	0.113	0.033	0.080
4.0	6.0	0.105	0.037	0.068
5.0	5.0	0.097	0.045	0.052
6.0	4.0	0.087	0.055	0.032
7.0	3.0	0.085	0.055	0.030
8.0	2.0	0.073	0.065	0.008

Fig.9, Curve 3.

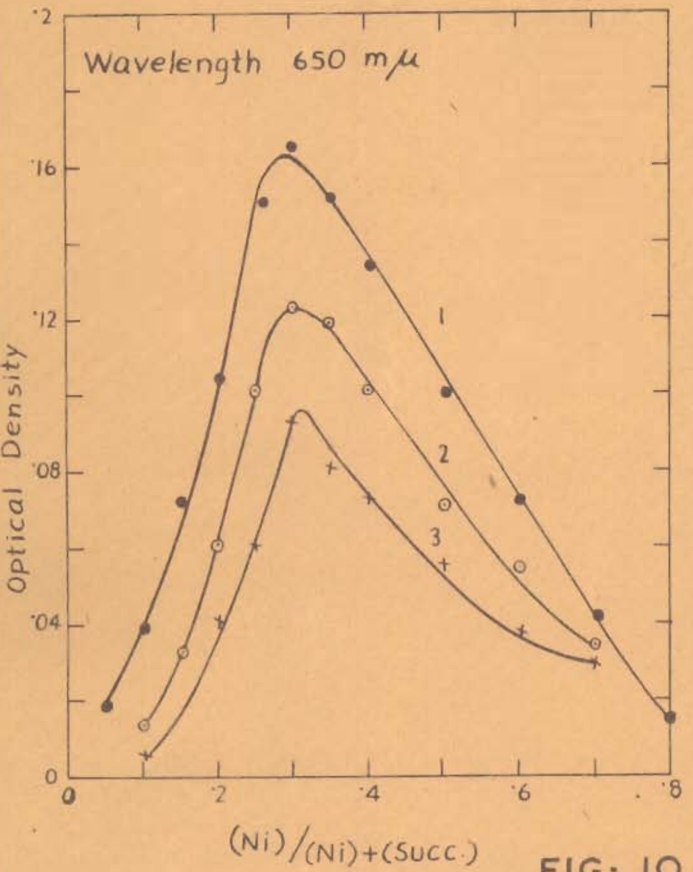
TABLE NO.21.

Wave length 650 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O.D. mixt.	O.D. $NiCl_2$	Difference
1.0	9.0	0.022	0.010	0.012
2.0	8.0	0.065	0.025	0.040
2.5	7.5	0.090	0.032	0.058
3.0	7.0	0.135	0.042	0.093
3.5	6.5	0.130	0.049	0.081
4.0	6.0	0.125	0.052	0.073
5.0	5.0	0.121	0.065	0.056
6.0	4.0	0.115	0.077	0.038
7.0	3.0	0.118	0.087	0.031
8.0	2.0	0.110	0.095	0.015

Fig.10, Curve 3.

JOB'S METHOD



FIG· 10

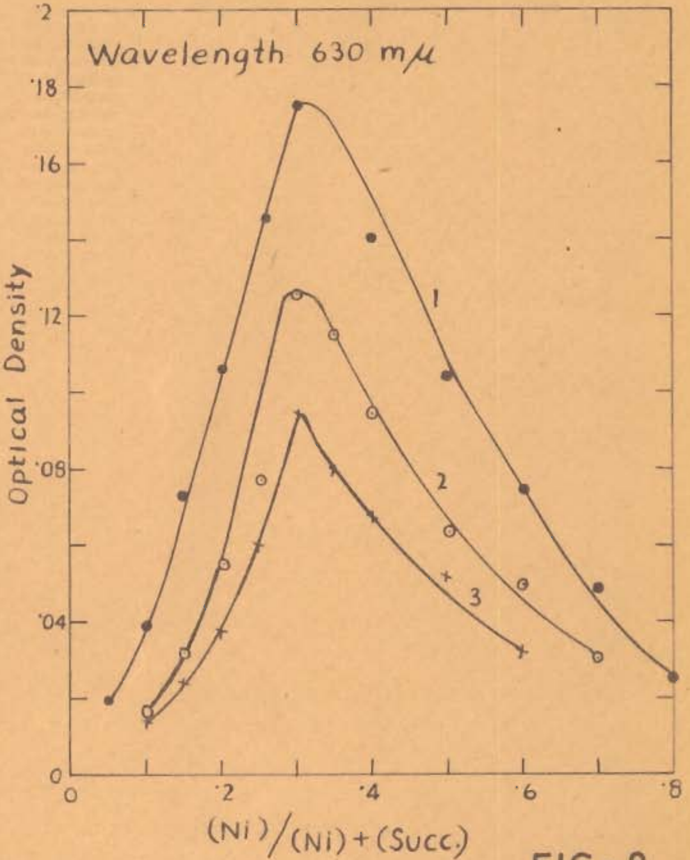


FIG · 9

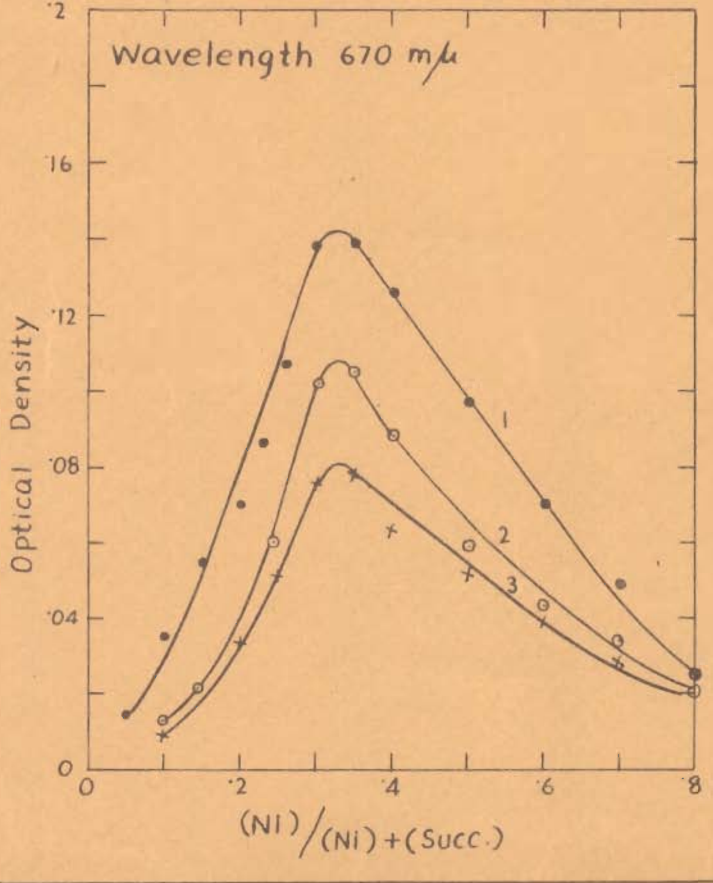


FIG. 11

TABLE NO.22.

Wave length 670 mu.

Vol. of $NiCl_2$	Vol. of succinimide	O.D. mixt.	O.D. $NiCl_2$	Difference
1.0	9.0	0.026	0.016	0.010
2.0	8.0	0.066	0.033	0.033
2.5	7.5	0.092	0.040	0.052
3.0	7.0	0.125	0.050	0.075
3.5	6.5	0.135	0.057	0.078
4.0	6.0	0.127	0.062	0.065
5.0	5.0	0.132	0.080	0.052
6.0	4.0	0.133	0.095	0.038
7.0	3.0	0.135	0.105	0.030
8.0	2.0	0.140	0.120	0.020

Fig. 11, Curve 3.

Mole ratio method: The mole ratio method was employed here also to confirm the results of the method of continued variation. The experiments were carried out at two different concentrations of nickel chloride (0.02M and 0.03M). The results were as follows;

O.D. values of mixtures prepared according to mole ratio method.

TABLE NO.23.

Concentration of nickel chloride = 0.03 M (in 10 ml.).

Concentration of succinimide = 0.2 M

Total volume made up = 10 ml.

Vol. of $NiCl_2$	Vol. of succinimide	630 mu	650 mu	670 mu
3.0	0.5	0.053	0.07	0.08
3.0	1.0	0.07	0.09	0.11
3.0	1.5	0.09	0.114	0.12
3.0	2.0	0.117	0.137	0.14
3.0	2.5	0.144	0.165	0.16
3.0	3.0	0.199	0.211	0.197
3.0	3.5	0.190	0.202	0.186
3.0	4.0	0.171	0.185	0.169
3.0	4.5	0.170	0.183	0.170
3.0	5.0	0.158	0.175	0.165
		Fig.12, Curve 1.	Fig.13, Curve 1.	Fig.14, Curve 1.

TABLE NO.24.

Concentration of nickel chloride = 0.02 M (in 10 ml.).

Concentration of succinimide = 0.2 M

Total volume made up = 10 ml.

Vol. of $NiCl_2$	Vol. of succinimide.	630 mu	650 mu	670 mu
4.0	0.5	0.039	0.052	0.062
4.0	1.0	0.055	0.07	0.072
4.0	1.3	0.076	0.093	0.091
4.0	1.7	0.100	0.115	0.109
4.0	2.0	0.120	0.132	0.122
4.0	2.3	0.117	0.127	0.115
4.0	2.7	0.108	0.114	0.102
4.0	3.0	0.109	0.109	0.100
		Fig.12, Curve 2.	Fig.13, Curve 2.	Fig.14, Curve 2.

MOLE-RATIO METHOD

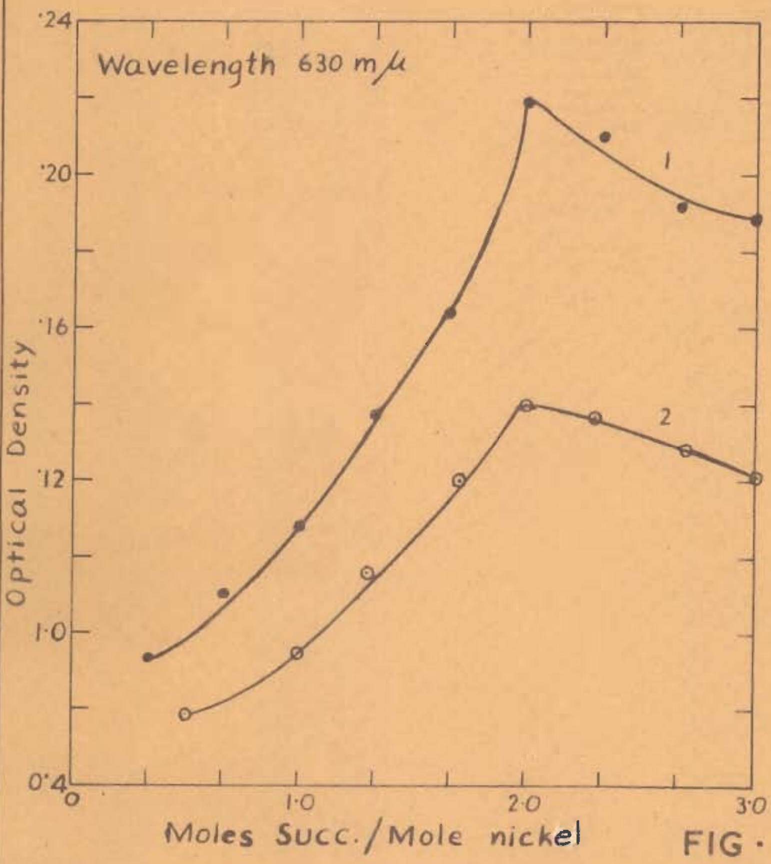


FIG · 12

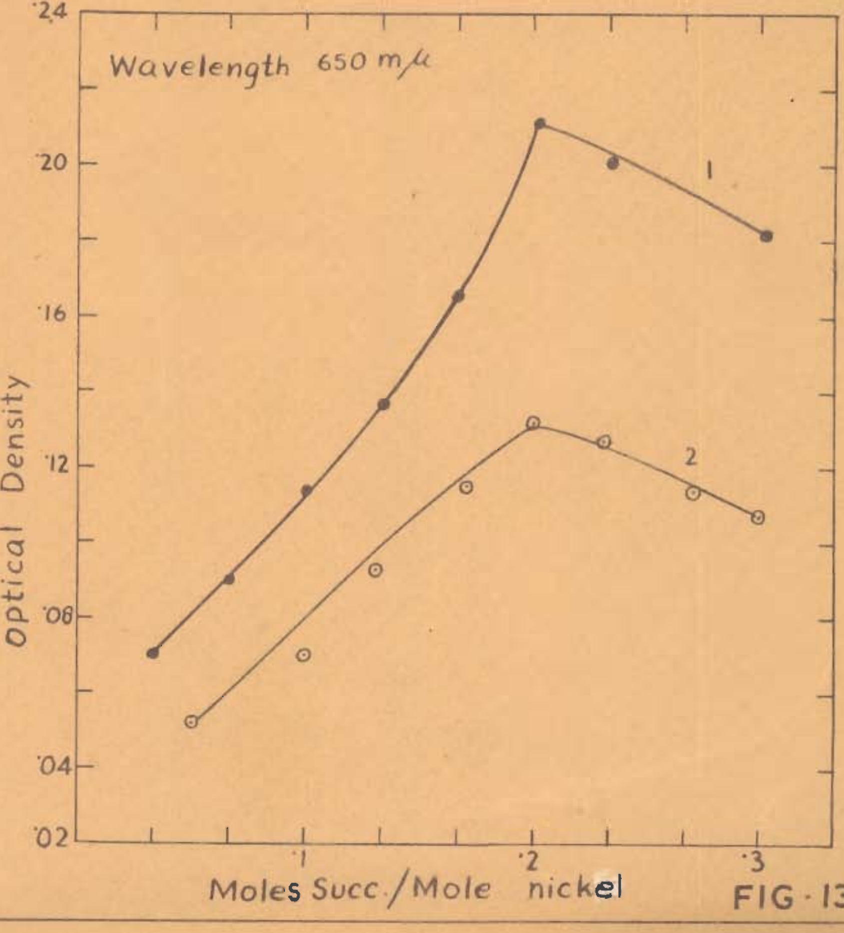


FIG · 13

Stability constants of the complexes.

A number of useful methods are known for the calculation of the stability constants of the complexes formed both in aqueous and non-aqueous media, using absorbance measurements. A brief account of some of the methods is presented here.

The determination of stability constant is essential for a proper understanding of a complex forming system. It is concerned with the reaction between different solvated reactants and products. The thermodynamic constants can also be calculated from a knowledge of the stability constant. However, it is doubtful wheather true thermodynamic quantities of complexes can be determined except in very simple cases, because the method is accompanied by many difficulties. Two main procedures are usually followed in studying the stability constants of the complexes. Lewis and Randall (11) first introduced the concept of ionic strength which later received theoretical justification from the Debye Huckel theory. The classical approach for the evaluation of thermodynamic equilibrium constants involved the determination of the equilibrium constant in media of different low ionic strengths, followed by extrapolation to zero ionic strength(infinite dilution). Some workers (12) have used the value of a single determination and attempted to correct this value to a thermodynamic equilibrium constant by the application to Debye Huckel theory. The second method was introduced by

Biedermann and Sillen (13) and the fundamental idea of the method is to control the activity coefficient by keeping ionic strength constant, because in dilute solutions the activity coefficient of a given strong electrolyte is the same in all the solutions of identical ionic strength. In view of the difficulties encountered in practical determination of true thermodynamic stability constants Rossotti and Rossotti (14) concluded " It would therefore seen better to obtain reliable values of stoichiometric constants (which describe the stability of species relative to the corresponding complexes with solvent molecules and medium ions) than less certain values of thermodynamic constants (which do not give absolute stability either, but only stability related to the solvated molecules)".

These values of the stoichiometry constants are reliable under a given set of experimental conditions and are useful for practical purposes. This constant has been termed as stability constant in the present work.

During present studies, it has not been possible to maintain ionic strength constant by swamping with an indifferent electrolyte, because of the insolubility of electrolyte in methyl alcohol or precipitation or fading of colour, on the addition of an electrolyte. The values of the stability constants determined in this work relate to the complex species formed under given set of experimental conditions.

Method of Anderson and coworkers: For the calculation of the stability constant of metal complexes from absorbance data, a well known method is that described by Anderson and coworkers (15) based on a treatment of composition of solutions having an identical intensity of colour i.e. the same absorbance value. In this method, both the reactants should be colourless.

Dey and coworkers (16,17) modified this method to cases where one of the reactants may be coloured. This method is described below.

In this method observations obtained for the method of continuous variation are utilised and the absorbances (not the difference in absorbance) are plotted against (M) /(M)+ (A), where M is the concentration of the metal ion and A that of complexing agent.

In the present studies the metal solutions are coloured while the ligands are colourless. Hence in the procedure adopted with the progressive increase of M , A decreases and it may be assumed that in the ascending portions of the curve where the ligand moles are in excess, a majority of the metal is bound up in the complex. Moreover the metal has a lower absorption than the complex at the wave lengths of observations. Therefore in this portion of the curve the absorbance of the free metal does not contribute substantially to the absorbances of the system, as a whole. The observed absorbance may, therefore be regarded to be due to the colour of the complex alone. We may therefore assume that in cases of sets of different concentrations, where the absorbances are the same, the respective amounts of the complexes formed in each case are identical.

Let us take the case of a system where a complex is formed with the composition of metal: complexing agent as 1:1 in the general equation

$$mM + nA = M_m A_n ,$$

$m/n = 1$ or $m = n$, the stability constant

$$K = \frac{X}{(a-X)(b-X)} \quad ......(1)$$

Taking two concentrations as a_1 , a_2 and b_1 , b_2 of the reactants (from two curves) having the same absorbance i.e. the same value of X, we have

$$K = \frac{X}{(a_1-X)(b_1-X)} = \frac{X}{(a_2-X)(b_2-X)}$$

$$\text{or} \quad X = \frac{a_1 b_1 - a_2 b_2}{(a_1+b_1) - (a_2+b_2)} \quad .... (2)$$

Knowing the value of X in (2), the value of K can be found by substitution in equation (1).

Now taking the case of a complex where the ratio of the reactants is 1:2 and the reaction takes place as

$$M + 2A = MA_2$$

$$K = \frac{x}{(a-x)(b-2x)^2} \quad .....(3)$$

Taking two concentrations a_1 , a_2 and b_1 , b_2 having the same absorbance i.e. the same value of x, we have

$$K = \frac{x}{(a_1-x)(b_1-2x)^2} = \frac{x}{(a_2-x)(b_2-2x)^2} \quad ....(4)$$

$$\text{or } x = \frac{-b_2^2 - b_1^2 + 4(a_2b_2 - a_1b_1) \pm \sqrt{b_2^2 + b_1^2 + 4(a_2b_2 - a_1b_1)^{\,2} - 16\,(a_1+b_1) - (a_2+b_2)\,(a_1b_1^2 - a_2b_2^2)}}{8\left[(a_1+b_1) - (a_2+b_2)\right]} \quad ..(5)$$

Knowing the value of x from equation (5), the value of K can be found out from equation (4) by substitution.

Comparitive study of the various methods for the determination of stability constants has been made by Anderson and coworkers(loc.cit.) and they concluded that the method involving the comparison of the solution of equal absorbance yeilds results which are more reproducible. Several other methods for the determination of the stability constants of coloured complexes have also been made spectrophotometrically (18,19).

Mole ratio method: Stability constant can also be evaluated from mole ratio method. The dissociation of the complex may be represented by

$$\begin{array}{llll} MA_n & = M & + nA & \\ c & 0 & 0 & \text{initial concentration} \\ c(1-\alpha) & \alpha c & n\alpha c, & \text{equilibrium concentration,} \end{array}$$

where c is the total concentration of the complex ion in moles per litre assuming no dissociation, and α is the degree of dissociation, the stability constant may be written as

$$K = c\ (1-\alpha)/(\alpha c) \times (n\alpha c)^n \quad \ldots(6)$$

The value of n for the complex having been established, value of α may be obtained from the mole ratio curves by the following relation

$$\alpha = \frac{E_M - E_S}{E_M} \quad ....(7)$$

E_M is the maximum extinction obtained from the horizantal portion of the curve, indicating that all the reagent is present in the form of complex. E_S is the extinction of stoichiometric molar ratio of metal to reagent in the complex, the total concentration of the complex being equal to the concentration of the reagent.

1:4,nickel-succinimide,yellow complex:

The stability constant was computed from data given in Fig.6, Curve 2, employing equation (6) page (45), for mole ratio method. The results are described in the discussion.

1:2,nickel-succinimide,green complex:

The stability constant was calculated by the method recommended by Anderson(loc.cit.) and extended by Dey and coworkers. The equation (5), page (45), was used for the purpose.

In actual experimentation two sets of mixtures of different concentration (0.1M and 0.077 M) of the reactants were prepared by mixing nickel chloride and succinimide, according to the method of continuous variation. Optical density of the mixtures containing nickel and succinimide was plotted against mole fraction of nickel at two concentration.

TABLE NO. 25.

O.D. values for stability constant of 1:2, nickel-succinimide, green complex.

Set I. Concentration of the reactants = 0.1M

Set II. Concentration of the reactants = 0.077M

Vol. of $NiCl_2$	Vol. of succinimide	Set I	Set II
1.0	9.0	0.065	0.035
1.5	8.5	0.100	0.058
2.0	8.0	0.140	0.090
2.5	7.5	0.200	0.138
3.0	7.0	0.225	0.164
3.5	6.5	0.227	0.168
4.0	6.0	0.212	0.162
5.0	5.0	0.200	0.145
6.0	4.0	0.190	0.143
7.0	3.0	0.185	0.141
	Fig.15.	Curve 1.	Curve 2.

MOLE-RATIO METHOD

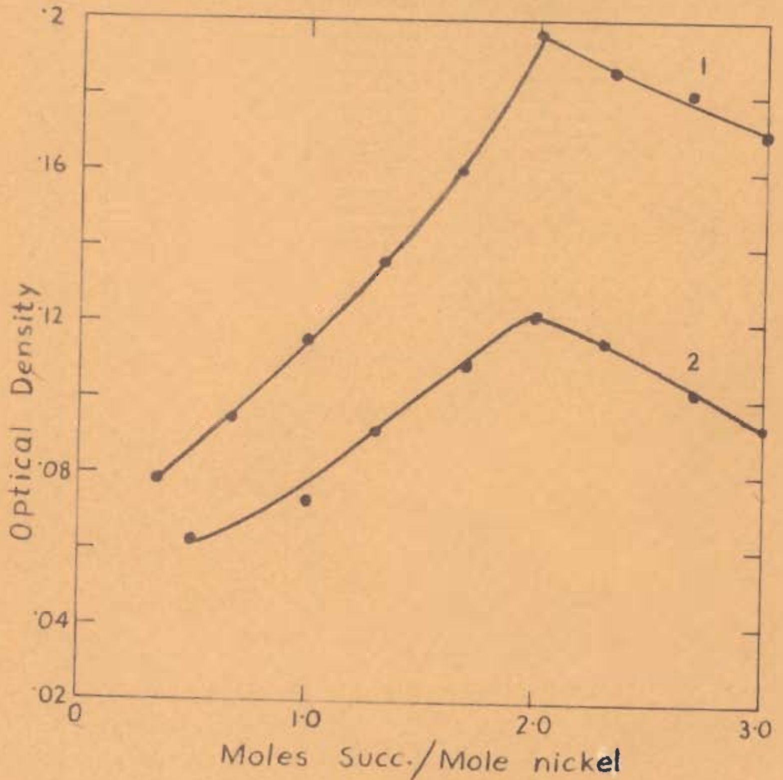


FIG · 14

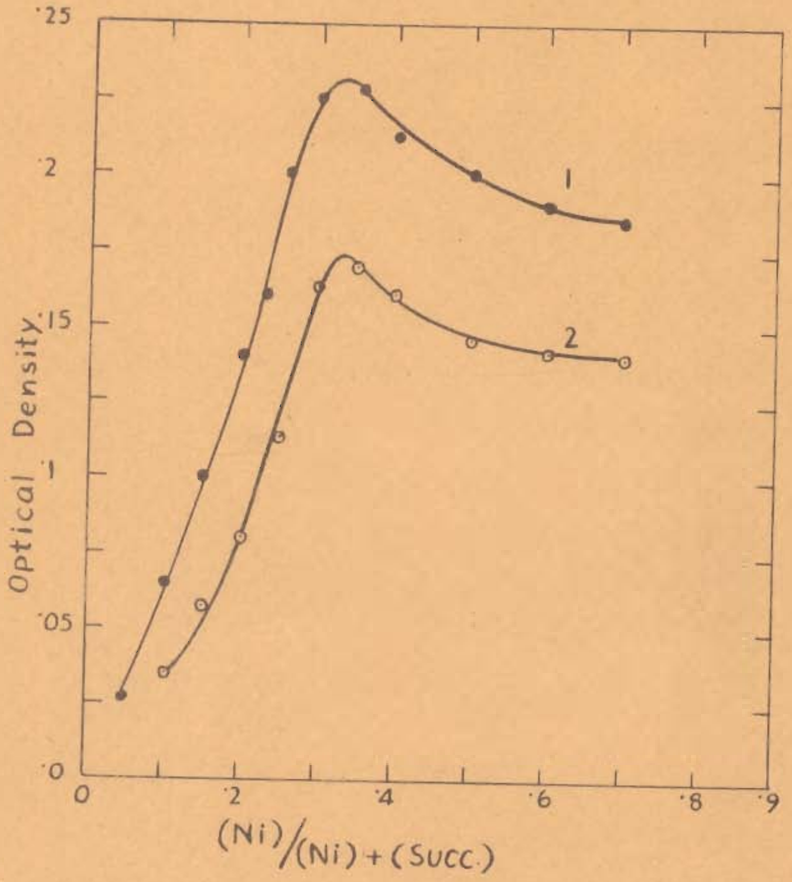


FIG · 15

STABILITY CONST. OF 1:2 (Ni-SUCC.) COMPLEX

Conductometric titrations.

Conductometric titrations of succinimide against nickel chloride were performed by taking methanolic succinimide solution(prepared in equivalent amount of KOH), at different concentrations, in the titration cell. Philips conductivity bridge with bridge type conductivity cell(cell constant 0.44) was used for conductance measurements.

Temperature effects on the conductance were minimised by putting the cell in a large beaker of water. Volume correction was applied by multiplying the conductance value with the fraction V + v/V where V is the volume taken in the cell and v is the volume of the titrant added. The results of the above titrations are given below.

Readings for direct titrations: Succinimide in cell.

TABLE NO. 26.

Concentration of succinimide = 0.5 M
Strength of Ni-chloride solution = 0.3 M
Volume of succinimide solution= 1.4 ml.made up to 25 ml.

Vol. of $NiCl_2$ (ml.)	Corrected conductance (mhosx10^{-3})	Volume of $NiCl_2$ (ml.)	Corrected conductance (mhosx10^{-3})
0.0	2.6178	0.9	2.8986
0.2	2.6247	1.0	2.9674
0.4	2.6247	1.1	3.0488
0.5	2.6810	1.3	3.2573
0.6	2.7248	1.5	3.5336
0.7	2.8011	2.0	3.8911
0.8	2.8524	2.5	4.3478

Fig.16

1.4 ml.of 0.5M succinimide
≡ 0.6 ml. of 0.3 M $NiCl_2$ ≡ 0.36 ml.of 0.5 M $NiCl_2$
Ni: succinimide ≡1:3.9.

TABLE NO.27.

Concentration of succinimide = 0.5 M

Strength of nickel chloride = 0.3 M

Volume of succinimide solution = 2.2 ml.made up to 25 ml.

Vol.of $NiCl_2$ (ml.)	Corrected conductance (mhosx10^{-3})	Volume of $NiCl_2$ (ml.)	Corrected conductance (mhosx10^{-3})
0.0	3.5336	1.1	3.7879
0.1	3.5587	1.2	3.8610
0.2	3.5587	1.3	3.9526
0.3	3.5587	1.4	4.0161
0.5	3.5587	1.5	4.1322
0.6	3.5714	1.7	4.3290
0.7	3.5714	1.8	4.3478
0.8	3.5714	1.9	4.4444
1.0	3.3704	2.0	4.5455

Fig.16, Curve

2.2 ml.of 0.5M succinimide

≡ 0.9 ml.of 0.3 M $NiCl_2$ ≡ 0.54 ml.of 0.5M $NiCl_2$

Ni: succinimide =1:4.08

TABLE NO.28.

Concentration of succinimide = 0.5 M

Strength of nickel chloride = 0.3 M

Volume of succinimide solution = 2.6 ml.made up to 25 ml.

Vol.of $NiCl_2$ (ml.)	Corrected conductance (mhosx10^{-3})	Volume of $NiCl_2$ (ml.)	Corrected conductance (mhosx10^{-3})
0.0	4.0323	1.5	4.3478
0.2	4.0323	1.7	4.5455
0.4	4.0000	1.9	4.7619
0.6	4.0000	2.1	4.9505
0.8	3.9683	2.3	5.0505
1.0	4.0000	2.5	5.2083
1.1	4.0323	2.7	5.3191
1.3	4.1667	3.0	5.5560

Fig.16,Curve

2.6 ml.of 0.5 M succinimide

≡1.1 ml.of 0.3M $NiCl_2$ ≡ 0.66 ml.of 0.5 M $NiCl_2$

Ni:succinimide = 1:3.94

TABLE NO.29.

Concentration of succinimide = 0.5 M

Strength of nickel chloride = 0.3 M

Volume of succinimide solution = 3.4 ml.made up to 25 ml.

Vol.of $NiCl_2$ (ml.)	Corrected conductance (mhosx10^{-3})	Vol.of $NiCl_2$ (ml.)	Corrected conductance (mhosx10^{-3})
0.0	4.9261	1.5	4.8309
0.2	4.9261	1.6	4.8780
0.4	4.8544	1.8	5.0000
0.6	4.8077	2.0	5.2520
0.8	4.8077	2.3	5.5556
1.0	4.8077	2.6	4.8140
1.2	4.7847	2.8	5.9172
1.3	4.7619	3.0	6.0976

Fig. 16,Curve

3.4 ml.of 0.5 M succinimide

$\equiv$ 1.4 ml. of 0.3 M $NiCl_2$ $\equiv$ 0.84 ml. of 0.5 M $NiCl_2$

Ni: succinimide = 1:4.05

Reverse titrations also were successfully performed by taking nickel chloride along with four equivalents of KOH,in the cell and titrating it against methanolic succinimide solution.

CONDUCTOMETRIC TITRATIONS

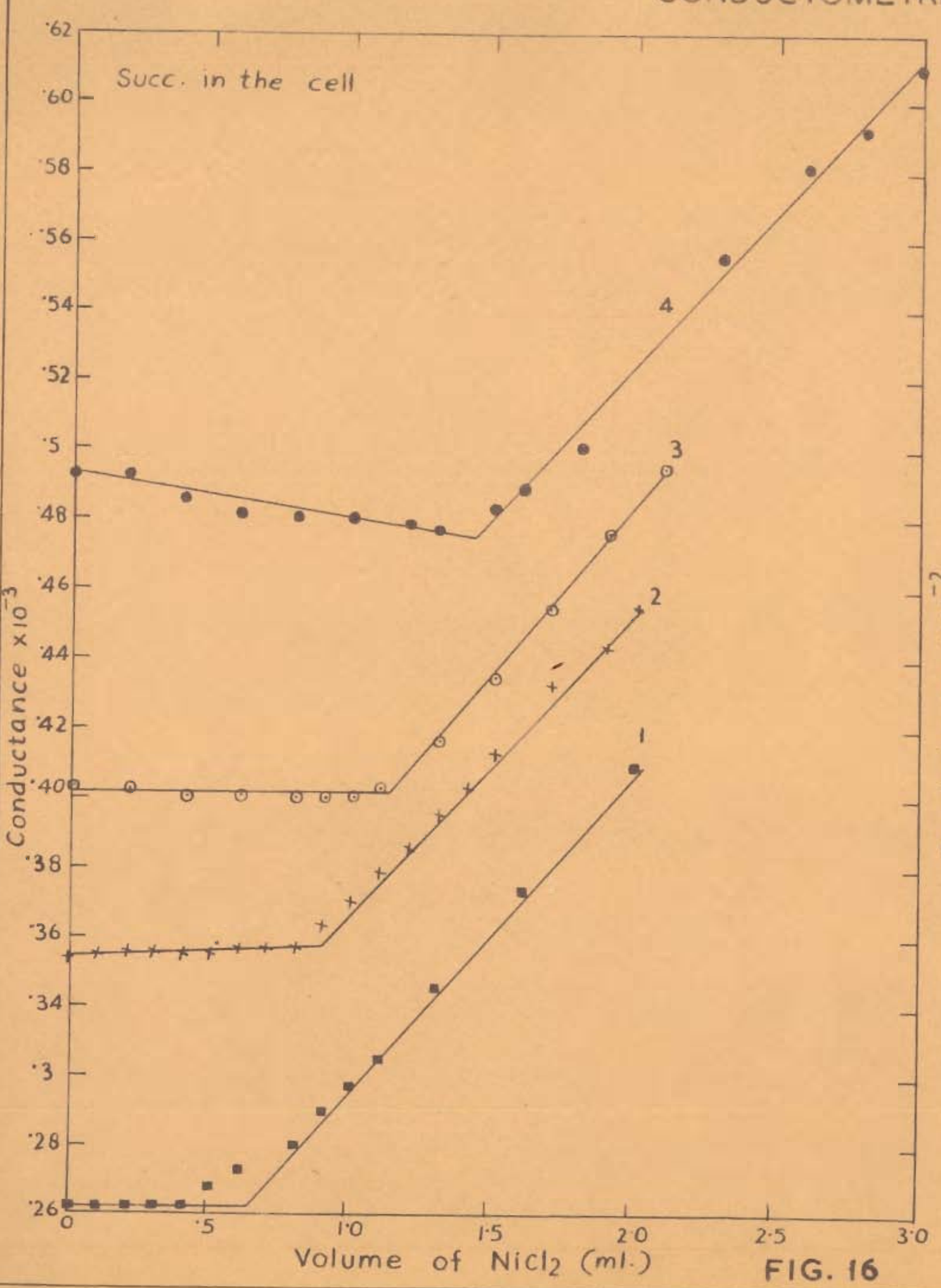


FIG. 16

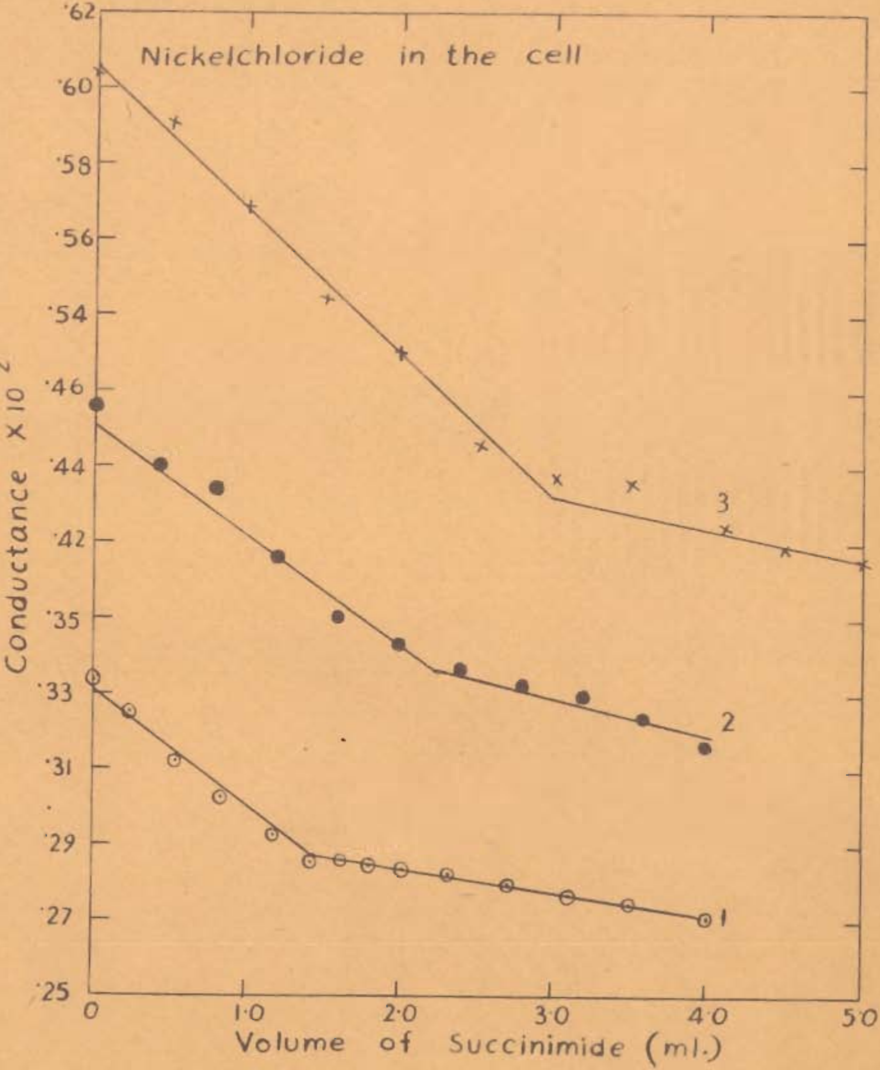


FIG · 17

Reverse titrations : $NiCl_2$ in the cell.

TABLE NO.30

Concentration of succinimide = 0.5 M

Strength of $NiCl_2$ solution = 0.1 M

Volume of $NiCl_2$ solution = 2.0 ml.

Vol. of succinimide. (ml.).	Corrected conductance (mhos $x10^{-2}$)	Volume of succinimide (ml.)	Corrected conductance (mhos $x10^{-2}$)
0.0	0.3344	2.0	0.2849
0.2	0.3257	2.3	0.2833
0.5	0.3125	2.7	0.2801
0.8	0.3012	3.1	0.2770
1.1	0.2915	3.5	0.2755
1.4	0.2862	4.0	0.2703
1.6	0.2860	-	-

Fig.17, Curve

2 ml. of 0.1M $NiCl_2$

= 1.5 ml. of 0.5 M succinimide= 7.5 ml. of 0.1M succinimide.

Ni: succinimide = 1:3.75

TABLE NO.31.

Concentration of succinimide = 0.5 M

Strength of $NiCl_2$ solutions = 0.1 M

Volume of $NiCl_2$ solution = 3.0 ml.

Vol. of succinimide(ml.)	Corrected conductance (mhos$x10^{-2}$)	Vol. of succinimide (ml.)	Corrected conductance (mhos$x10^{-2}$)
0.0	0.4560	2.4	0.3876
0.4	0.4400	2.8	0.3831
0.8	0.4348	3.2	0.3802
1.2	0.4167	3.6	0.3745
1.6	0.4016	4.0	0.3663
2.0	0.3937	-	-

Fig.17, Curve

3 ml. of 0.1M $NiCl_2$

=2.3 ml. of 0.5 M succinimide=11.5 ml. of 0.1M succinimide

Ni: succinimide =1:3.83.

TABLE NO.32.

Concentration of succinimide = 0.5 M

Strength of $NiCl_2$ solution = 0.1 M

Volume of $NiCl_2$ solution = 4.0 ml.

Vol. of succinimide (ml.)	Corrected conductance (mhos $\times 10^{-2}$)	Vol. of succinimide (ml.)	Corrected conductance (mhos $\times 10^{-2}$)
0.0	0.6050	3.0	0.4975
0.5	0.5952	3.5	0.4950
1.0	0.5600	4.1	0.4831
1.5	0.5376	4.5	0.4785
2.0	0.5305	5.0	0.4739
2.5	0.5051	-	-

Fig.17, Curve

4 ml. of o.1M $NiCl_2$

= 3.1 ml. of 0.5 M succinimide = 15.5 ml. of 0.1 M succinimide

Ni: succinimide = 1:3.88

pH metric studies.

Most significant advance in the chemistry of co-ordination compounds started with the publication of Bjerrum's work (1941) in his famous book on "Metal Ammine Formation In Aqueous solutions" for determining the stability constants by pH measurements. Bjerrum emphasised that complex formation usually follows stepwise course. The general equilibrium between a metal ion M and ligand A is written in steps.

$$M + A = MA$$

$$MA + A = MA_2$$

$$MA_{N-1} + A = MA_N$$

The individual formation constants are given by

$$K_1 = (MA)/(M)(A)$$

$$K_2 = (MA_2)/(MA)(A)$$

$$K_N = (MA_N)/(MA_{N-1})(A)$$

The quantity $\bar{n}$ has been defined by Bjerrum as the average number of co-ordinated groups per metal ion present ; all metal ions wheather co-ordinated or not are taken into consideration.

$$\bar{n} = \frac{(MA) + 2(MA_2) + 3\,(MA_3) + \ldots\ldots N(MA_N)}{(M) + (MA) + (MA_2) + \ldots\ldots (MA_N)}$$

The value of $\bar{n}$ is determined experimentally by measurement of pH since the removal of free donor groups by co-ordination alters in pH by amounts which may be used to calculate the number of groups co-ordinated. The difference between concentration of ligand added and the concentration of ligand co-ordinated is the concentration of free ligand, (A). $\bar{n}$ is also named as formation function and a plot of $\bar{n}$ against -log (A) as the formation curve. Bjerrum has shown mathematically that when experimental conditions are adjusted to specific values for $\bar{n}$, the following relations hold good for the case N = 2

If $\bar{n} = 0.5$, $K_1 = 1/(A)$

If $\bar{n} = 1.5$, $K_2 = 1/(A)$

If $\bar{n} = 1$ $\sqrt{K_1K_2} = K = 1/(A)$

The "average constant" K, is also the square root of the constant K of the over-all reaction

$$M + 2A \overset{K}{=} MA_2 \quad (N = 2).$$

The Bjerrum's method has been extensively used by workers in the field of co-ordination chemistry. The method was examplified by the work of Calvin and Melchior(20) with the 5-sulpho-salicylaldehyde complex of copper (II). 5-sulpho-salicylaldehyde was titrated with sodium hydroxide and the titration was repeated in the presence of copper (II) ions. At any value of pH the distance between the two curves gave the amount of alkali, needed to neutralise the protons, freed by the co-ordinating organic groups. This amount of hydroxide gives the quantity of the coordinated ligand, and, when divided by the known metal concentration, gave the value of $\bar{n}$. The dissociation constant of the aldehyde and the known concentration of the uncoordinated aldehyde, were used for the calculation of (A), the concentration of free aldehyde anion.

In order to study the structure of the metal-imide complexes, formed in the aqueous and methanolic media, Bjerrum's method extended by Calvin and Melchior(loc.cit.) was applied. For the case of 1:4 metal-ligand complex, the sum of the reaction is $M + 4A = MA_4$. The stability constant in terms of equilibrium constants for this reaction is given by

$$K = \frac{(MA_4)}{(M)(A)^4} = K_1 \times K_2 \times K_3 \times K_4$$, where K_1 , K_2 , K_3 and K_4 represent the stepwise constants of the four steps. If T_{HA} represents the total concentration of the ligand and T_M that of the metal ion and (A) of free ligand, then

$$T_{HA} = (HA) + (A) + (MA) + 2(MA)_2 + 3\ (MA_3) + 4\ (MA_4)$$

$$T_M = (M) + (MA) + (MA_2) + (MA_3) + (MA_4).$$

$$(HA) + (A) = T_{HA} - (MA) - 2(MA_2) - 3\ (MA_3) - 4\ (MA_4)$$

$$(A) + \frac{(A)(H)}{K} = T_{HA} - (MA) - 2\ (MA_2) - 3\ (MA_3) - 4\ (MA_4)$$

$$(A) = \frac{T_{HA} - (MA) - 2(MA_2) - 3(MA_3) - 4(MA_4)}{1 + (H)/K}$$

Thus at various values of pH, a set of $\bar{n}$ values was determined, and the concentration of free ligand (A) was calculated from the above equation. The values of $\bar{n}$ were plotted against the corresponding values of -log (A) to give formation curve. The stepwise stability constants, log K_1 , log K_2 , log K_3 , log K_4 are equal to the values of -log A at $\bar{n}$, 0.5, 1.5, 2.5, and 3.5 respectively.

Bjerrum has introduced a spreading factor x, between two successive stability constants, such that

$$\frac{K_n}{K_{n+1}} = \frac{(n+1)(N-n+1)}{n(N-n)} \times x^2$$

and showed that the above equation holds in general case, where N may be any integer. Therefore "the average constant", or the N<u>th</u> root of the over all constant K, is equal to the reciprocal of the free ligand concentration when the degree of formation, n/N, is 0.5. Thus regardless of spreading factor, x, the value of the average formation constant may be determined graphically from the plot of $\bar{n}$ versus the reciprocal values of (A). In actual practice $\bar{n}$ is plotted against log (1/(A)), or pA and value of log K is read directly from the graph.

<u>Nickel succinimide complex in methanolic medium:</u>

pH-metric titrations of succinimide, with and without the presence of nickel chloride, were performed against standard methanolic solution of potassium hydroxide, according to the method of Calvin and Melchior (loc. cit.). Cambridge bench type pH meter in conjunction with Cambridge glass electrode and S.C.E. was used for pH measurements. Standard potassium hydroxide methanolic solution was added to the reaction vessel from an automatic micro burette. Nitrogen gas (free from oxygen, carbondioxide and moisture) was used for maintaining an inert atmosphere, as well as for stirring the solution.

The solution of succinimide was separately titrated pH metrically, and the value of pK was calculated at half titration value. The results of the pH metric titrations, performed at three different concentrations of metal ion, are tabulated in the following tables, each accompanied by the calculation table for formation curve, i.e. the values of $\bar{n}$ and -log A.

TABLE NO.33.

Titration for pK value of succinimide(methanolic solution).

10.0 ml. of 0.1 M succinimide,titrated against(0.1M) KOH.

Vol.of KOH(ml.).	pH	Vol.of KOH(ml.).	pH
0.0	6.43	2.5	9.45
0.2	8.83	3.0	9.5
0.4	9.02	4.0	9.6
0.8	9.25	5.0	9.75
1.5	9.34	6.0	9.8
2.0	9.4	7.0	9.86

Fig.18

pK value of succinimide = 9.74

TABLE NO.34

Titration of succinimide in absence of nickel chloride.

10.0 ml. of 0.5 M succinimide,titrated against (0.15 M)KOH.

Total volume made up-to 15 ml. by methyl alcohol.

Vol.of KOH(ml.)	pH	Vol.of KOH(ml.)	pH
0.0	6.33	2.0	9.08
0.1	8.38	2.5	9.1
0.2	8.62	3.2	9.14
0.4	8.82	4.0	9.16
0.6	8.9	4.5	9.18
0.8	8.95	5.0	9.19
1.2	9.01	-	-
1.5	9.04	-	-

Fig.19,Curve 1.

Titrations of succinimide in presence of $NiCl_2$:

Concentration of succinimide = 0.5 M

Strength of $NiCl_2$ solution = 0.1 M

Strength of KOH solution = 0.15 M

TABLE NO. 35.

10 ml. succinimide - 0.3 ml. $NiCl_2$, total volume made upto 15 ml. by methyl alcohol.

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.)	pH
0.0	3.93	1.4	8.9
0.1	4.96	2.2	9.03
0.2	5.96	2.6	9.07
0.3	7.3	3.0	9.1
0.4	7.88	3.5	9.12
0.5	8.3	4.0	9.14
0.6	8.53	4.5	9.15
0.8	8.69	5.0	9.17
1.0	8.79	-	-

Fig. 19, Curve 2.

TABLE NO. 35(A).

Calculations table for formation curve.
For 0.3 ml. of $NiCl_2$ (0.1M) $\equiv 0.3 \times 10^{-4}$ moles.

pH	Δ KOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	- log. Succ.
5.0	0.117	0.16	0.59	5.2204
5.5	0.15	0.225	0.75	4.7214
6.0	0.2	0.3	1.0	4.2229
6.33	0.233	0.359	1.20	3.8937
6.67	0.24	0.36	1.20	3.5540
7.0	0.24	0.36	1.20	3.2240
7.33	0.25	0.375	1.25	2.8943
7.67	0.28	0.42	1.5	2.5557
8.0	0.34	0.51	1.75	2.2268
8.33	0.40	0.60	2.0	1.8985
8.67	0.50	0.75	2.5	1.5614
8.83	0.725	1.08	3.6	1.4069
9.0	0.80	1.20	4.0	1.2397
9.1	0.80	1.20	4.0	1.1397

Fig. 20, Curve 1.

TABLE NO.36.

10 ml.succinimide, 0.8 ml.$NiCl_2$, total volume made upto 15 ml. by methyl alcohol.

Vol.of KOH(ml.).	pH	Vol.of KOH(ml.).	pH
0.0	3.10	1.40	8.52
0.1	4.45	1.60	8.62
0.2	4.89	1.80	8.69
0.3	5.24	2.00	8.74
0.40	5.62	2.50	8.87
0.5	6.26	3.00	9.00
0.6	6.90	3.50	9.06
0.7	7.27	4.00	9.10
0.8	7.54	4.50	9.13
1.0	8.02	5.00	9.17
1.2	8.36	-	-

Fig.19,Curve 3.

TABLE NO.36(A).

Calculations table for formation curve,

For 0.8 ml.of $NiCl_2$ (0.1 M) ≡ 0.8×10^{-4} moles.

pH	Δ KOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log.Succ.
5.0	0.25	0.333	0.416	5.2243
5.5	0.375	0.550	0.69	4.7279
6.0	0.475	0.713	0.891	4.2307
6.33	0.50	0.75	0.937	3.9014
6.67	0.525	0.787	0.984	3.5621
7.0	0.60	0.90	1.125	3.2334
7.33	0.68	1.02	1.27	2.9065
7.67	0.75	1.125	1.41	2.5683
8.0	0.875	1.313	1.73	2.2417
8.33	1.05	1.696	2.12	1.9165
8.67	1.35	2.248	2.81	1.5845
9.0	2.12	3.248	4.06	1.2624

Fig.20,Curve 2.

TABLE NO.37.

10 ml. of succinimide,1.2 ml. $NiCl_2$,total volume made upto 15 ml. by methyl alcohol.

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.).	pH
0.0	3.13	1.4	7.90
0.1	4.35	1.6	8.19
0.2	4.68	1.8	8.37
0.3	4.91	2.0	8.47
0.4	5.18	2.6	8.66
0.5	5.44	3.0	8.74
0.6	5.68	3.5	8.84
0.7	6.06	4.0	8.94
0.8	6.54	4.5	9.01
1.0	7.2	5.0	9.06
1.2	7.55	6.0	9.14

Fig. 19,Curve 4.

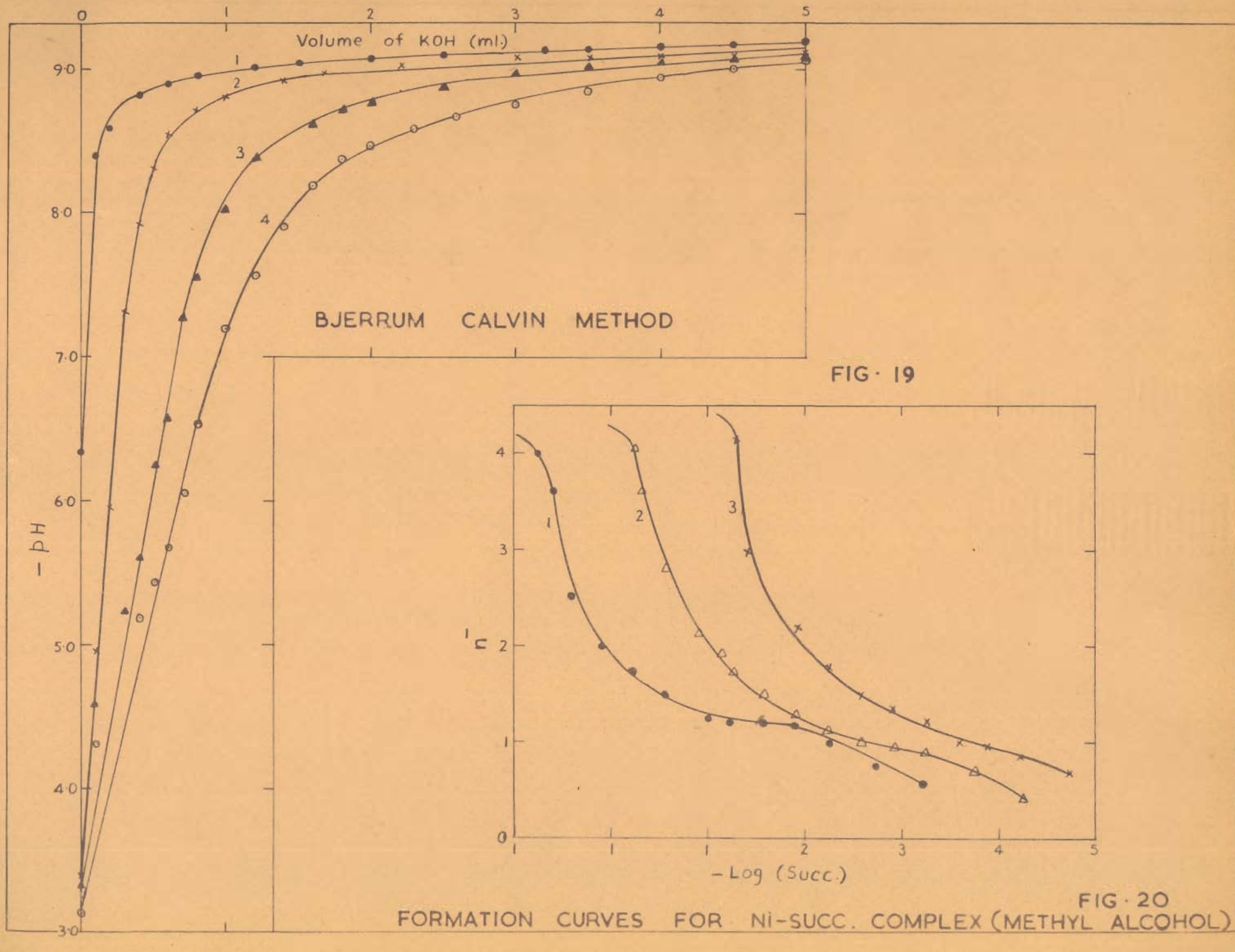
TABLE NO. 37(A).

Calculations table for formation curve,

For 1.2 ml. of $NiCl_2$ (0.1 M) = 1.2×10^{-4} moles.

pH	Δ KOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log. $\overline{\text{Succ}}$.
5.0	0.35	0.525	0.437	5.2279
5.5	0.55	0.825	0.688	4.7328
6.0	0.675	1.1013	0.844	4.2334
6.33	0.75	1.125	0.938	3.9083
6.67	0.775	1.162	0.97	3.5690
7.0	0.90	1.45	1.21	3.2400
7.33	1.07	1.60	1.33	2.9151
7.67	1.20	1.80	1.50	2.5805
8.0	1.40	2.10	1.75	2.2552
8.33	1.73	2.60	2.17	1.9325
8.67	2.37	3.55	2.96	1.4053
9.00	3.30	4.95	4.12	1.2828

Fig.20,Curve 3.



BJERRUM CALVIN METHOD

FIG · 19

FIG · 20
FORMATION CURVES FOR Ni-SUCC. COMPLEX (METHYL ALCOHOL)

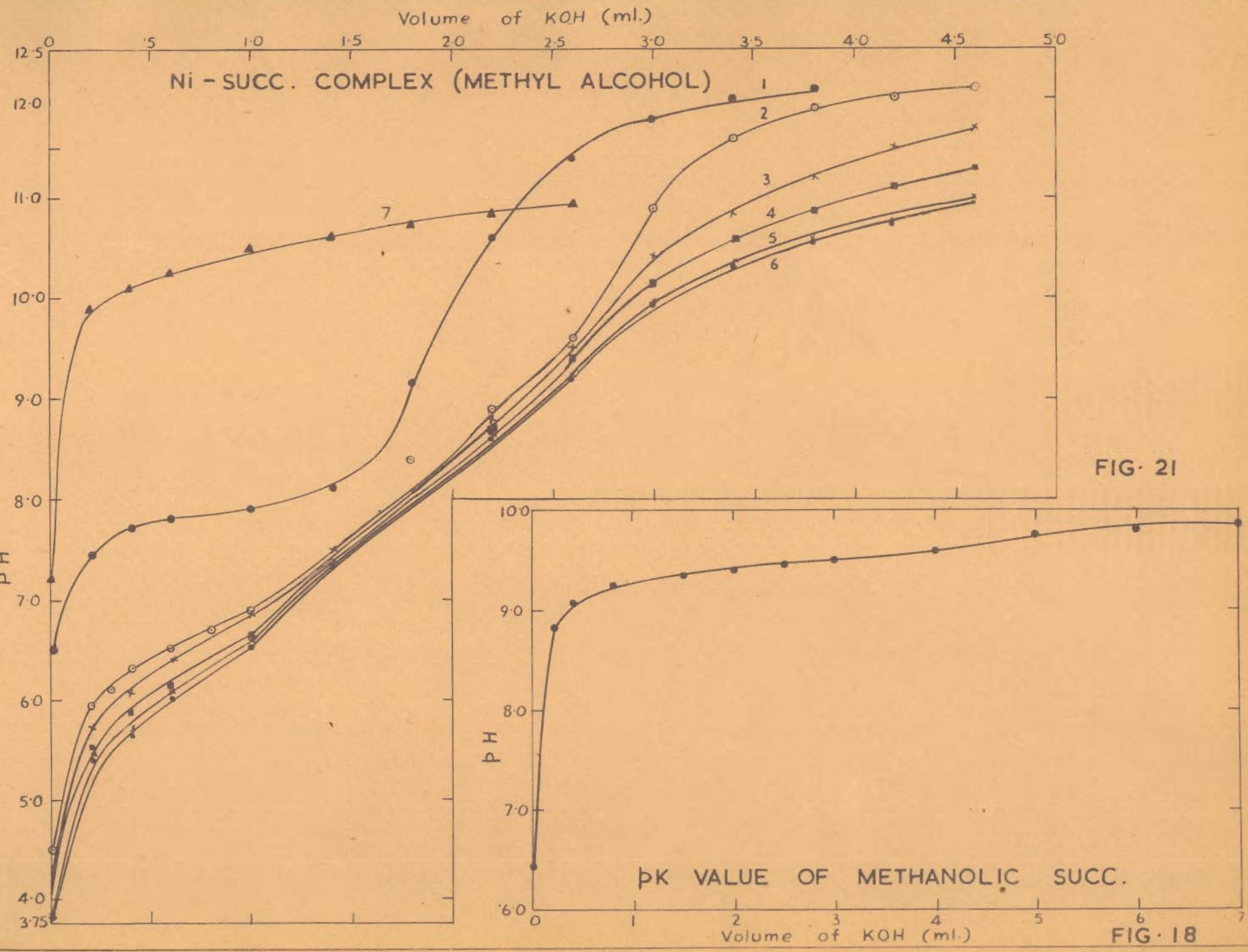
For obtaining further confirmation of the composition of complex, nickel chloride as such and also in presence of one, two, three, four and five fold equivalents of succinimide solution, were separately titrated against potassium hydroxide solution. Succinimide alone was also titrated against potassium hydroxide solution. Details of concentrations and volumes of the reactants, used, for this purpose are summarised below. Actual observations can be read from Fig. 21.

TABLE NO. 38.

Concentration of succinimide solution = 0.05M
Concentration mf nickel chloride = 0.05 M
Concentration of potassium hydroxide = 0.1 M
Total volume in each set made upto 20 ml. by methylalcohol.

$NiCl_2$ Vol. (ml.).	Succinimide (Vol. (ml.)	$NiCl_2$: Succinimide	Curve No.
3.0	0.0	1:0	1
3.0	3.0	1:1	2
3.0	6.0	1:2	3
3.0	9.0	1:3	4
3.0	12.0	1:4	5
3.0	15.0	1:5	6
0.0	15.0	0:1	7

Fig. 21.


Volume of KOH (ml.)
Ni - SUCC. COMPLEX (METHYL ALCOHOL)
1
2
3
4
5
6
7
pH
0
·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0
12·5
12·0
11·0
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·75
pK VALUE OF METHANOLIC SUCC.
pH
10·0
9·0
8·0
7·0
6·0
0
1
2
3
4
5
6
7
Volume of KOH (ml.)

FIG· 21

FIG· 18

Nickel succinimide complex in aqueous medium:

Nickel chloride A.R.(B.D.H.) was dissolved in doubly distilled water to obtain stock solution. Its strength was determined gravimetrically by weighing as nickel-dimethyl-glyoxime. Succinimide solution was prepared by direct weighing and dissolving the calculated amount in double distilled water. Stock solution of potassium hydroxide was standardised by titrating against standard oxalic acid solution. The apparatus and details of procedure in these pH titrations, were similar to those employed for methanolic medium. The scheme adopted for tabulating results was also same as for nickel succinimide complex in non-aqueous medium.

TABLE NO. 39.

Titration for pK values of succinimide(aqueous solution).

10 ml. of 0.1 M succinimide,titrated against(0.1 M) KOH.

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.).	pH
0.0	4.56	3.5	9.04
0.1	6.94	4.0	9.13
0.2	7.41	4.5	9.20
1.0	8.36	5.0	9.29
1.5	8.55	6.0	9.42
2.0	8.71	7.0	9.58
2.5	8.84	8.0	9.76
3.0	8.95	9.0	9.98

Fig.22

pK value of succinimide = 9.29

TABLE NO.40.

Titration of succinimide in absence of $NiCl_2$.

10.0 ml. of 0.5 M succinimide titrated against(0.1M) KOH.

Total volume made upto 15 ml.by water.

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.).	pH
0.0	4.63	2.5	8.10
0.1	5.22	3.0	8.19
0.2	6.36	4.0	8.30
0.3	6.85	5.0	8.40
0.4	7.12	6.0	8.49
0.6	7.40	7.0	8.57
0.8	7.57	8.0	8.64
1.0	7.68	9.0	8.70
1.57	7.87	10.0	8.75
2.0	8.00	-	-

Fig.23,Curve 1.

Titrations of succinimide in presence of $NiCl_2$:

Concentration of succinimide = 0.5 M
Strength of $NiCl_2$ solution = 0.1 M
Strength of KOH solution = 0.1 M

TABLE NO. 41

10 ml. succinimide, 0.7 ml. $NiCl_2$, total volume made upto 15 ml. by water.

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.).	pH
0.0	4.45	2.0	7.80
0.1	5.07	2.4	7.92
0.2	5.63	2.8	8.03
0.3	6.02	3.2	8.11
0.4	6.28	3.6	8.18
0.5	6.51	4.0	8.25
0.7	6.84	4.5	8.32
0.9	7.10	5.0	8.38
1.2	7.37	5.5	8.43
1.6	7.63	6.0	8.48
1.8	7.73	7.0	8.55

Fig. 23, Curve 2.

TABLE NO. 41(A).

Calculations table for formation curve.
For 0.7 ml. of $NiCl_2$ (0.1M) = 0.7×10^{-4} moles.

pH	△ KOH (ml.).	Moles of KOH $\times 10^{-4}$	$\bar{n}$	$-\log.\overline{\text{Succ}}$.
5.0	0.04	0.04	0.06	4.7683
5.33	0.075	0.075	0.107	4.4363
5.67	0.10	0.10	0.143	4.1000
6.0	0.15	0.15	0.214	3.7714
6.333	0.25	0.25	0.357	3.4413
6.67	0.35	0.35	0.50	3.1071
7.00	0.50	0.50	0.71	2.7814
7.333	0.60	0.60	0.85	2.4511
7.50	0.65	0.65	0.93	2.2855
7.67	0.70	0.70	1.00	2.1199
8.00	0.72	0.70	1.02	1.7869

Fig. 24, Curve 1.

þK VALUE OF AQUOUS SUCC.

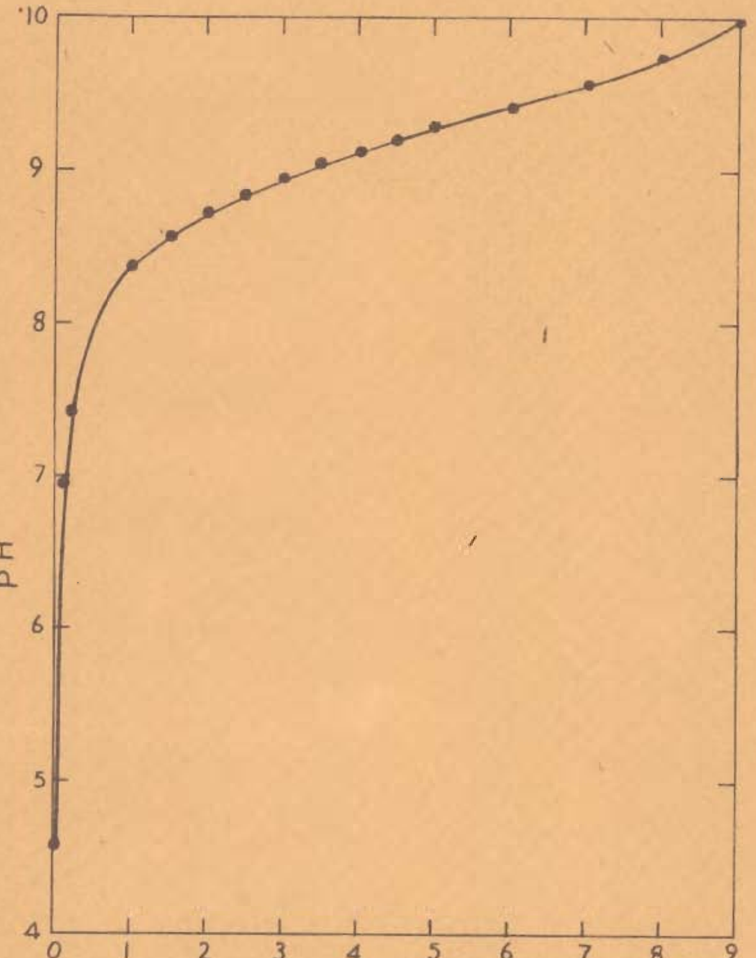


FIG · 22

TABLE NO.42.

10 ml.succinimide,1.0 ml.$NiCl_2$,total volume made upto 15 ml.by water.

Vol.of KOH(ml.).	pH	Vol.of KOH(ml.).	pH
0.0	4.35	2.0	7.62
0.1	4.98	2.5	7.80
0.2	5.48	3.0	7.93
0.3	5.83	3.5	8.04
0.4	6.10	4.0	8.13
0.5	6.28	4.5	8.20
0.6	6.46	5.0	8.26
1.0	6.94	5.5	8.30
1.2	7.13	6.0	8.36
1.7	7.47	7.0	8.44

Fig.23,Curve 3.

TABLE NO.42(A).

Calculations table for formation curve.
For 1.0 ml.of $NiCl_2$ (0.1 M) =1.0 x 10^{-4} moles.

pH	△ KOH (ml.).	Moles of KOH x 10^{-4}	$\bar{n}$	-log $\bar{Succ}$.
5.0	0.05	0.05	0.05	4.7684
5.333	0.10	0.10	0.10	4.4370
5.67	0.15	0.15	0.15	4.1014
6.00	0.175	0.175	0.175	3.7722
6.333	0.30	0.30	0.30	3.4427
6.67	0.50	0.50	0.50	3.1114
7.00	0.725	0.725	0.725	2.7876
7.333	0.95	0.95	0.95	2.4608
7.67	1.05	1.05	1.05	2.1265
8.00	1.10	1.10	1.10	1.7979
8.17	1.10	1.10	1.10	1.6279

Fig.24,Curve 2.

TABLE NO. 43.

10 ml. succinimide, 1.5 ml. $NiCl_2$, total volume made upto 15 ml. by water.

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.).	pH
0.0	4.32	2.0	7.48
0.1	4.87	2.5	7.70
0.2	5.35	3.0	7.87
0.3	5.71	3.5	8.00
0.4	5.99	4.0	8.10
0.5	6.18	4.5	8.19
0.7	6.45	5.0	8.27
0.9	6.66	6.0	8.40
1.2	6.94	6.5	8.44
1.4	7.10	7.0	8.47
1.6	7.22	7.5	8.51

Fig. 23, Curve 4.

TABLE NO. 43(A).

Calculations table for formation curve.

For 1.5 ml. of $NiCl_2$ (0.1 M) =1.5 x 10^{-4} moles.

pH	△ KOH (ml.).	Moles of KOH $x10^{-4}$	$\bar{n}$	-log Succ^{-}.
5.333	0.10	0.10	0.067	4.4370
5.67	0.15	0.15	0.10	4.1014
6.00	0.25	0.25	0.167	3.7743
6.333	0.375	0.375	0.25	3.4449
6.67	0.65	0.65	0.433	3.1155
7.00	0.90	0.90	0.60	2.7924
7.333	1.15	1.15	0.767	2.4662
7.67	1.45	1.45	0.967	2.1372
8.00	1.50	1.50	1.00	1.8085
8.20	1.50	1.50	1.00	1.6085

Fig. 24, Curve 3.

TABLE NO.44.

10 ml. of succinimide, 2.0 ml. of $NiCl_2$, total volume made upto 15 ml. by water.

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.).	pH
0.0	4.30	2.5	7.44
0.1	4.88	3.0	7.65
0.2	5.31	3.5	7.80
0.3	5.62	4.0	7.93
0.4	5.86	4.5	8.03
0.5	6.00	5.0	8.12
0.7	6.23	6.0	8.20
1.0	6.53	6.5	8.26
1.4	6.83	7.0	8.32
2.0	7.20	7.5	8.37

Fig.23, Curve 5.

TABLE NO.44(A).

Calculations table for formation curve.

For 2.0 ml. of $NiCl_2$(0.1 M) = 2.0×10^{-4} moles.

pH	△ KOH (ml.).	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log $\overline{\text{Succ}}$.
5.0	0.075	0.075	0.038	4.7693
5.333	0.125	0.125	0.0625	4.4377
5.67	0.20	0.20	0.10	4.1029
6.00	0.35	0.35	0.175	3.7771
6.333	0.60	0.60	0.30	3.4511
6.67	0.925	0.925	0.462	3.1231
7.00	1.30	1.30	0.65	2.8032
7.333	1.75	1.75	0.875	2.4820
7.67	2.05	2.05	1.025	2.1527
8.00	2.20	2.20	1.10	1.8266

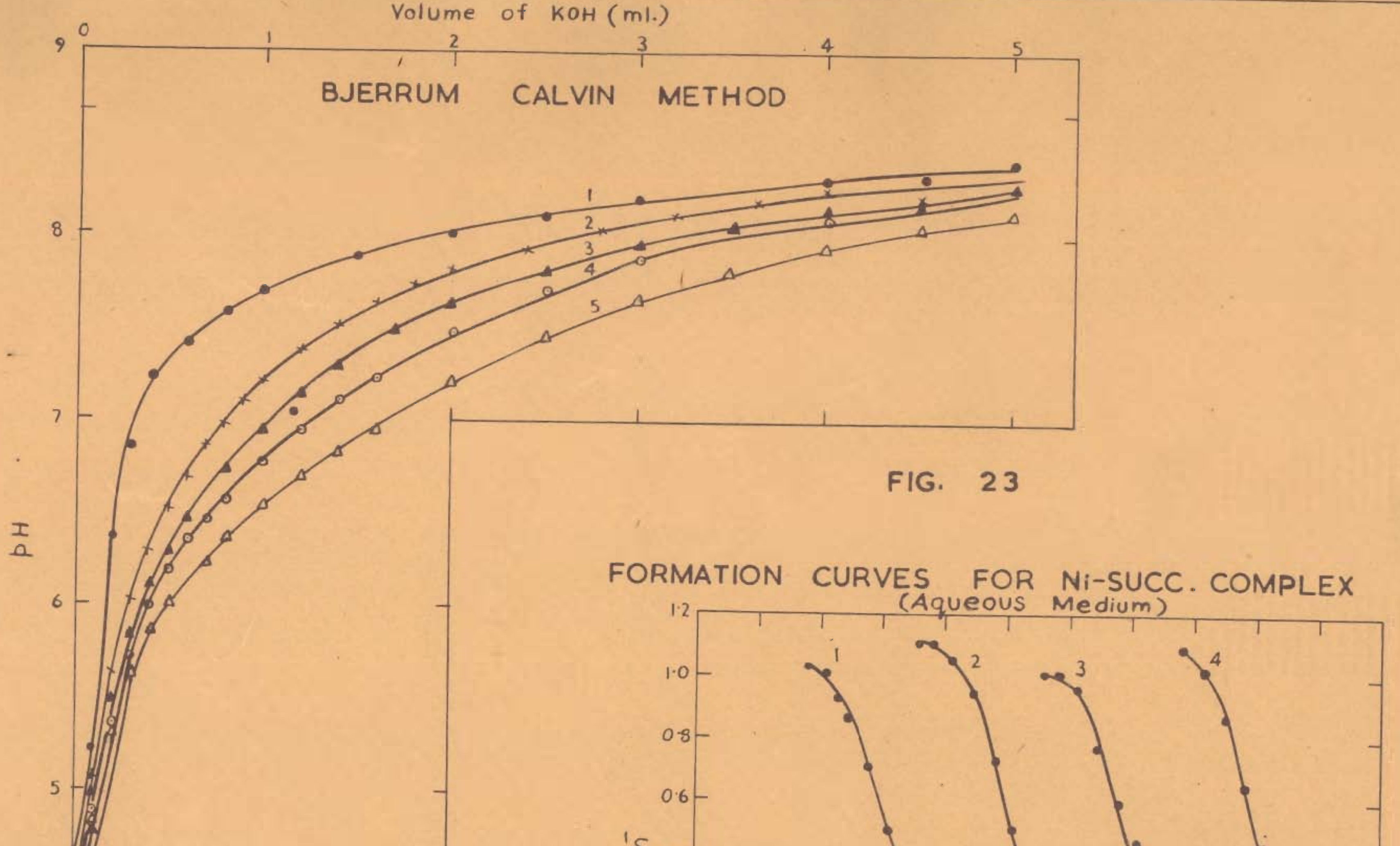
Fig.24, Curve 4.

Isolation and chemical analysis of the yellow nickel succinimide complex:

1:4, nickel succinimide complex was found to decompose in presence of higher proportions (more than 1:4, Ni:Succ.) of nickel, therefore 500 ml. of 0.1M nickel chloride was gradually added to 500 ml. of 0.5 M succinimide, prepared in equivalent amount of potassium hydroxide. The pH was adjusted in the vicinity of 9.5. The resulting mixture was concentrated in a vacuum dessicator, when the golden yellow crystals of nickel succinimide complex were isolated. These crystals were washed several times with methyl alcohol in order to remove adhering impurities of caustic potash, nickel chloride and succinimide, and then dried in a vacuum dessicator.

For estimation of nickel, a weighed amount of dried sample of the complex was digested with aqua-regia and its nickel content was estimated gravimetrically by dimethyl glyoxime.

The nitrogen estimation of the complex was carried out using Kjeldahl's volumetric method. 0.2 gms. of the complex was taken in Kjeldahl's flask and 2 ml. of concentrated sulphuric acid and 150 mg of catalyst (32 parts by weight of potassium sulphate, 5 parts of mercuric chloride and 1 part of selenium powder) were added. The flask was heated first slowly on a small flame and then boiled vigorously until the solution became clear and straw yellow in colour. The distillation of ammonia was carried out using Parnas and Wagner's apparatus and was absorbed in standard hydrochloric acid which was titrated back with



BJERRUM CALVIN METHOD

FIG. 23

FORMATION CURVES FOR Ni-SUCC. COMPLEX
(Aqueous Medium)

FIG. 24

NaOH.

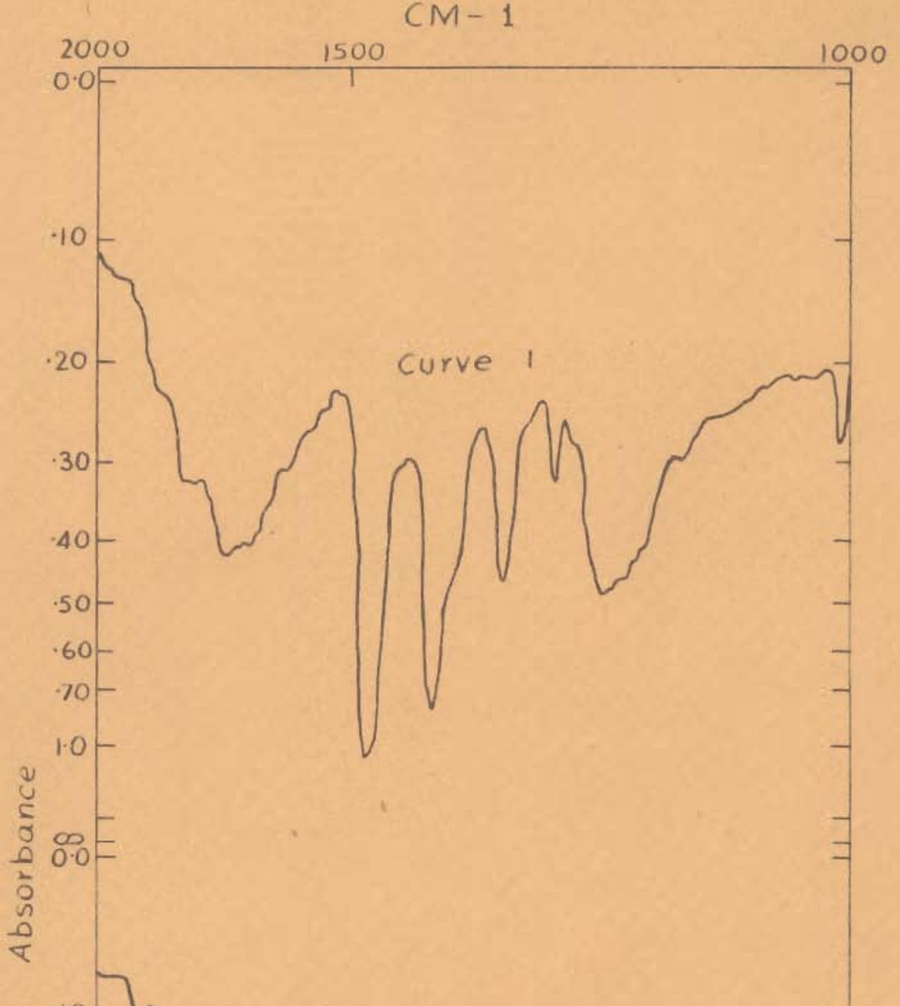
The results of analysis are as follows:

Percentage of nickel = 12.9 %

Percentage of nitrogen = 12.33%

Infra-red of spectroscopy:

I.R. Spectrum of nickel succinimide complex was taken in the nujol medium by the method of fast scanning, in the infra red region. For comparing this spectrum with that of ligand, infra red spectrum of succinimide was also scanned by the above method. Perkin Elmer, Infra cord was used for carrying out these studies. The spectra obtained are depicted in Fig.25.



Curve 1. Succinimide

Curve 2. Ni - Succinimide Complex

I. R. SPECTRA

FIG. 25

DISCUSSION

The following information on the composition of the nickel-succinimide complexes, studied in the non-aqueous medium, was obtained on employing the various physico-chemical methods.

Spectrophtometric studies:

On applying VosBurgh and Cooper's method for the mixtures (nickel chloride to succinimide as 2:1, 1:1, 1:2, 1:4, 1:6 and 1:8) at different wavelengths, two maxima corresponding to 400 and 650 mu (Fig. 2) were obtained, indicating thereby the existence of two complexes. The choice of the wave-lengths at which these complexes could be studied was not easy to make, since the first peak was very close to that of the methanolic solution of nickel chloride, obtained at 405 mu irrespective of the metal ligand ratio in the mixtures. However, in the wave-length region 430 to 480 mu. mixtures containing excess of succinimide showed much greater absorption than those, containing higher proportions of the metal (Fig. 2, Curves 4-6). The yellow complex formed in excess of succinimide could, therefore, be successfully studied spectrophotometrically in the wave-length region 430 to 480 mu.. The methanolic solution of nickel chloride showed negligible absorption in this region of wave-lengths. On the other hand there was no difficulty in making a choice of wave-lengths for the second complex, since the second peak was pronounced, only for mixtures containing excess of nickel chloride (Fig. 2, Curves 1-3).

Composition and stability constant of the yellow complex:- The maximum peaks in Job's curves(Figs.3-5) corresponding to the formation of 1:4 (Ni-succinimide)complex were obtained when the difference of O.D. of the mixtures of succinimide and metal ions against ratio (Ni)/(Ni)+(Succinimide), was plotted at wave-lengths 440,450 and 460 mu.. The range of the mixtures analysed was,however,limited due to the decomposition of the complex in excess of nickel chloride.

Further confirmation regarding the composition of this complex was obtained on the basis of molar ratio method. The plot of O.D. vs. molar ratio of succinimide to nickel,(keeping nickel constant and varying succinimide) gave curves with the inflexion points corresponding to the ratio 1:4 (nickel : succinimide) (Figs.6-8).

The stability constant of the complex was determined by the molar ratio method due to Harvey and Manning. The formation of 1:4 complex can be represented by the equation $M + 4\,A = MA_4$, for which the stability constant K is given by $K = C\,(1-\alpha) / \alpha C \times (4\alpha C)^4$, where α is the degree of dissociation and C the concentration of the complex. The degree of dissociation of the complex is given by $\alpha = Em - Es / Em$, where E_m is the maximum absorption obtained from the horizantal portion of the plot of O.D. of the solution against,moles of reagent/ mole of nickel and E_s is the observed absorption at the stoichiometric molar ratio.

Fig.6,Curve 2, has been utilised for the calculations of stability constant of 1:4 yellow complex. The value of stability constant K was found to be, 2.869×10^5.

Composition and stability constant of green complex:- As already stated the complex was found stable in excess of nickel-chloride. A larger number of nickel-succinimide mixtures could be subjected to analysis by Job's method in this case than for the yellow complex. In the region of wavelengths 630-670 mu, the plots of difference of O.D. against molar fraction of nickel, gave a peak for the existence of 1:2 (nickel-succinimide)complex (Figs.9-11).

In the monovariation method the nature of the curves (Figs.12-14) was slightly different from those of the typical molar ratio curves. The O.D. values were found to decrease after the stoichiometric ratio had been realised, instead of remaining constant. This decrease could be explained due to the formation of 1:4 (nickel-succinimide) yellow complex in presence of excess of succinimide. This was also evident from the fact that the absorption of yellow coloured complex was much less than that of the green variety in this region of wavelengths(630-670 mu), Fig.2.

The stability constant K of this complex was determined by the method of Anderson and coworkers (loc.cit.) using equations 3 and 5, Pages 44 and 45. From Fig.15, the values of a_1 , b_1 and a_2 , b_2 from first and second sets were, 1.8×10^{-2}M, 8.2×10^{-2}M and 2×10^{-2}M, 5.7×10^{-2}M, respectively. The value of K calculated from the above equation, came out to be, 6.14×10^4.

Conductometric studies:

Direct conductometric titrations with methanolic succinimide(prepared in equivalent amount of KOH) in the cell gave sharp inflexion points(Figs.16,Curve 1-4) corresponding to the formation of 1:4 complex.

As regards the reverse titrations(nickel chloride in the cell), it looked in the beginning as if the precipitation of nickel hydroxide in presence of four equivalents of methanolic potassium hydroxide would interfere with the titrations. But it was later found that gradual addition of succinimide to freshly precipitated hydroxide,resulted in its decomposition and subsequent change into the yellow complex. The conductometric titrations,under this condition, were quite successful, again giving a sharp inflexion for the combining ratio: 1 nickel to 4 succinimide(Fig.17,Curves 1-3). The steep fall in conductance before the realisation of the inflexion point was due to the removal of caustic potash during the formation of the complex. Afterwards, very little variations in conductance took place on addition of excess of succinimide.

pH-metric studies:

Bjerrum's method has certain limitations when applied to systems studied in non-aqueous medium,since the pH scale set for aqueous medium is not applicable to non-aqueous medium. The values of stability constant determined for these systems would not,therefore,be the real values but would be the apparent ones. The K,calculated from -log succ. and $\bar{n}$ i.e. the formation curves(Fig.20) in the non-aquéous medium,have therefore,been designated as"apparent stability constants. Henceforth the term apparent stability constant has been used in subsequent discussions.

pH-metric titrations of succinimide alone and in presence of nickel ions,performed according to the method recommended by Calvin and Melchior gave typical pH-metric curves(Fig.19). From the shift of the curves the excess amount of alkali consumed was calculated. The plots of $\bar{n}$ against - log succ. (Fig.20,Curves 1-3),were employed for determining the average apparent stability constant of the 1:4 complex. The value of over all apparent stability constant,was computed from the average stability constant value as shown below:

Curves	Average stability constant log k=-log A at $\bar{n}$=2.	Over all stability constant log K=4 log k	Mean log K
1	1.95	7.80	7.93
2	2.00	8.00	
3	2.00	8.00	

The gradual increase in the value of $\bar{n}$ with increase of pH showed that the anionic form of succinimide was responsible for the complex-ion with nickel.

Further confirmation was forthcoming from the pH-metric titrations of succinimide alone and of nickel-succinimide mixtures prepared in ratios as 1:1,1:2,1:3,1:4, and 1:5. From these curves (Fig.21) it could be concluded that the reaction between nickel and succinimide takes place with the liberation of protons,the limiting condition was reached with 1:4,nickel succinimide mixture. Afterwards overlapping of the curves was observed showing thereby that a maximum of four protons can be liberated in the reaction per metal ion. This confirmed the existence of 1:4 nickel-succinimide complex.

Analysis of the yellow complex:

Analysis of the isolated complex gave : Ni = 12.9% and N_2 = 12.33 %. The values are in quite agreement with theoretical values.

I.R.spectra:

The I.R.spectra of succinimide and its 1:4 complex with nickel were recorded in the sodium chloride region(Fig. 25). The main feature of the spectrum was a marked shift in the carbonyl stretching frequency from 1750 cm^{-1} (succinimide) to 1660 cm^{-1} (complex), pointing towards metal-oxygen binding in the complex. This may be true for the isolated complex which may change its nature on heating and drying,but is not possible for the complex in solution where both chemical evidence and pH-metric data gave strong indication of co-ordination through nitrogen. Moreover, the complex showed interesting splitting of the band of the type shown by the parent imides due to vibrational coupling. This fact also goes against possible metal-oxygen binding in the complex.

Another interesting feature of the complex was to lower the frequencies of 1180 cm^{-1} band,which may have a strong component of the C-N vibration stretching band. Further the duplet found around 830 cm^{-1} (probably due to ring vibration) also shifts to lower frequency on complexion.

Nickel succinimide complex formed in aqueous medium:

Unlike the complexes in the non-aqueous medium, the one formed in the aqueous medium is stable only in presence of excess of succinimide. The spectrophotometric technique could not be employed since the mixtures prepared according to Job's and molar ratio methods got precipitated in most of the cases. The conductometric titrations failed to give any inflexion in view of the originally high conductance of the succinimide solution (prepared in equivalent amount of KOH).

The pH-metric method could only be successfully employed to study the composition and stability of the complex in the aqueous medium.

Typical titration curves were obtained when succinimide was titrated against standard potassium hydroxide solution, with and without the presence of nickel ions(Fig.23). The horizantal distance(excess of alkali consumed) gave the amount of protons liberated by complex-ion i.e. the amount of ligand complexed. This value divided by the total metal ion in the system gave the value of $\bar{n}$. Thus at various values of pH, a set of $\bar{n}$ values was determined. The value of $\bar{n}$ was found to increase with pH and attained a constant value in the region of one at pH 7.5, suggesting thereby 1:1 (Ni : succinimide) composition of the complex.

If HA (succinimide) complexes with Ni, the equilibrium involved in the reaction may be expressed as:

$$Ni^{2+} + A^{-} = Ni\ A^{+}$$

$$(Ni\ A)^{+} / (Ni^{2+})\ (A^{-}) = K_e \quad \ldots\ldots(1)$$

where K_e represents the equilibrium constant of the above reaction.

If T_A represents the total concentration of the ligand and T_M, that of the metal, then

$$T_A = (HA) + (A^{-}) + (Ni\ A^{+}) \quad \ldots\ldots.(2)$$

and $$T_M = (Ni^{2+}) + (Ni\ A^{+})$$

If K_a be the dissociation constant of the ligand

$$(H^{+})\ (A^{-}) / (HA) = K_a \quad \ldots\ldots\ldots\ (3)$$

Equations 2 and 3 reduce to,

$$(A^{-}) = \frac{T_A - (Ni\ A^{+})}{1 + \frac{(H^{+})}{K_a}} \quad \ldots\ldots \quad (4)$$

The concentration of free ligand (A^{-}) was calculated from equation (4). The values of $\bar{n}$ were plotted against the corresponding values of $-\log A$ to obtain formation curve(Fig.24). The value of stability constant log K of the complex was determined at $\bar{n} = 0.5$ from the formation curve. The mean value of log K came out to be 3.025 as shown in the following table.

Stability constant of nickel-succinimide complex.

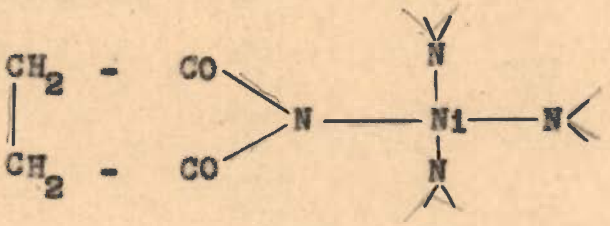
Curves	Stability constant log K = - log A at $\bar{n}$ = 0.5	Mean log K.
1	3.05	3.025
2	3.05	
3	3.00	
4	3.00	

Fig. 30

Mechanism of the reactions between nickel chloride and succinimide in aqueous and methanolic media.

(i) 1:4 nickel-succinimide complex(yellow in colour), formed in methyl-alcohol.

This reaction is essentially a biuret reaction for the reason that four basic nitrogen atoms are involved in co-ordination with nickel. A similar mechanism was proposed by Rising and Yang (loc.cit.) for the amide complexes of copper involving co-ordination with four basic nitrogen, accompanied by the splitting of four hydrogen atoms from two amide molecules. The structure of 1:4 complex may be represented as,



or $((C_4H_4O_2N)_4\,Ni)^{2-}$

For the above complex both chemical evidence and pH metric data gave strong indication of co-ordination through nitrogen. However, I.R. spectrum of the isolated complex gave indication of the metal oxygen binding. This may be true for the isolated complex, which may have changed its nature on heating and drying, but is not likely for the complex in solution.

(ii) 1:2 nickel succinimide complex (green in colour), formed in methyl alcohol.

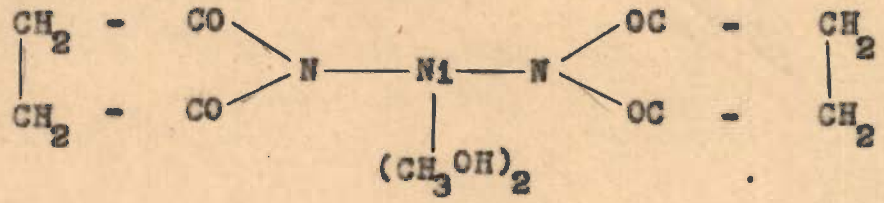
Assuming that two molecules of methyl-alcohol are associated with one atom of nickel in the methanolic solution the formula of 1:2 complex may be represented as follows:

$(C_4H_4O_2N)_2$ Ni $(CH_3OH)_2$, the co-ordination number of nickel is completed by two molecules of methyl-alcohol.

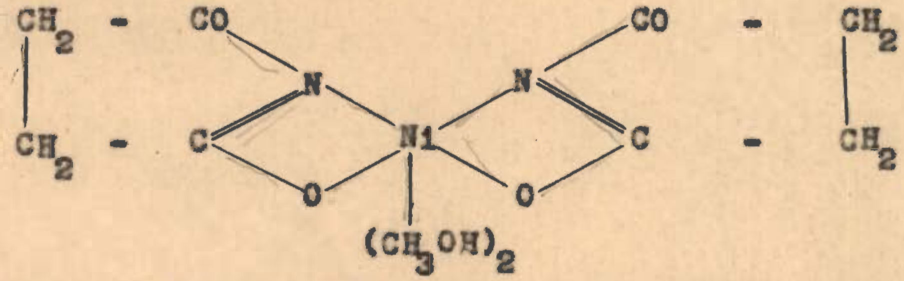
The formation of this green complex involves co-ordination with two basic nitrogen instead of four. The biuret reaction mechanism cannot therefore be put forward here.

The possibility of chelation also exists in this complex since co-ordination through both nitrogen and oxygen also is possible. Therefore either of the following two structures may be assigned,

(i)



(ii)



Since the complex could not be isolated in the pure form, chemical evidence as well I.R. analysis was not possible to give any specific structure to this complex.

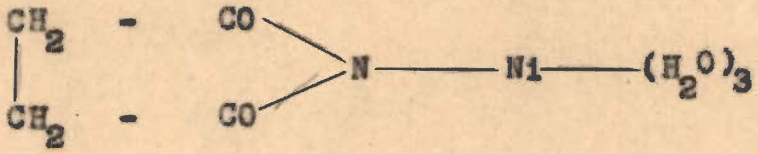
(iii) 1:1 Ni-succinimide complex(green in colour)formed in aqueous medium.

The reaction between succinimide and Ni^{2+} ions,below pH 8 may be represented by the following mechanism,

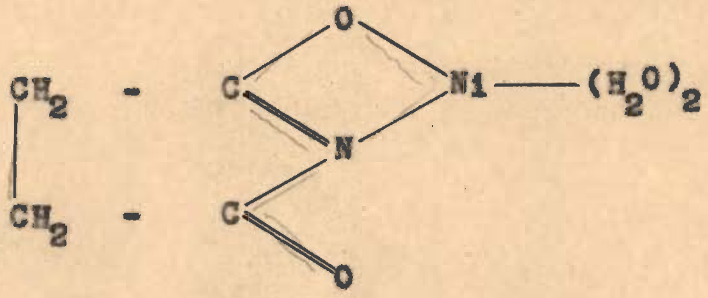
$$Ni^{2+}(H_2O)_4 + (C_4H_4O_2N)^- = ((C_4H_4O_2N)\ Ni\ (H_2O)_3)^+$$

The possibility of chelation exists here also as in case of 1:2,nickel-succinimide complex,and therefore following two structures may be envisaged for this complex,

(i)



(ii)



But due to lack of evidence in favour of either of the two structures,the complex may be formulated as,

$$((C_4H_4O_2N)\ Ni\ (H_2O)_3)^+$$

The biuret reaction mechanism can not be assigned for the formation of the above complex.

CHAPTER II.

Nickel complexes of phthalimide and glutarimide(biuret and non biuret reaction mechanisms).

INTRODUCTION

Very little work has been done on nickel-imides because of the instability of these complexes in aqueous medium. Tayabji and Gibson(1) had mentioned the formation of potassium salt of gold-phthalimide complex, which they prepared by mixing the boiling solutions of $KAuBr_4$ and potassium phthalimide, and extracted gold phthalimide from the solid product, by the acetone extraction method. This gold derivative of phthalimide was not found to be very stable and got decomposed on heating to give back phthalimide. The structure of this complex was determined by means of chemical analysis only.

Livio Cambi (2) reported the magnetic susceptibility of the complexes of nickel with phthalimide and hexahydrophthalimide, and also those of palladium complexes of phthalimide and succinimide. The nickel-phthalimide complex $Ni(C_8H_4O_2N)_2$. 3 EtOH was obtained on evaporating under vacuum the product of the interaction of nickel acetate and potassium phthalimide.

Except for the above passing references on imide complexes, nothing worth mentioning has so far been done on the metal imide complexes, and a comprehensive study on the chemistry of these complexes is worth under taking. Preliminary investigations revealed that nickel(II) did not react with phthalimide in aqueous medium, both in acidic and alkaline media. The reaction was, however, possible in the methanolic medium in the higher pH range($pH > 9$). Evidence for the existence of two complexes i.e. a yellow one formed with excess of phthalimide, and a green one in excess of the metal ion was forthcoming. Both the complexes were found to be highly susceptible to moisture. This necessitated the use of purely methanolic solutions of the reactants. Further indication of complex-ion formation between nickel chloride and phthalimide was obtained from the fact that, although precipitation of nickel hydroxide took place on addition of nickel chloride to caustic potash(methanolic solutions), but no such precipitation in the alkaline medium was observed in presence of phthalimide. Instead of precipitation, two complexes were obtained. Moreover, just like the nickel-succinimide complex, the yellow complex got changed into a green one on the addition of excess of nickel(II).

In this chapter, composition and stability of the yellow complex have been established by spectrophotometric, conductometric and pH metric methods. The results have been further confirmed from chemical analysis of the isolated complex and also from its I.R. spectrum. As regards the green complex, only spectrophotometric method could be employed to study its composition and stability.

Another interesting aspect of the study of the metal-imide complexes is to examine the effect of the nature of the ring of the imides on the complexes formed. A comparison could, therefore, be possible by studying the interaction of nickel chloride with glutarimide, which is a six membered ring compound compared as against a five membered ring present in phthalimide. Here too, the preliminary studies revealed that the corresponding complex was stable only in the non-aqueous medium. However, unlike nickel phthalimide, no yellow complex was obtained with excess of the complexing agent, but only a green product was obtained irrespective of the metal glutarimide ratio. Further-more, the reaction could be carried out at a little higher pH (pH $>$ 10). The same difficulty regarding the isolation of the complex was encountered in this case as met with in the case of green variaties of nickel succinimide and nickel phthalimide. Chemical analysis and I.R. studies were, therefore, not possible.

EXPERIMENTAL

Phthalimide was prepared by the action of urea on phthalic anhydride by the method recommended by Vogel(3). An intimate mixture of 99 gms. of pure phthalic anhydride and 20 gms. of urea was placed in one litre long necked round bottomed flask. The flask was heated in an oil bath at 130-135°C., when the contents melted, effervescence commenced and increased in vigour. After 10 to 20 minutes, the mixture frothed at about (150-160°C) and became solid. The flame was removed to allow the flask to cool. The solid mass was disintegrated by adding about 10 ml. of water. This product was filtered at vacuum pump, washed with a little water and then dried at 100°C.

This phthalimide was recrystallised from 1200 ml. of methylated spirit and the first crop was collected, which was pure phthalimide(m.p. 233°).

Preparation of glutarimide: In order to prepare glutarimide, the corresponding acid was first of all prepared from cyclopentanone (4). Details of the method are given below:

An intimate mixture of 200 gms. of adipicacid and 10 gms. of barium hydroxide(crystallised) was placed in a two litre distilling flask fitted with thermometer reaching within 5 mm. of distilling liquid. The flask was connected with a condenser and a receiver . The temperature of the flask was maintained between 285° and 290°C, not allowing to rise more than 300°C, as adipic acid distilled over. The cyclopentanone was separated from water in the distillate and dried with anhydrous potassium carbonate. This treatment removed the traces of adipic acid, if any, from the distillate. Finally cyclopentanone was collected by distilling the crude product at 128° to 131°C.

For obtaining glutaric acid from cyclopentanone, two litre round bottom flask was fitted with a long condenser and a dropping funnel. A mixture of 350 ml. of concentrated nitric acid and 550 ml. of water, was heated nearly to boiling: 90 gms. of cyclopentanone was allowed to enter the hot acid dropwise taking care that the first few drops were acted upon by the acid, otherwise explosion might have occurred, the addition was completed in about one hour. As the reaction was exothermic the flame below the flask was kept considerably lower.

After the completion of the reaction the solution was transferred to a large evaporating dish and evaporated the solution to dryness on a water bath; an oil was obtained which solidified on cooling m.p. 80-85° and consisted of a mixture of glutaric acid and succinic acid. This mixture was dissolved in 100 ml. of water, and was boiled to expel the excess of ammonia. Slight excess of 40% barium chloride solution was added and the precipitate of barium succinate was filtered off. The filterate was acidified with dilute hydrochloric acid, and the glutaric-acid was extracted with 100 ml. portions of ether, three to four times. The etherial extract of glutaric acid was dried with anhydrous magnesium sulphate, and the ether was distilled off. The crude glutaric acid obtained, was recrystallised from benzene to get the pure product, m.p.97 °C.

Glutarimide was prepared by the distillation of its ammonium salt, by the similar method as was employed in case of succinimide.

Phthalimide solution was prepared in methanol by direct weighing. Concentrated solutions of phthalimide could not be prepared, on account of its limited solubility, in methanol. However, solutions of strength upto 0.067 M could be obtained on prolong shaking. For spectrophotometric studies phthalimide solution was obtained in equivalent amount of potassium hydroxide.

Glutarimide solution was prepared by dissolving the requisite amount of the reagent in methanol. Methanolic solutions of nickel chloride and potassium hydroxide were prepared by the method discussed earlier in Chapter I.

Spectronic '20', Bausch and Lomb was used for spectrophotometric studies, after allowing a sufficient warming up period. pH metric measurements were carried out with Cambridge bench type pH meter in conjunction with Cambridge glass electrode and S.C.E.. Conductometric studies were performed using Philips conductivity bridge.

Composition of nickel-phthalimide complexes in methanolic medium, by spectrophotometric methods:

VosBurgh and Cooper's method(loc.cit.) was employed to know the number of complexes formed and for choosing wavelength, suitable for performing further studies. Several mixtures were prepared by mixing nickel chloride and phthalimide solutions in various proportions(1:1, 1:2, 1:3, 1:4, 1:5 and 1:7), maintaining the sum of concentrations of nickel and phthalimide as 0.067 M. These mixtures were, then scanned on the spectrophotometer. From O.D. values at different wavelength, two maxima corresponding to 360 mu and 650 mu were obtained(Fig.1). In order to ascertain the nature of the curves in wavelength region (425-550 mu), VosBurgh and Cooper's curves have been plotted in two parts on separate scales. The results have been depicted in the following table.

<u>Selection of wave-lengths</u>.

<u>TABLE</u> <u>NO</u>.1.

Absorbance of nickel chloride-phthalimide mixtures, mixed according to VosBurgh Cooper's method.

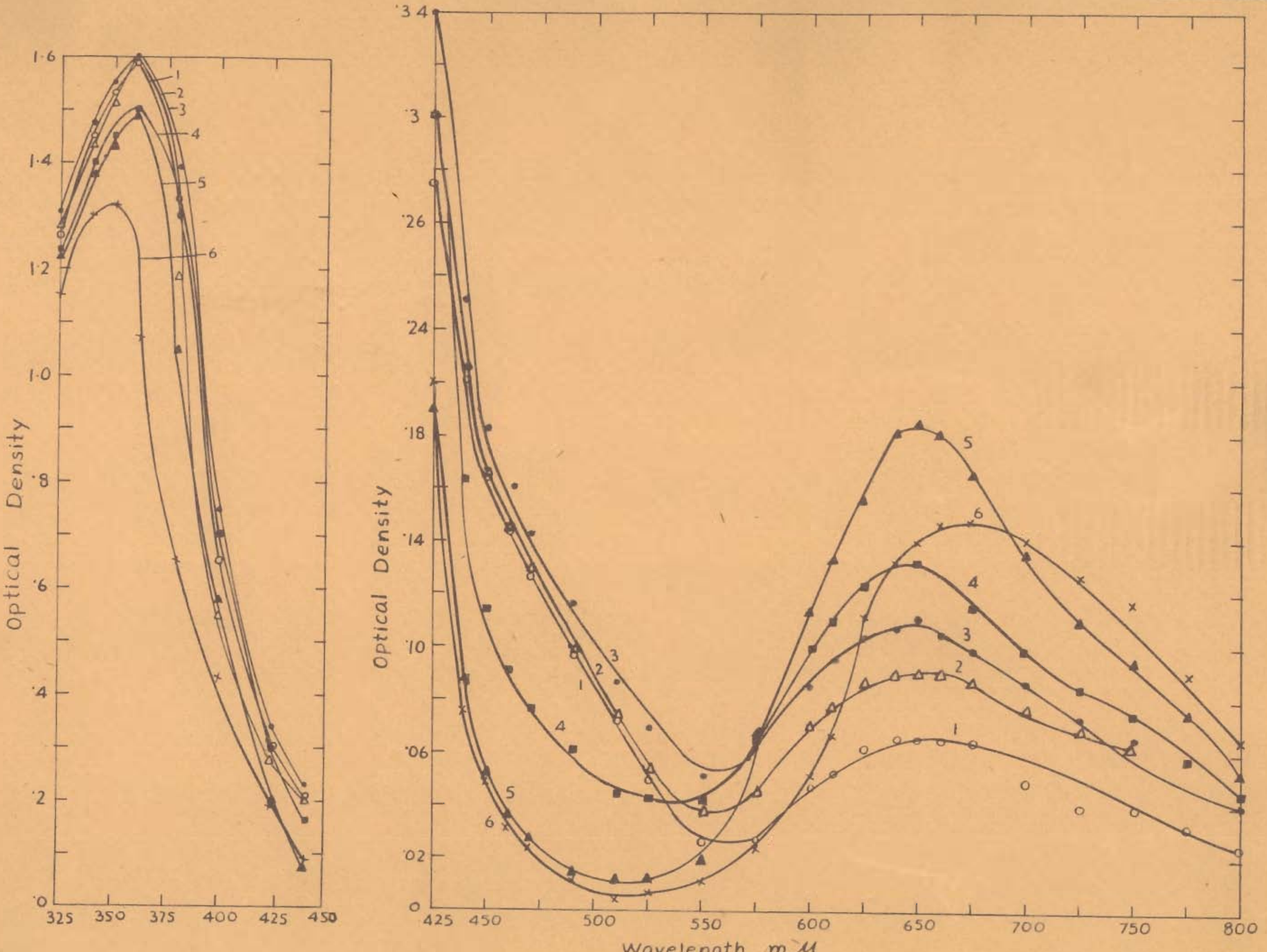
Concentration of nickel chloride $= 6.67 \times 10^{-2}$ M
Concentration of phthalimide $= 6.67 \times 10^{-2}$ M

Wave length.	Ratio of nickel chloride to phthalimide.					
mu	1:7	1:5	1:4	1:3	1:2	1:1
325	1.284	1.260	1.301	1.222	1.222	1.143
340	1.432	1.450	1.470	1.398	1.377	1.301
350	1.510	1.530	1.550	1.452	1.430	1.320
360	1.602	1.598	1.606	1.500	1.490	1.071
380	1.187	1.301	1.398	1.337	1.097	0.650
400	0.550	0.650	0.745	0.700	0.580	0.430
425	0.275	0.295	0.340	0.300	0.200	0.190
440	0.200	0.205	0.230	0.163	0.077	0.089
450	0.165	0.165	0.182	0.115	0.050	0.053
460	0.145	0.150	0.160	0.092	0.032	0.037
470	0.127	0.130	0.143	0.078	0.025	0.028
490	0.097	0.100	0.117	0.062	0.013	0.015
510	0.073	0.075	0.087	0.045	0.012	0.003
525	0.060	0.055	0.070	0.044	0.013	0.007
550	0.028	0.040	0.052	0.043	0.020	0.012
575	0.028	0.046	0.062	0.065	0.068	0.025
600	0.048	0.070	0.085	0.100	0.114	0.062
610	0.053	0.078	0.096	0.110	0.133	0.067
625	0.063	0.087	0.102	0.125	0.156	0.112
640	0.065	0.090	0.108	0.125	0.182	0.132
650	0.062	0.090	0.112	0.132	0.185	0.140
660	0.063	0.090	0.105	0.125	0.180	0.147
675	0.065	0.087	0.099	0.116	0.165	0.148
700	0.050	0.077	0.087	0.098	0.135	0.140
725	0.040	0.070	0.073	0.085	0.110	0.127
750	0.040	0.065	0.067	0.075	0.095	0.117
775	0.033	0.049	-	0.058	0.075	0.090
800	0.025	0.040	0.040	0.043	0.050	0.065
Fig.1	Curve 1.	Curve 2.	Curve 3.	Curve 4.	Curve 5.	Curve 6.

The above absorbance curves besides giving information for the existence of two complexes, gave sufficient indication of the decomposing nature of yellow complex in presence of excess of nickel. The absorbance, of mixtures in all proportions, was fairly high in the wavelength region of 360 mu (Fig.1). But in the region of wavelength 425 mu to 480 mu, the mixtures having higher proportions of phthalimide absorbed appreciably, as against those with low proportions which showed little absorption. The absorbance of nickel chloride was not appreciable in the above region of wavelengths. From the scanning, it was concluded that stoichiometry of yellow complex could best be carried out in the wavelength range 430 to 480 mu.. No such difficulty existed in choosing wavelengths for the second complex, as the second maximum peak occurred at 650 mu, which appeared quite far from the second maximum of nickel chloride occurring at 750 mu.

Composition of yellow complex: Job's method(loc.cit.)of continued variation was followed for determining the composition of the complex. Equimolar solutions of nickel chloride and phthalimide were mixed as under:

$NiCl_2$: 0.5,1.0,1.3,1.7,2.0,2.4 -----5.0 ml. and phthalimide: 9.5,9.0,8.7,8.3,8.0 ----5.0 ml, and O.D. of mixtures was measured at three wavelengths(425,440 and 460 mu). Such three sets of experiments were carried out at three concentrations viz.,(0.05,0.044, and 0.04 M). The difference of O.D. of the mixtures and metal ions was plotted against mole fraction of nickel, (Ni)/(Ni) +(phthalimide). The results of Job's method are given below:



VOS BURGH & COOPER'S METHOD Nicl$_2$-PHTHALIMIDE MIXTURE

FIG· 1

Set I. Concentration of the reactants = 0.05 M.

TABLE NO.2.

Wave length 425 mμ.

Vol. of $NiCl_2$	Vol. of phthalimide	O.D. mixt.	O.D. $NiCl_2$	Difference
0.5	9.5	0.112	0.012	0.100
1.0	9.0	0.207	0.020	0.187
1.3	8.7	0.255	0.023	0.232
1.7	8.3	0.290	0.028	0.262
2.0	8.0	0.38	0.040	0.340
2.4	7.6	0.375	0.047	0.328
2.8	7.2	0.355	0.057	0.298
3.3	6.7	0.255	0.071	0.184
4.0	6.0	0.192	0.090	0.102
4.5	5.5	0.182	0.102	0.080
5.0	5.0	0.182	0.117	0.065

Fig.2, Curve 1.

TABLE NO. 3.

Wave length 440 mμ.

Vol. of $NiCl_2$	Vol. of phthalimide	O.D. mixt.	O.D. $NiCl_2$	Differance
0.5	9.5	0.089	0.005	0.084
1.0	9.0	0.162	0.010	0.152
1.3	8.7	0.200	0.012	0.188
1.7	8.3	0.286	0.016	0.270
2.0	8.0	0.310	0.018	0.292
2.4	7.6	0.280	0.020	0.260
2.8	7.2	0.245	0.025	0.220
3.3	6.7	0.108	0.035	0.073
4.0	6.0	0.075	0.047	0.028
5.0	5.0	0.087	0.057	0.030

Fig.3, Curve 1.

TABLE NO.4.

Wave length 460 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	9.5	0.065	0.00	0.065
1.0	9.0	0.119	0.002	0.116
1.3	8.7	0.155	0.004	0.151
1.7	8.3	0.23	0.006	0.224
2.0	8.0	0.25	0.008	0.242
2.4	7.6	0.202	0.007	0.195
2.8	7.2	0.173	0.010	0.163
2.3	6.7	0.048	0.012	0.036
4.0	6.0	0.025	0.017	0.008
5.0	5.0	0.030	0.020	0.010

Fig.4, Curve 1.

Set II. Concentration of the reactants = 0.044 M.

TABLE NO.5.

Wave length 425 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	9.5	0.08	0.045	0.035
1.0	9.0	0.16	0.04	0.120
1.3	8.7	0.19	0.05	0.140
1.7	8.3	0.218	0.05	0.168
2.0	8.0	0.265	0.057	0.208
2.4	7.6	0.262	0.063	0.199
2.8	7.2	0.23	0.070	0.160
3.3	7.7	0.187	0.080	0.107
4.0	6.0	0.146	0.090	0.056
5.0	5.0	0.155	0.117	0.038
6.0	4.0	0.183	0.145	0.038

Fig.2, Curve 2.

TABLE NO.6.

Wave length 440 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	9.5	0.062	0.020	0.042
1.0	9.0	0.120	0.020	0.100
1.3	8.7	0.140	0.025	0.115
1.7	8.3	0.152	0.029	0.133
2.0	8.0	0.182	0.030	0.152
2.4	7.6	0.165	0.032	0.133
2.8	7.2	0.119	0.038	0.081
3.3	6.7	0.077	0.040	0.037
4.0	6.0	0.064	0.048	0.016
5.0	5.0	0.071	0.060	0.011
6.0	4.0	0.092	0.075	0.017

Fig. 3, Curve 2.

TABLE NO. 7.

Wave length 460 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O. D. mixt.	O. D. $NiCl_2$	Difference
0.5	9.5	0.047	0.01	0.037
1.0	9.0	0.088	0.012	0.076
1.3	8.7	0.105	0.012	0.093
1.7	8.3	0.120	0.014	0.106
2.0	8.0	0.136	0.015	0.121
2.4	7.6	0.105	0.016	0.089
2.8	7.2	0.067	0.019	0.048
3.3	6.7	0.031	0.020	0.011
4.0	6.0	0.029	0.018	0.011
5.0	5.0	0.028	0.023	0.005
6.0	4.0	0.038	0.026	0.012

Fig. 4, Curve 2.

Set III. Concentration of the reactants =0.04 M.

TABLE NO. 8.

Wave length 425 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O.D. mixt.	O.D. $NiCl_2$	Difference
0.5	9.5	0.059	0.022	0.037
1.0	9.0	0.115	0.028	0.087
1.3	8.7	0.135	0.035	0.100
1.7	8.3	0.170	0.040	0.130
2.0	8.0	0.210	0.042	0.168
2.4	7.6	0.210	0.050	0.160
2.8	7.2	0.205	0.050	0.155
3.3	6.7	0.156	0.062	0.094
4.0	6.0	0.120	0.072	0.048
4.5	5.5	0.110	0.085	0.025

Fig. 2, Curve 3.

TABLE NO. 9.

Wave length 440 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O.D. mixt.	O.D. $NiCl_2$	Difference
0.5	9.5	0.042	0.020	0.022
1.0	9.0	0.080	0.020	0.060
1.3	8.7	0.090	0.022	0.068
1.7	8.3	0.110	0.023	0.087
2.0	8.0	0.131	0.024	0.107
2.4	7.6	0.127	0.027	0.100
2.8	7.2	0.100	0.028	0.072
3.3	6.7	0.065	0.035	0.030
4.0	6.0	0.049	0.038	0.011
4.5	5.5	0.048	0.048	0.000

Fig. 3, Curve 3.

JOB'S METHOD

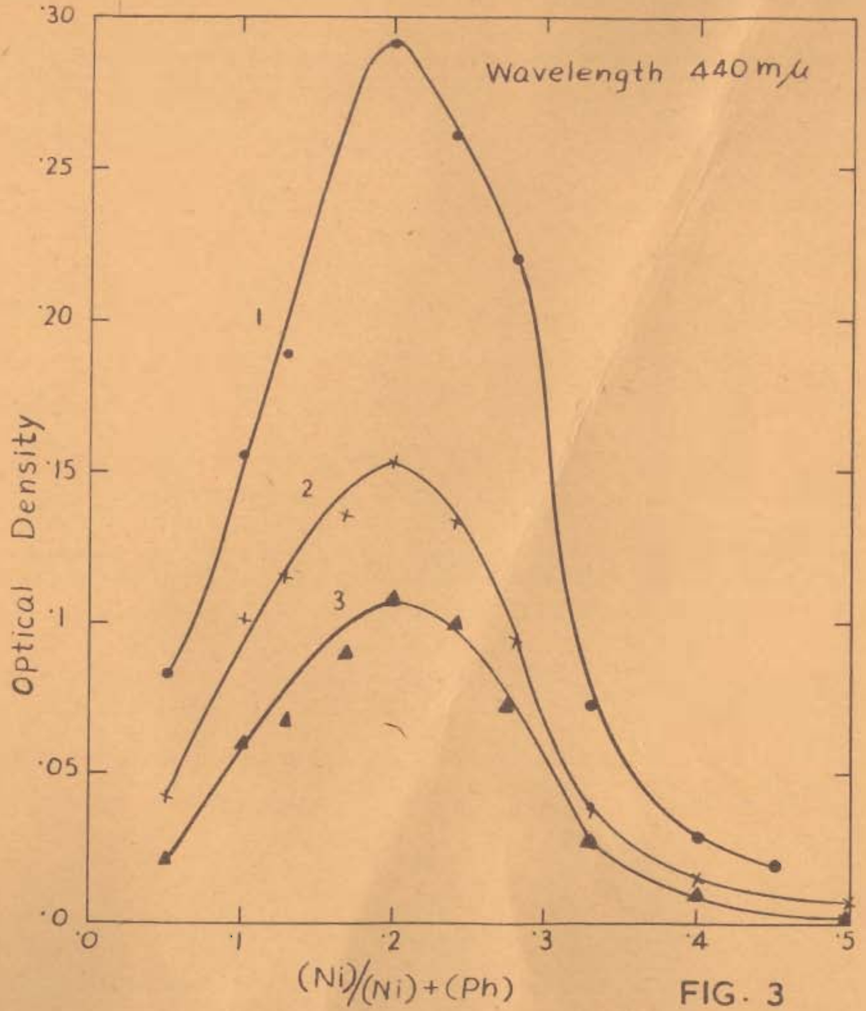


FIG. 3

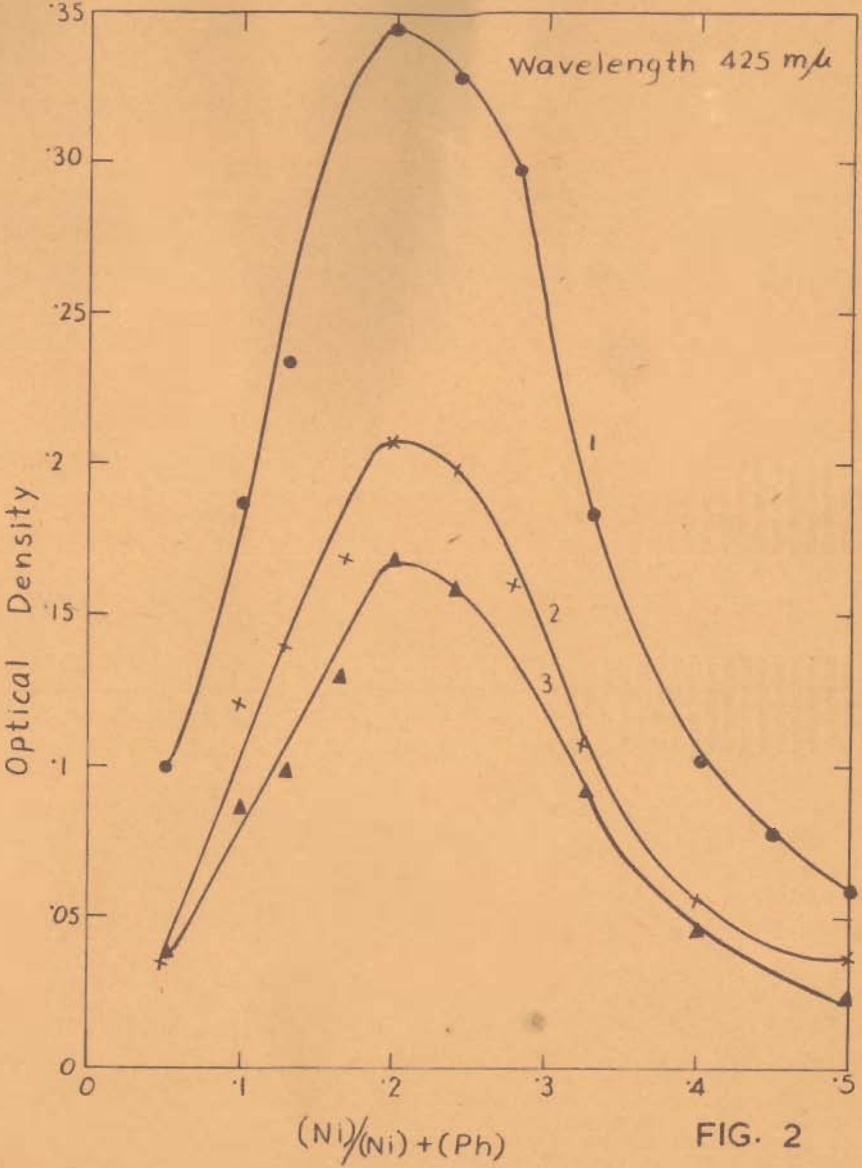


FIG. 2

TABLE NO. 10.

Wave length 460 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O.D. mixt.	O.D. $NiCl_2$	Difference
0.5	9.5	0.027	0.013	0.014
1.0	9.0	0.033	0.015	0.028
1.3	8.7	0.054	0.015	0.039
1.7	8.3	0.069	0.016	0.053
2.0	8.0	0.080	0.018	0.062
2.4	7.6	0.073	0.018	0.055
2.8	7.2	0.056	0.019	0.037
3.3	7.7	0.034	0.024	0.010
4.0	6.0	0.022	0.020	0.002
4.5	5.5	0.022	0.022	0.000

Fig.4, Curve 3.

Mono variation method:

Mole ratio method (loc. cit.) was tried here also for confirmation of the results of Job's method on composition, and also for determining the stability constant of the yellow complex. Solutions were mixed by the method described earlier (keeping constant amount of nickel and varying the concentration of phthalimide) and experiments were carried out at two different concentrations of nickel chloride. The optical density measurements were made at 440 and 460 mu. The results are tabulated below:

O.D. values of mixtures prepared according to mole ratio method.

TABLE NO.11.

Concentration of nickel chloride = 0.01 M(in 10 ml.).

Concentration, phthalimide solution = 0.067 M.

Total volume made up =10 ml.

Vol. of $NiCl_2$	Vol. of phthalimide	440 mu	460 mu
1.5	1.0	0.022	0.01
1.5	1.5	0.022	0.01
1.5	2.0	0.025	0.011
1.5	2.5	0.04	0.012
1.5	3.0	0.065	0.028
1.5	3.5	0.07	0.03
1.5	4.0	0.10	0.051
1.5	5.0	0.19	0.132
1.5	5.5	0.245	0.170
1.5	6.5	0.265	0.190
1.5	7.0	0.268	0.195
		Fig.5, Curve 1.	Fig.6, Curve 1.

TABLE NO.12.

Concentration of nickel chloride = 0.0067 M.(in 10 ml.).

Concentration of phthalimide solution =0.067M.

Total volume made up = 10 ml.

Vol. of $NiCl_2$	Vol. of phthalimide	440 mu	460 mu
1.0	1.0	0.019	0.01
1.0	2.0	0.034	0.015
1.0	2.5	0.048	0.021
1.0	3.0	0.06	0.028
1.0	3.5	0.075	0.048
1.0	4.0	0.115	0.085
1.0	4.5	0.119	0.105
1.0	5.0	0.156	0.110
1.0	5.5	0.16	0.112
1.0	6.0	0.158	0.114
		Fig.5, Curve 2.	Fig.6, Curve 2.

The reverse method(keeping phthalimide amount constant and varying the amount of nickel chloride) was employed for obtaining information of the decomposition of yellow complex in presence of excess of nickel chloride. Absorption measurements of different mixtures were carried out at wavelengths 440 and 460 mu, and were plotted against mole ratio of nickel chloride and phthalimide. Following results were obtained.

TABLE NO.13.

Concentration of phthalimide = 0.033 M.(in 10 ml.).

Concentration of nickel chloride = 0.067 M.

Total volume made up = 10 ml.

Vol. of phthalimide	Vol. of $NiCl_2$	440 mu	460 mu
5.0	0.2	0.021	0.013
5.0	0.4	0.044	0.024
5.0	0.6	0.057	0.035
5.0	0.8	0.073	0.045
5.0	1.0	0.095	0.061
5.0	1.2	0.106	0.066
5.0	1.5	0.090	0.050
5.0	1.8	0.077	0.037
5.0	2.0	0.075	0.032
		Fig.7, Curve 1.	Fig.8, Curve 1.

TABLE NO.14.

Concentration of phthalimide = 0.0267 M.(in 10 ml.).

Concentration of nickel chloride =0.067 M.

Total volume made up = 10 ml.

Vol.of phthalimide	Vol.of $NiCl_2$	440 mu	460 mu
4.0	0.2	0.02	0.014
4.0	0.4	0.044	0.026
4.0	0.6	0.059	0.038
4.0	0.8	0.081	0.052
4.0	1.0	0.107	0.069
4.0	1.2	0.099	0.055
4.0	1.4	0.092	0.050
4.0	1.6	0.086	0.042
4.0	1.8	0.080	0.037
		Fig.7, Curve 2.	Fig.8, Curve 2.

Stability constant of 1:4, yellow complex:

The value of K, stability constant of yellow,nickel-phthalimide complex was calculated by the mole ratio method, as recommended by Harvey and Manning (loc.cit.5). The data given in Fig.6,Curve 1 were used for calculations. The results are discussed later on.

Composition of green complex:

Solutions were mixed according to the Job's method of continued variation at three different concentrations 0.067 M, 0.05 M and 0.04 M respectively and absorbance measurements were carried out at wavelengths 630,650 and 670 mu respectivel for Sets I,II and III. Here also difference of O.D.of mixtures and metal ions, was plotted against the ratio (Ni)/ (Ni) + (Phthalimide). The results are given below:

Set I. Concentration of the reactants = 0.067 M

TABLE NO. 15.

Wave length 630 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O.D. mixt.	O.D. $NiCl_2$	Difference
1.0	9.0	0.028	0.01	0.018
2.0	8.0	0.074	0.016	0.058
2.5	7.5	0.107	0.017	0.090
3.0	7.0	0.128	0.026	0.102
3.33	6.67	0.129	0.027	0.102
4.0	6.0	0.113	0.028	0.084
5.0	5.0	0.096	0.038	0.058
6.0	4.0	0.089	0.046	0.043
7.0	3.0	0.086	0.053	0.033
8.0	2.0	0.084	0.065	0.019

Fig. 9, Curve 1.

TABLE NO. 16.

Wave length 650 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O.D. mixt.	O.D. $NiCl_2$	Difference
1.0	9.0	0.029	0.012	0.017
2.0	8.0	0.080	0.023	0.057
2.5	7.5	0.122	0.027	0.095
3.0	7.0	0.143	0.038	0.105
3.33	6.67	0.145	0.040	0.105
4.0	6.00	0.135	0.045	0.090
5.0	5.00	0.124	0.060	0.064
6.0	4.00	0.121	0.070	0.051
7.0	3.00	0.118	0.080	0.038
8.0	2.00	0.122	0.100	0.022

Fig. 10, Curve 1.

TABLE NO.17.

Wave length 670 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O. D. mixt.	O. D. $NiCl_2$	Difference
1.0	9.0	0.027	0.016	0.011
2.0	8.0	0.078	0.029	0.049
2.5	7.5	0.117	0.035	0.082
3.0	7.0	0.138	0.048	0.090
3.33	6.67	0.142	0.050	0.092
4.00	6.0	0.135	0.058	0.077
5.0	5.0	0.135	0.075	0.060
6.0	4.0	0.140	0.090	0.050
7.0	3.0	0.143	0.105	0.038
8.0	2.0	0.150	0.127	0.023

Fig.11, Curve 1.

Set II. Concentration of the reactants = 0.05 M.

TABLE NO. 18.

Wave length 630 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O. D. mixt.	O. D. $NiCl_2$	Difference
1.0	9.0	0.024	0.012	0.012
2.0	8.0	0.049	0.012	0.037
2.4	7.6	0.070	0.017	0.053
2.8	7.2	0.085	0.020	0.065
3.3	6.7	0.113	0.023	0.090
4.0	6.0	0.10	0.029	0.071
4.5	5.5	0.088	0.030	0.058
5.0	5.0	0.081	0.030	0.051
6.0	4.0	0.070	0.035	0.035
7.0	3.0	0.065	0.042	0.023
8.0	2.0	0.062	0.051	0.011

Fig.9, Curve 2.

MOLE RATIO METHOD

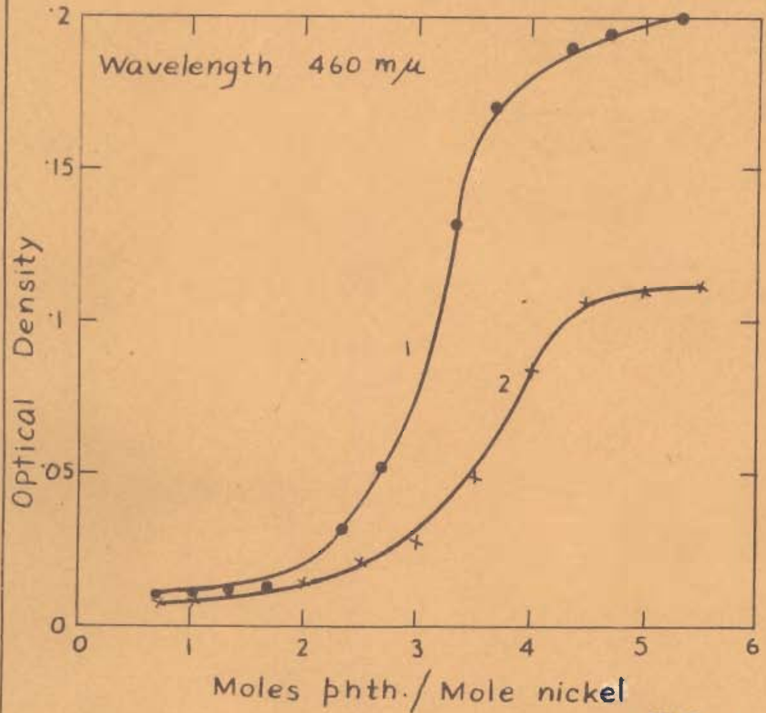


FIG. 6

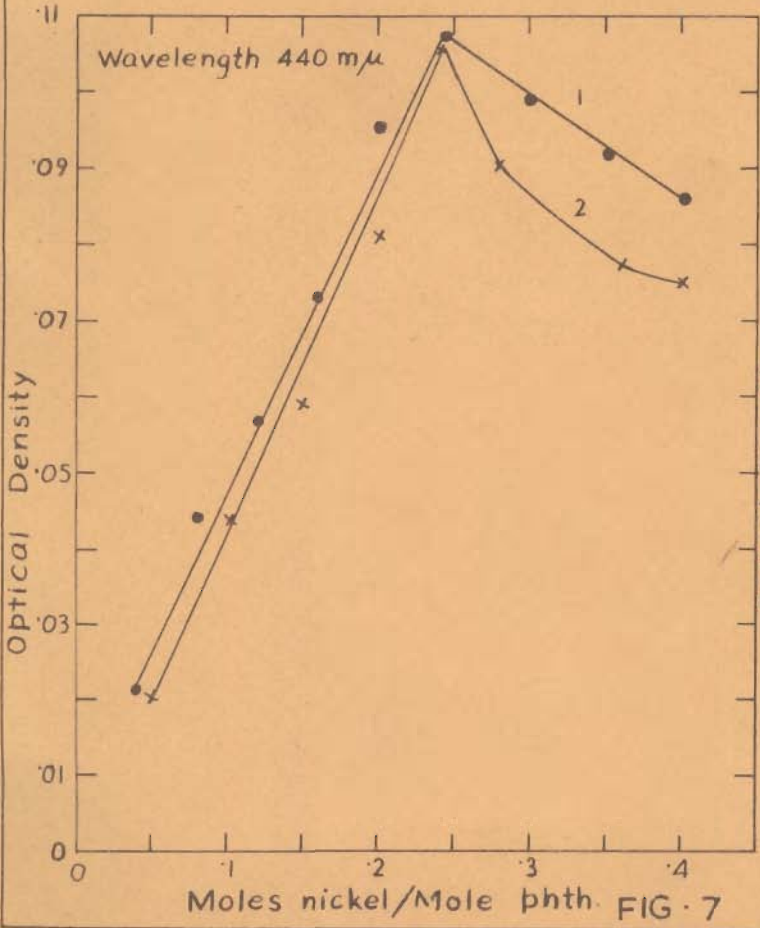


FIG · 7

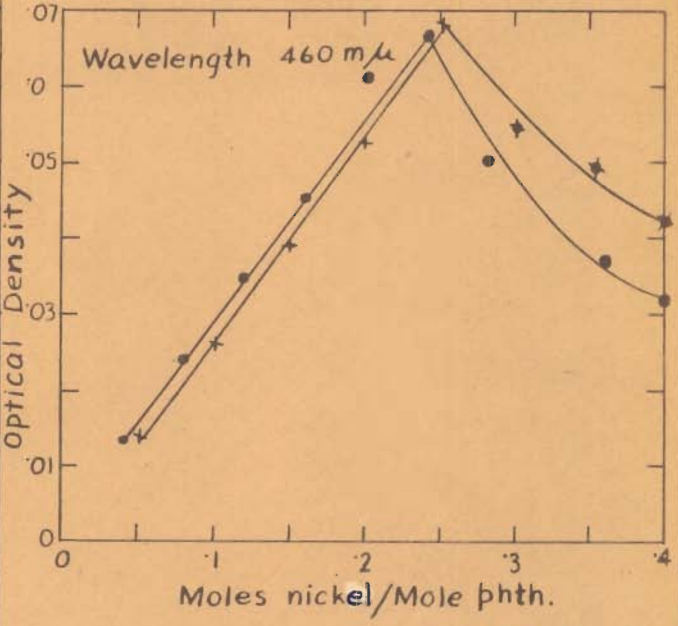


FIG · 8

TABLE NO.19.

Wave length 650 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O. D. mixt.	O. D. $NiCl_2$	Difference
1.0	9.0	0.026	0.013	0.013
2.0	8.0	0.052	0.020	0.032
2.4	7.6	0.070	0.025	0.045
2.8	7.2	0.093	0.027	0.066
3.3	6.7	0.122	0.033	0.089
4.0	6.0	0.117	0.042	0.075
4.5	5.5	0.105	0.045	0.060
5.0	5.0	0.102	0.050	0.052
6.0	4.0	0.093	0.055	0.038
7.0	3.0	0.090	0.065	0.025
8.0	2.0	0.088	0.078	0.010

Fig.10, Curve 2.

TABLE NO. 20.

Wave length 670 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O. D. mixt.	O. D. $NiCl_2$	Difference
1.0	9.0	0.022	0.012	0.010
2.0	8.0	0.048	0.022	0.026
2.4	7.6	0.064	0.027	0.037
2.8	7.2	0.087	0.031	0.056
3.3	6.7	0.115	0.043	0.072
4.0	6.0	0.115	0.050	0.065
4.5	5.5	0.112	0.053	0.059
5.0	5.0	0.113	0.058	0.055
6.0	4.0	0.109	0.068	0.041
7.0	3.0	0.110	0.083	0.027
8.0	2.0	0.113	0.099	0.014

Fig. 11, Curve 2.

Set III. Concentration of the reactants = 0.04 M.

TABLE NO.21.

Wave length 630 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O.D. mixt.	O.D. $NiCl_2$	Difference
1.0	9.0	0.020	0.009	0.011
2.0	8.0	0.043	0.013	0.030
2.4	7.6	0.058	0.016	0.042
2.8	7.2	0.074	0.018	0.056
3.3	6.7	0.087	0.021	0.066
4.0	6.0	0.074	0.023	0.051
4.5	5.5	0.068	0.030	0.038
5.0	5.0	0.062	0.030	0.032
6.0	4.0	0.059	0.038	0.021
7.0	3.0	0.053	0.041	0.012
8.0	2.0	0.052	0.044	0.008

Fig. 9, Curve 3.

TABLE NO.22.

Wave length 650 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O.D. mixt.	O.D. $NiCl_2$	Difference
1.0	9.0	0.022	0.008	0.014
2.0	8.0	0.041	0.013	0.028
2.4	7.6	0.057	0.018	0.039
2.8	7.2	0.075	0.020	0.055
3.3	6.7	0.090	0.022	0.068
4.0	6.0	0.080	0.026	0.054
4.5	5.5	0.075	0.033	0.042
5.0	5.0	0.070	0.037	0.033
6.0	4.0	0.070	0.045	0.025
7.0	3.0	0.065	0.049	0.016
8.0	2.0	0.061	0.052	0.009

Fig.10, Curve 3.

JOB'S METHOD

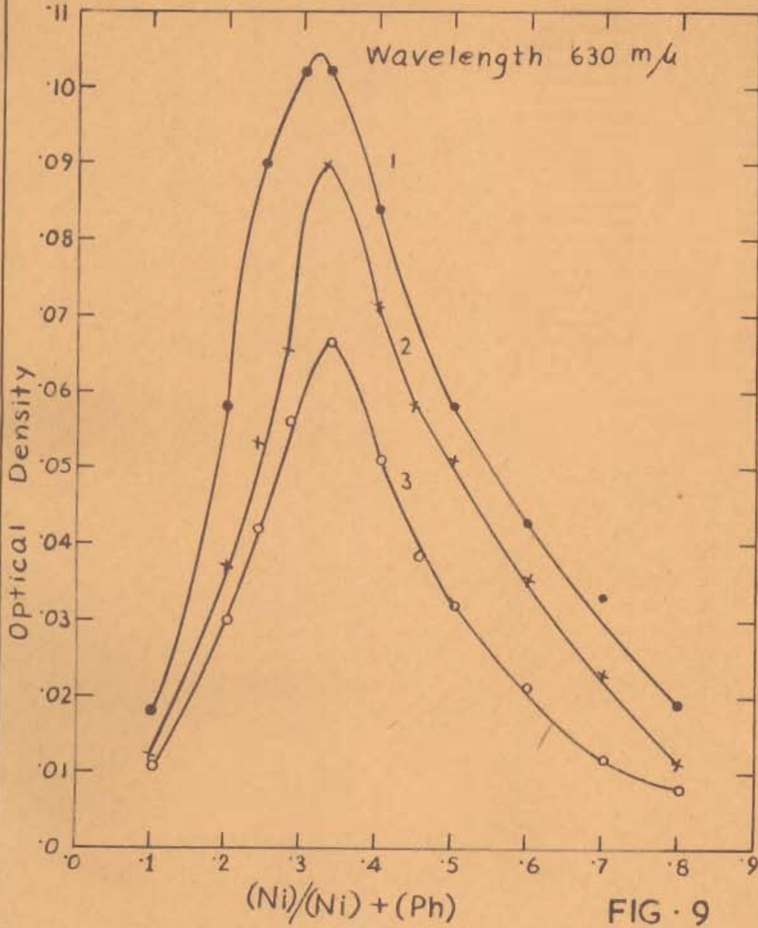


FIG · 9

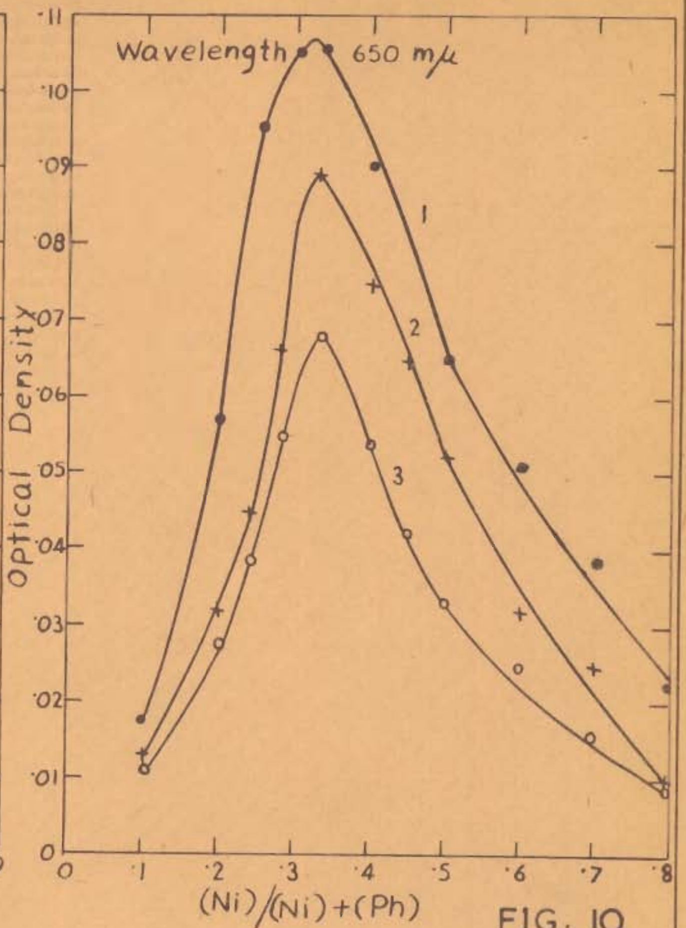
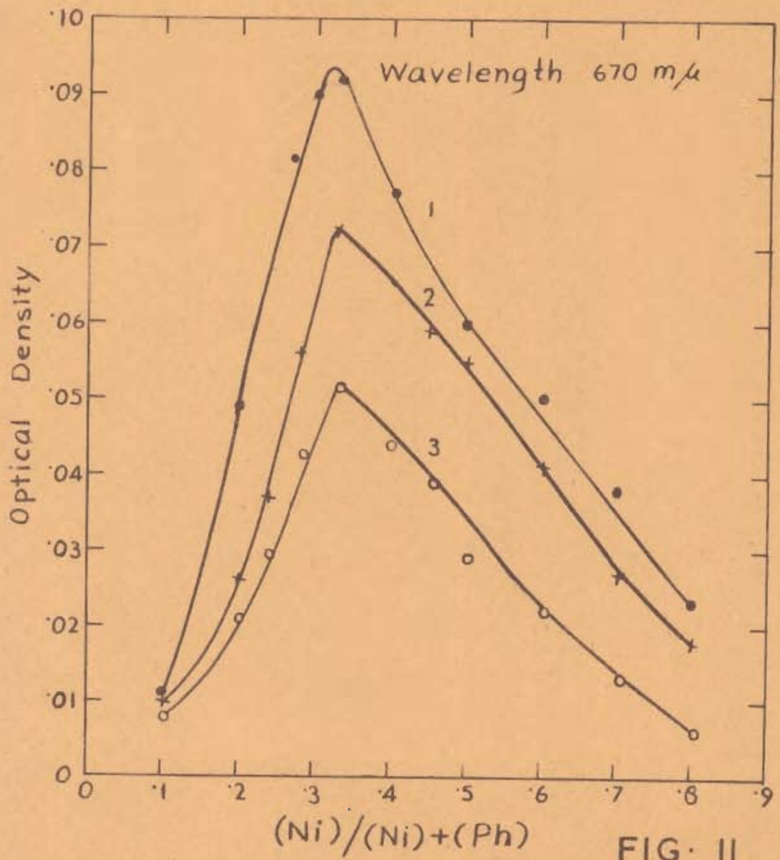


FIG. 10



FIG· 11

TABLE NO.23.

Wave length 670 mu.

Vol. of $NiCl_2$	Vol. of phthalimide	O. D. mixt.	O. D. $NiCl_2$	Difference
1.0	9.0	0.020	0.011	0.009
2.0	8.0	0.039	0.017	0.022
2.4	7.6	0.052	0.022	0.030
2.8	7.2	0.068	0.025	0.043
3.3	6.7	0.081	0.030	0.051
4.0	6.0	0.079	0.035	0.044
4.5	5.5	0.080	0.041	0.039
5.0	5.0	0.075	0.044	0.029
6.0	4.0	0.077	0.055	0.022
7.0	3.0	0.075	0.062	0.013
8.0	2.0	0.075	0.069	0.006

Fig. 11, Curve 3.

Mole ratio method:- The results of Job's method were further confirmed by mole ratio method. The method of mixing the solutions was the same as described earlier. The experiments were performed at two different concentrations of nickel chloride, and absorption measurements were carried out at wave lengths 630,650 and 670 mu. The results are tabulated below:

O.D. values of mixtures, prepared according to the mole ratio method.

TABLE NO. 24.

Concentration of nickel chloride = 0.0133 M (in 10 ml.).

Concentration of phthalimide = 0.067 M.

Total volume made up = 10 ml.

Vol. of $NiCl_2$	Vol. of phthalimide	630 mu	650 mu	670 mu.
2.0	1.0	0.028	0.038	0.041
2.0	2.0	0.043	0.050	0.051
2.0	2.5	0.053	0.062	0.061
2.0	3.0	0.063	0.070	0.070
2.0	2.5	0.077	0.083	0.076
2.0	4.0	0.092	0.097	0.087
2.0	4.5	0.095	0.100	0.090
2.0	5.0	0.093	0.098	0.088
2.0	5.5	0.086	0.093	0.085
2.0	6.0	0.085	0.092	0.083
		Fig. 14, Curve 1.	Fig. 13, Curve 1.	Fig. 12, Curve 1.

TABLE NO. 25.

Concentration of nickel chloride = 0.01M. (in 10 ml.).

Concentration of phthalimide = 0.067 M.

Total volume made up = 10 ml.

Vol. of $NiCl_2$	Vol. of phthalimide	630 mu	650 mu	670 mu
1.5	1.0	0.033	0.035	0.039
1.5	1.5	0.040	0.043	0.041
1.5	2.0	0.048	0.051	0.050
1.5	2.5	0.060	0.062	0.059
1.5	3.0	0.072	0.073	0.065
1.5	3.5	0.076	0.075	0.067
1.5	4.0	0.074	0.073	0.065
1.5	5.0	0.069	0.068	0.062
1.5	5.5	0.063	0.062	0.058
		Fig. 14, Curve 2.	Fig. 13, Curve 2.	Fig. 12, Curve 2.

Stability constant of green complex:- The value of K, stability constant was determined by the method of Anderson(loc.cit.), using the expression described in Chapter I, for 1:2, complex. Two sets of mixtures, of concentrations 0.05 M and 0.067 M of the reactants, were prepared according to the Job's method. The O.D.(not the difference) was then plotted against the ratio (Ni)/(Ni) + (Phthalimide).

TABLE NO.26.

O.D. values for stability constant of 1:2, nickel phthalimide, green complex.

Set. I. Concentration of the reactants = 0.05 M.

Set II. Concentration of the reactants= 0.067 M

Vol. of $NiCl_2$	Vol. of phthalimide	Set I O.D.	Set II O.D.
1.0	9.0	0.016	0.029
2.0	8.0	0.050	0.082
2.5	7.5	0.070	0.120
2.8	7.2	0.092	0.144
3.3	6.7	0.120	0.148
4.0	6.0	0.118	0.140
4.5	5.5	0.111	0.132
5.0	5.0	0.109	0.132
6.0	4.0	0.102	0.134
7.0	3.0	0.101	0.137
	Fig.15,	Curve 2.	Curve 1.

MOLE - RATIO METHOD

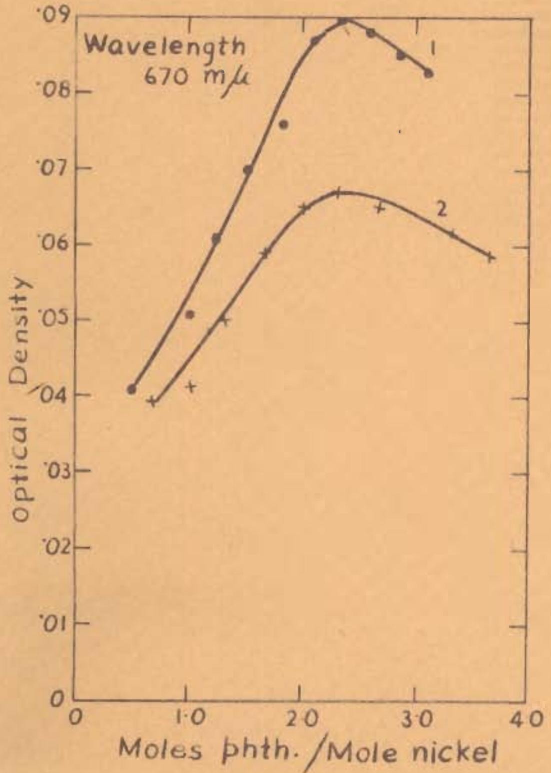


FIG. 12

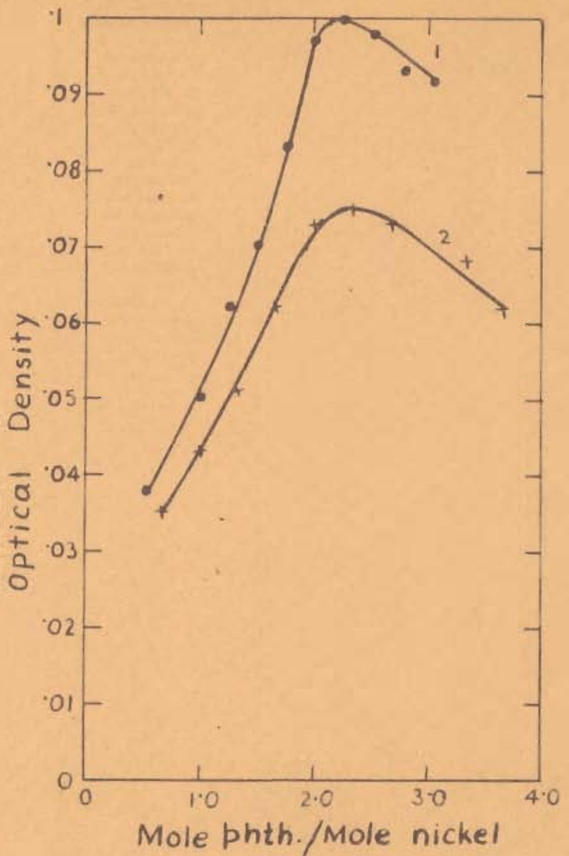


FIG. 13

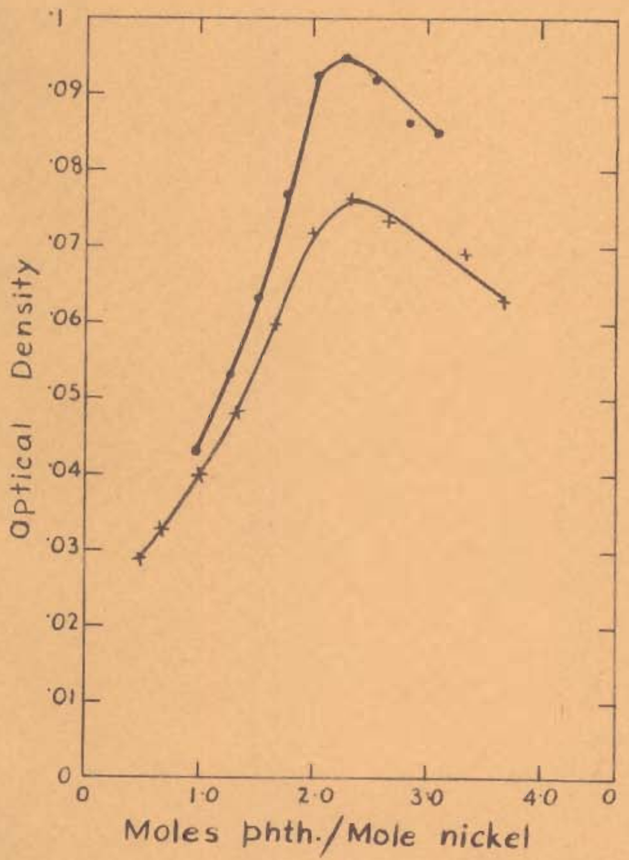


FIG. 14

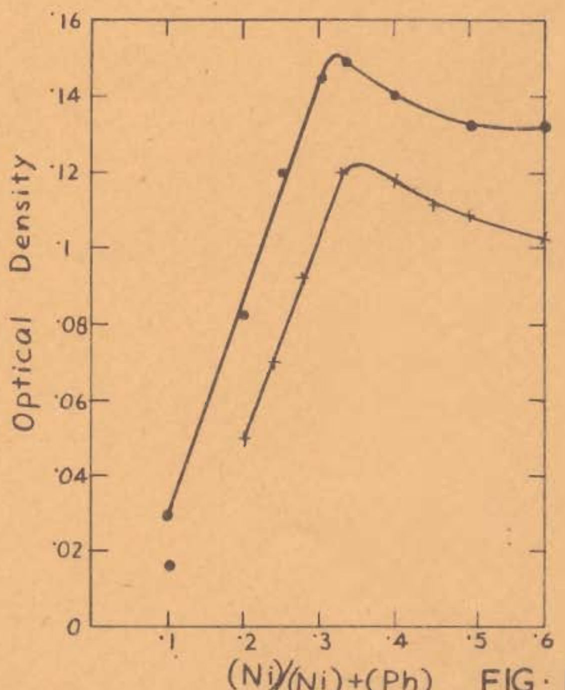


FIG · 15

STABILITY CONST. OF (Ni-PHTH.) COMPLEX

Conductometric titrations

Conductometric titrations of phthalimide(prepared in equivalent amount of KOH) against nickel chloride were carried out in order to obtain further confirmation of the composition of nickel-phthalimide complexes. The procedure and other details, for performing these studies were kept the same, as described in Chapter I.

Readings for direct titrations: Phthalimide in cell.

TABLE NO. 27.

Concentration of phthalimide solution = 0.066 M.

Concentration of nickel chloride solution = 0.30 M.

Volume of phthalimide solution = 10 ml.

Total volume made up to 25 ml. with methyl alcohol.

Vol. of $NiCl_2$ (ml.).	Corrected conductance (mhos x 10^{-3})	Vol. of $NiCl_2$ (ml.).	Corrected conductance (mhos x 10^{-3})
0.0	2.545	1.0	2.941
0.1	2.500	1.1	3.086
0.2	2.463	1.2	3.226
0.4	2.404	1.3	3.356
0.5	2.381	1.5	3.623
0.6	2.469	1.7	3.876
0.7	2.577	1.9	4.167
0.8	2.688	2.1	4.405
0.9	2.817	2.4	4.762

Fig. 16

10.0 ml. of 0.066 M phthalimide

≡ 0.55 ml. of 0.3 M $NiCl_2$ ≡ 2.5 ml. of 0.066 M $NiCl_2$

Ni: phthalimide = 1:4

TABLE NO. 28.

Concentration of phthalimide solution = 0.066 M.

Concentration of nickel chloride solution=0.30 M.

Volume of phthalimide solution = 12 ml.

Total volume made up to 25 ml. with methyl alcohol.

Vol. of $NiCl_2$ (ml.)	Corrected conductance (mhosx10^{-3})	Vol. of $NiCl_2$ (ml.).	Corrected conductance (mhosx10^{-3})
0.0	2.817	0.9	2.778
0.1	2.793	1.0	2.899
0.2	2.762	1.2	3.106
0.3	2.732	1.4	3.300
0.4	2.703	1.6	3.534
0.5	2.681	1.8	3.731
0.6	2.667	2.0	3.922
0.7	2.653	2.4	4.292
0.8	2.688	-	-

Fig.17

12.0 ml. of 0.066 M phthalimide

≡ 0.675 ml. of 0.3 M $NiCl_2$ ≡ 3.07 ml. of 0.066 M $NiCl_2$

Ni: phthalimide = 1:3.9

TABLE NO. 29.

Concentration of phthalimide solution = 0.066 M.

Concentration of $NiCl_2$ solution = 0.30 M.

Volume of phthalimide solution = 15 ml.

Total volume made up to 25 ml. with methyl alcohol.

Vol. of $NiCl_2$ (ml.).	Corrected conductance (mhosx10^{-3})	Vol. of $NiCl_2$ (ml.).	Corrected conductance (mhosx10^{-3})
0.0	3.246	1.4	3.571
0.2	3.215	1.6	3.717
0.4	3.164	1.8	3.891
0.6	3.134	2.0	4.132
0.8	3.077	2.2	4.292
1.0	3.125	2.4	4.587
1.2	3.333	-	-

Fig.18.

15 ml. of 0.066 M phthalimide

≡ 0.85 ml. of 0.3M $NiCl_2$ ≡ 3.87 ml. of 0.066M $NiCl_2$

Ni: phthalimide = 1:3.88

TABLE NO.30.

Concentration of phthalimide solution = 0.066 M.

Concentration of nickel chloride solution =0.3 M.

Volume of phthalimide solution =21.0 ml.

Total volume made up to 25 ml.with methyl alcohol.

Vol. of $NiCl_2$ (ml.).	Corrected conductance (mhosx10^{-3})	Vol. of $NiCl_2$ (ml.).	Corrected conductance (mhosx10^{-3})
0.0	4.292	1.5	4.098
0.2	4.255	1.6	4.167
0.4	4.167	1.7	4.348
0.6	4.132	1.9	4.545
0.7	4.115	2.2	4.762
0.8	4.098	2.4	5.002
0.9	4.082	2.6	5.155
1.0	4.049	2.8	5.319
1.2	3.984	3.0	5.556
1.4	3.968	-	-

Fig.19.

21.0 ml. of 0.066 M phthalimide

= 1.2 ml. of 0.3 M of $NiCl_2$ = 5.4 ml. of 0.066 M $NiCl_2$

Ni: phthalimide = 1:3.85

For reverse titrations,1.0 ml.and 2.0 ml.of 0.066M nickel chloride were taken in the cell. To these four equivalents of potassium hydroxide solution were added,and total volume was made up to 10 ml.in each case. An interesting feature of these titrations was that although,nickel hydroxide precipitate was originally present in the titration cell, it got decomposed on the addition of phthalimide solution, resulting in appreciable variations in conductance values and subsequent appearence of a well defined inflexion point. The results are tabulated below:

Readings for reverse titrations:nickel chloride in the cell.

Concentration of nickel chloride solution = 0.0667 M.

Concentration of phthalimide solution = 0.0667 M.

Total volume made up to 10 ml.with methyl alcohol.

TABLE NO.31.

Volume of nickel chloride solution =1.0 ml.

Vol.of phthalimide (ml.).	Corrected conductance (mhosx10^{-3})	Vol.of phthalimide (ml.).	Corrected conductance (mhosx10^{-3})
0.0	1.299	4.3	1.093
0.7	1.242	5.0	1.081
1.4	1.180	5.8	1.058
2.1	1.180	6.4	1.036
2.8	1.130	7.4	1.020
3.5	1.111	8.0	1.020
3.8	1.111	-	-

Fig.20.

1.0 ml. of 0.0667 M $NiCl_2$ = 3.80 ml.of 0.0667 M phthalimid

Ni: phthalimide = 1:3.8

TABLE NO. 32.

Volume of nickel chloride solution = 2.0 ml.

Vol.of phthalimide (ml.).	Corrected conductance (mhosx10^{-3})	Vol.of phthalimide (ml.).	Corrected conductance (mhosx10^{-3})
0.0	2.381	8.0	1.724
1.2	2.232	9.0	1.681
2.4	2.083	10.0	1.645
3.6	1.969	11.2	1.613
5.0	1.887	12.4	1.575
6.2	1.812	13.4	1.538
7.0	1.770	-	-

Fig.21.

2.0 ml.of 0.0667 M $NiCl_2$ = 7.8 ml. of 0.0667 M phthalimide

Ni:phthalimide = 1:3.9

CONDUCTOMETRIC TITRATIONS (Ni-PHTH COMPLEX)

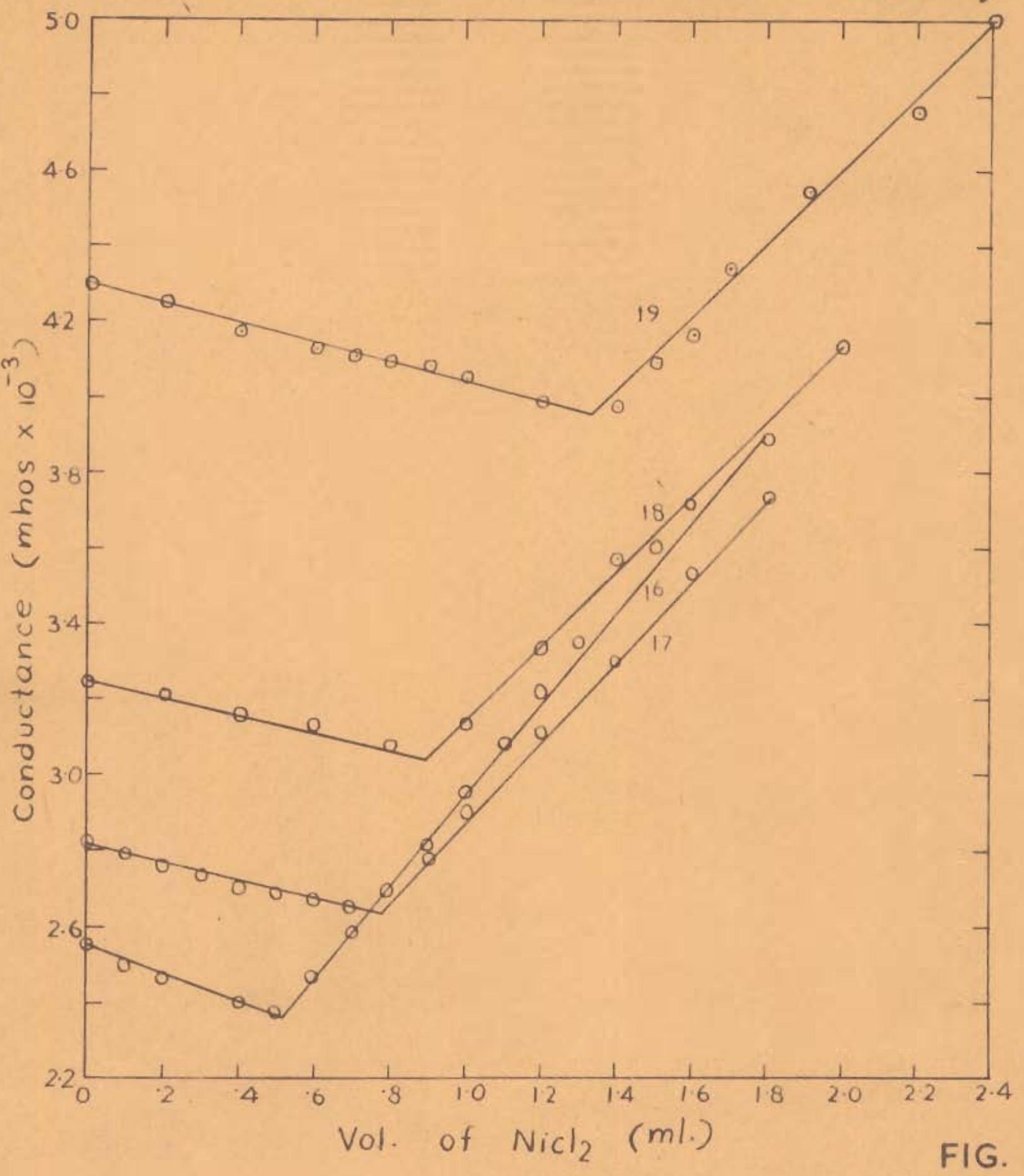


FIG. 16-19

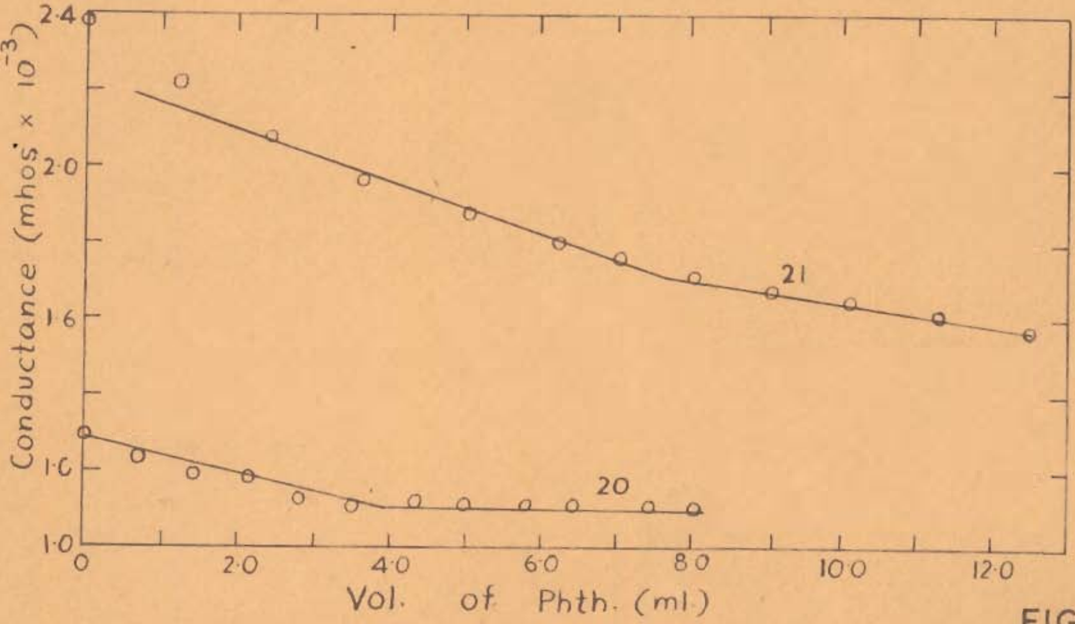


FIG. 20-21

pH-metric titrations

The method recommended by Calvin and Melchoir(loc.cit.) was employed here also, for performing pH metric studies of nickel complexes of phthalimide and glutarimide, in methanolic medium. The experimental details and the apparatus employed for these studies, were same as described earlier in Chapter I. Both in case of phthalimide and glutarimide, typical titration curves were obtained with and without the presence of metal ion.

Ni-phthalimide complex:

20 ml. of 0.05M phthalimide solution was mixed with 1.0 ml. and 1.5 ml. of nickel chloride, and was titrated against 0.1 M potassium hydroxide solution. For pK value phthalimide solution was separately titrated pH metrically. Corrected values of $\bar{n}$ and -log A (free ligand concentration) were calculated using the equation described in Chapter I. Tables showing calculations of $\bar{n}$ and -log A have been given, along with each titration table.

TABLE NO.33.

Titration for pK value of phthalimide(methanolic solution).

20.0 ml.of 0.05 M phthalimide,titrated against 0.1 M KOH.

Vol.of KOH(ml.).	pH	Vol.of KOH(ml.).	pH
0.0	6.87	4.0	9.48
0.2	9.12	5.0	9.495
0.3	9.26	6.0	9.50
0.5	9.32	7.0	9.52
0.8	9.38	8.0	9.54
1.4	9.39	9.0	9.57
2.0	9.42	10.0	9.59
3.0	9.47	-	-

Fig.22.

pK value of phthalimide = 9.50

TABLE NO. 34.

Titration of phthalimide solution in absence of nickelchloride.

20.0 ml. of 0.05 M phthalimide titrated against 0.1 M KOH.

Total volume made up to 25 ml. by methyl alcohol.

Vol.of KOH(ml.).	pH	Vol.of KOH(ml.).	pH
0.0	6.79	1.8	9.45
0.1	8.75	2.5	9.48
0.2	9.02	3.0	9.48
0.4	9.21	4.0	9.49
0.8	9.35	5.0	9.51
1.2	9.40	-	-

Fig.23,Curve 1.

Titrations of phthalimide in presence of nickel chloride:

Concentration of phthalimide = 0.05 M

Strength of $NiCl_2$ solution = 0.02 M

Strength of KOH solution = 0.1 M

TABLE NO.35.

20 ml. of phthalimide -1.0 ml. of nickel chloride,total volume made upto 25 ml. by methyl alcohol.

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.).	pH
0.0	4.46	1.0	8.98
0.1	5.40	1.4	9.22
0.2	5.91	1.8	9.31
0.4	7.20	2.5	9.40
0.5	7.93	3.0	9.44
0.6	8.24	4.0	9.52
0.8	8.70	5.0	9.58

Fig.23,Curve 2.

TABLE NO.35(A)

Calculations for formation curve.

For 1.0 ml.of 0.02 M,$NiCl_2$ = 0.2×10^{-4} moles.

pH	△ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log phth.
5.0	0.075	0.075	0.375	5.8027
5.5	0.125	0.125	0.625	5.3038
6.0	0.225	0.225	1.125	4.8060
6.5	0.325	0.325	1.515	4.3081
7.0	0.375	0.375	1.875	3.8083
7.5	0.425	0.425	2.125	3.3102
8.0	0.475	0.475	2.375	2.8113
8.5	0.625	0.625	3.125	2.3145
9.0	0.80	0.80	4.000	1.8181
9.25	0.85	0.85	4.25	1.5692

Fig.24,Curve 1.

TABLE NO. 36.

20 ml. of phthalimide -1.5 ml. of nickel chloride,total volume made upto 25 ml. by methyl alcohol.

Vol.of KOH(ml.).	pH	Vol.of KOH(ml.).	pH
0.0	4.42	1.2	8.80
0.1	5.00	1.8	9.25
0.25	5.55	2.5	9.35
0.3	5.90	3.0	9.47
0.4	6.25	4.0	9.53
0.5	6.75	5.0	9.57
0.8	8.10	-	-

Fig.23,Curve 3.

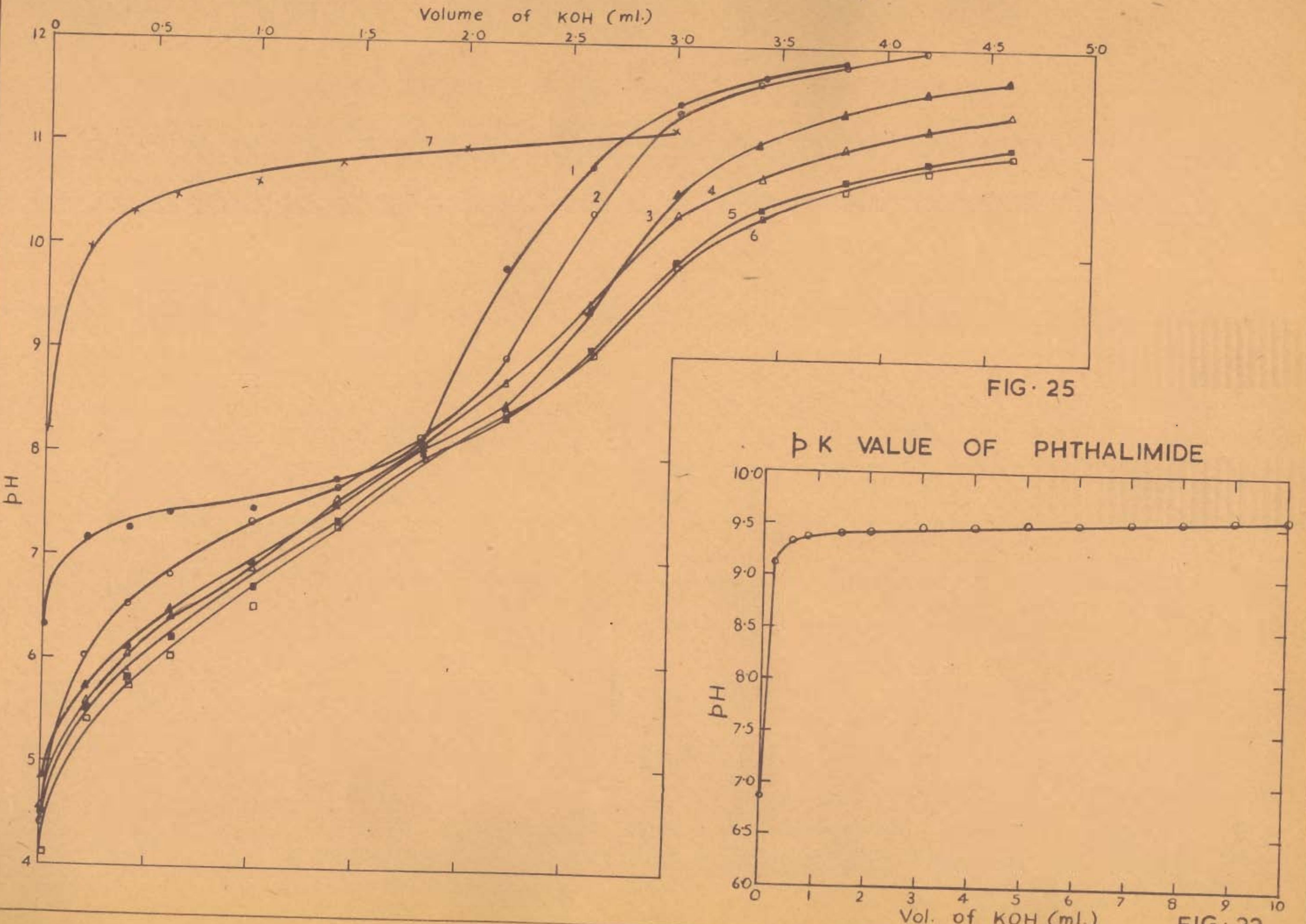
TABLE NO.36(A).

Calculations for formation curve.

For 1.5 ml. of 0.02 M,$NiCl_2$ = 0.3 x 10^{-4} moles.

pH	Δ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log phth.
5.0	0.125	0.125	0.416	5.8031
5.5	0.20	0.20	0.666	5.3054
6.0	0.35	0.35	1.166	4.8086
6.5	0.45	0.45	1.50	4.3107
7.0	0.55	0.55	1.833	3.8129
7.5	0.65	0.65	2.166	3.3150
8.0	0.75	0.75	2.50	2.8170
8.5	0.95	0.95	3.166	2.3212
9.0	1.175	1.175	3.916	1.8259
9.25	1.30	1.30	4.333	1.5784

Fig.24,Curve 2.



NI-PHTH. COMPLEX (METHYL ALCOHOL)

FIG · 25

þK VALUE OF PHTHALIMIDE

FIG · 22

For further confirmation of the composition of yellow complex, metal alone and with increasing proportions of phthalimide as (1:1, 1:2, 1:3, 1:4 and 1:5), were separately titrated against standard potassium hydroxide solution. Titration of phthalimide alone, against KOH, was also performed under similar condition. Details have been summarised in the following table and observation of different titrations are shown in Fig. 25.

TABLE NO. 37.

Concentration of phthalimide solution = 0.05 M.

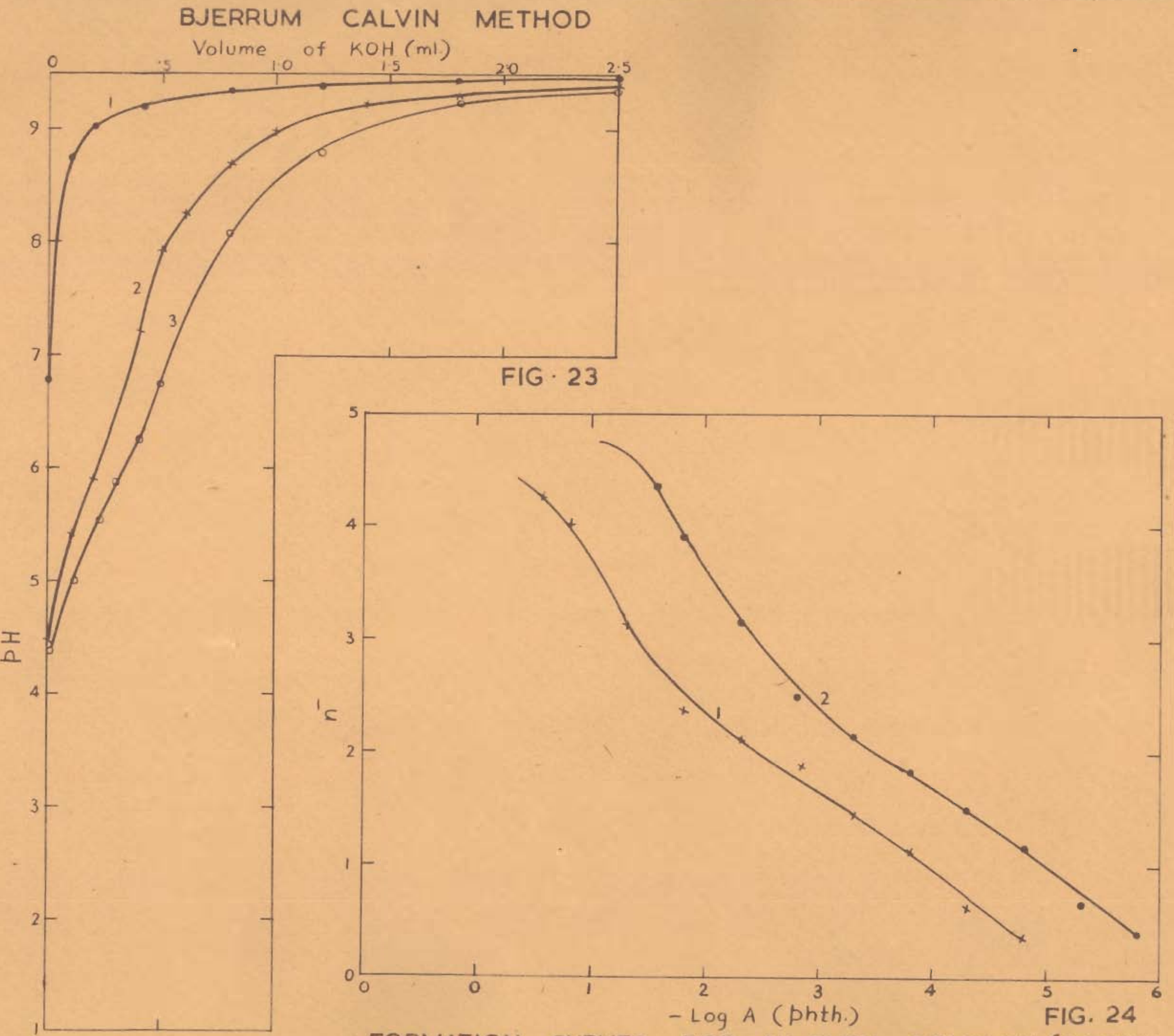
Concentration of nickel chloride = 0.05 M.

Concentration of KOH solution = 0.1 M.

Total volume in each set made upto 20 ml. by methyl alcohol.

Vol. of $NiCl_2$ (ml.).	Vol. of phthalimide (ml.).	$NiCl_2$: phthalimide	Curve No.
3.0	0.0	-	1
3.0	3.0	1:1	2
3.0	6.0	1:2	3
3.0	9.0	1:3	4
3.0	12.0	1:4	5
3.0	15.0	1:5	6
0.0	15.0	-	7

Fig. 25.



BJERRUM CALVIN METHOD

FIG · 23

FIG. 24

FORMATION CURVES FOR Ni-PHTH. COMPLEX (METHYL ALCOHOL)

Nickel-glutarimide complex:

pH metric titrations of 10 ml. of 0.1 M glutarimide alone and in presence of 0.5, 1.0 and 1.5 ml. of (0.05M) nickel chloride (total volume made upto 12 ml. with methyl-alcohol in each case), were performed against standard potassium hydroxide solution. pK value of glutarimide was determined by a separate titration and was found to be 11.06 at half titration point. Calculation tables for $\bar{n}$ and - log A (free ligand concentration) are given along with each titration table.

TABLE NO.38.

Titration of glutarimide solution in absence of nickel-chloride.

10.0 ml. of 0.1 M glutarimide solution titrated against 0.1 M KOH. Total volume made upto 12 ml. by methyl alcohol.

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.).	pH
0.0	7.15	1.5	11.9
0.1	10.38	2.0	12.05
0.2	10.70	3.0	12.20
0.3	10.95	4.0	12.30
0.4	11.13	5.0	12.35
0.5	11.28	5.5	12.40
1.0	11.70	6.2	12.42

Fig. 26, Curve 1.

Titrations of glutarimide in presence of nickel chloride:

Concentration of glutarimide = 0.1 M.

Strength of $NiCl_2$ solution = 0.05 M.

Strength of KOH solution = 0.1 M

TABLE NO.39.

10 ml. glutarimide - 0.5 ml. nickel chloride, total volume made upto 12 ml. by methyl alcohol.

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.).	pH
0.0	4.20	1.0	11.43
0.1	6.20	1.5	11.78
0.2	7.05	2.0	11.98
0.4	8.95	2.5	12.10
0.5	10.05	3.0	12.20
0.6	10.60	4.0	12.30
0.7	10.93	5.0	12.37
0.8	11.15	-	-

Fig.26, Curve 2.

TABLE NO.39(A)

Calculations for formation curve.

For 0.5 ml. of 0.05 M $NiCl_2$ = 0.25×10^{-4} moles.

pH	Δ KOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log glut.
7.0	0.20	0.20	0.80	5.1464
7.5	0.25	0.25	1.00	4.6482
8.0	0.275	0.275	1.10	4.1492
8.5	0.30	0.30	1.20	3.6499
9.0	0.35	0.35	1.40	3.1517
9.5	0.40	0.40	1.60	2.6534
10.0	0.425	0.425	1.70	2.1544
10.5	0.450	0.450	1.80	1.6552
11.0	0.45	0.45	1.80	1.1552
11.5	0.45	0.45	1.80	0.6552

Fig.27, Curve 1.

TABLE NO.40.

10 ml. glutarimide - 1.0 ml. nickel chloride, total volume made upto 12 ml. by methyl alcohol.

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.).	pH
0.0	4.27	1.0	10.40
0.1	5.95	1.2	11.10
0.2	6.40	1.4	11.40
0.3	6.80	1.8	11.70
0.4	7.28	2.2	11.89
0.5	7.60	3.0	12.1
0.6	7.90	3.5	12.20
0.7	8.30	4.3	12.30
0.8	8.85	5.0	12.35

Fig.26, Curve 3.

TABLE NO.40(A).

Calculations for formation curve.

For 1.0 ml. of 0.05 M $NiCl_2$ $\equiv 0.5 \times 10^{-4}$ moles.

pH	△ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log glut.
7.0	0.35	0.35	0.70	5.1517
7.5	0.45	0.45	0.90	4.6552
8.0	0.575	0.575	1.15	4.1597
8.5	0.70	0.700	1.40	3.6638
9.0	0.75	0.75	1.50	3.1655
9.5	0.85	0.85	1.70	2.7029
10.0	0.90	0.90	1.80	2.1706
10.5	0.91	0.91	1.82	1.6709
11.0	0.90	0.90	1.80	1.1706

Fig. 27, Curve 2.

TABLE NO.41.

10 ml. glutarimide - 1.5 ml. nickel chloride, total volume made upto 12 ml. by methyl alcohol.

KOH Vol. (ml.).	pH	KOH Vol. (ml.).	pH
0.0	4.17	1.2	8.33
0.1	5.60	1.4	10.40
0.2	6.12	1.7	11.10
0.3	6.43	2.0	11.50
0.4	6.75	2.4	11.79
0.5	7.00	2.8	12.02
0.6	7.30	3.2	12.13
0.82	7.30	3.8	12.23
1.0	7.78	5.0	12.38

Fig. 26, Curve 4.

TABLE NO. 41(A).

Calculation for formation curve.

For 1.5 ml. of 0.05 M $NiCl_2$ = 0.75×10^{-4} moles.

pH	Δ KOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log glut.
7.0	0.50	0.50	0.667	5.1569
7.5	0.75	0.75	1.00	4.6655
8.0	1.00	1.00	1.33	4.1739
8.5	1.15	1.15	1.533	3.6789
9.0	1.20	1.20	1.60	3.1806
9.5	1.25	1.25	1.667	2.6822
10.0	1.30	1.30	1.733	2.1839
10.5	1.35	1.35	1.80	1.6855
11.0	1.32	1.32	1.76	1.1846

Fig. 27, Curve 3.

BJERRUM CALVIN METHOD

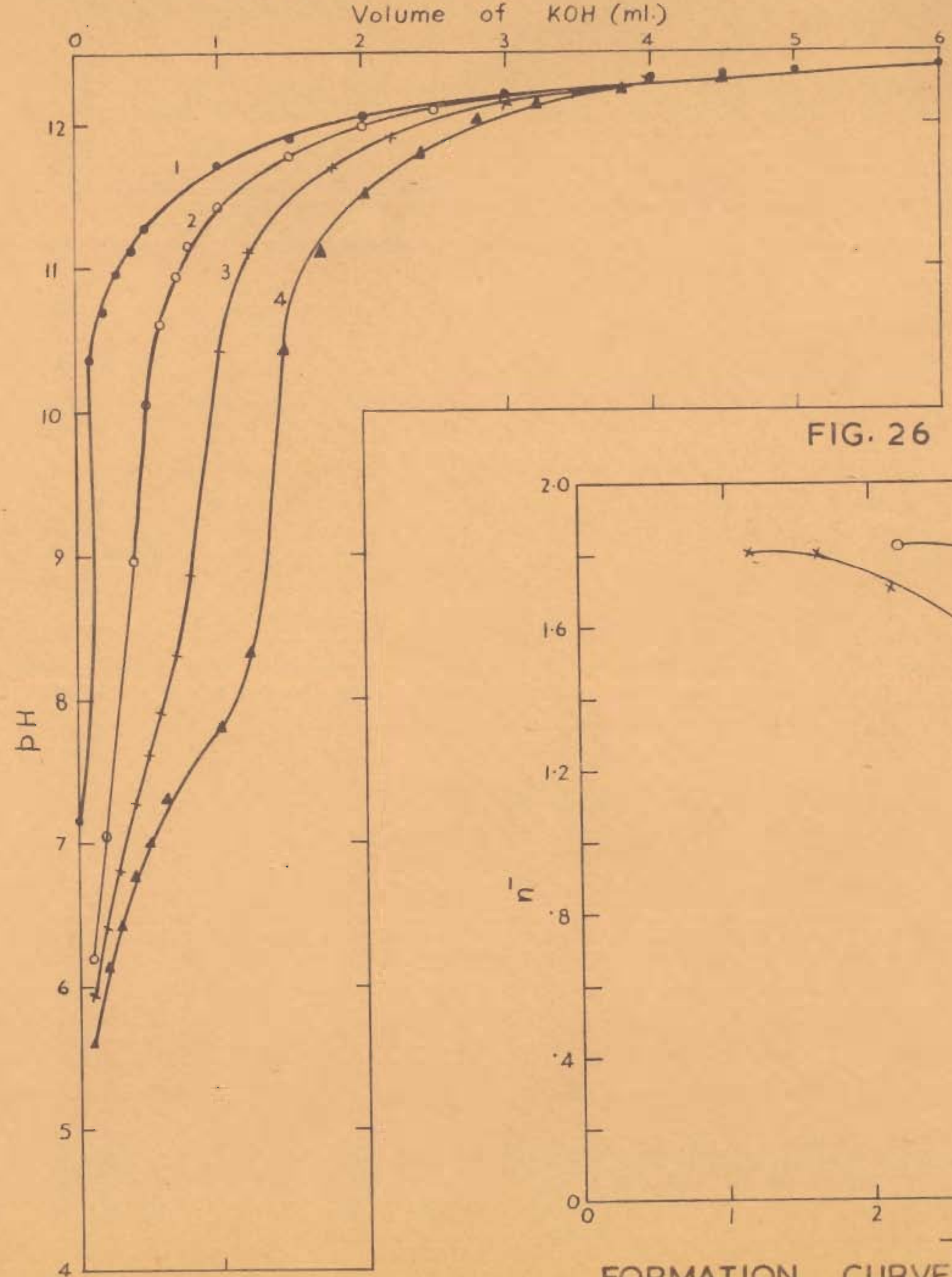


FIG. 26

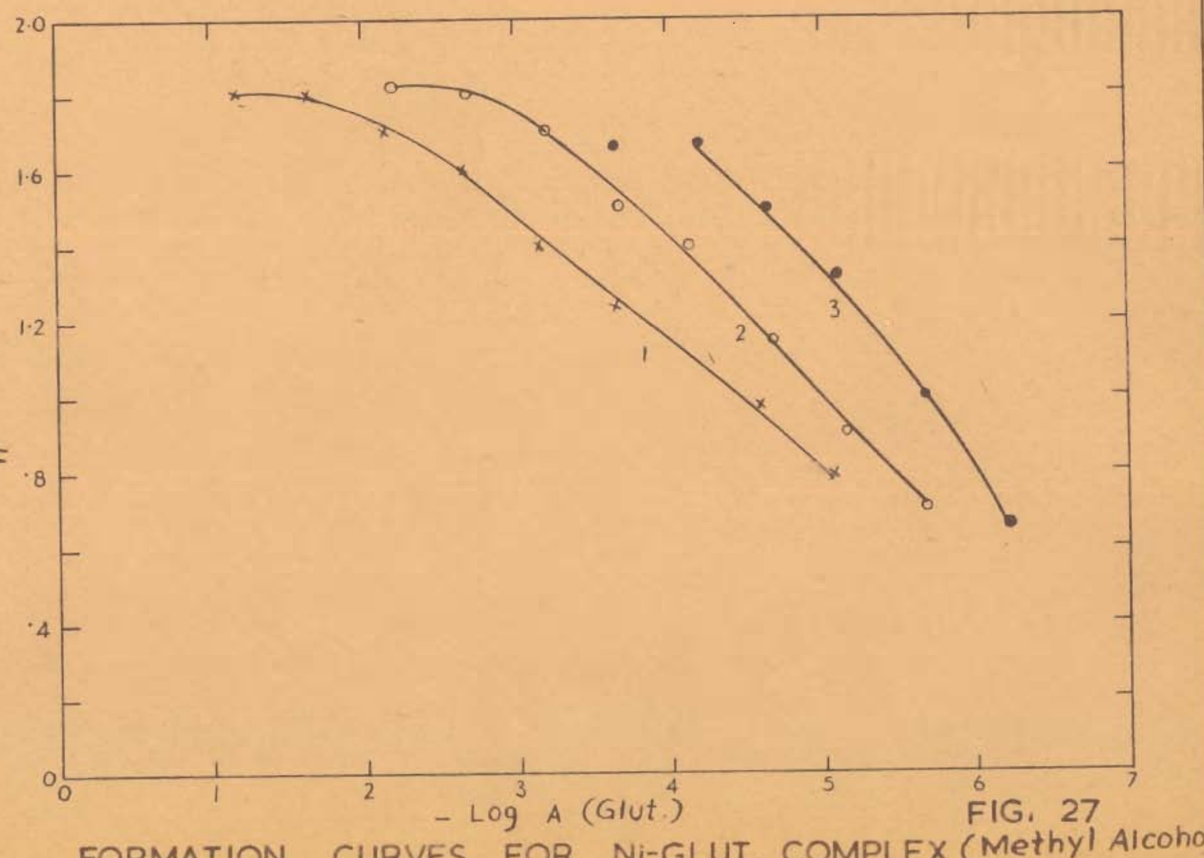


FIG. 27

FORMATION CURVES FOR Ni-GLUT. COMPLEX (Methyl Alcohol)

Here again solutions containing nickel chloride and glutarimide in different proportions, giving ratios of nickel to glutarimide as 1:1, 1:2 and 1:3, were titrated pH metrically against 0.1 M potassium hydroxide solution. Blank titrations of nickel chloride and glutarimide were also carried out separately, under similar conditions. The results of titration have been shown in Fig. 28 and details of concentrations etc. of the reagents are summarised below:

TABLE NO. 42.

Concentration of glutarimide solution = 0.1 M.

Concentration of nickel chloride = 0.05 M.

Concentration of KOH solution = 0.1 M.

Total volume in each set made upto to 15 ml. by methyl-alcohol.

Vol. of $NiCl_2$ (ml.).	Vol. of glutarimide (ml.).	$NiCl_2$: glutarimide	Curve No.
6.0	0.0	-	1
6.0	3.0	1:1	2
6.0	6.0	1:2	3
6.0	9.0	1:3	4
0.0	9.0	-	5

Fig. 28.

Isolation and chemical analysis of the yellow coloured nickel phthalimide complex:

50 ml. of nickel chloride (0.05 M) solution was added to 250 ml. of phthalimide solution of strength 0.05 M (phthalide solution was prepared in equivalent amount of potassium hydroxide), when a pH in the vicinity of ten was adjusted. The yellow coloured, crystalline precipitate of nickel phthalimide complex, was obtained, on concentrating the above mixture in a vacuum dessicator. Chemical analysis of this complex was done by the method described in Chapter I. The results of analysis are as follows:

Percentage of nitrogen = 8.51 %

Percentage of nickel = 8.98 %

Infra red spectroscopy:- I.R. Spectra of isolated yellow coloured, nickel phthalimide complex and of phthalimide were obtained in nujol medium by the method of fast scanning. Perkin and Elmer, spectrophotometer was employed for the above studies. The spectra obtained are depicted in Fig.29.

DISCUSSION

As described earlier nickel did not undergo complexion with phthalimide in aqueous medium, in either acidic neutral or alkaline media. In methanolic medium two complexes of yellow and green varieties were formed in presence of potassium hydroxide above pH 9. The yellow complex was found stable in presence of excess of phthalimide while the other complex was formed in presence of excess of nickel. Similar to the yellow coloured nickel succinimide complex, this yellow complex also changed into the green variety on increasing nickel proportions in the mixtures.

Spectrophotometric studies:

On applying VosBurgh and Cooper's method for the mixtures of nickel chloride : phthalimide as (1:1, 1:2, 1:3, 1:4, 1:5 and 1:7), two maxima corresponding to 360 mu and 650 mu were realised (Fig.1). Formation of two complexes was evident from these observations.

A much remarkable information to ascertain the nature of the two complexes was obtained by critically examining the variations in optical density values for the different mixtures, in the wavelength region 425 to 480 mu. The mixtures having higher proportions of phthalimide showed appreciable absorption, while the mixtures with low proportions absorbed very little in the above wavelength region. An abrupt fall in optical density values for the mixtures containing higher proportions of nickel than 1:4 (Ni : phthalimide), indicated the decomposition of yellow complex.

Therefore the stoichiometry of the yellow complex was carried out at wavelengths 425,440 and 460 mu. The absorption of methanolic solution of nickel chloride in this wavelength region,was negligible. The studies for the green complex were performed at wavelengths 630,650 and 670 mu,as the second absorption peak was obtained at 650 mu, which was quite far apart from the second peak of nickel chloride(750 mu).

Composition and stability constant of yellow complex:-

From Job's method of continued variation,the plots of the difference of O.D. of mixtures and metal ions against molar fraction of nickel,gave peaks corresponding to 1:4 (Ni-phthalimide) complex (Figs.2-4).

A slightly modified version of the molar ratio method was employed. In one case phthalimide was constant while in the other like the conventional procedure,nickel was kept constant. With mixtures containing fixed amount of nickel chloride,the plots of(moles of phthalimide)/(moles of nickel) vs.optical density,gave a sharp break corresponding to 1:4,nickel-phthalimide complex (Figs.5 and 6). The second procedure (mixtures containing fixed amount of phthalimide), besides providing information about the composition of the complex, also furnished definite evidence for the decomposition of the yellow complex in presence of excess of nickel (Figs.7 and 8) since optical density values beyond the inflexion point,showed gradual decrease instead of remaining constant. This decrease in optical density was due to the formation of green complex which as already stated, showed lesser absorption on the wavelengths 440 and 460 mu.

Formation constant of 1-4, nickel phthalimide complex was calculated using the method of Harvey and Manning(loc.cit. The equation described earlier in Chapter I, for 1:4 complex, was employed here also for this purpose. From Fig.6, curve 1, the value of stability constant K, came out to be, 3.89×10^6.

Composition and stability constant of green complex:- Unlike 1:4 complex in non-aqueous medium, this complex was quite stable in presence of excess of nickel chloride. The plots of difference in optical density against molar fraction of nickel gave maxima corresponding to 1:2 (Ni : phthalimide) composition(Figs.9-11).

Further confirmation of the results of Job's method was obtained by molar ratio method, inflexion points corresponding to 1:2(nickel-phthalimide) ratio were realised (Figs.12-14). However, the curves slightly deviated from the normal curves for the molar ratio method. The optical density values after the inflexion point instead of remaining constant, decreased due to the formation of yellow complex (due to excess of phthalimide).

The stability constant of this complex was determined by Anderson's method (equations 3 and 5, Pages 44 and 45). The values of a_1, b_1 and a_2, b_2 were 1.467×10^{-2}, 5.2×10^{-2} and 1.45×10^{-2}, 4.05×10^{-2}M respectively (Fig.15, Curves 1 and 2). The value of stability constant K, came out to be, 9.61×10^5.

Conductometric titrations:

Conductometric direct (phthalimide in the cell) titrations were quite successful in methanolic medium. A sharp inflexion point corresponding to 1:4(nickel-phthalimide) ratio was realised (Figs.16-19). Reverse (nickel chloride in the cell) titrations, exhibited a behaviour similar to the nickel-succinimide complex. The precipitate of nickel hydroxide got dissolved on gradual addition of phthalimide, giving a sharp inflextion corresponding to 1:4, nickel phthalimide complex (Figs.20-21).

pH-metric studies:

Here also, as in the case of nickel-succinimide complex, Bjerrum's method was subjected to the limitation of arbitrary units of pH in non-aqueous medium. However, from the shift in pH-metric titration curves the values of $\bar{n}$ and apparent average stability constant were determined. The value of, apparent over all stability constant, of the nickel phthalimide complex was obtained by multiplying the average value by four(Fig.23). From the titration curves it was evident that the value of $\bar{n}$ showed gradual increase with increase of pH, till a constant value of four was reached, suggesting thereby that the anionic form of phthalimide was taking part in the complex— ion(Fig.23). The mean value of apparent stability constant of the yellow complex, calculated from formation curves is given below:

Curves	Average stability constant log k =-log A at $\bar{n}$ =2	Over all stability constant log K = 4 log k	Mean log K
1	3.45	13.80	13.9
2	3.50	14.00	

Fig.24

The difference in the values of stability constant of yellow complex, as obtained by spectrophotometric and pH-metric methods, is quite understandable, since the pH in non-aqueous medium is not in the same units as in case of aqueous medium. Therefore the value of the stability constant obtained from pH-metric method, gives only the apparent value of stability constant.

The further confirmation of the composition of nickel phthalimide complex was obtained from the pH-metric titration curves of phthalimide alone and of mixtures having nickel and phthalimide in proportions of 1:1, 1:2, 1:3, 1:4 and 1:5. The shift of curves towards lower pH region, with increasing proportion of phthalimide, suggested continuous liberation of protons during complex – ion with nickel. The limiting case was reached corresponding to the mixtures having, nickel : phthalimide in the ratio of 1:4 (Fig.25).

Analysis of the yellow complex:

The results of analysis of the isolated complex (Ni = 8.98 % and N = 8.5 %), also confirmed the existence of

1:4 complex.

I.R.Spectra:

The I.R.Spectra of phthalimide and its 1:4 complex with nickel were recorded in the sodium chloride region (Fig.29).

The main characteristic of the spectrum of the complex was a marked shift in the carbonyl stretching frequency. The parent ligand, phthalimide showed carbonyl absorption band around 1750 cm^{-1} while the complex showed the band around 1660 cm^{-1}. The splittings of the band were also shown by the complex. However, it may be pointed out that even the parent imides must show splitting due to vibrational coupling.

Since the pH titrations and other chemical evidence seems to indicate that the co-ordination is through nitrogen, the decrease in carbonyl frequency could be interpreted due to the mass effect of the heavy metal atoms, which must have some perturbation in these ring complexes. Furthermore some of the decomposed metal might have reacted with carbonyl group, resulting the decrease in its frequency.

Nickel-glutarimide complex formed in methyl-alcohol:

Interaction of nickel with glutarimide was studied by pH-metric method only since conductometric and spectrophotometric methods could not be employed due to the limitations similar to those as encountered in case of nickel succinimide complex, in the aqueous medium.

pH-metric titration curves obtained were in accordance with the shape of the typical curves of Bjerrum's method (Fig.26). A set of $\bar{n}$ values was determined at different pH values. The value of $\bar{n}$ was found to increase with pH and attained a constant value at $\bar{n} = 2$, indicating thereby the formation of 1:2 (nickel glutarimide) complex.

Free ligand concentration(A^-) was calculated by the method described earlier in Chapter I. Formation curves (Fig.27) were obtained by plotting $\bar{n}$ against -log A. The apparent values of average and over all stability constants, as determined from the formation curves are tabulated below:

Curves	Average stability constant log k=-log A at $\bar{n}$=1	Over all stability constant log K=2 log k	Mean log K
1	4.40	8.80	
2	4.55	9.10	9.0333
3	4.60	9.20	

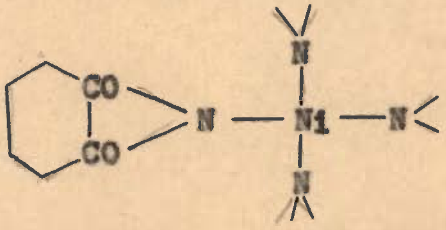
Fig.27

Further confirmation of the composition of nickel glutarimide complex was obtained from pH titration curves of mixtures containing nickel chloride and glutarimide in different proportions (Fig.28). A gradual shift of curves towards lower pH range was observed till the ratio of nickel: glutarimide approached, 1:2. No further shift of the curves to the lower pH range was observed beyond 1:2, nickel-glutarimide ratio. This clearly indicated that the maximum capacity per metal ion for displacing hydrogen ions of glutarimide, is two.

Mechanism of the reactions of nickel(II)with phthalimide and glutarimide,in methanolic medium:

(i) 1:4 Ni-phthalimide complex(yellow coloured).

Analogous to the behaviour of Ni-succinimide,this complex was also formed by a biuret mechanism. The following structure may therefore be assigned to this complex,



or $\left((C_8H_4O_2N)_4\ Ni\right)^{2-}$

In view of the evidence gathered from physico-chemical studies, the co-ordination of nickel has been visualized through four basic nitrogen atoms. However, I.R.spectrum of the isolated complex does not seems to support above observations,probably due to change in the nature of complex on heating and drying.

(ii) 1:2 Ni-phthalimide complex(green coloured).

The following structure may be proposed,based on exactly similar reasonings as in case of 1:2,nickel-succinimide complex,

$$\left((C_8H_4O_2N)_2\ \ Ni\ \ (CH_3OH)_2\right)$$

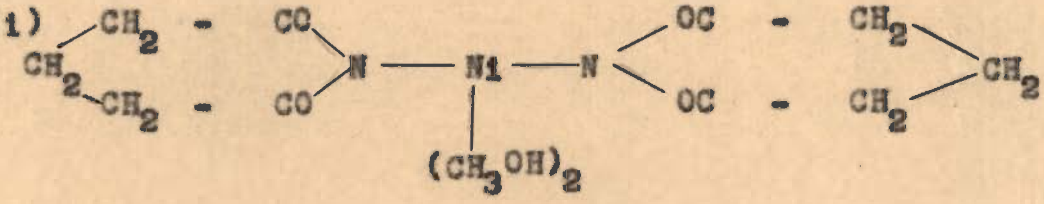
The possibility of chelation exists here also analogous to 1:2,succinimide complex of nickel.

Since two basic nitrogen instead of four are involved in co-ordination,biuret reaction mechanism cannot be assigned.

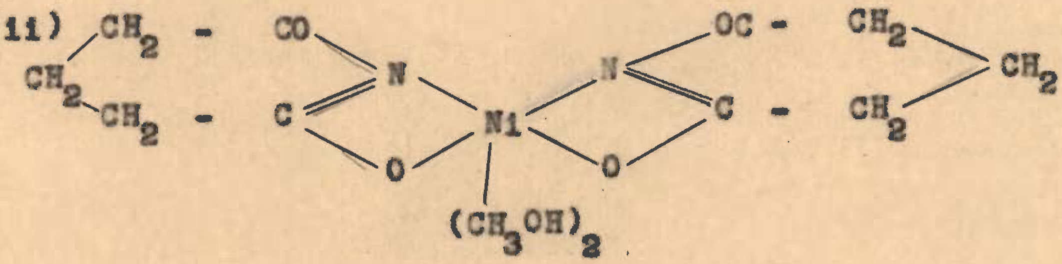
(iii) 1:2 Ni-glutarimide complex(green coloured).

The structure of 1:2, nickel-glutarimide complex may be represented by the following formulae,

(i)



(ii)



However, for lack of evidence in favour of any of the two structures, the complex may be represented as,

$$\left[(C_5H_6O_2N)_2 \quad Ni \quad (CH_3OH)_2\right]$$

This complex again is not formed by biuret reaction, since only two nitrogen atoms are involved in complex-ion.

CHAPTER III.

Insoluble copper complexes of succinimide, phthalimide, and glutarimide (biuret reaction mechanism).

INTRODUCTION

Copper complexes involving biuret reaction are quite familiar. Mary M. Rising and coworkers (1) studied the biuret reaction of di-acid amides and copper, in presence of alkali. The colour change was explained due to simultaneous salt and complex ion formation. It was therefore, suggested that in each molecule of di-acid amide there must be two acid hydrogen atoms and one or more amine nitrogen atoms, for salt and complex ion formation respectively.

Biuret reaction of copper with amino acid amides(2) involves appearance of pink colour even in absence of alkali. This behaviour was attributed to their ready enolisation. Thus copper gets coordinated with four nitrogen atoms of two molecules of acid amides. The literature on these reactions, besides being meagre, deals mostly with the studies based on the methods of chemical analysis only. Some of it is, however, worth describing. Schiff(3) in his generalisation of the groups, responsible for the biuret reaction did not include di-acid imides. However, Tschugaeff (4) reported biuret reaction of imides in the ammonical, aqueous-ethanolic and pyridine media. The hydrolytic nature of the copper succinimide complex was reported by Ley and Werner (5). Owing to its hydrolytic decomposition, Rising and Johnson (6) investigated the copper succinimide complex in ethanolic solution of barium hydroxide, and tried to establish its composition by the method of chemical analysis.

L.Cambi (7) studied the magnetic properties of complex derivatives of succinimide and phthalimide,with iron,nickel,cobalt and copper,and these complexes were shown to be paramagnetic.

From what has been said above,it is evident that only reactions involving coordination of the metal with four basic nitrogen are designated as biuret reaction, while other reactions like the interaction of copper and nickel with imides in the aqueous medium,involving two basic nitrogen or that of cobalt in non aqueous medium involving combination with two ionic nitrogen are non biuret reactions.

Preliminary investigations performed in aqueous medium revealed that copper got precipitated as hydroxide on mixing with alkaline solution of succinimide and glutarimide. However, on carrying out the reactions in methanolic medium,complex-ion between metals and imides was possible to realise. It was thus observed that bluish violet insoluble complex was obtained,on mixing methanolic potassium hydroxide to a methanolic metal-imide mixture. This bluish violet precipitate was found highly sensitive towards moisture and traces of water decomposed it,resulting in the formation of copper hydroxide. Moreover,these complexes got decomposed in excess of copper sulphate also.

In this chapter composition and stability of insoluble copper complexes of succinimide,phthalimide and glutarimide, formed in methanolic medium have been studied,employing conductometric, potentiometric, amperometric and pH-metric methods. The results of the above studies have been further confirmed by I.R.spectra and chemical analysis, of the isolated products.

EXPERIMENTAL

Solutions of succinimide, phthalimide and glutarimide were prepared by dissolving the requisite amounts in double distilled methyl alcohol. Copper sulphate (A.R.) solution was prepared by direct weighing and dissolving in methanol. Freshly prepared methanolic solution of copper sulphate was used through out these studies, since it got turbid on keeping.

Copper (I) chloride:- No copper(I) salts soluble in water, much less in methanol to give copper(I) ions are known. The only known stable copper(I) salts are either slightly soluble compounds in water or are complex salts (8). Cuprous chloride was prepared by dissolving 42 gms. of crystalline cupric chloride in 200 ml. of hydrochloric acid (sp.gr.1.17) and mixing with 100 ml. of water. 25 gms. of copper turnings were added and the mixture was heated on a water bath until the dark colour disappeared. The clear liquid was then poured into a vessel containing two litres of cold, air free water, acidified with a little sulphurous acid. White precipitate of cuprous chloride was collected by means of suction filter, washed with dilute sulphuric acid(1:20) and then successively with absolute alcohol and ether. The product was dried in a vacuum dessicator over concentrated sulphuric acid.

Cuprous chloride solution was prepared by dissolving the salt in methanolic solution of sodium chloride.

Stock solution of methanolic potassium hydroxide was prepared by dissolving the alkali in methanol. Its strength was determined volumetrically.

Conductometric titrations.

Conductometric titrations of succinimide, phthalimide and glutarimide against freshly prepared copper sulphate solution were carried out at different concentrations. Both direct(copper sulphate as the titrant) and reverse (imides as the titrant) titrations were performed in purely methanolic medium. For direct (metal ion as the titrant) titrations, imide solution prepared in equivalent amount of potassium hydroxide, was taken in the cell, while for reverse (imide as titrant) titrations, copper sulphate in presence of four equivalents of potassium hydroxide was taken in the cell.

The technique of reverse titration was based on decomposing the freshly precipitated copper hydroxide (formed due to the addition of four equivalents of methanolic potassium hydroxide) by gradual addition of the imide from the burette. As stated earlier, a sharp inflexion point corresponding to the formation of a definite complex was realised here also.

Phillips conductivity bridge with bridge type conductivity cell was used for conductance measurements. The effect of temperature on the conductance was minimised by putting the cell in a beaker of water. Volume correction was applied by multiplying the conductance value by the V + v / V , where V is the volume taken in the cell and v is the volume of the titrant added. The readings for the direct and reverse titrations are tabulated below:

Copper-succinimide complex:

Readings for direct titrations: succinimide in the cell.

TABLE NO.1.

Concentration of succinimide solution = 0.1 M.

Concentration of copper sulphate solution = 0.2 M.

Volume of succinimide solution = 10 ml.

Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos x 10^{-3})	Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos x 10^{-3})
0.0	3.8462	1.8	0.5263
0.2	3.4483	2.0	0.4348
0.4	3.0303	2.2	0.3328
0.6	2.5907	2.4	0.2320
0.8	2.1552	2.6	0.1786
1.0	1.7544	2.8	0.1408
1.2	1.2987	3.0	0.1075
1.4	0.8333	3.2	0.0833
1.6	0.6410	-	-

Fig.1

10 ml. of 0.1 M succinimide.

= 1.2 ml. of 0.2 M $CuSO_4$ = 2.4 ml. of 0.1 M $CuSO_4$

Cu: succinimide = 1:4.15

TABLE NO.2.

Concentration of succinimide solution = 0.1 M.

Concentration of copper sulphate solution = 0.2 M.

Volume of succinimide solution = 15 ml.

Vol. of $CuSO_4$(ml.).	Corrected conductance (mhosx10^{-3})	Vol. of $CuSO_4$(ml.).	Corrected conductance (mhosx10^{-3})
0.0	4.3860	2.0	1.2987
0.2	4.1152	2.2	1.0000
0.4	3.8610	2.4	0.7692
0.8	3.2258	2.6	0.7521
1.0	2.9240	2.8	0.6554
1.2	2.6110	3.4	0.3703
1.4	2.2883	4.0	0.2024
1.6	1.9231	4.5	0.1298
1.8	1.6077	-	-

15 ml. of 0.1M succinimide. Fig.2.

= 1.95 ml. of 0.2M $CuSO_4$ = 3.9 ml. of 0.1 M $CuSO_4$

Cu: succinimide = 1:3.85.

TABLE NO.3.

Concentration of succinimide solution = 0.1 M.

Concentration of copper sulphate solution =0.1 M.

Volume of succinimide solution = 9.0 ml.

Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-3}$)	Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x 10^{-3}$)
0.0	2.5707	1.9	0.8695
0.2	2.3981	2.1	0.7143
0.3	2.3310	2.3	0.5814
0.5	2.1413	2.7	0.4504
0.7	1.9531	3.0	0.3636
0.9	1.7794	3.3	0.2915
1.1	1.5873	3.8	0.1886
1.3	1.4085	4.1	0.1492
1.5	1.2195	4.4	0.1219
1.7	1.0638	4.8	0.0909

Fig.3.

9.0 ml. of 0.1M succinimide.
≡ 2.3 ml. (0.1M) $CuSO_4$.
Cu:succinimide =1:3.9.

TABLE NO.4.

Concentration of succinimide solution = 0.1 M.

Concentration of $CuSO_4$ solution = 0.133M.

Volume of succinimide solution = 7.5 ml.

Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x 10^{-3}$)	Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-3}$)
0.0	2.5641	1.6	0.6250
0.2	2.3148	1.8	0.4878
0.4	2.0576	2.0	0.4115
0.6	1.8149	2.2	0.3496
0.8	1.5625	2.4	0.2801
1.0	1.3245	2.6	0.2127
1.2	1.0638	2.8	0.1795
1.4	0.8196	3.0	0.1526

Fig.4.

7.5 ml. of 0.1 M succinimide.
≡ 1.45 ml. of 0.133M $CuSO_4$ ≡ 1.93 ml. of 0.1M $CuSO_4$.
Cu: succinimide = 1:3.88.

Readings for the reverse titration: CuSO$_4$ solution in cell.

TABLE NO. 5.

Concentration of succinimide solution = 0.5 M.

Concentration of CuSO$_4$ solution = 0.04 M.

Volume of CuSO$_4$ solution = 5.0 ml.

Vol. of succinimide (ml.).	Corrected conductance (mhos x 10^{-3})	Vol. of succinimide (ml.).	Corrected conductance (mhos x 10^{-3})
0.0	3.3898	2.6	1.8116
0.4	3.0303	2.9	1.7699
0.8	2.6882	3.2	1.7301
1.2	2.3753	3.5	1.6667
1.6	2.1053	3.8	1.3245
2.0	1.9531	4.1	1.2987
2.3	1.8727	4.4	1.2821

Fig.5.

5.0 ml. of 0.04 M CuSO$_4$
= 1.6 ml. of 0.5 M succinimide solution = 20 ml. of 0.04 M succinimide.

Cu: succinimide = 1:4.0

TABLE NO. 6.

Concentration of succinimide solution = 0.5 M.

Concentration of CuSO$_4$ solution = 0.02 M.

Volume of CuSO$_4$ solution = 6.0 ml.

Vol. of succinimide (ml.)	Corrected conductance (mhos x 10^{-3})	Vol. of succinimide (ml.).	Corrected conductance (mhos x 10^{-3})
0.0	2.2124	1.1	1.4388
0.2	2.0576	1.3	1.3889
0.4	1.9157	1.5	1.3605
0.6	1.1700	1.7	1.3423
0.7	1.6667	1.9	1.3158
0.8	1.5924	2.1	1.2987
0.9	1.5385	2.3	1.2821
1.0	1.4706	2.5	1.2658

Fig.6.

6.0 ml. of 0.02 M CuSO$_4$
= 1.0 ml. of 0.5 M succinimide = 25 ml. of 0.02 M succinimide.

Cu: succinimide = 1:4.17.

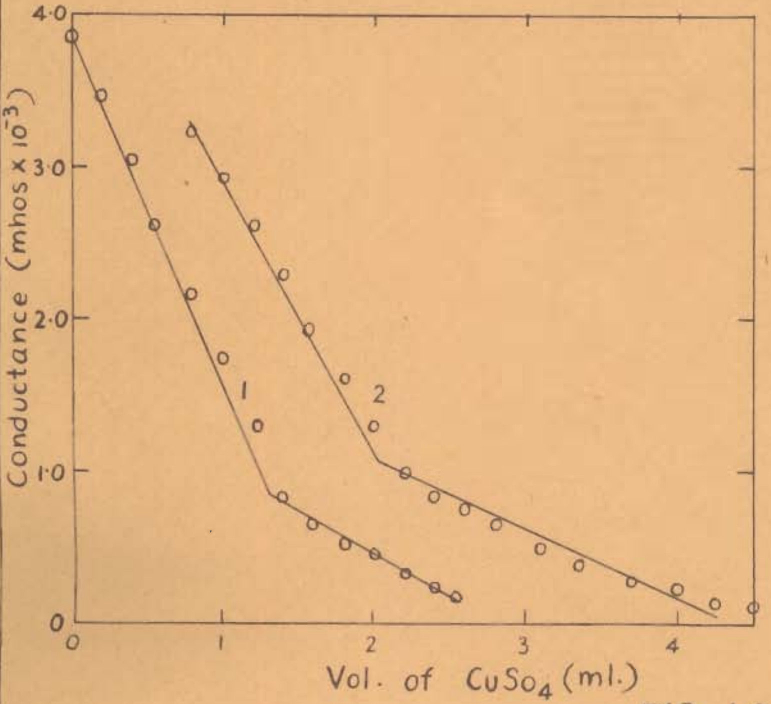


FIG. 1-2

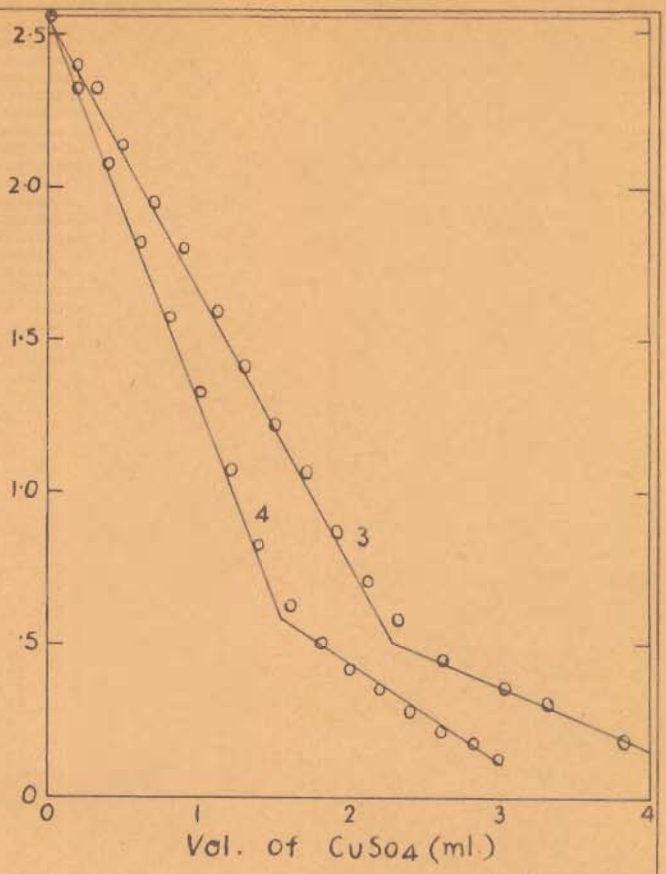


FIG. 3-4

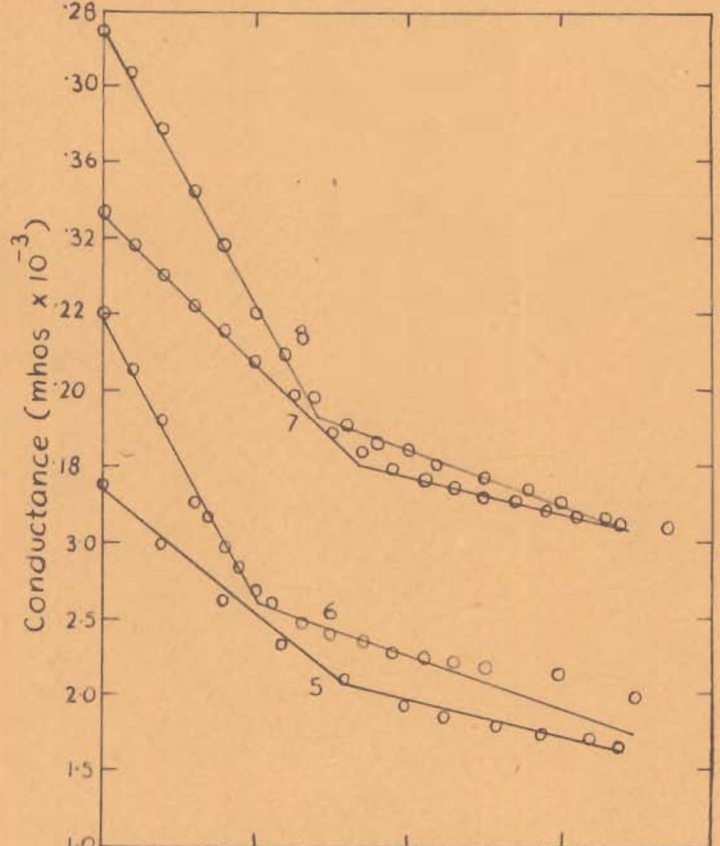


FIG. 5-8

CONDUCTOMETRIC TITRATIONS: Cu-SUCCINIMIDE COMPLEX

Concentration of succinimide solution = 0.5 M.

Concentration of $CuSO_4$ solution = 0.02 M.

TABLE NO.7.

Volume of $CuSO_4$ solution = 10 ml.

Vol. of succinimide (ml.).	Corrected conductance (mhos $\times 10^{-3}$)	Vol. of succinimide (ml.).	Corrected conductance (mhos $\times 10^{-3}$)
0.0	3.3333	1.9	1.9920
0.2	3.1746	2.1	1.9231
0.4	3.0211	2.3	1.8762
0.6	2.8571	2.5	1.8349
0.8	2.7100	2.7	1.8116
1.0	2.5445	2.9	1.7699
1.2	2.3810	3.1	1.7544
1.5	2.1692	3.4	1.7094
1.7	2.0833	3.7	1.6835

Fig.7.

10.0 ml. of 0.02 M $CuSO_4$
≡ 1.65 ml. of 0.5 M succinimide ≡ 40 ml. of 0.02M succinimide
Cu: succinimide = 1:4

TABLE NO. 8.

Vol. of $CuSO_4$ solution = 8.0 ml.

Vol. of succinimide (ml.).	Corrected conductance (mhos $\times 10^{-3}$)	Vol. of succinimide (ml.).	Corrected conductance (mhos $\times 10^{-3}$)
0.0	2.7548	1.8	1.6584
0.2	2.6316	2.0	1.6393
0.4	2.4876	2.2	1.6000
0.6	2.3256	2.5	1.5625
0.8	2.1834	2.8	1.5385
1.0	2.0000	3.0	1.5038
1.2	1.8868	3.3	1.4493
1.4	1.7794	3.5	1.3699
1.6	1.7094	3.7	1.1765

Fig. 8.

8.0 ml. of 0.02 M $CuSO_4$

≡ 1.3 ml. of 0.5 M succinimide ≡32.5 ml. of 0.02M succinimide

Cu: succinimide = 1:4.06

Copper-phthalimide complex:

Readings for direct titrations: phthalimide in the cell.

Concentration of phthalimide solution = 0.0667 M.

Concentration of $CuSO_4$ solution = 0.0667 M.

TABLE NO.9.

Volume of phthalimide solution = 5.0 ml.

Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-3}$)	Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-3}$)
0.0	1.2900	1.4	0.4566
0.2	1.1630	1.6	0.3922
0.4	1.0260	1.9	0.3236
0.6	0.8696	2.1	0.2604
0.8	0.7576	2.4	0.1916
1.0	0.6061	2.7	0.1307
1.2	0.5102	3.0	0.0925

Fig.9.

5.0 ml. of 0.0667 M phthalimide= 1.25 ml. of 0.0667M $CuSO_4$

Cu: phthalimide = 1:4.0

TABLE NO.10.

Volume of phthalimide solution = 12.0 ml.

Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-3}$)	Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x 10^{-3}$)
0.0	2.439	2.4	0.8403
0.4	2.169	2.7	0.6250
0.8	1.923	3.0	0.4255
1.1	1.724	3.3	0.2950
1.5	1.471	3.8	0.2273
1.8	1.282	4.2	0.1859
2.1	1.058	4.5	0.1639

Fig.10.

12 ml. of 0.0667 M phthalimide =3.0 ml. of 0.0667 M $CuSO_4$

Cu: phthalimide = 1.4.0

TABLE NO.11.

Volume of phthalimide solution = 18.0 ml.

Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-3}$)	Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-3}$)
0.0	3.236	4.5	0.7825
0.5	2.967	4.9	0.6267
1.0	2.732	5.5	0.4250
1.5	2.488	6.0	0.3541
2.0	2.247	6.5	0.2481
2.6	1.934	7.0	0.2169
3.0	1.724	7.5	0.1869
3.6	1.360	8.0	0.1562
4.0	1.120	-	-

Fig.11.

18.0 ml. of 0.0667 M phthalimide= 4.60 ml. of 0.0667 M $CuSO_4$

Cu : phthalimide = 1:3.91

TABLE NO. 12.

Volume of phthalimide solution = 21 ml.

Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-3}$)	Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-3}$)
0.0	3.226	5.5	0.9253
0.8	2.874	5.5	0.7025
1.6	2.494	6.1	0.4762
2.4	2.160	6.8	0.3527
3.2	1.818	7.6	0.2735
4.0	1.481	8.0	0.2213
4.5	1.266	8.6	0.1379

Fig.12.

21.0 ml. of 0.0667 M phthalimide= 5.5 ml. of 0.0667M $CuSO_4$

Cu : phthalimide = 1:3.82.

CONDUCTOMETRIC TITRATIONS : Cu-PHTHALIMIDE COMPLEX

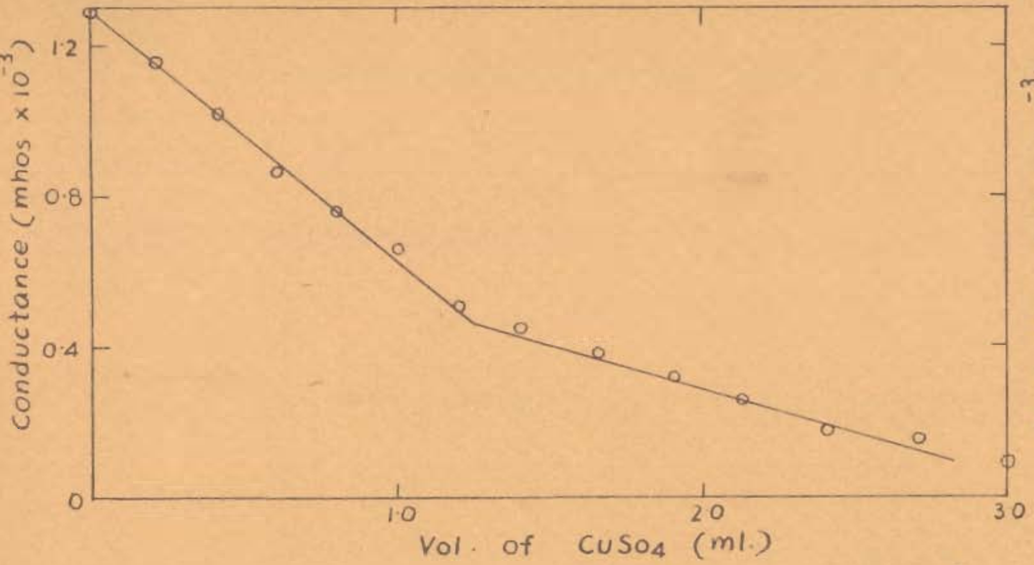


FIG. 9

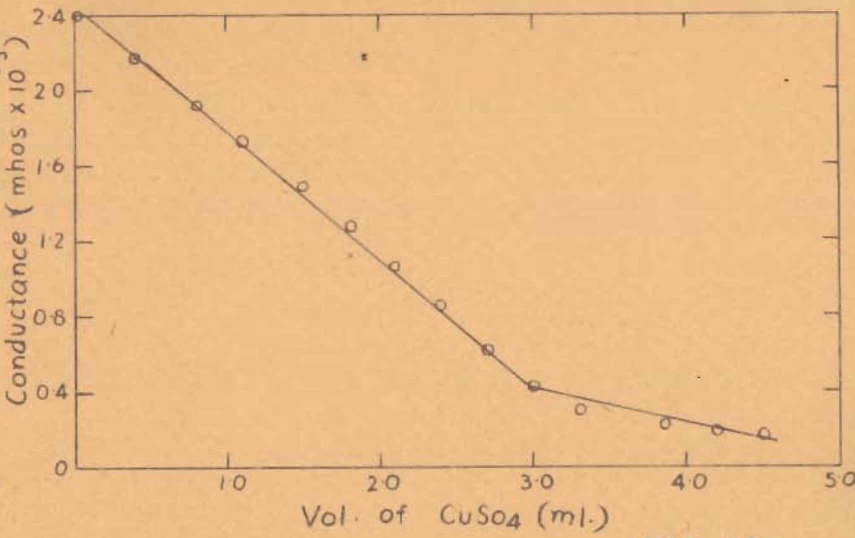


FIG. 10

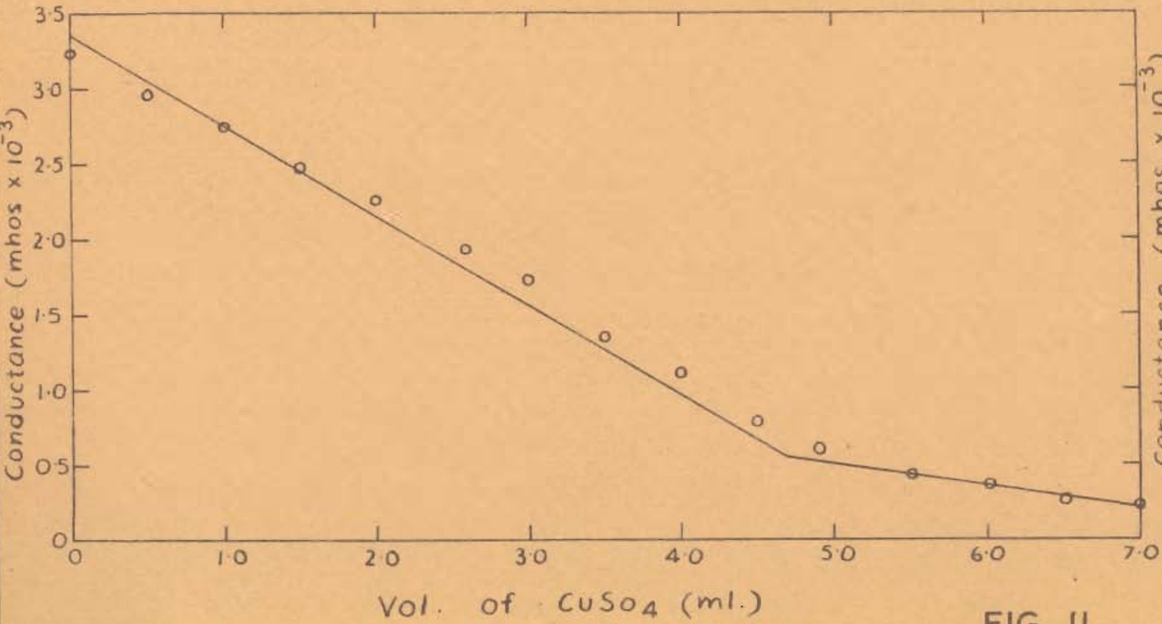


FIG. 11

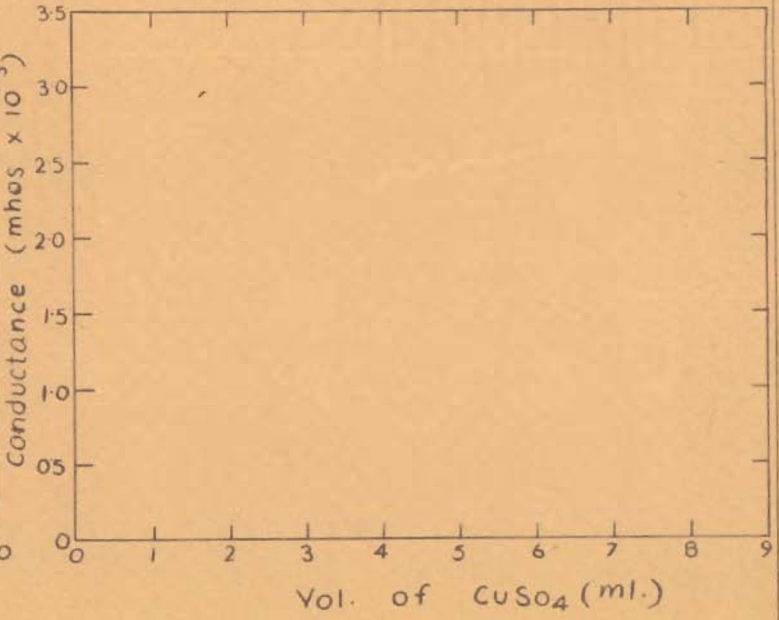


FIG. 12

Readings for reverse titrations: $CuSO_4$ in the cell.

Concentration of phthalimide solution = 0.0667 M.

Concentration of $CuSO_4$ solution = 0.0167 M.

TABLE NO. 13.

Volume of $CuSO_4$ solution = 5.0 ml.

Vol. of phthalimide (ml.).	Corrected conductance (mhos x 10^{-3})	Vol. of phthalimide (ml.).	Corrected conductance (mhos x10^{-3})
0.0	1.562	5.7	0.9709
0.7	1.481	6.4	0.9346
1.4	1.408	7.1	0.9091
2.1	1.333	7.8	0.8929
2.8	1.235	8.5	0.8850
3.5	1.149	9.2	0.8696
4.2	1.075	10.0	0.8475
5.0	1.005	-	-

Fig. 13.

5 ml. of 0.0167 M $CuSO_4$

≡ 5.0 ml. of 0.0667 M phthalimide ≡ 20.0 ml. of 0.0167 M phthalimide.

Cu : phthalimide = 1:4.0

TABLE NO. 14.

Volume of $CuSO_4$ solution = 7.5 ml.

Vol. of phthalimide (ml.).	Corrected conductance (mhos x10^{-3})	Vol. of phthalimide (ml.).	Corrected conductance (mhos x 10^{-3})
0.0	2.326	7.0	1.379
1.0	2.174	8.0	1.316
2.0	2.041	9.0	1.266
3.0	1.908	9.5	1.242
4.0	1.754	10. 0	1.220
5.0	1.587	11.0	1.120
6.0	1.481	-	-

Fig. 14

7.5 ml. of 0.0167 M $CuSO_4$

≡ 7.4 ml. of 0.0667 M phthalimide ≡ 29.6 ml. of 0.0167M phthalimide.

Cu: phthalimide = 1:3.95.

TABLE NO.15.

Volume of $CuSO_4$ solution = 10.0 ml.

Vol. of phthalimide (ml.).	Corrected conductance (mhos x10^{-3})	Vol. of phthalimide (ml.).	Corrected conductance (mhos x10^{-3})
0.0	1.462	8.8	0.7813
1.5	1.385	10.0	0.7407
3.0	1.269	11.0	0.7246
4.0	1.163	12.0	0.7092
5.0	1.047	13.0	0.7042
6.5	0.9091	14.0	0.6803
7.5	0.833	15.0	0.6667

Fig.15.

10 ml. of 0.0167 M $CuSO_4$

≡ 9.5 ml. of 0.0667 M phthalimide ≡ 38.0 ml. of 0.0167 M phthalimide.

Cu: phthalimide =1:3.8.

TABLE NO. 16.

Volume of $CuSO_4$ solution = 12.5 ml.

Vol. of phthalimide (ml.).	Corrected conductance (mhos x10^{-3})	Vol. of phthalimide (ml.).	Corrected conductance (mhos x10^{-3})
0.0	1.6535	11.5	0.8929
2.0	1.4433	12.5	0.8696
3.5	1.430	13.5	0.8403
5.0	1.389	14.5	0.8330
6.5	1.227	15.0	0.8197
8.0	1.094	16.0	0.8130
9.0	1.020	17.0	0.7183
10.0	0.9346	18.0	0.7692

Fig. 16.

12.5 ml. of 0.0167 M $CuSO_4$

≡ 12.4 ml. of 0.0667 M phthalimide ≡ 49.6 ml. of 0.0167M phthalimide

Cu : phthalimide = 1:3.97.

CONDUCTOMETRIC TITRATIONS : Cu-PHTHALIMIDE COMPLEX

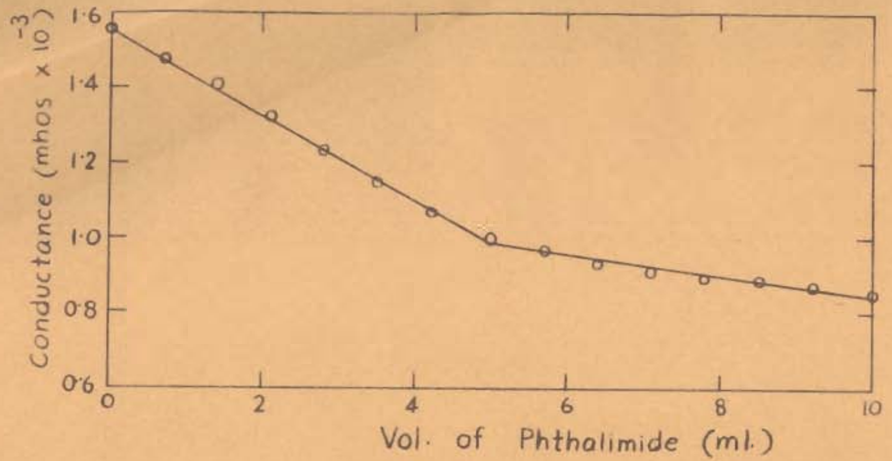


FIG. 13

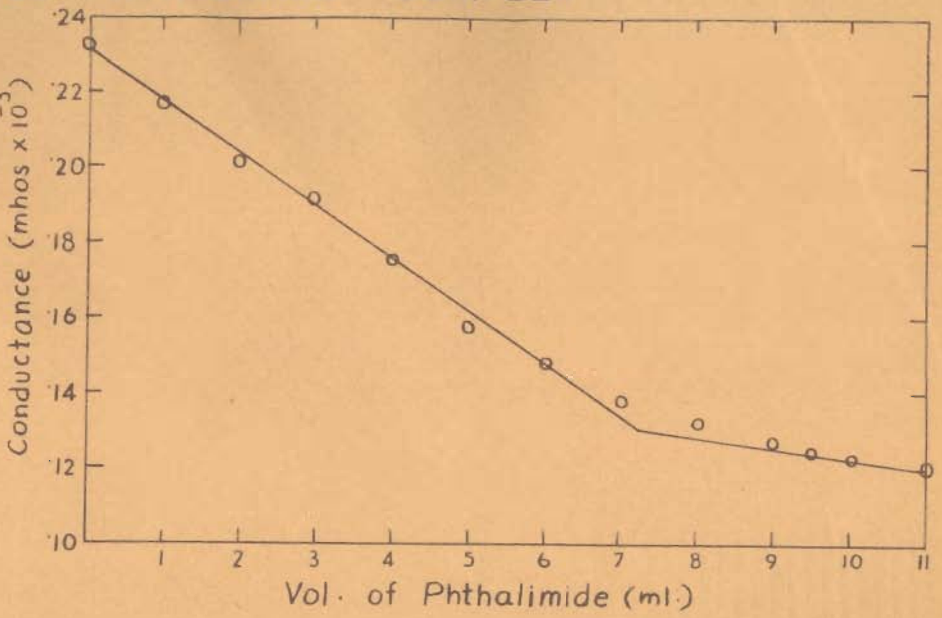


FIG. 14

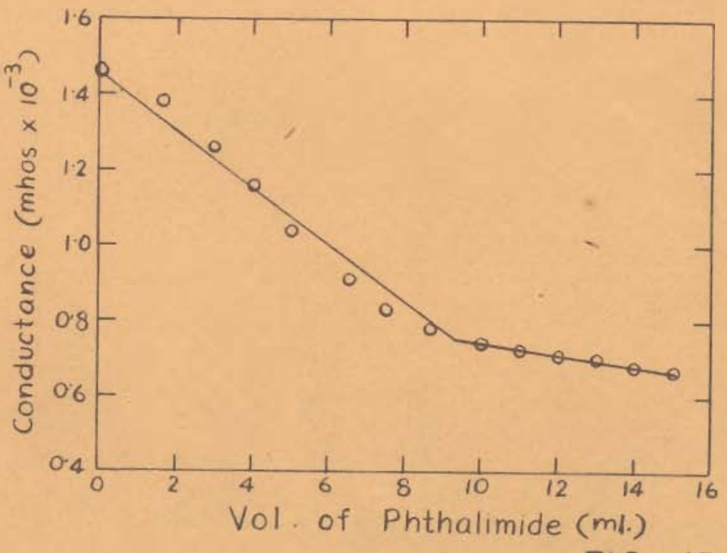


FIG. 15

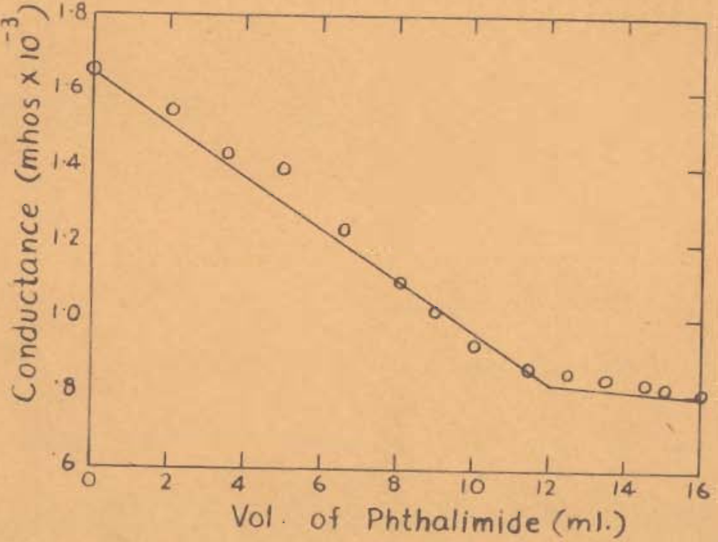


FIG. 16

Copper-glutarimide complex:

Readings for direct titrations: glutarimide in the cell.

Concentration of glutarimide solution =0.2 M.

Concentration of $CuSO_4$ solution =0.1 M.

TABLE NO.17.

Volume of glutarimide solution = 8.0 ml.

Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos x10^{-2})	Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos x10^{-2})
0.0	1.124	4.0	0.3704
0.4	1.010	4.4	0.3226
0.8	0.9424	4.8	0.2778
1.2	0.8696	5.2	0.2326
1.6	0.7692	5.6	0.1869
2.0	0.7042	6.0	0.1587
2.4	0.6250	6.4	0.1282
2.8	0.5556	6.8	0.0833
3.2	0.500	7.2	0.555
3.6	0.4348	-	-

Fig.17.

8.0 ml. of 0.2 M glutarimide
≡ 4.0 ml. of 0.1 M $CuSO_4$ ≡ 2.0 ml. of 0.2M $CuSO_4$

Cu : glutarimide = 1:4.

TABLE NO.18.

Volume of glutarimide solution = 10.0 ml.

Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos x10^{-2})	Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos x10^{-2})
0.0	1.010	4.8	0.4082
0.6	1.000	5.3	5.3571
1.2	0.9091	5.8	0.3077
1.8	0.8333	6.3	0.2597
2.4	0.7143	6.8	0.2128
3.0	0.6250	7.3	0.1695
3.6	0.5556	7.8	0.1299
4.2	0.4831	-	-

Fig. 18.

10.0 ml. of 0.2 M glutarimide
≡ 4.9 ml. of 0.1 M $CuSO_4$ ≡ 2.45 ml. of 0.2M $CuSO_4$

Cu : glutarimide = 1:4.08

TABLE NO. 19.

Volume of glutarimide solution = 12.0 ml.

Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-2}$)	Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-2}$)
0.0	1.111	7.0	0.2941
1.0	0.9524	8.0	0.2198
2.0	0.8333	9.0	0.1481
3.0	0.7143	10.0	0.0896
4.0	0.5882	11.0	0.0513
5.0	0.4762	12.0	0.0294
6.0	0.3704	-	-

Fig. 19.

12.0 ml. of 0.2 M glutarimide

≡ 6.0 ml. of 0.1 M $CuSO_4$ ≡ 3.0 ml. of 0.2M $CuSO_4$

Cu : glutarimide = 1:4

TABLE NO. 20.

Concentration of glutarimide = 0.134 M.

Concentration $CuSO_4$ solution = 0.1 M.

Volume of glutarimide solution = 13.5 ml.

Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-2}$)	Vol. of $CuSO_4$ (ml.).	Corrected conductance (mhos $x10^{-2}$)
0.0	0.800	4.8	0.2500
0.6	0.7143	5.2	0.2174
1.2	0.6250	5.8	0.1835
1.8	0.5556	6.4	0.1527
2.4	0.4878	7.0	0.1227
3.0	0.4255	7.6	0.0954
3.6	0.3636	8.2	0.0769
4.2	0.3077	-	-

Fig. 20.

13.5 ml. of 0.134 M glutarimide

≡ 4.6 ml. of 0.1 M $CuSO_4$ ≡ 3.4 ml. of 0.134 M $CuSO_4$

Cu : glutarimide = 1:4.08

Readings for the reverse titrations: $CuSO_4$ in the cell.

Concentration of $CuSO_4$ solution = 0.02 M.

Concentration of glutarimide = 0.2 M.

TABLE NO.21.

Volume of $CuSO_4$ solution = 6.0 ml.

Vol. of glutarimide (ml.).	Corrected conductance (mhos $\times 10^{-3}$)	Vol. of glutarimide (ml.).	Corrected conductance (mhos $\times 10^{-3}$)
0.0	0.1538	3.2	3.448
0.4	0.0392	3.6	3.922
0.8	0.0476	4.0	4.338
1.2	0.1562	4.4	4.651
1.6	1.000	4.8	5.000
2.0	1.667	5.2	5.263
2.4	2.410	5.6	5.556
2.8	2.985	6.0	5.714

Fig.21.

6 ml. of 0.02 M $CuSO_4$
≡ 2.5 ml. of 0.2 M glutarimide ≡ 25 ml. of 0.02 M glutarimide
Cu : glutarimide = 1:4.17

TABLE NO.22.

Volume of $CuSO_4$ solution = 10 ml.

Vol. of glutarimide (ml.).	Corrected conductance (mhos $\times 10^{-3}$)	Vol. of glutarimide (ml.).	Corrected conductance (mhos $\times 10^{-3}$)
0.0	0.1429	4.8	3.077
0.6	0.0425	5.4	3.509
1.2	0.0434	6.0	3.846
1.8	0.0869	6.6	4.167
2.4	0.6667	7.2	4.545
3.0	1.333	8.0	4.762
3.6	2.020	8.6	5.000
4.2	2.564	-	-

Fig. 22.

10 ml. of 0.02 M $CuSO_4$
≡ 4.0 ml. of 0.2 M glutarimide ≡ 40.0 ml. of 0.02M glutarimide.
Cu : glutarimide = 1:4

TABLE NO.23.

Volume of $CuSO_4$ solution = 15.0 ml.

Vol.of glutarimide (ml.).	Corrected conductance (mhos x10^{-3})	Vol.of glutarimide (ml.).	Corrected conductange (mhosx10^{-3})
0.0	0.133	7.0	3.175
1.0	0.339	8.0	3.650
2.0	0.0689	9.0	4.082
3.0	0.2985	10.0	4.546
4.0	1.176	11.0	4.762
5.0	1.980	12.0	5.000
6.0	2.632	-	-

Fig.23.

15 ml. of 0.02 M $CuSO_4$

≡ 6.2 ml. of 0.2 M glutarimide ≡ 62.0 ml.of 0.02 M glutarimide.

Cu : glutarimide = 1:4.13.

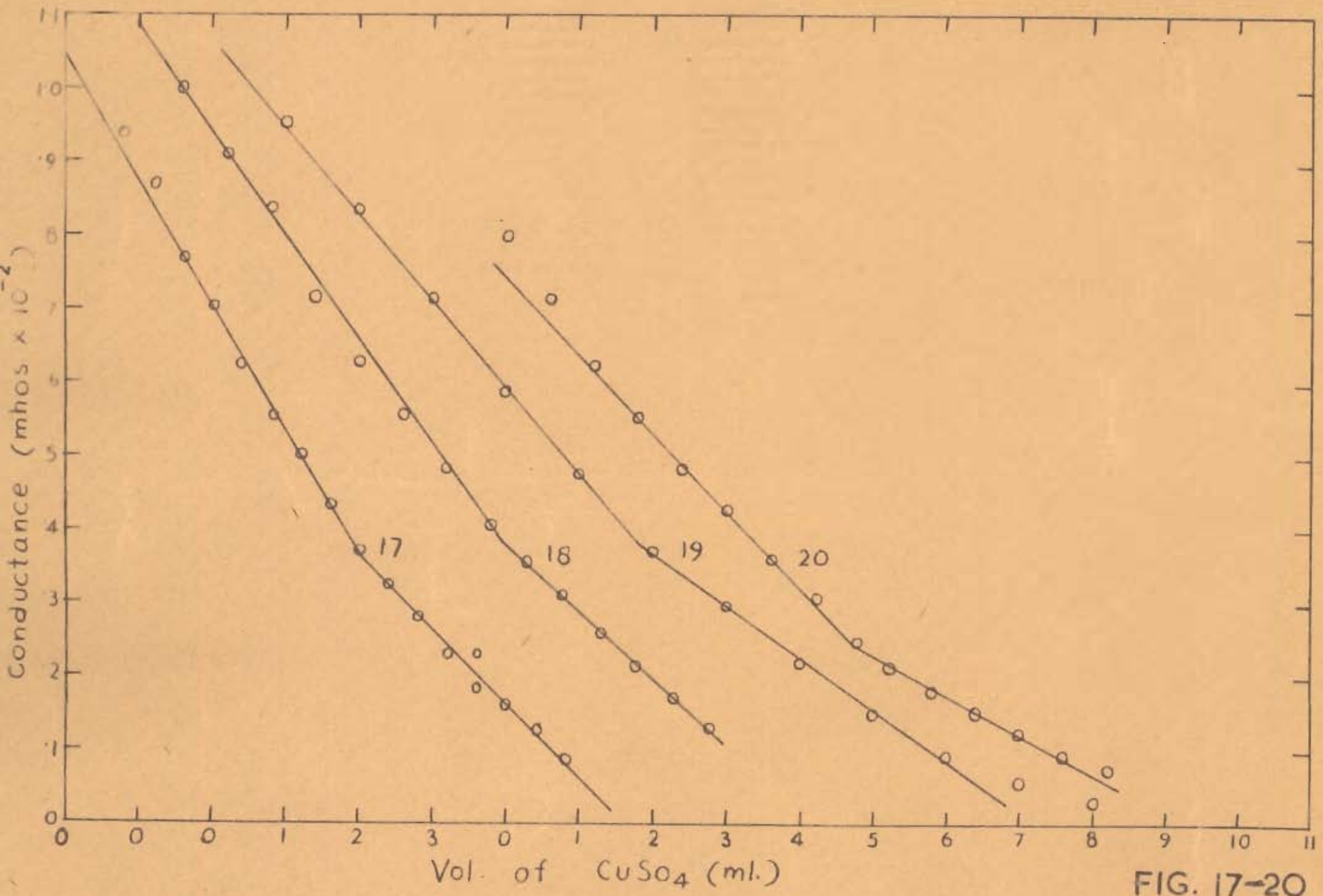


FIG. 17-20

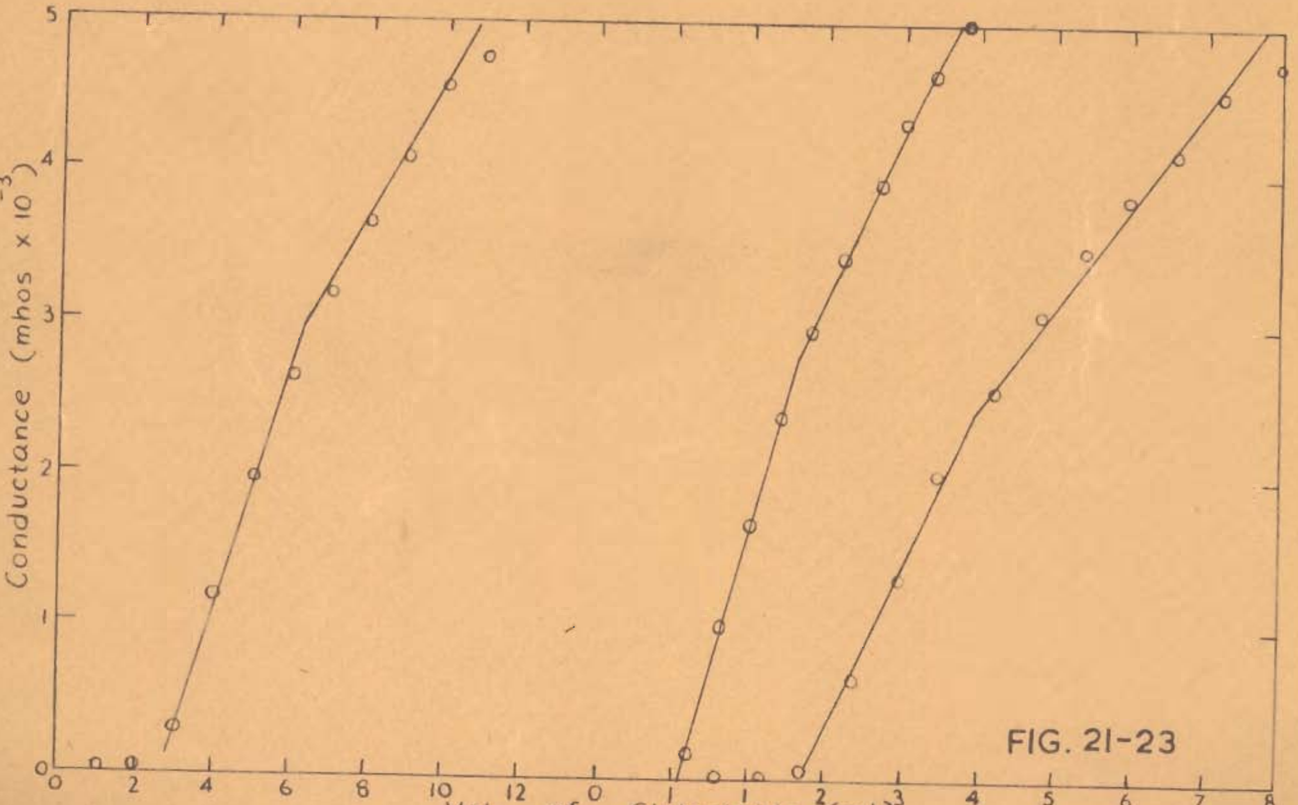


FIG. 21-23

Potentiometric titrations.

Potentiometric titrations of succinimide,phthalimide and glutarimide against copper sulphate were performed with a view to confirm the results on the composition of these complexes by conductometric studies.

E.M.F.measurements were carried out using Pye,bench type potentiometer in conjunction with a ballistic galvanometer with lamp scale arrangement. Platinum electrode served the purpose of an indicator electrode for the redox system by adding minute quantity of methanolic cuprous chloride solution(1 ml.of 0.01M was added,to imides solution in direct titrations,and to copper sulphate solutions in reverse titrations). For direct titrations imides solutions were prepared in equivalent amount of potassium hydroxide,while for reverse titrations four equivalents of potassium hydroxide were added to copper sulphate solution, in order to ensure complete reaction. Nitrogen free from oxygen and carbon dioxide was passed through the cell to create an inert atmosphere and also to serve the stirring purpose. All the experiments were performed at room temperature. The results are given below:

Copper-succinimide complex:

Readings for direct titrations: succinimide in the cell.

Concentration of succinimide solution = 0.05M.

Concentration of $CuSO_4$ solution = 0.0667 M.

TABLE NO.24.

Volume of succinimide solution = 8.0 ml.

Vol. of $CuSO_4$ (ml.).	Pot. vs. S.C.E. mV.	Vol. of $CuSO_4$ (ml.).	Pot. vs. S.C.E. mV.
0.0	173	1.8	-116
0.2	146	2.0	-144
0.4	120	2.2	-166
0.8	95	2.4	-174
1.2	70	2.6	-194
1.4	- 11	2.8	-206
1.6	- 65	3.0	-212

Fig.24.

8 ml. of 0.05 M succinimide
≡ 1.5 ml. of 0.0667 M $CuSO_4$ ≡ 2.0 ml. of 0.05 M $CuSO_4$
Cu : succinimide = 1:4

TABLE NO.25.

Volume of succinimide solution = 5.0 ml.

Vol. of $CuSO_4$ (ml.).	Pot. vs. S.C.E. mV.	Vol. of $CuSO_4$ (ml.).	Pot. vs. S.C.E. mV.
0.0	151	1.2	-167
0.2	86	1.4	-187
0.4	73	1.6	-197
0.6	29	1.8	-205
0.8	- 37	2.0	-208
1.0	-125	-	-

Fig.25.

5.0 ml. of 0.05 M succinimide
≡ 0.95 ml. of 0.0667 M $CuSO_4$ ≡ 1.26 ml. of 0.05 M $CuSO_4$

Cu : succinimide = 1:3.94

TABLE NO. 26.

Volume of succinimide solution = 11.0 ml.

Vol. of $CuSO_4$ (ml.).	Pot. vs. S.C.E. mV.	Vol of $CuSO_4$ (ml.).	Pot. vs. S.C.E. mV.
0.0	154	2.0	-58
0.4	101	2.2	-92
0.6	81	2.4	-130
1.0	44	2.6	-164
1.4	14	3.0	-190
1.6	-04	3.4	-208
1.8	- 28	3.8	-216

Fig. 26.

11.0 ml. of 0.05 M succinimide

≡ 2.1 ml. of 0.0667 M $CuSO_4$ ≡ 2.8 ml. of 0.05M $CuSO_4$

Cu : succinimide = 1:3.93

TABLE NO. 27.

Volume of succinimide solution = 9.5 ml.

Vol. of $CuSO_4$ (ml.).	Pot. vs. S.C.E. mV.	Vol. of $CuSO_4$ (ml.).	Pot. vs. S.C.E. mV.
0.0	144	1.8	- 78
0.4	82	1.9	- 92
0.8	50	2.1	-130
1.2	08	2.3	-162
1.4	- 17	2.5	-178
1.5	- 31	2.7	-187
1.6	- 45	2.9	-192
1.7	- 59	3.0	-194

Fig. 26.

9.5 ml. of 0.05 M succinimide

≡ 1.7 ml. of 0.0667 M $CuSO_4$ ≡ 2.27 ml. 0.05 M $CuSO_4$

Cu : succinimide = 1:4.18

Readings for the reverse titrations: $CuSO_4$ in the cell.

Concentration of $CuSO_4$ solution = 0.01 M.

Concentration of succinimide solution =0.4 M.

TABLE NO.28.

Voluem of $CuSO_4$ solution = 10.0 ml.

Vol. of succinimide (ml.).	Pot. vs. S.C.E. mV.	Vol. of succinimide (ml.).	Pot. vs. S.C.E. mV.
0.0	-392	0.9	-130
0.1	-388	1.0	-107
0.2	-362	1.1	- 94
0.3	-220	1.2	- 83
0.4	-195	1.3	- 73
0.5	-178	1.4	- 64
0.6	-165	1.5	- 56
0.8	-155	1.6	- 49

Fig.28.

10 ml. of 0.01 M $CuSO_4$

≡ 1.0 ml. of 0.4 M succinimide ≡ 40 ml. of 0.01 M succinimide.

Cu : succinimide =1:4.

TABLE NO.29.

Volume of $CuSO_4$ solution =8.0 ml.

Vol. of succinimide (ml.).	Pot. vs. S.C.E. mV.	Vol. of succinimide (ml.).	Pot. vs. S.C.E. mV.
0.0	-388	0.7	-138
0.1	-381	0.8	-110
0.2	-280	0.9	- 91
0.3	-200	1.0	- 75
0.4	-188	1.1	- 64
0.5	-177	1.2	- 55
0.6	-166	1.3	- 46

Fig. 29.

8.0 ml. of 0.01 M $CuSO_4$

≡ 0.8 ml. of 0.4 M succinimide ≡ 32.0 ml. of 0.01 M succinimide.

Cu : succinimide = 1:4

TABLE NO. 30.

Volume of $CuSO_4$ solution = 12.0 ml.

Vol. of succinimide (ml.).	Pot. vs. S.C.E. mV.	Vol. of succinimide (ml.).	Pot. vs. S.C.E. mV.
0.0	-379	1.0	-157
0.2	-360	1.1	-141
0.4	-210	1.2	-125
0.6	-195	1.3	-114
0.7	-189	1.4	-103
0.8	-181	1.6	- 87
0.9	-171	1.8	- 71

Fig. 30.

12 ml. of 0.01 M $CuSO_4$

≡ 1.2 ml. of 0.4 M succinimide≡ 48 ml. of 0.01 M succinimide

Cu : succinimide = 1:4

TABLE NO. 31

Volume of $CuSO_4$ solution = 15 ml.

Vol. of succinimide (ml.).	Pot. vs. S.C.E. mV.	Vol. of succinimide (ml.).	Pot. vs. S.C.E. mV.
0.0	-396	1.4	-106
0.2	-380	1.6	- 90
0.4	-358	1.8	- 47
0.6	-170	2.0	- 41
0.8	-152	2.2	- 34
1.0	-141	2.4	- 26
1.2	-131	2.6	- 18

Fig. 31.

15 ml. of 0.01 M $CuSO_4$

≡ 1.55 ml. of 0.4 M succinimide ≡62.0 ml. of 0.01 M succinimide.

Cu : succinimide = 1: 4.13

Copper-phthalimide complex:

Readings for the direct titrations: phthalimide in the cell.

Concentration of phthalimide solution = 0.05 M.

Concentration of $CuSO_4$ solution = 0.05 M.

TABLE NO.32.

Volume of phthalimide solution = 4.0 ml.

Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.	Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.
0.0	63	1.2	- 93
0.2	13	1.4	-185
0.4	08	1.6	-196
0.6	- 06	1.8	-203
0.8	- 20	2.0	-209
1.0	- 50	2.2	-213

Fig.32.

4 ml. of 0.05 M phthalimide = 1.0 ml. of 0.05 M $CuSO_4$

Cu : phthalimide = 1:4

TABLE NO.33.

Volume of phthalimide solution = 7.0 ml.

Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.	Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.
0.0	108	1.6	- 53
0.2	37	1.8	-107
0.4	26	2.0	-190
0.8	19.5	2.2	-198
1.0	13	2.4	-204
1.2	09	2.6	-209
1.4	- 25	2.8	-214

Fig. 33.

7.0 ml. of 0.05 M phthalimide =1.75ml. of 0.05 M $CuSO_4$

Cu : phthalimide =1:4.

POTENTIOMETRIC TITRATIONS : Cu-SUCCINIMIDE COMPLEX

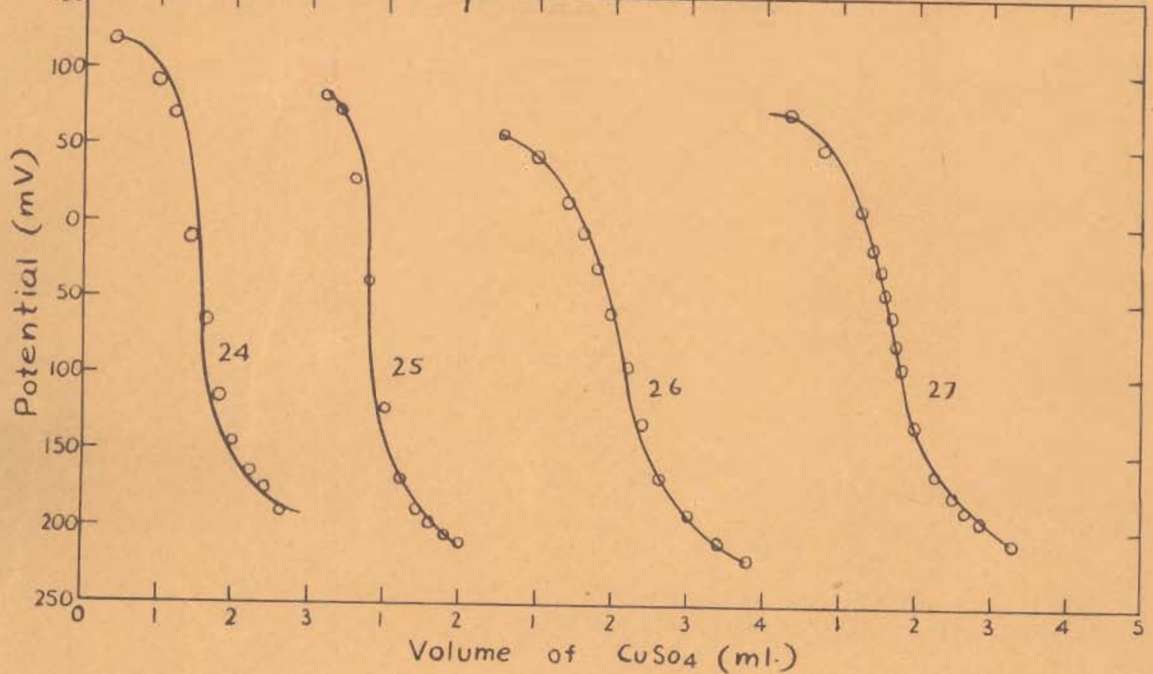


FIG. 24-27

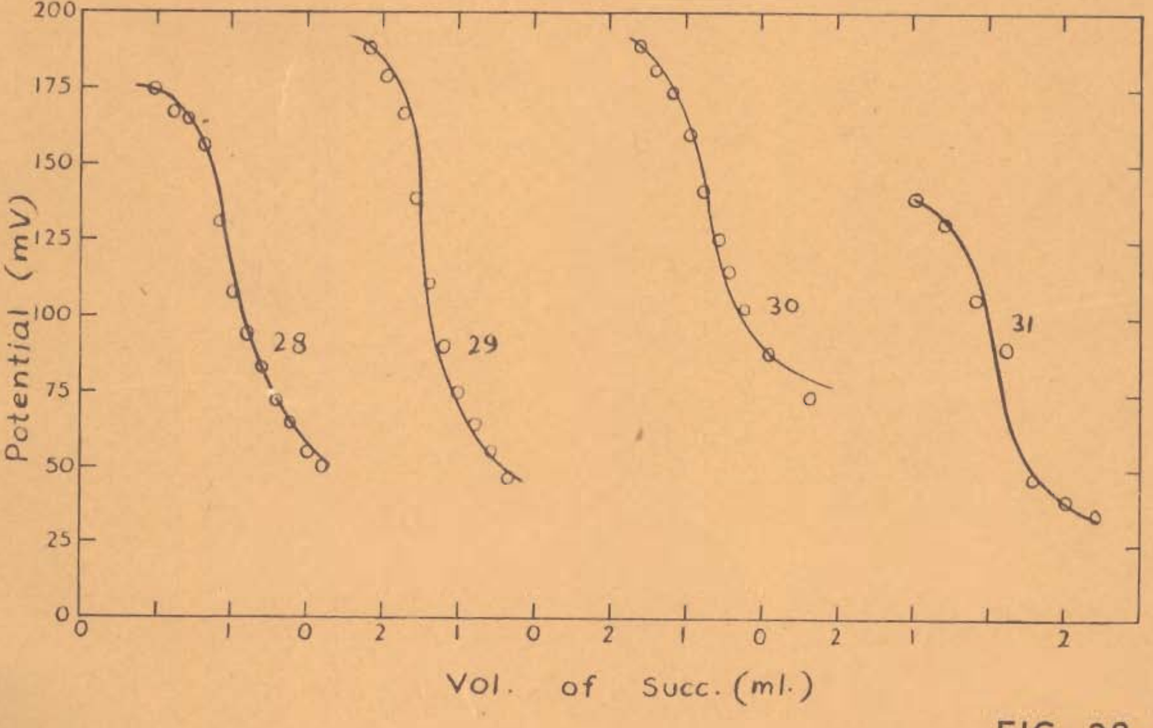


FIG. 28-31

TABLE NO.34.

Volume of phthalimide solution = 9.0 ml.

Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.	Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.
0.0	25	2.0	- 53
0.3	15	2.2	- 78
0.6	- 06	2.4	-121
0.9	- 22	2.6	-197
1.2	- 33	2.8	-205
1.5	- 35	3.0	-209
1.8	- 38	3.2	-211

Fig. 34.

9.0 ml. of 0.05 M phthalimide ≡ 2.25 ml. of 0.05 M $CuSO_4$

Cu : phthalimide = 1:4.

TABLE NO. 35.

Volume of phthalimide solution = 11.0 ml.

Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.	Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.
0.0	110	2.6	- 43
0.4	28	2.8	- 77.5
0.8	- 03	3.0	-141
1.2	- 24	3.2	-192
1.6	- 34	3.5	-200
2.0	- 32	3.8	-204
2.3	- 40.5	4.0	-205

Fig. 35.

11.0 ml. of 0.05 M phthalimide ≡ 2.8 ml. of 0.05 M $CuSO_4$

Cu : phthalimide = 1:3.93

Readings for the reverse titrations: <u>$CuSO_4$ in the cell.</u>

Concentration of $CuSO_4$ solution = 0.01 M.

Concentration of phthalimide solution = 0.1 M.

TABLE NO.36.

Volume of $CuSO_4$ solution = 9.0 ml.

Vol. of phthalimide ml.	Pot. vs. S.C.E. mV.	Vol. of phthalimide ml.	Pot. vs. S.C.E. mV.
0.0	-378	2.6	-109.5
0.4	-364	2.8	-101.5
0.8	-194	3.0	- 98.5
1.2	-164	3.2	- 93.5
1.6	-140	3.6	- 78.0
1.8	-134	4.0	- 07.5
2.0	-131	4.4	25.0
2.2	-122	4.6	32.0
2.4	-117	4.8	35.5

Fig.36.

9.0 ml. of 0.01 M $CuSO_4$

≡ 3.7 ml. of 0.1 M phthalimide ≡ 37.0 ml. of 0.01M phthalimide.

Cu : phthalimide = 1:4.11

TABLE NO. 37.

Volume of $CuSO_4$ solution = 10.0 ml.

Vol. of phthalimide ml.	Pot. vs. S.C.E. mV.	Vol. of phthalimide ml.	Pot. vs. S.C.E. mV.
0.0	-380	3.6	- 93
0.6	-353	4.0	- 64
1.2	-191	4.4	- 34
1.8	-165	4.8	- 15
2.4	-151	5.0	- 07
2.8	-141	5.4	06
3.2	-139	5.8	14
3.4	-113	6.0	20

Fig. 37.

10 ml. of 0.01 M $CuSO_4$

≡ 4.0 ml. of 0.1 M phthalimide ≡ 40.0 ml. of 0.01 M Phthalimide.

Cu : phthalimide = 1:4

TABLE NO. 38.

Volume of $CuSO_4$ solution = 5.0 ml.

Vol.of phthalimide ml.	Pot.vs. S.C.E. mV.	Vo.of phthalimide ml.	Pot.vs. S.C.E. mV.
0.0	-376.5	1.8	-130
0.3	-353.5	2.0	- 81
0.6	-187.5	2.2	- 49
0.9	-163.0	2.4	- 29
1.1	-150.5	2.6	- 09
1.3	-143.5	2.8	06
1.6	-135.5	3.0	17

Fig. 38.

5.0 ml. of 0.01M $CuSO_4$

≡ 2.0 ml. of 0.1 M phthalimide≡20.0 ml.of 0.01 M phthalimide.

Cu : phthalimide = 1:4

TABLE NO. 39.

Volume of $CuSO_4$ solution = 11.0 ml.

Vol.of phthalimide ml.	Pot.vs. S.C.E. mV.	Vol.of phthalimide ml.	Pot.vs. S.C.E. mV.
0.0	-377	3.2	-129
0.4	-370	3.6	-119
0.8	-242	4.0	- 61.5
1.2	-189	4.4	- 27.5
1.6	-169	4.8	- 04
2.0	-159	5.0	05
2.4	-149	5.4	09
2.8	-137	-	-

Fig. 39.

11.0 ,1. of 0.01 M $CuSO_4$

≡ 4.2 ml. of 0.1 M phthalimide ≡ 42.0 ml. of 0.01 M phthalimide.

Cu : phthalimide = 1:3.82.

POTENTIOMETRIC TITRATIONS : Cu-PHTHALIMIDE COMPLEX

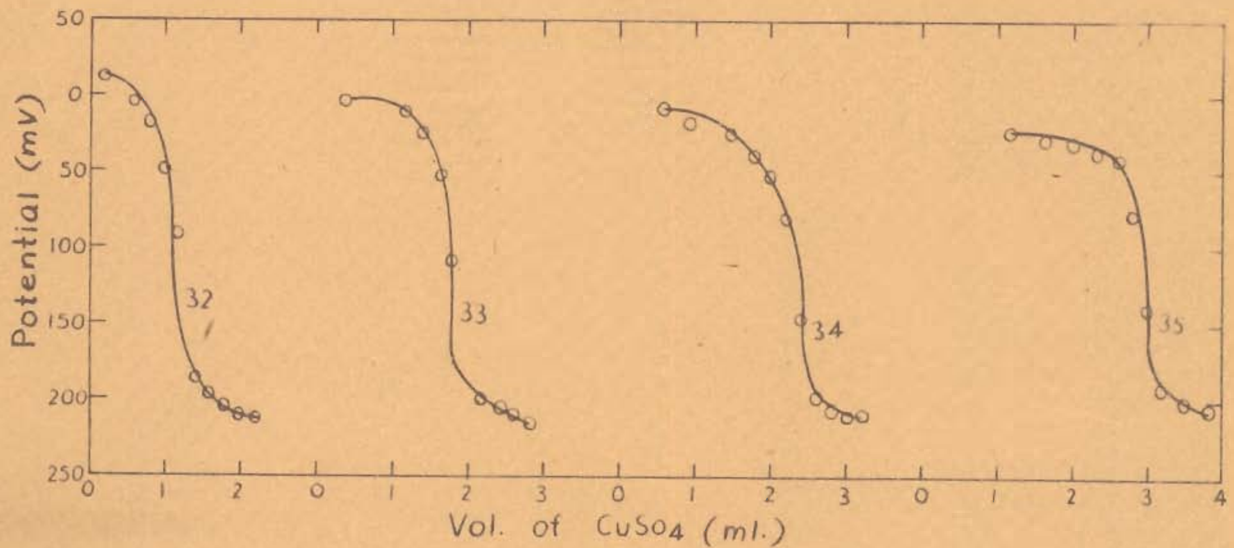


FIG. 32-35

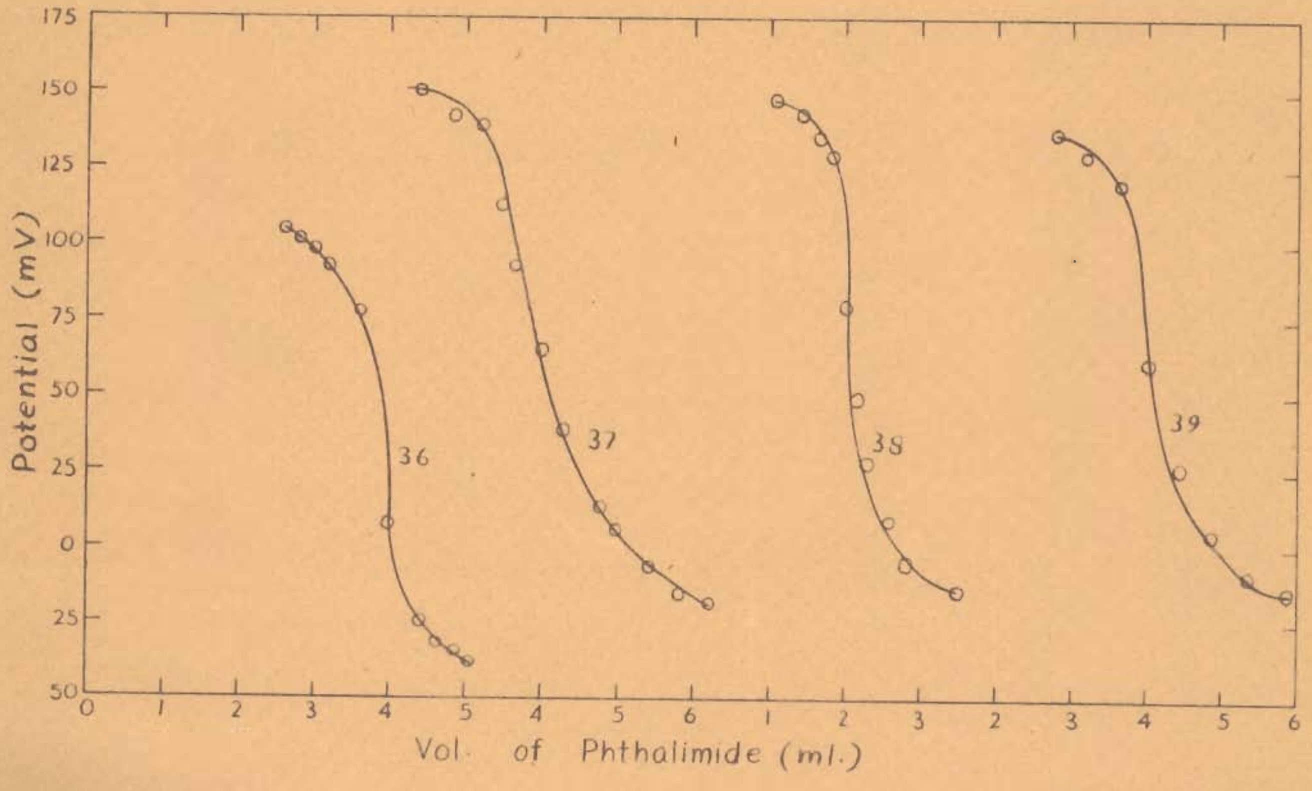


FIG. 36-39

Copper-glutarimide complex:

Readings for the direct titrations: glutarimide in the cell.

Concentration of glutarimide solution = 0.2 M.

Concentration of $CuSO_4$ solution = 0.0667 M.

TABLE NO.40.

Volume of glutarimide solution = 4.0 ml.

Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.	Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.
0.0	154.0	2.0	71.5
0.4	143.5	2.6	19.5
0.8	129.0	2.8	-129.0
1.2	119.0	3.2	-165.0
1.4	111.0	3.6	-197.5
1.6	96.0	4.0	-210.0
1.8	85.5	-	-

Fig. 40.

4.0 ml. of 0.2 M glutarimide
≡ 2.85 ml. of 0.0667 M $CuSO_4$ ≡ 0.95 ml. of 0.2M $CuSO_4$
Cu : glutarimide = 1:4.21

TABLE NO.41.

Volume of glutarimide solution = 6.0 ml.

Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.	Vol. of $CuSO_4$ ml.	Pot. vs. S.C.E. mV.
0.0	156.0	3.0	78.5
0.4	144.5	2.4	54.0
0.8	136.5	3.8	15.0
1.2	127.5	4.2	- 66.0
1.6	118.0	4.6	-153.5
2.0	106.5	5.0	-171.0
2.4	102.5	5.3	-184.0
2.7	89.0	5.6	-196.0

Fig. 41.

6.0 ml. of 0.2 M glutarimide
≡ 4.2 ml. of 0.0667 M $CuSO_4$ ≡ 1.57 ml. of 0.2 M $CuSO_4$
Cu : glutarimide = 1:3.82.

TABLE NO.42.

Volume of glutarimide solution = 7.0 ml.

Vol.of $CuSO_4$ ml.	Pot.vs. S.C.E. mV.	Vol.of $CuSO_4$ ml.	Pot.vs. S.C.E. mV.
0.0	169.0	4.2	53.5
0.6	152.0	4.8	15.0
1.2	136.0	5.4	-107.0
1.8	125.0	6.0	-138.0
2.4	111.5	6.5	-142.5
2.8	102.0	7.0	-155.0
3.2	89.0	7.5	-160.0
3.6	74.0	-	-

Fig.42.

7.0 ml. of 0.2 M glutarimide
≡ 5.2 ml. of 0.0667 M $CuSO_4$ ≡ 1.74 ml. of 0.2M $CuSO_4$
Cu : glutarimide = 1:4.02

Readings for the reverse titrations:$CuSO_4$ in the cell.

Concentration of $CuSO_4$ solution = 0.02 M.

Concentration of glutarimide solution = 0.2 M.

TABLE NO.43.

Volume of $CuSO_4$ solution = 4.0 ml.

Vol.of glutarimide ml.	Pot.vs. S.C.E. mV.	Vol.of glutarimide ml.	Pot.vs. S.C.E. mV.
0.0	-375.5	2.0	86.5
0.4	-341.5	2.2	102.5
0.8	-141.5	2.4	111.0
1.2	-101.0	2.6	116.5
1.4	- 57.5	2.8	119.0
1.6	+04 .0	3.0	121.0
1.8	+ 54.5	-	-

Fig.43.

4.0 ml. of 0.02 M $CuSO_4$
≡ 1.6 ml. of 0.2M glutarimide ≡ 16.0 ml.of 0.02 M glutarimide.
Cu : glutarimide = 1:4.0.

TABLE NO.44.

Volume of $CuSO_4$ solution = 5.0 ml.

Vol.of glutarimide ml.	Pot.vs. S.C.E. mV.	Vol.of glutarimide ml.	Pot.vs. S.C.E. mV.
0.0	-383.5	2.3	53.0
0.4	-365.0	2.5	80.5
0.8	-177.5	2.7	99.0
1.2	-118.5	2.9	109.0
1.6	- 70.0	3.1	113.0
1.8	- 27.0	3.3	115.0
2.0	+ 09.0	-	-

Fig.44.

5.0 ml. of 0.02 M $CuSO_4$

≡ 2.0 ml. of 0.2 M glutarimide≡ 20.0 ml. of 0.02 M glutarimide.

Cu : glutarimide = 1:4

TABLE NO. 45.

Volume of $CuSO_4$ solution = 7.0 ml.

Vol.of glutarimide ml.	Pot.vs. S.C.E. mV.	Vol.of glutarimide ml.	Pot.vs. S.C.E. mV.
0.0	-370.5	3.4	57.5
0.6	-361.5	3.8	85.0
1.2	-175.0	4.2	97.5
1.8	-123.0	4.6	108.0
2.2	- 93.0	5.0	115.0
2.6	- 38.5	5.4	117.0
3.0	+ 19.0	-	-

Fig. 45.

7.0 ml. of 0.02 M $CuSO_4$

≡ 2.8 ml. of 0.2 M glutarimide ≡ 28.0 ml.of 0.02 M glutarimide.

Cu : glutarimide = 1:4.

POTENTIOMETRIC TITRATIONS : Cu-GLUTARIMIDE COMPLEX

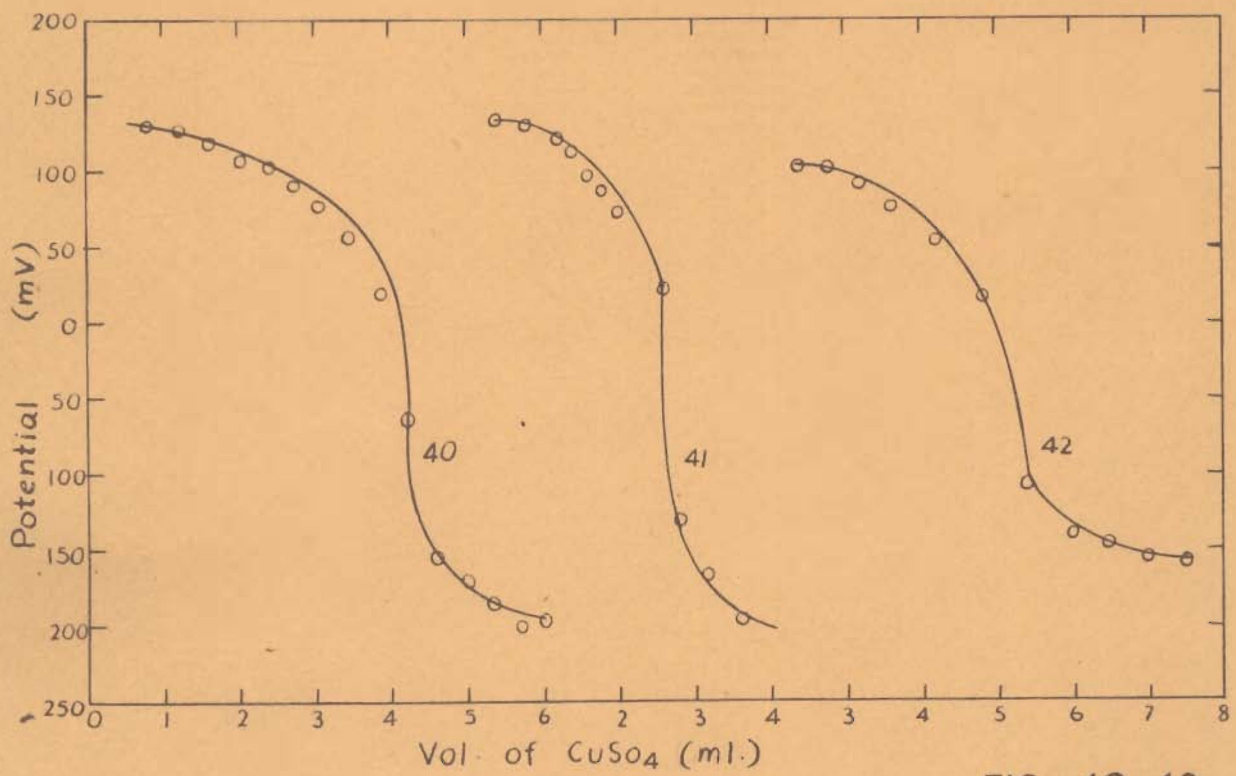


FIG. 40-42

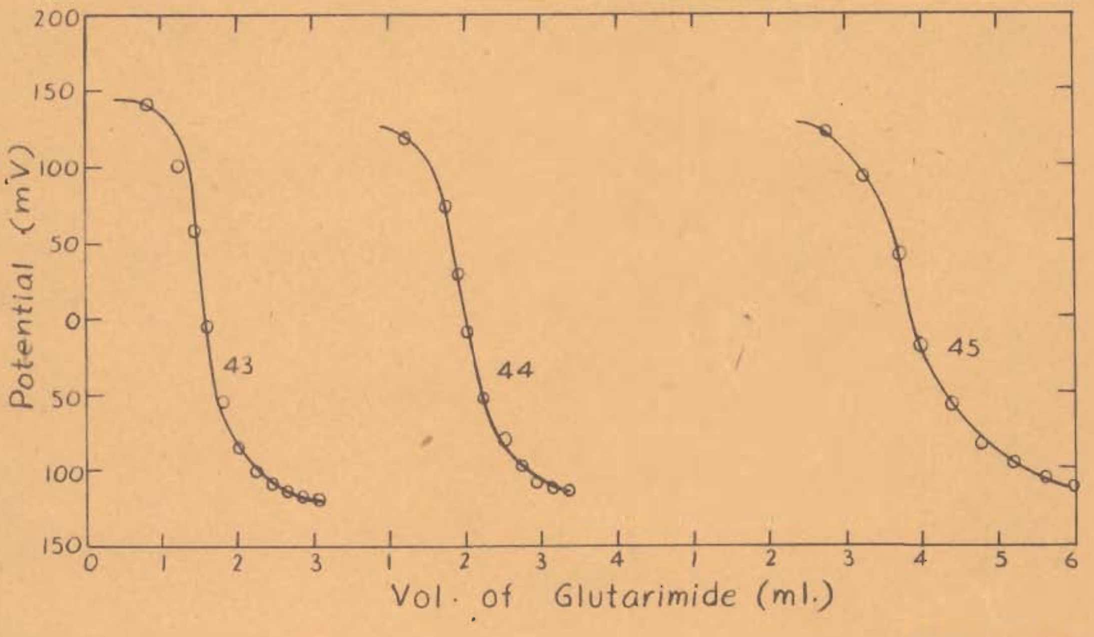


FIG. 43-45

Amperometric titrations.

Amperometric titrations of succinimide, phthalimide and glutarimide against copper sulphate were carried out using potassium hydroxide as supporting electrolyte. In direct (imides in the cell) titrations, imide solutions were prepared in equivalent amount of potassium hydroxide, while in reverse (copper sulphate in the cell) titrations four equivalents of potassium hydroxide were added in the cell. In case of succinimide and phthalimide, only direct titrations (imide in the cell) could be carried out, while with glutarimide, inflexion points could be realised only in the reverse titrations($CuSO_4$ in the cell). Method of preparing copper sulphate and imides, methanolic solutions was the same as already described.

Toshniwal S.No.(031) India, with scalamp galvanometer model Pye (sensitivity 1:10) in the external circuit was used for carrying out these titrations. Nitrogen gas (purified after passing through alkaline pyrogallol and chromous chloride) was passed for keeping an inert atmosphere. The cell was kept immersed in a thermostat maintained at $30 \pm 0.1^{o}C$. The drop time was kept at 4.0 seconds.

Unlike usual amperometric titrations(for choice of potential and shape of titration curves vide under discussion), it was difficult to choose the constant potential for the respective titrations. However, the following potentials were found suitable for these titrations:

Titration	Potential applied
$CuSO_4$ succinimide(direct titration)	-1.2 volts
$CuSO_4$ phthalimide(direct titration)	-0.8 volts
$CuSO_4$ glutarimide(reverse titration)	-0.8 volts

Copper-succinimide complex:

Readings for direct titrations: succinimide in the cell.

TABLE NO.46.

6.0 ml. of 0.1 M succinimide against 0.05 M $CuSO_4$

Volume of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})	Volume of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})
0.0	0.4	2.8	4.7
0.5	1.8	3.0	4.9
1.0	2.9	3.4	4.6
1.5	3.5	3.8	4.1
2.0	4.0	4.0	3.8
2.4	4.4	4.5	2.9

Fig.46.

6.0 ml. of 0.1 M succinimide

= 2.95 ml. of 0.05 M $CuSO_4$ = 1.475 ml. of 0.1 M $CuSO_4$

Cu : succinimide = 1:4.1

TABLE NO.47

6.0 ml. of 0.066 M succinimide against 0.066M $CuSO_4$

Vol. of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})	Vol. of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})
0.0	0.9	1.4	8.8
0.4	2.8	1.8	8.0
0.7	4.3	2.0	7.5
1.0	5.8	2.4	6.7
1.2	8.3	2.6	6.3

Fig.47.

6 ml. of 0.066 M succinimide ≡ 1.45 ml. of 0.066 M $CuSO_4$

Cu : succinimide = 1:4.13

TABLE NO.48

12.0 ml. of 0.066 M succinimide against 0.066M $CuSO_4$

Vol. of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})	Vol. of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})
0.0	0.3	2.8	8.3
0.5	1.2	3.0	8.7
1.0	2.6	3.2	8.4
1.4	2.5	3.6	7.8
1.8	4.9	4.0	7.6
2.5	7.2	5.0	6.8

Fig.48

12.0 ml. of 0.066 M succinimide ≡ 3.0 ml. of 0.066 M $CuSO_4$

Cu : succinimide = 1:4

AMPEROMETRIC TITRATIONS : Cu-SUCCINIMIDE COMPLEX

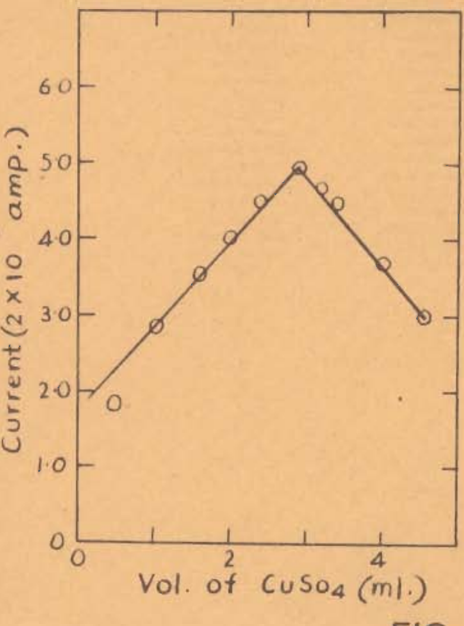


FIG. 46

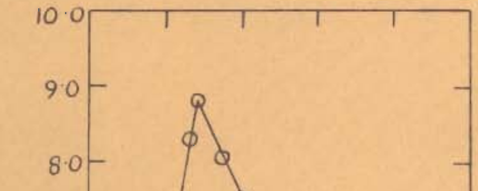


FIG · 47

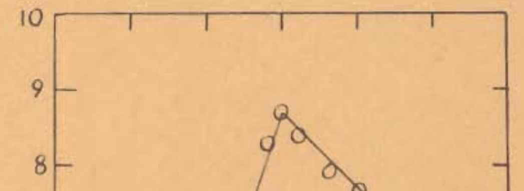


FIG. 48

Copper-phthalimide complex:

Readings for direct titrations: phthalimide in the cell.

TABLE NO.49.

3.0 ml. of 0.066 M phthalimide against 0.033 M $CuSO_4$

Vol. of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})	Vol. of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})
0.0	8.6	1.6	12.9
0.3	9.9	1.8	12.0
0.7	11.2	2.0	10.9
1.0	12.3	2.2	9.8
1.3	13.0	2.4	8.2

Fig.49.

3.0 ml. of 0.066 M phthalimide
≡ 1.45 ml. of 0.033 M $CuSO_4$ ≡ 0.725 ml. of 0.066 M $CuSO_4$
Cu : phthalimide = 1:4.14.

TABLE NO.50

4.0 ml. of 0.066 M phthalimide against 0.033 M $CuSO_4$

Vol. of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})	Vol. of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})
0.0	1.0	1.8	6.0
0.4	2.4	2.0	4.0
0.8	4.1	2.4	2.5
1.2	5.0	2.8	1.2
1.6	5.5	-	-

Fig.50

4.0 ml. of 0.066 M phthalimide
≡ 1.9 ml. of 0.033 M $CuSO_4$ ≡ 0.95 ml. of 0.066M $CuSO_4$
Cu : phthalimide = 1:4.2

TABLE NO.51

5.0 ml. of 0.066 M phthalimide against 0.033 M $CuSO_4$

Vol. of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})	Vol. of $CuSO_4$ ml.	Current (amp. 2.0×10^{-6})
0.5	4.7	2.4	11.5
0.8	6.6	2.7	12.2
1.2	8.3	3.0	10.0
1.6	9.4	3.4	8.2
2.0	10.4	4.0	6.2

Fig. 51.

5 ml. of 0.066 M phthalimide
≡ 2.6 ml. of 0.033 M $CuSO_4$ ≡ 1.3 ml. of 0.066M $CuSO_4$
Cu : phthalimide = 1:3.86.

Copper-glutarimide complex:

Readings for reverse titrations: $CuSO_4$ in the cell.

TABLE NO.52.

0.5 ml. of 0.05 M $CuSO_4$, total volume made upto 10 ml., titrated against 0.1 M glutarimide.

Vol.of glutarimide ml.	Current (amp.2.0 $x10^{-6}$)	Vol.of glutarimide ml.	Current (amp.2.0$x10^{-6}$)
0.0	1.4	1.3	5.1
0.2	1.9	1.7	5.1
0.5	3.1	2.0	5.0
0.7	4.1	2.5	4.9
1.0	5.2	-	-

Fig. 52.

0.5 ml. of 0.05 M $CuSO_4$
≡ 1.0 ml. of 0.1 M glutarimide≡2.0 ml.of 0.05 M glutarimide

Cu : glutarimide = 1:4

TABLE NO.53

2.0 ml.of 0.05 M $CuSO_4$, total volume made up to 10 ml., titrated against 0.1 M glutarimide.

Vol.of glutarimide ml.	Current (amp.2.0 $x10^{-6}$)	Vol.of glutarimide ml.	Current (amp.2.0$x10^{-6}$)
0.0	1.6	4.0	6.2
1.0	2.5	4.5	6.1
2.0	3.9	5.0	6.0
3.0	5.2	6.0	5.9
2.5	5.8	-	-

Fig.53.

2.0 ml.of 0.05 M $CuSO_4$
≡ 4.0 ml.of 0.1 M glutarimide ≡ 8.0 ml.of 0.05 M glutarimide

Cu : glutarimide = 1:4

TABLE NO.54.

1.0 ml.of 0.05 M $CuSO_4$ total volume made up to 10 ml., titrated against 0.1 M glutarimide.

Vol.of glutarimide ml.	Current (amp.2.0$x10^{-6}$)	Vol.of glutarimide ml.	Current (amp.2.0$x10^{-6}$)
0.0	1.0	2.0	5.4
0.5	2.1	2.5	5.3
1.0	3.2	3.0	5.2
1.5	4.0	3.5	5.15

Fig. 54.

1.0 ml. of 0.05 M $CuSO_4$
≡ 2.0 ml. of 0.1 M glutarimide ≡ 4.0 ml. of 0.05 M glutarimide

Cu : glutarimide = 1:4

AMPEROMETRIC TITRATIONS : Cu-GLUTARIMIDE COMPLEX

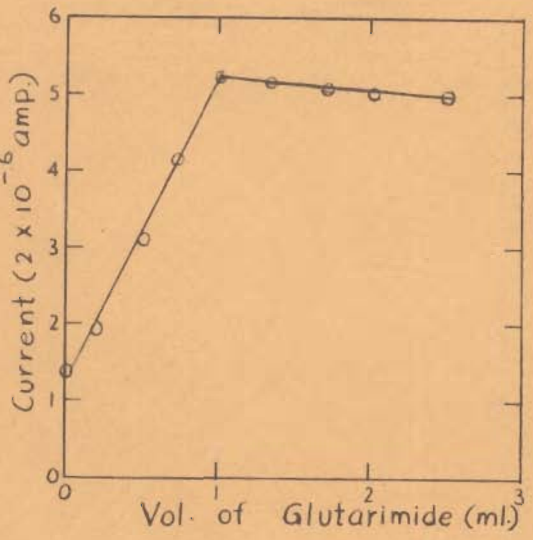


FIG. 52

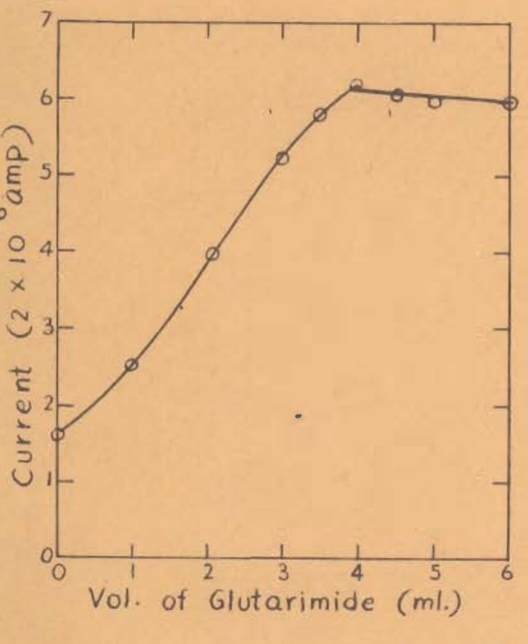


FIG. 53

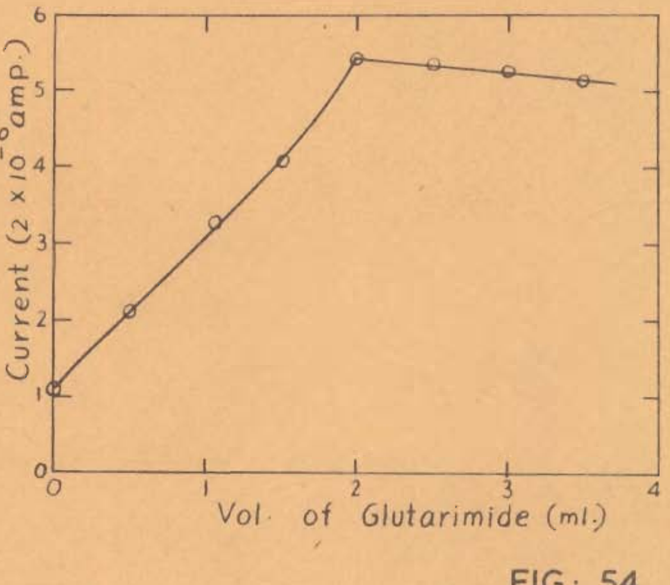


FIG. 54

AMPEROMETRIC TITRATIONS : Cu - PHTHALIMIDE COMPLEX

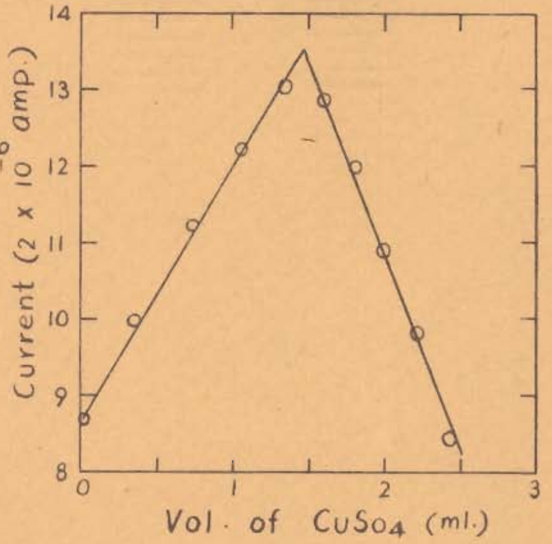


FIG. 49

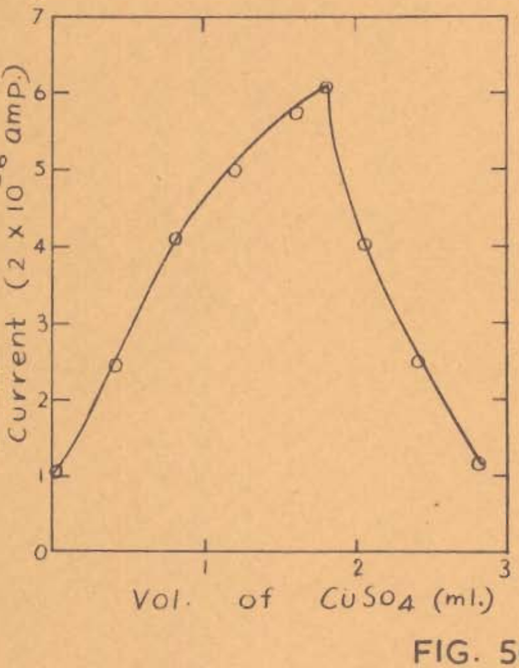


FIG. 50

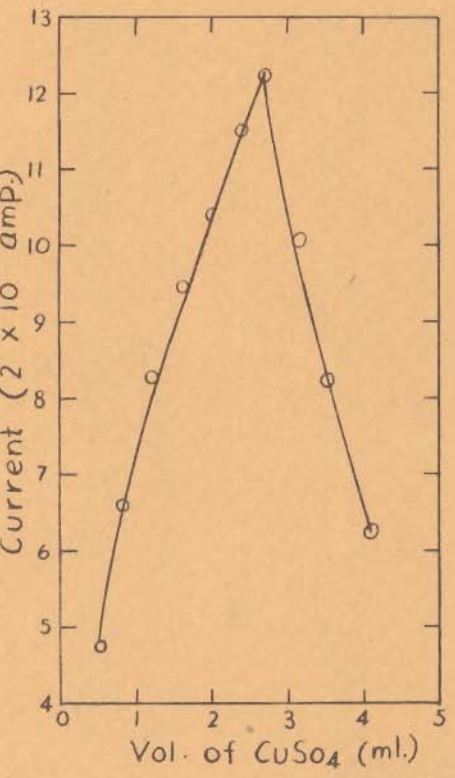


FIG. 51

pH-metric studies

Methanolic solutions of imides and copper sulphate were prepared in the manner described earlier. pH-metric titrations of imides alone and in presence of copper sulphate were performed against standard methanolic solution of potassium hydroxide, according to the method recommended by Calvin and Melchoir(loc.cit.). Cambridge bench type pH meter in conjunction with Cambridge glass electrode and S.C.E. was used for pH measurements. Standard potassium hydroxide methanolic solution was added to the reaction vessel from an automatic micro burette. Nitrogen (free from oxygen, carbondioxide and moisture) was used for maintaining inert atmosphere as well as for stirring the solutions.

Typical titration curves were obtained when imides, alone and in presence of copper sulphate, were titrated against potassium hydroxide solution. The distance between the two curves gave the excess amount of alkali(Δ KOH) consumed, which on dividing by the metal ion concentration gave the value of $\bar{n}$, the average number of ligand moles undergoing complex ion formation per metal ion.

The solutions of different imides were separately titrated pH metrically and apparent pK values were calculated at half titration values(described earlier in Chapter I and II).

pK value of succinimide = 9.74

pK value of phthalimide = 9.50

pK value of glutarimide = 11.06

The titration data together with the values of $\bar{n}$ and -log A (free ligand concentration) are given below:

Copper succinimide complex.

TABLE NO. 55.

Titration of succinimide in absence of copper sulphate.

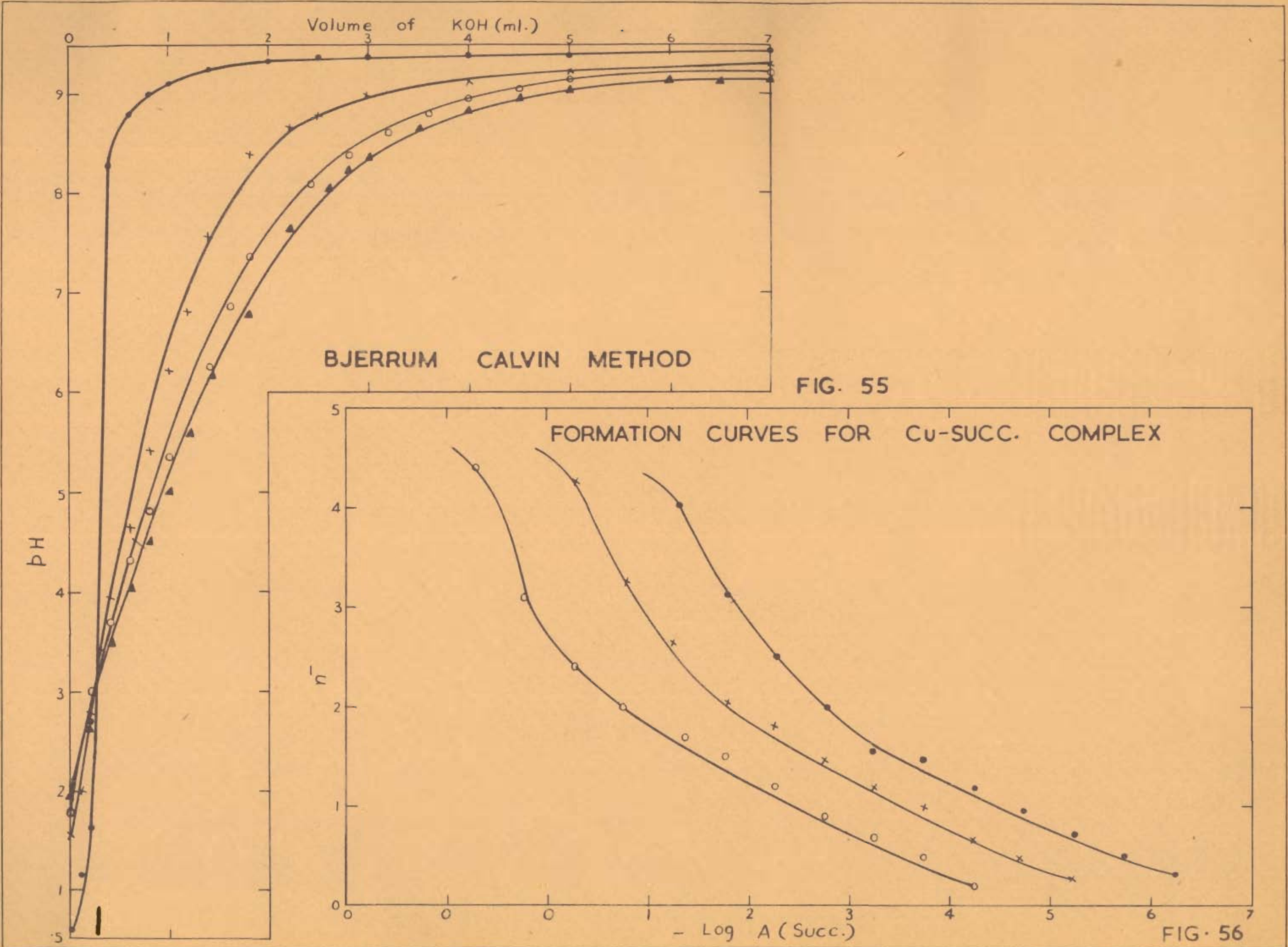
10.0 ml. of 0.5 M succinimide - 1.0 ml. of 0.01 M H_2SO_4.

Total volume made up with methyl alcohol = 15.0 ml.

Concentration of KOH solution = 0.1 M

Vol. of KOH(ml.).	pH	Vol. of KOH(ml.).	pH
0.0	0.84	1.4	9.22
0.1	1.14	2.0	9.31
0.2	1.61	2.5	9.36
0.4	8.26	3.0	9.37
0.6	8.79	4.0	9.40
0.8	8.99	5.0	9.40
1.0	9.10	-	-

Fig. 55, Curve 1.



BJERRUM CALVIN METHOD

FIG. 55

FORMATION CURVES FOR Cu-SUCC. COMPLEX

FIG. 56

Titrations of succinimide in presence of copper sulphate.

Concentration of succinimide = 0.5 M

Concentration of copper sulphate = 0.05 M

Strength of H_2SO_4 solution = 0.01 M

Strength of KOH solution = 0.1 M

TABLE NO.56.

10 ml. of succinimide - 1.0 ml. of $CuSO_4$ - 1.0 ml. of H_2SO_4, total volume made upto 15 ml. by methyl alcohol.

Vol. of KOH(ml.)	pH	Vol. of KOH(ml.)	pH
0.0	1.55	1.2	6.81
0.1	2.00	1.4	7.54
0.2	2.77	1.8	8.64
0.3	3.42	2.2	8.62
0.4	3.94	2.5	8.75
0.6	4.66	3.0	8.90
0.8	5.42	4.0	9.10
1.0	6.23	5.0	9.20

Fig.56, Curve 2.

TABLE NO.56(A)

Calculations for formation curve.
For 1.0 ml. of 0.05 M $CuSO_4$ ≡ 0.5×10^{-4} moles.

pH	Δ KOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log succ.
4.0	0.10	0.10	0.2	6.2300
4.5	0.25	0.25	0.5	5.7343
5.0	0.35	0.35	0.7	5.2371
5.5	0.45	0.45	0.9	4.7400
6.0	0.60	0.60	1.2	4.2442
6.5	0.75	0.75	1.5	3.7483
7.0	0.85	0.85	1.7	3.3411
7.5	1.00	1.00	2.0	2.7551
8.0	1.20	1.20	2.4	2.2605
8.5	1.55	1.55	3.1	1.7689
9.0	2.20	2.20	4.4	1.2866

Fig. 56, Curve 1.

TABLE NO.57.

10 ml. of succinimide - 1.5 ml. of $CuSO_4$ -1.0 ml.of H_2SO_4 ,total volume made upto 15 ml. by methyl-alcohol.

Vol.of KOH(ml.)	pH	Vol.of KOH(ml.)	pH
0.0	1.75	2.0	7.76
0.2	3.00	2.45	8.09
0.4	3.70	2.80	8.37
0.6	4.32	3.20	8.61
0.8	4.82	3.60	8.80
1.0	5.37	4.00	8.95
1.4	6.28	4.50	9.10
1.8	7.41	5.00	9.15

Fig.55,Curve 3.

TABLE NO.57 (A)

Calculations for formation curve.

For 1.5 ml. of 0.05 M $CuSO_4$ = 0.75 x 10^{-4} moles.

pH	Δ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log succ.
4.0	0.20	0.20	0.27	6.2329
4.5	0.35	0.35	0.467	5.7371
5.0	0.50	0.50	0.667	5.2414
5.5	0.70	0.70	0.933	4.7469
6.0	0.90	0.90	1.20	4.2524
6.5	1.10	1.10	1.46	3.7579
7.0	1.35	1.35	1.80	3.2645
7.5	1.55	1.55	2.06	2.7698
8.0	2.00	2.00	2.667	2.2816
8.5	2.55	2.55	3.267	1.7953
9.0	3.20	3.20	4.23	1.3111

Fig. 56,Curve 2.

TABLE NO.58

10 ml. of succinimide -1.8 ml.of $CuSO_4$ -1.0 ml. of H_2SO_4 ,total volume made upto 15 ml. by methyl-alcohol.

Vol.of KOH(ml.).	pH	Vol.of KOH(ml.).	pH
0.0	1.78	1.8	6.78
0.2	2.64	2.2	7.66
0.4	3.50	3.6	8.04
0.6	4.02	2.8	8.22
0.8	4.49	3.0	8.36
1.0	5.00	3.55	8.85
1.2	5.58	4.5	9.00
1.4	6.15	5.0	9.10

Fig. 55,Curve 4.

TABLE NO. 58 (A)

Calculations for formation curve.

For 1.8 ml. of 0.05 M $CuSO_4$ = 0.9 x 10^{-4} moles.

pH	Δ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log succ.
4.0	0.30	0.30	0.333	6.2357
4.5	0.45	0.45	0.500	5.7400
5.0	0.65	0.65	0.722	5.2455
5.5	0.85	0.85	0.944	4.7411
6.0	1.05	1.05	1.167	4.2465
6.5	1.30	1.30	1.444	3.7532
7.0	1.50	1.50	1.555	3.2585
7.5	1.80	1.80	2.000	2.7663
8.0	2.25	2.25	2.500	2.2778
8.5	2.80	2.80	3.110	1.7914
9.0	3.60	3.60	4.000	1.3105

Fig. ~~56~~,Curve 3.

Copper-phthalimide complex

Titration of phthalimide in absence of copper sulphate.

TABLE NO. 59.

20.0 ml. of 0.0667 M phthalimide - 1.0 ml. of 0.01 M H_2SO_4.

Total volume made up with methyl-alcohol = 25 ml.

Concentration of KOH solution = 0.05 M.

Vol. of KOH ml.	pH	Vol. of KOH ml.	pH
0.0	1.02	1.24	8.70
0.1	1.12	1.40	8.81
0.2	1.23	1.80	9.04
0.4	1.48	2.20	9.14
0.5	1.68	2.60	9.19
0.6	2.04	3.00	9.24
0.7	3.70	4.00	9.32
0.8	7.50	5.00	9.35
1.0	8.32	-	-

Fig. 58, Curve 1.

Titrations of phthalimide in presence of copper sulphate.

Concentration of phthalimide = 0.0667 M.

Concentration of $CuSO_4$ = 0.02 M.

Strength of H_2SO_4 = 0.01 M.

Strength of KOH = 0.05 M.

TABLE NO. 60.

20 ml. phthalimide - 0.7 ml. $CuSO_4$ - 1.0 ml. H_2SO_4 ; total volume made up to 25 ml. by methyl-alcohol.

Vol. of KOH ml.	pH	Vol. of KOH ml.	pH
0.0	1.34	1.6	8.08
0.2	1.64	2.0	8.54
0.4	2.06	2.5	8.82
0.6	3.17	3.0	9.00
0.8	5.11	3.5	9.08
1.0	6.35	4.0	9.13
1.2	7.02	5.0	9.21

Fig.58, Curve 2.

TABLE NO. 60(A)

Calculation for formation curve.

For 0.7 ml. of 0.02 M $CuSO_4$ ≡ 0.14×10^{-4} moles.

pH	Δ KOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log phth.
5.0	0.10	0.05	0.357	5.7748
5.5	0.15	0.075	0.535	5.2757
6.0	0.20	0.10	0.714	4.7765
6.5	0.30	0.15	1.070	4.2782
7.0	0.45	0.225	1.60	3.7801
7.5	0.55	0.275	1.96	3.2825
8.0	0.75	0.375	2.67	2.7859
8.5	0.85	0.425	3.35	2.2876
9.0	1.10	0.55	3.92	1.7917

Fig.59, Curve 1.

- -

TABLE NO.61.

20 ml.phthalimide - 1.0 ml.$CuSO_4$ - 1.0 ml. H_2SO_4 ,
Total volume made upto 25 ml. by methyl-alcohol.

Vol.of KOH ml.	pH	Vol.of KOH ml.	pH
0.0	1.17	1.6	7.42
0.1	1.35	2.0	8.10
0.2	1.54	2.5	8.56
0.4	2.21	3.0	8.78
0.6	3.28	3.5	8.92
0.8	4.35	4.0	9.00
1.0	5.44	4.5	9.06
1.2	6.18	5.0	9.13

Fig. 58,Curve 3.

TABLE NO. 61 (A)

Calculation for formation curve.

For 1.0 ml. of 0.02 M $CuSO_4 \equiv 0.2 \times 10^{-4}$ moles.

pH	Δ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log phth.
5.0	0.175	0.088	0.437	5.7762
5.5	0.25	0.125	0.675	5.2774
6.0	0.30	0.15	0.75	4.7782
6.5	0.50	0.25	1.25	4.2816
7.0	0.70	0.35	1.75	3.7850
7.5	0.85	0.425	2.125	3.2876
8.0	1.05	0.525	2.625	2.7909
8.5	1.35	0.675	3.375	2.2959
9.0	1.85	0.925	4.25	1.8032

Fig. 59,Curve 2.

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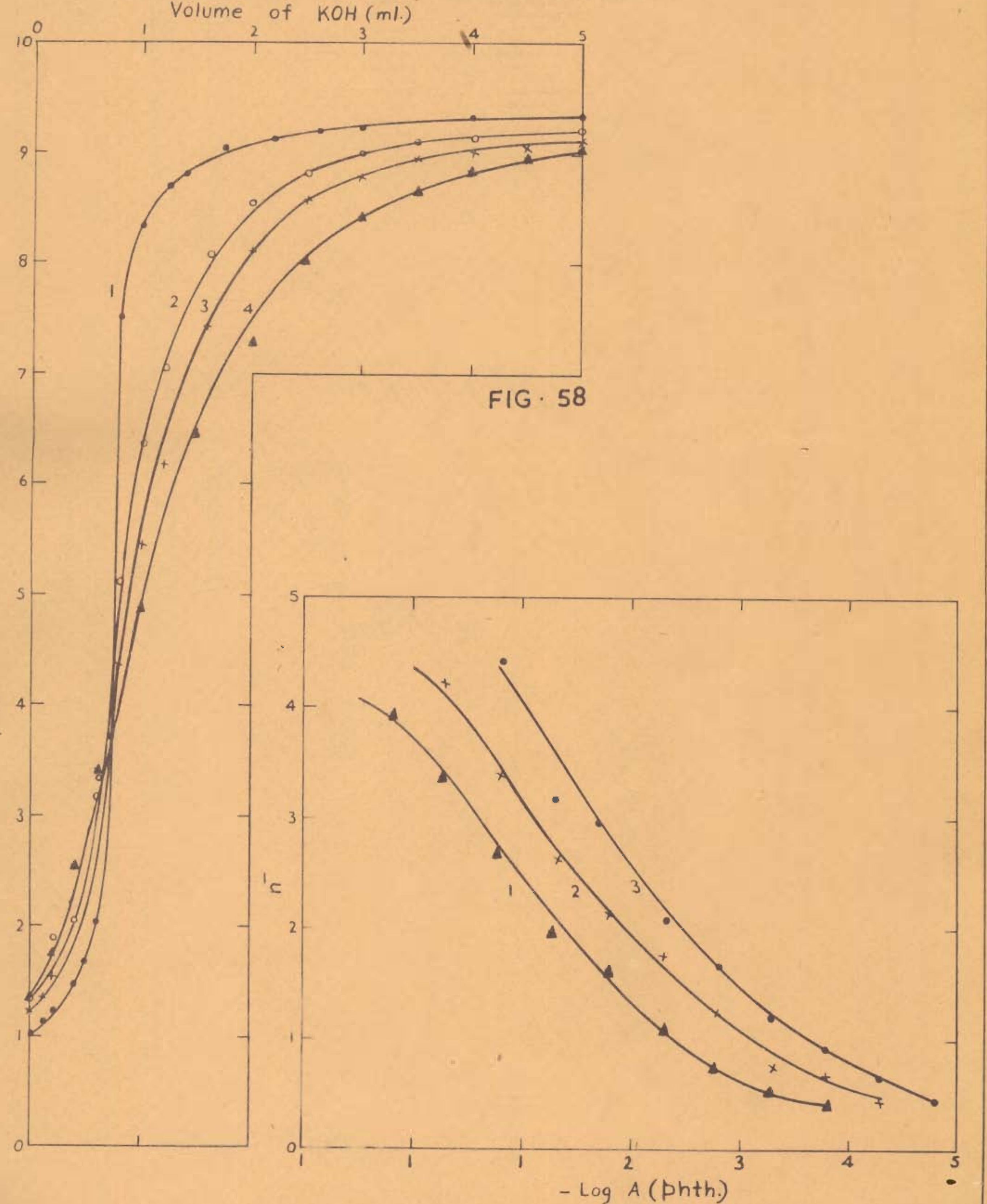

FIG · 58

FORMATION CURVES FOR Cu-PHTH. COMPLEX

FIG · 59

TABLE NO.62.

20 ml. phthalimide - 1.5 ml. $CuSO_4$ -1.0 ml. H_2SO_4 ; total volume made upto 25 ml. by methyl-alcohol.

Vol. of KOH ml.	pH	Vol. of KOH ml.	pH
0.0	1.30	2.5	8.00
0.2	1.74	3.0	8.41
0.4	2.54	3.5	8.68
0.6	3.43	4.0	8.84
1.0	4.86	4.5	8.95
1.5	6.46	5.0	9.05
2.0	7.28	-	-

Fig.58, Curve 4.

TABLE NO. 62 (A)

Calculation for formation curve.

For 1.5 ml. of 0.02 M $CuSO_4$ $\equiv$ 0.3 x 10^{-4} moles.

pH	Δ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log phth.
5.0	0.275	0.138	0.458	5.7779
5.5	0.40	0.20	0.666	5.2799
6.0	0.55	0.275	0.916	4.7825
6.5	0.75	0.375	1.240	4.2859
7.0	1.00	0.500	1.666	3.7901
7.5	1.25	0.625	2.082	3.2942
8.0	1.80	0.900	2.973	2.7032
8.5	1.90	0.950	3.153	2.3049
9.0	2.70	1.350	4.430	1.8176

Fig. 59, Curve 3.

Copper-glutarimide complex

Titration of glutarimide in absence of copper sulphate.

TABLE NO. 63.

10.0 ml. of 0.2 M glutarimide, total volume made upto 11 ml. by methyl-alcohol.

Concentration of KOH solution = 0.1 M

Vol. of KOH ml.	pH	Vol. of KOH ml.	pH
0.0	6.10	0.5	10.46
0.1	9.50	0.8	10.62
0.2	10.02	1.0	10.68
0.3	10.22	1.8	10.80

Fig. 60, Curve 1.

Titration of glutarimide in presence of copper sulphate.

Concentration of glutarimide = 0.2 M.

Concentration of $CuSO_4$ = 0.04 M.

Strength of KOH = 0.1 M.

TABLE NO. 64.

10 ml. glutarimide - 0.3 ml. $CuSO_4$,total volume made upto 11 ml. by methyl-alcohol.

Vol. of KOH ml.	pH	Vol. of KOH ml.	pH
0.0	4.06	1.2	10.66
0.2	7.06	1.6	10.80
0.4	9.12	2.0	10.92
0.6	10.00	2.5	11.00
0.8	10.34	3.0	11.06
1.0	10.54	3.4	11.10

Fig. 60, Curve 2.

TABLE NO. 64 (A)

Calculations for formation curve.

For 0.3 ml. of 0.04 M $CuSO_4$ = 0.12×10^{-4} moles.

pH .	Δ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log glut.
6.0	0.10	0.10	0.833	5.8043
6.5	0.12	0.12	1.000	5.3051
7.0	0.15	0.15	1.250	4.8062
7.5	0.19	0.19	1.583	4.3078
8.0	0.22	0.22	1.833	3.8089
8.5	0.26	0.26	2.17	3.3104
9.0	0.30	0.30	2.50	2.8121
9.5	0.37	0.37	3.083	2.3118
10.0	0.42	0.42	3.50	1.8167

Fig. 61, Curve 1.

TABLE NO. 65.

10 ml. glutarimide -0.45 ml. $CuSO_4$,total volume made upto 11 ml. by methyl-alcohol.

Vol. of KOH ml.	pH	Vol. of KOH ml.	pH
0.0	3.94	1.0	10.35
0.1	5.34	1.1	10.46
0.2	6.48	1.2	10.54
0.3	7.43	1.3	10.62
0.4	8.18	1.4	10.72
0.5	8.86	1.6	10.82
0.6	9.54	1.8	10.90
0.7	9.84	2.0	10.98
0.9	10.18	2.5	11.06

Fig. 60, Curve 3.

TABLE NO. 65 (A)

Calculations for formation curve.

For 0.45 ml. of 0.04 M $CuSO_4 \equiv 0.18 \times 10^{-4}$ moles.

pH	Δ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log glut.
6.0	0.15	0.15	0.833	5.8062
6.5	0.18	0.18	1.000	5.3073
7.0	0.22	0.22	1.220	4.8099
7.5	0.26	0.26	1.445	4.3105
8.0	0.32	0.32	1.778	3.8129
8.5	0.38	0.38	2.111	3.3152
9.0	0.43	0.43	2.390	2.8172
9.5	0.52	0.52	2.890	2.3205
10.0	0.62	0.62	3.445	1.8243

Fig.61, Curve 2.

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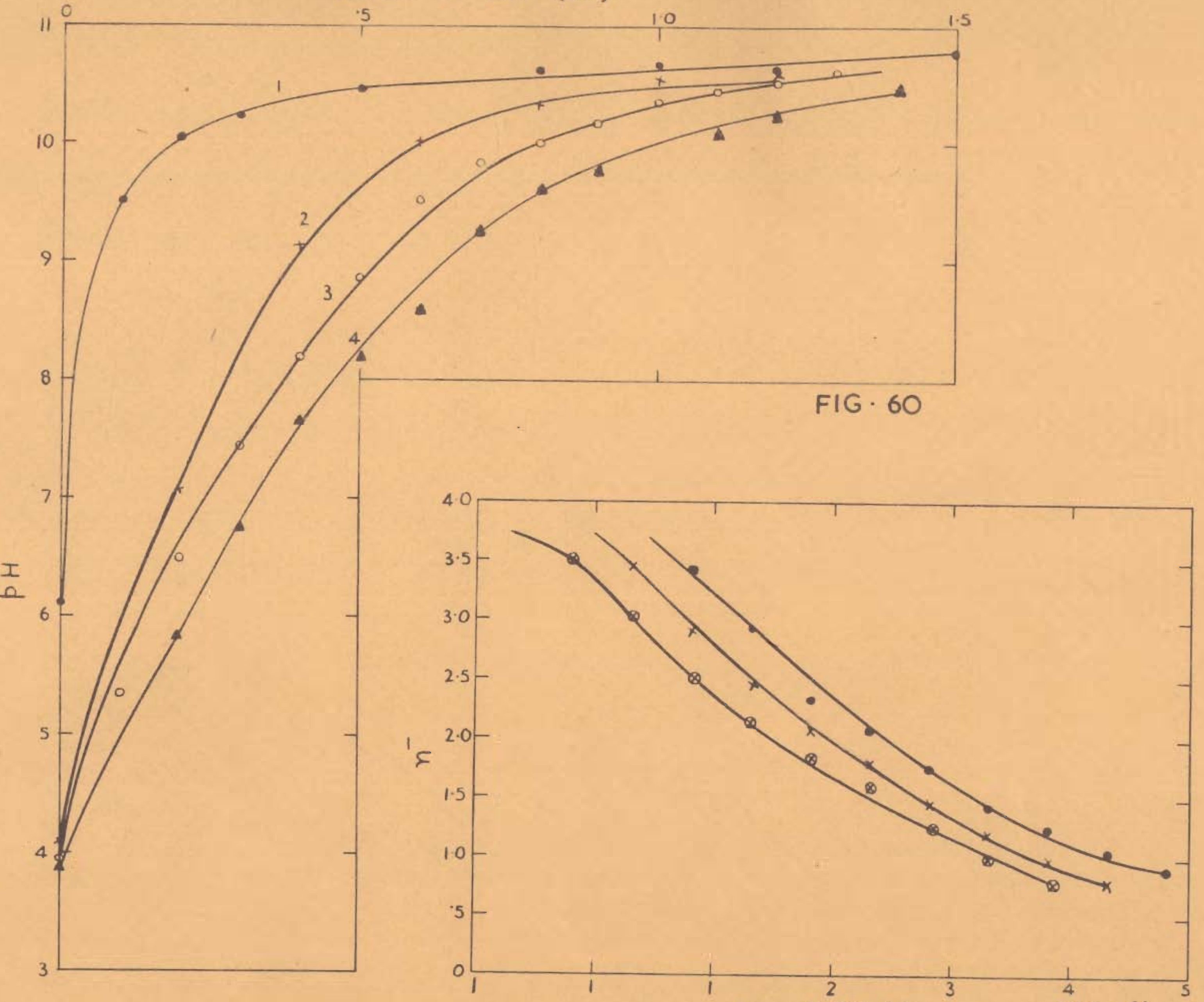


FIG · 60

FIG · 61

FORMATION CURVES FOR Cu-GLUT. COMPLEX

TABLE NO. 66.

10 ml. glutarimide -0.6 ml. $CuSO_4$, total volume made upto 11 ml. by methyl-alcohol.

Vol. of KOH ml.	pH	Vol. of KOH ml.	pH
0.0	3.70	0.9	9.77
0.1	5.08	1.1	10.09
0.2	5.80	1.2	10.24
0.3	6.74	1.4	10.44
0.4	7.67	1.6	10.57
0.5	8.20	1.8	10.65
0.6	8.56	2.2	10.77
0.7	9.29	2.6	10.84
0.8	9.60	3.0	10.90

Fig. 60, Curve 4.

TABLE NO. 66 (A)

Calculations for formation curve.

For 0.6 ml. of 0.04 M $CuSO_4$ ≡ 0.24×10^{-4} moles.

pH	△ KOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log glut.
6.0	0.22	0.22	0.916	5.8090
6.5	0.25	0.25	1.04	5.3101
7.0	0.30	0.30	1.25	4.8121
7.5	0.35	0.35	1.46	4.3140
8.0	0.42	0.42	1.75	3.8167
8.5	0.50	0.50	2.08	3.3197
9.0	0.56	0.56	2.33	2.8219
9.5	0.69	0.69	2.89	2.3267
10.0	0.82	0.82	3.417	1.8316

Fig. 61, Curve 3.

In order to ensure that hydrogen ions are liberated during complex-ion of copper with imides, and for further confirming the stoichiometry of the copper-imide complexes, copper sulphate alone and also in presence of one, two, three, four and five fold equivalents of imides solutions were separately titrated against potassium hydroxide solution. Imide solutions were also titrated separately against potassium hydroxide solution.

Details of concentrations and volumes of the reactants, used for this purpose, are summarised below. Actual observations can be read from corresponding figures.

TABLE NO. 67

Copper-succinimide complex.

Concentration of succinimide solution 0.05 M.

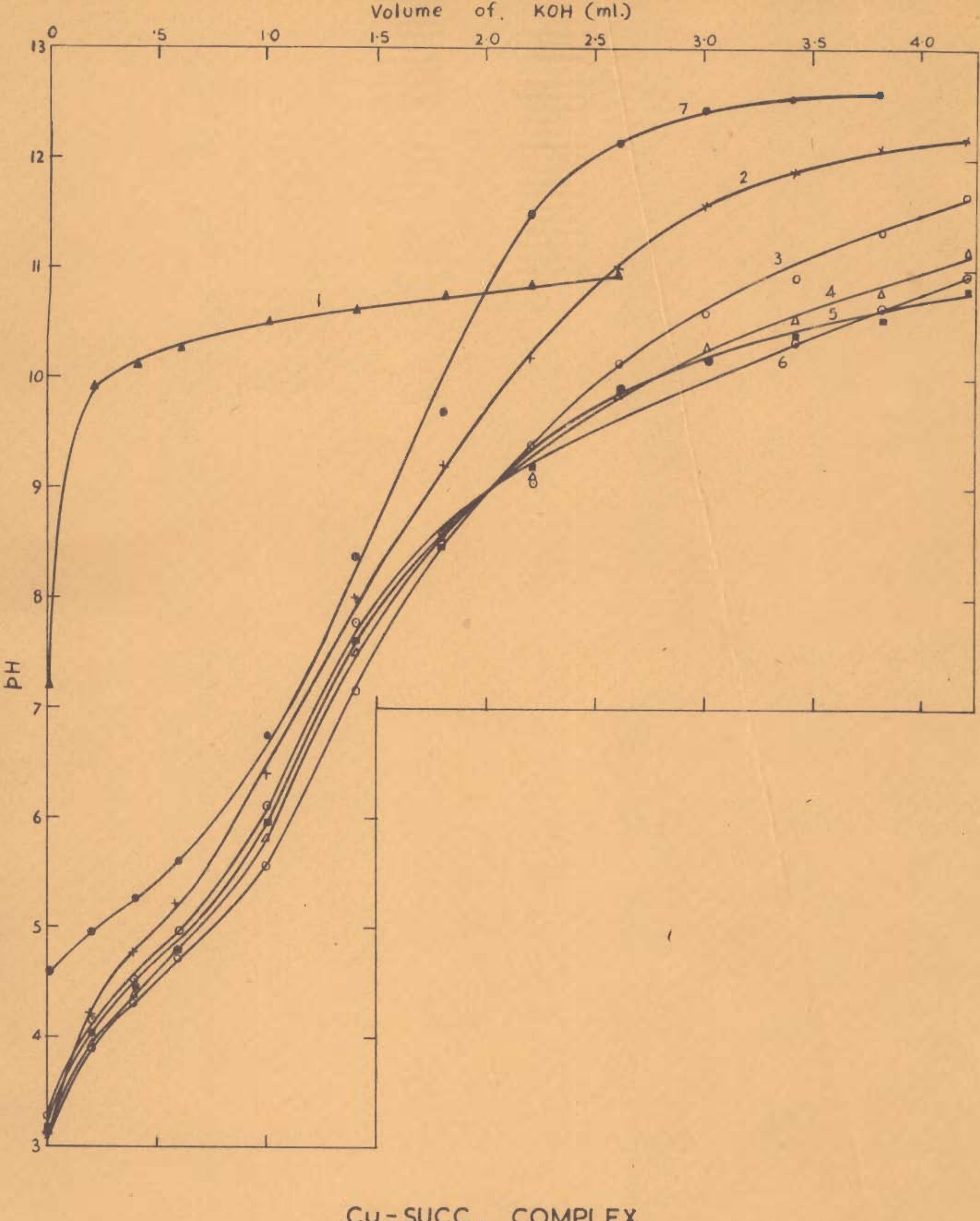
Concentration of copper sulphate solution =0.05 M.

Concentration of potassium hydroxide =0.1 M.

Total volume in each set made upto 20 ml. by methyl-alcohol.

Vol. of $CuSO_4$ ml.	Vol. of succinimide ml.	$CuSO_4$: Succinimide	Curve No.
0.0	15.0	-	1
3.0	3.0	1:1	2
3.0	6.0	1:2	3
3.0	9.0	1:3	4
3.0	12.0	1:4	5
3.0	15.0	1:5	6
3.0	0.0	-	7

Fig. 62



Cu-SUCC. COMPLEX

FIG· 62

TABLE NO. 68

Copper-phthalimide complex

Concentration of phthalimide solution = 0.05 M.

Concentration of copper sulphate solution = 0.05 M.

Strength of potassium hydroxide solution = 0.1 M.

Total volume in each set made upto 20 ml. by methyl-alcohol.

Vol. of $CuSO_4$ ml.	Vol. of phthalimide ml.	$CuSO_4$: phthalimide	Curve No.
0.0	15.0	-	1
3.0	3.0	1:1	2
3.0	6.0	1:2	3
3.0	9.0	1:3	4
3.0	12.0	1:4	5
3.0	15.0	1:5	6
3.0	0.0	-	7

Fig. 63

TABLE NO. 69

Copper-glutarimide complex

Concentration of glutarimide solution = 0.2 M.

Concentration of copper-sulphate solution = 0.04 M.

Concentration of potassium hydroxide = 0.1 M.

Total volume in each set made upto 10 ml. by methyl-alcohol.

Vol. of $CuSO_4$ ml.	Vol. of glutarimide ml.	$CuSO_4$: glutarimide	Curve No.
0.0	5.0	-	1
5.0	0.0	-	2
5.0	3.0	1:3	3
5.0	4.0	1:4	4
5.0	5.0	1:5	5

Fig. 64

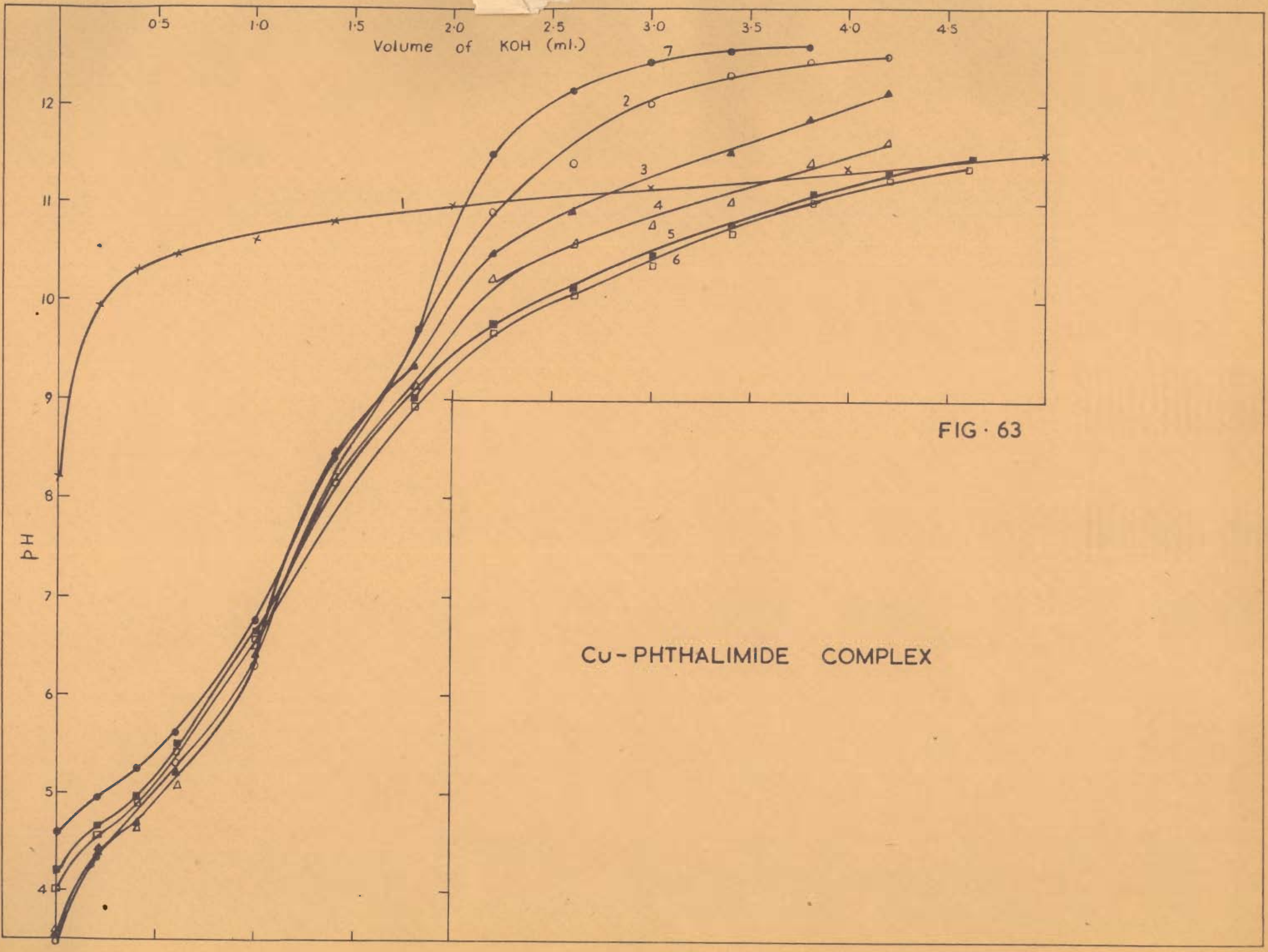


FIG · 63

Cu-PHTHALIMIDE COMPLEX

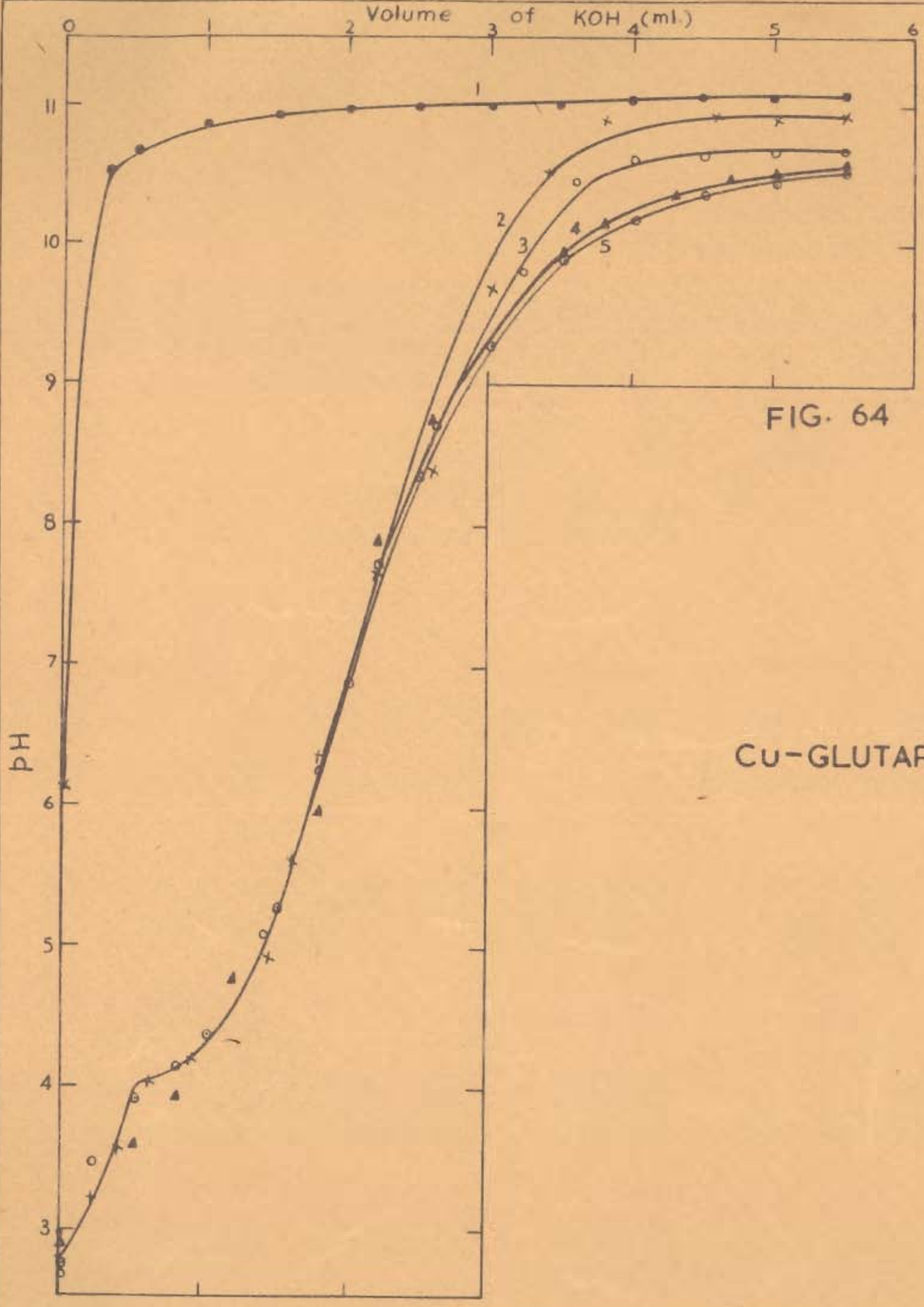


FIG. 64

CU-GLUTARIMIDE COMPLEX

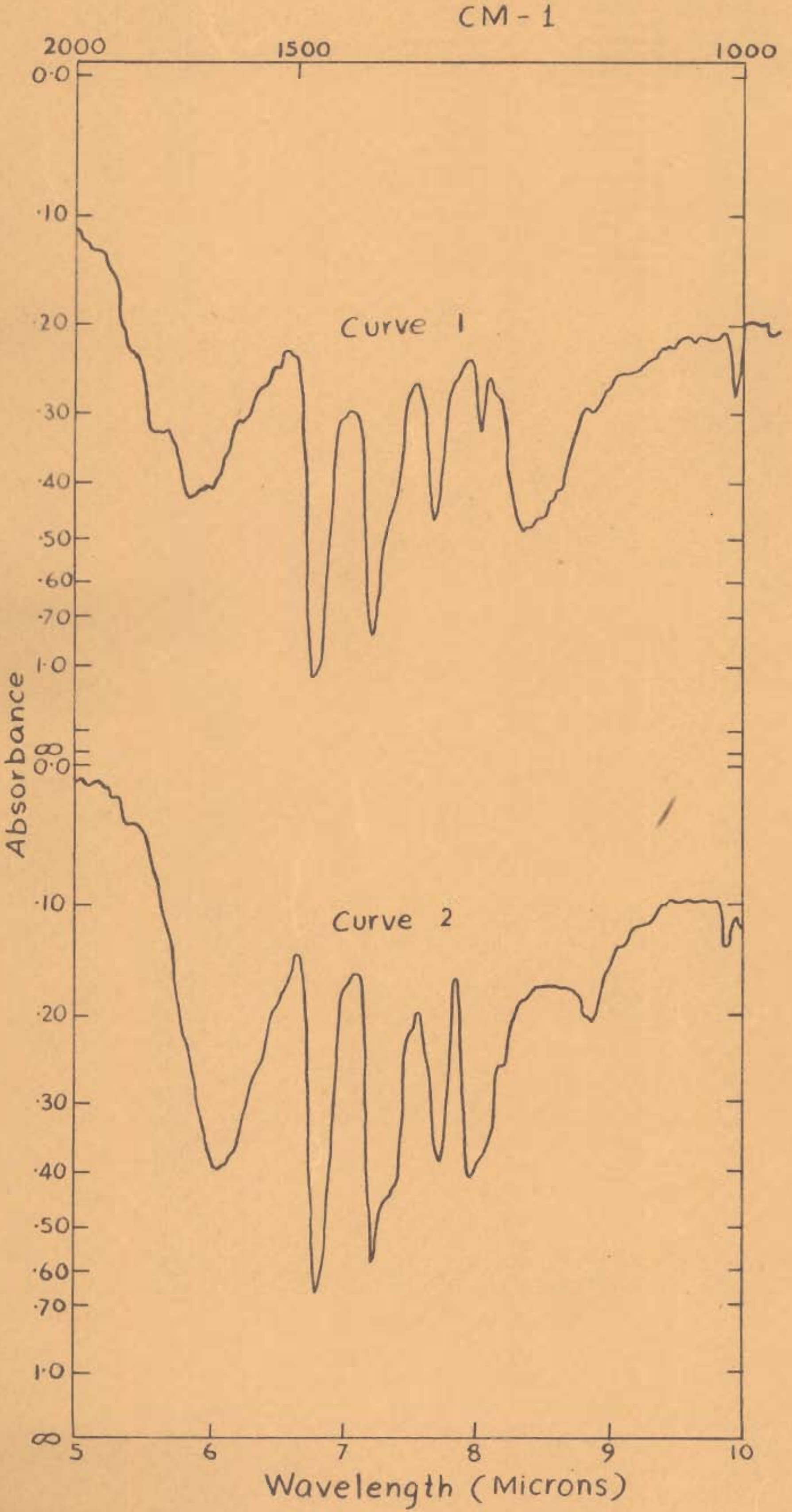
Isolation and chemical analysis of the complexes:

In view of the unstability of these complexes in presence of excess of copper ions, the reagents were mixed keeping the proportion of the imide a little higher than determined by the various physico-chemical methods described above. Since a 1:4 complex was indicated by these methods, methanolic solutions of copper sulphate and the imide were mixed, and the pH of the resulting mixture was adjusted to 10. The resulting precipitate was thoroughly washed with methyl alcohol till it was free from adsorbed caustic potash and excess of imide. It was then kept in a vacuum dessicator and dried over calcium chloride. The bluish violet precipitate remained almost unchanged in colour on drying.

Copper succinimide complex: 500 ml. of 0.5 M succinimide having one equivalent amount of potassium hydroxide, taken in a beaker and 500 ml. of 0.1 M copper sulphate were added to it, when dark blue coloured crystals of copper succinimide complex were formed.

Copper phthalimide complex: 500 ml. of 0.05 M phthalimide having equivalent amount of potassium hydroxide were mixed with 50 ml. of 0.1 M copper sulphate solution, when a pink violet precipitate was obtained.

Copper glutarimide complex: 200 ml. of 0.1 M glutarimide having equivalent amount of potassium hydroxide were mixed with 40 ml. of 0.1 M copper sulphate solution, when a blue coloured complex was obtained.

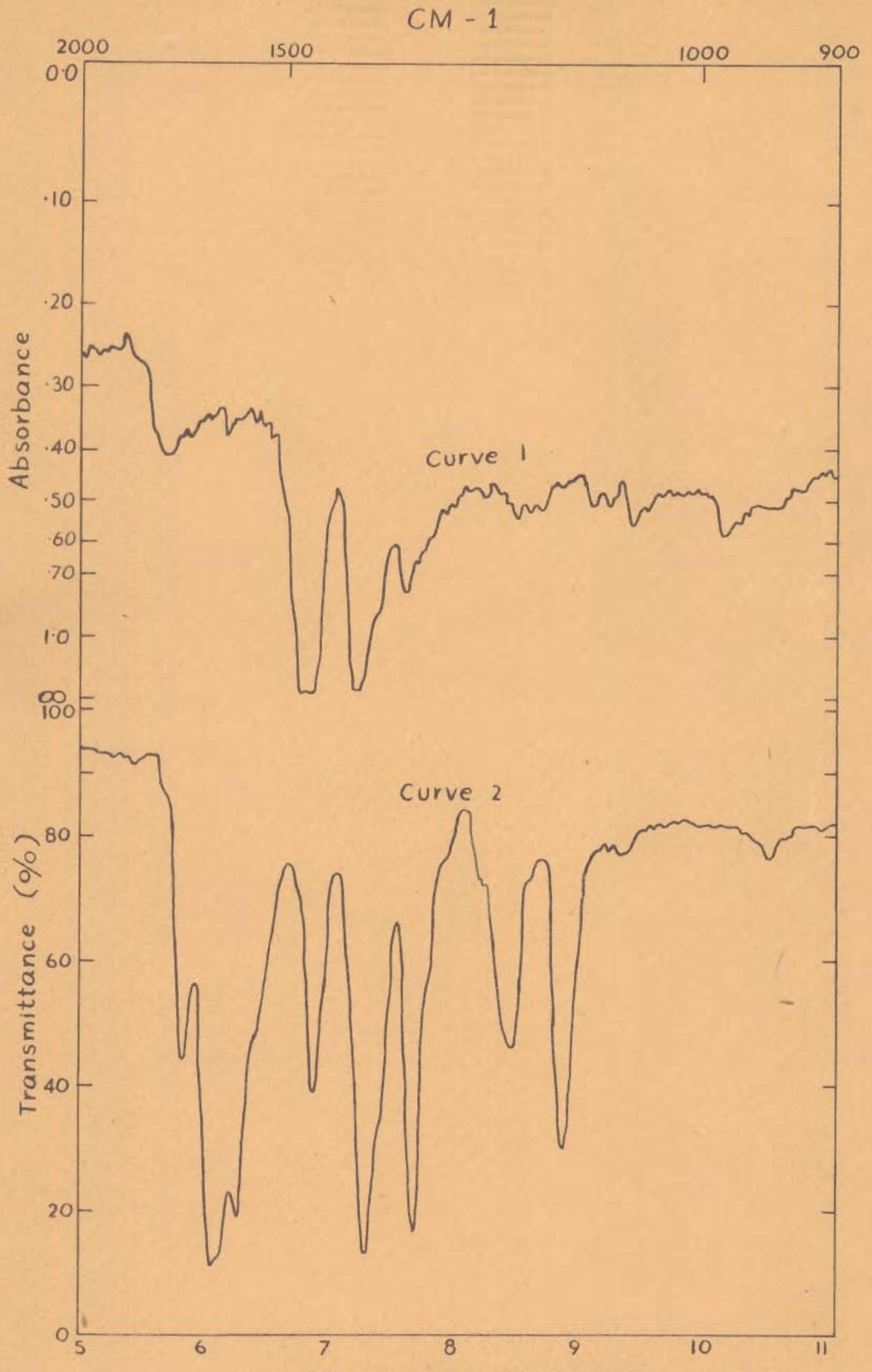


Curve 1. Succinimide

Curve 2. Cu-Succinimide Complex

I. R. SPECTRA

FIG. 65



Curve 1. Phthalimide
Curve 2. Cu-Phthalimide Complex

I.R. SPECTRA

FIG. 66

Chemical analysis: A weighed amount of the dried sample was digested with aqua regia and its copper content was estimated gravimetrically as cuprous thiocyanate.

The nitrogen estimation of copper imide complexes was carried out using Kjeldahl's volumetric method.

Following results were obtained.

	Nitrogen %	Copper %
Copper-succinimide complex	12.14	13.43
Copper-phthalimide complex	9.38	10.42
Copper-glutarimide complex	10.68	12.12

Infra-red spectroscopy:

Spectra of copper-succinimide and copper-phthalimide complexes were taken in nujol medium by the method of fast scanning, in the infra-red region. For comparing the spectra of complexes with those of ligands, I.R. spectra of succinimide and phthalimide were also recorded by the above method. The apparatus used in these studies was Perkin and Elmer infra cord. The spectra obtained are depicted in Fig.65 for succinimide complex and in Fig. 66 for phthalimide complex.

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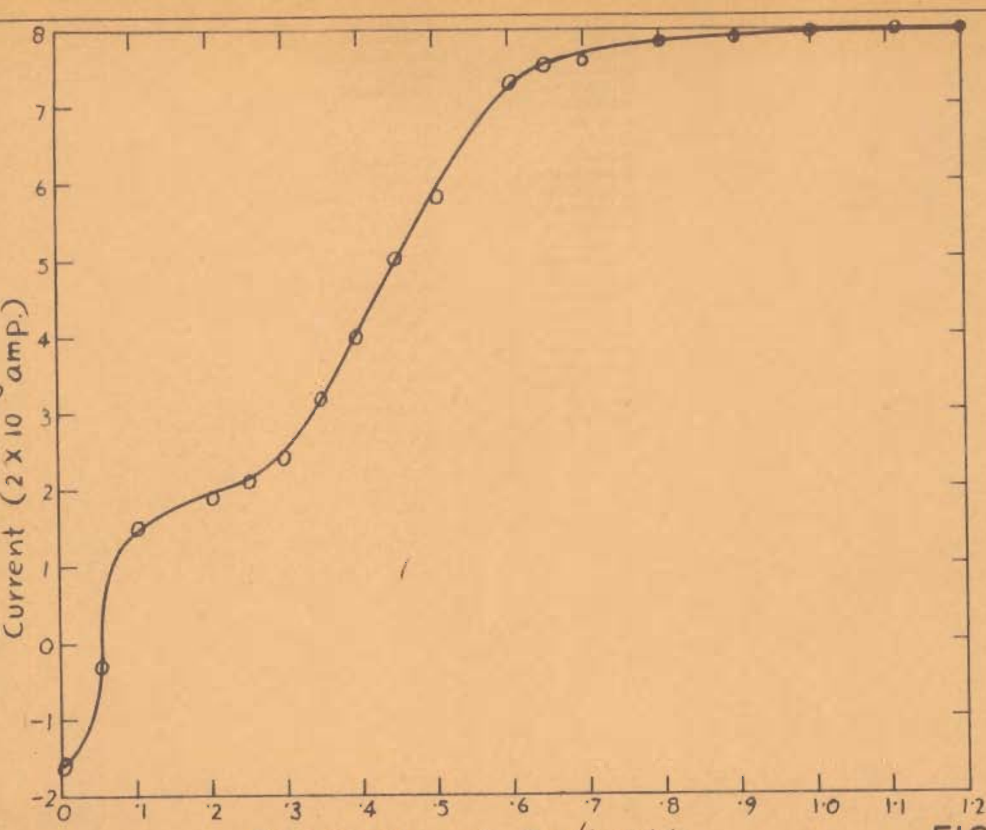
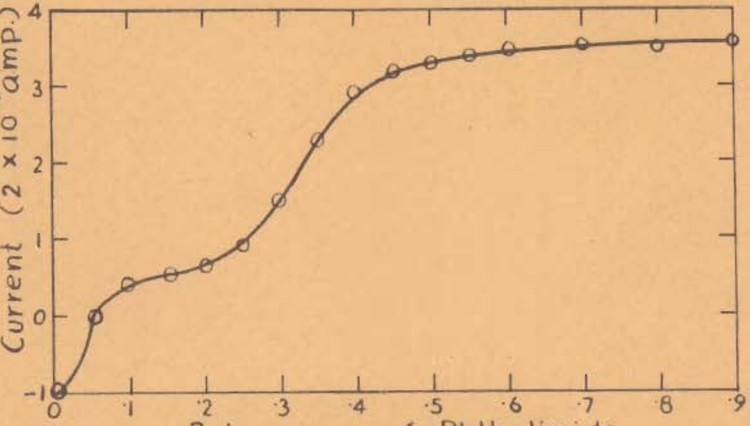


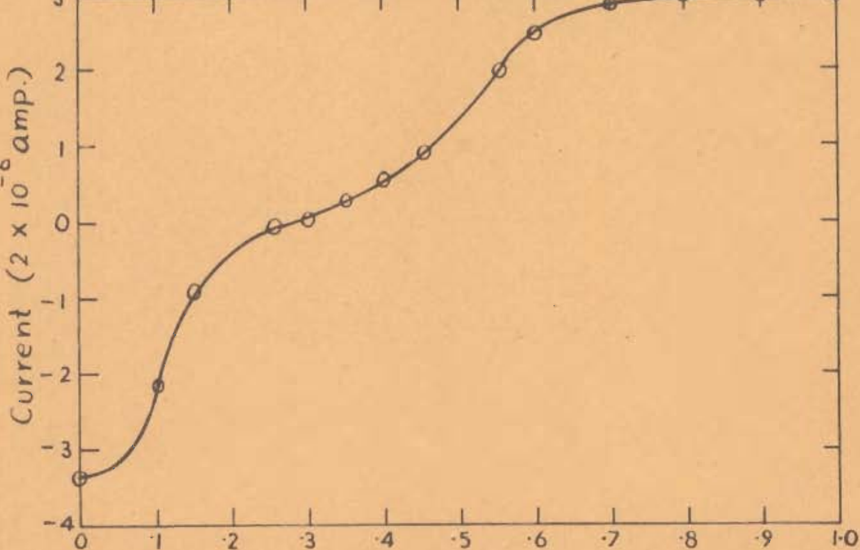
Polarogram of Succinimide

FIG. 67



Polarogram of Phthalimide

FIG. 68



Polarogram of Glutarimide

FIG. 69

DISCUSSION

Results on the conductometric, potentiometric, amperometric and pH metric methods between the copper sulphate and imides at high pH presents the following interesting features.

Conductometric titrations:

In both direct (imides in the cell) and reverse (copper sulphate in the cell) titrations, the combining ratio of Cu : imide comes out to be 1:4 (Figs. 1-4, 9-12 and 21-23). The imide solutions for direct titrations were prepared in equivalent amount of potassium hydroxide.

The copper-glutarimide complex, studies could not, however, be carried out at low dilution of caustic potash. Instead a concentrated solution of potassium hydroxide (0.2 M) was added to obtain glutarimide in one equivalent of caustic potash.

Reverse titrations, performed with copper sulphate, containing four equivalents of caustic potash (each equivalent for one mole of succinimide and since evidence of 1:4 complex was forthcoming, four equivalents of potassium hydroxide were added in the very beginning). On gradual addition of the titrant (imide), the copper hydroxide precipitate got decomposed and got converted into the violet blue complex completely, when imide corresponding to the equivalence point in the conductometric titrations was added. Similarly in the direct titrations the violet complex got decomposed into the green hydroxide when copper sulphate beyond the equivalence point was added to the imides.

The inflexion points from the titration curves, both direct and reverse, gàve the combining ratio,1 mole of Cu^{++} to 4 moles of the imide (Figs.1-23).

Potentiometric titrations:

The potentiometric titration technique could not be applied in investigating the composition of these complexes due to the non-availability of a suitable indicator electrode. A copper electrode(obtained by electrolytic deposition of copper on platinum) used as such did not remain steady. Satisfactory results could not also be obtained with the amalgam electrode(prepared by the method recommended by Nielson and Brown(9)) since this too failed to give stable potentials in the required pH range. The possibility of employing a new electrode system was,therefore,sought for. It was found that a redox indicator electrode could be developed if a platinum wire electrode was kept dipped in a solution of cupric ions containing extremely small amount of cuprous ions ($- Cu^{++} : - Cu^{+}$). Variations in e.m.f. at this electrode, on adding the titrant (imides) gave typical potentiometric titration curves with sharp breaks. Reverse titrations (imides in the cell) could also be carried out successfully. An extra advantage of this redox system was that its performance was equally good in non aqueous medium.

From the inflexion points precise information about the binding ratio is obtained both from the direct as well as the reverse titrations. The ratio comes out to be 1,Cu : 4,imide. These results confirm the data of conductometric titrations. Moreover the titration curves obtained with phthalimide and glutarimide gave sharp inflexion points as compared to those of the succinimide. This may be attributed to the structural difference between the complexing agents.

Amperometric titrations:

The amperometric titrations confirm the results of the other studies. Here-too the combining ratio of 1:4 (Cu : imide) was realised for all the three imides. However, the shape of the curves was unusual and in no case typical titration curves were realised.

Ordinarily copper complexes are studied amperometrically by applying a constant potential corresponding to the plateau of the reduction wave of cupric ions,it was not possible to do so in the case of the copper-imide complexes, since a well defined wave of copper was not obtained in the methanolic medium. Polarograms of the chelating agents, viz., succinimide,phthalimide and glutarimide were then recorded using methanolic caustic potash as the supporting electrolyte(caustic potash was chosen since the reactions studied,took place only in highly alkaline medium).Two reduction waves (one anodic and the other cathodic) were obtained(Fig.67-69).

The constant potential to be applied for the amperometric titration was determined from the plateau of these waves. The potentials employed were -1.2,-0.8 and

-0.8 volts, for succinimide, phthalimide and glutarimide respectively.

Direct titrations(imide in the cell) could only be carried out with succinimide and phthalimide. Reverse titrations(copper sulphate in the cell) were not successful with these two imides. However, in the case of glutarimide only reverse titrations could be performed, titrations with the reagent in the cell did not give sharp inflexion point.

Considering the titrations with succinimide and phthalimide, it would be observed that the current should decrease with the removal of the imides on adding gradually, increasing amount of the cupric ions. After the completion of the reaction, the current should become constant since excess of the metal ion would not be reduced at the applied potential. But as already stated this typical behaviour was not observed. Instead, the current first goes on increasing, followed by an equally sharp decrease in current after the inflexion point(Fig. 46-51).

The initial increase in current can be due to two factors (i) reduction of the resulting complex at the applied potential; (ii) appearance of adsorption or kinetic current(depending on the nature of the reaction and reaction products). These currents will manifest themselves as long as the complex is present and this behaviour should persist unless the complex formed starts decomposing.

Since these complexes, like the nickel-imide complexes, also get decomposed in presence of excess of metal, a decrease in current should be observed after the completion of the reaction. This is what has actually been observed in both cases.

Amperometric titrations, therefore, not only confirm the existence of 1-4 complex but also give experimental support to the observation that the copper complexes of succinimide and phthalimide can remain in the stable form, only in excess of the complexing agent. Once metal ion is in slight excess than the stoichiometric ratio for the formation of the complex, it decomposes.

The titrations with glutarimide(copper sulphate in the cell) should normally show a constancy upto the inflexion point, followed by an increase in current due to excess of glutarimide. This typical behaviour is not met-with and shape of the titration curves is just as unusual as observed for copper complexes of phthalimide and succinimide. The explanation for the inital increase can be based on the same reasoning, namely, the reduction of the complex or the existence of adsorption or kinetic current, but since in these titrations excess of the ligand instead of the metal ions are being added, after the inflexion point, a decrease in current due to the decomposition of the complex should not be observed. A constancy in current instead of gradual increase beyond the inflexion point may point towards the adsorption of the glutarimide by the resulting complex. A large affinity of the complex for the imides is quite understandable since the complex attains greater stability in presence of excess of the glutarimide.

pH-metric studies:

Bjerrum's method is normally employed to determine the composition and stability constant of soluble complexes. It was observed that the experimental procedure of this method could be used to determine the composition and stability constants of complexes showing tendency to exist as colloidal precipitate. Since the complexes remained in highly dispersed form in excess of the ligand, and flocculation sets in, only in the higher pH range, average stability constant of the copper-imide complexes could be computed from the curves (with and without the metal ions) upto the pH range in which precipitation of the complexes was not started.

The pH-metric titrations performed according to the method of Calvin and Melchior, gave typical curves in all the three cases. The value of $\bar{n}$ was found to increase regularly with the increase of pH and attained constant value of approximately four in each case, confirming thereby the existence of 1:4 metal-imide complexes. The use of this method was based on the assumption that the methanolic medium would not effect the $\bar{n}$ value as it was calculated from the excess amount of alkali consumed in presence of metal ions (Figs.55,58 and 60).

For determining the apparent stability constant of different complexes the plots of $\bar{n}$ against -log A, were used as done previously. The results are given below:

Apparent stability constants of the copper-imide complexes.

Copper-succinimide complex:

Curves	Average stability constant $\log k = -\log A$ at $\bar{n} = 2$	Over all stability constant $\log K = 4 \log k$	Mean log K
1	2.75	11.00	
2	2.85	11.40	11.333
3	2.90	11.60	

Fig.56

Copper-phthalimide complex:

1	3.40	13.60	
2	3.45	13.80	13.80
3	3.50	14.00	

Fig.59

Copper-glutarimide complex:

1	3.45	13.80	
2	3.50	14.00	13.933
3	3.50	14.00	

Fig.61

The pH-metric titrations performed with copper alone and with different proportions of imides as, 1:1, 1:2, 1:3, 1:4, 1:5 (Cu : imide) (Figs.62-64), exhibit a continuous shift of curves towards the lower pH range with increasing proportions of imides. This shift of curves continued till a metal-imide ratio of 1:4 was reached. In case of mixtures having 1:5 metal-imide ratio, the pH shift was almost negligible, showing thereby that maximum of four protons can be liberated from four molecules of imides per metal ion.

Chemical analysis of the complexes:

Chemical analysis of the isolated complex also confirmed 1:4 (metal-imide) combining ratio.

I.R. Studies:

The I.R. Spectra of imides and their 1:4 complexes with copper revealed a marked shift in carbonyl stretching frequency (Figs. 65 and 66) pointing towards oxygen-metal binding. Since the pH-metric, conductometric and other chemical evidences seem to indicate that the co-ordination is through nitrogen, the decrease in carbonyl frequency could be interpreted due to the mass effect of the heavy metal atoms which would definitely have some perturbation in these ring compounds. The NH vibration frequency could not be examined due to the interference from the OH absorption bands of methanol, which probably is present in the complexes. An additional feature of succinimide complex was to lower frequencies of the 1180 cm^{-1} band which may have a strong component of the C-N vibration stretching band. Further duplet formed around 830 cm^{-1} (probably due to ring vibration) also shifts to lower frequency on complexation.

In view of the above results, the structure of copper complexes of succinimide, phthalimide and glutarimide, may be represented by the following formulae,

Copper-succinimide complex, $((C_4H_4O_2N)_4\ Cu\ (CH_3OH)_2)^{2-}$

Copper-phthalimide " $((C_8H_4O_2N)_4\ Cu\ (CH_3OH)_2)^{2-}$

Copper-glutarimide " $((C_5H_6O_2N)_4\ Cu\ (CH_3OH)_2)^{2-}$

The solvation of metal ions with methanol is not unusal as has also been reported in the literature (10). Evidence for this is also available from I.R.spectra where OH absorption bands of methanol are observed.

Moreover, since four basic nitrogen atoms are involved in complexation with copper, all the three complexes are essentially formed by biuret reaction mechanism.

CHAPTER IV.

Soluble copper complexes of succinimide and saccharin (non biuret reaction mechanism).

INTRODUCTION

Livio Cambi (1) studied the magnetic properties of insoluble copper complex of succinimide and showed it to be paramagnetic. Malik and coworkers(2) studied copper-succinimide complex polarographically in aqueous and aqueous-ethanolic media, at high pH (1.0 M KOH) and reported the formation of a soluble violet coloured copper-succinimide complex.

Preliminary experiments in aqueous medium have revealed the formation of a bluish coloured copper-succinimide complex in the lower pH range($pH < 8$),stable only in excess of succinimide. The polarographic method was found unsuitable to study this complex due to the irreversible nature of its reduction. Other physico-chemical methods, viz.,conductometric and potentiometric methods were therefore, tried. The conductometric method failed to give any inflexion in view of the originally high conductance of succinimide solution. So was the case with spectrophotometric methods, since mixtures containing excess of copper sulphate got precipitated,not allowing wide concentration range necessary for the use of Job's or slope ratio methods,for the determination of the composition of complex. Of the available methods in the laboratory,it was only the pH-metric method which could be employed for these studies. The Bjerrum's method(loc.cit.) was tried and was found to give satisfactory results on the composition and stability of the complex.

Formation of another soluble copper-imide complex was noticed when copper sulphate was mixed with saccharin in methanolic medium. Potassium-bis-o benzoic sulfanimide dibromo aurate ($C_{14}H_8O_6N_2Br_2S_2$ K Au), a red coloured derivative of potassium saccharin was studied by Tyabji and Gibson(4), which was found to decompose by the action of water. Crystal structures of saccharin derivatives of manganese, nickel and cobalt have also been cited in the literature(5). Klasen's and Terpstra(6) have shown the formation of light blue crystals of $(C_6H_4COSO_2N)_2$ Cu $(H_2O)_6$ upon addition of concentrated copper sulphate solution to an equally concentrated solution of sodium saccharinate.

Owing to the decomposing action of water on these complexes of saccharin, probably no physico-chemical method was employed to study the nature of this complex. It was, therefore, thought worth investigating this complex, in non aqueous medium, using the available physico-chemical methods. Unlike the copper-succinimide complex described above, the spectrophotometric as well as conductometric methods could be employed to determine its composition. The pH metric method could, however, not be employed since this reaction, unlike the others described earlier, does not take place in alkaline medium.

The results of spectrophotometric and conductometric methods were confirmed by the methods of chemical analysis and I.R. spectroscopy.

EXPERIMENTAL

Stock solution of succinimide of strength 0.5 M was prepared by dissolving 12.3912 gms. of the reagent in 250 ml. of double distilled water. Aqueous (for the succinimide complex) and methanolic (for the saccharin complex) solutions of copper sulphate A.R.(B.D.H.) were prepared by direct weighing and their strength checked gravimetrically as cuprous thiocyanate. The standard solution of saccharin A.R. (B.D.H.) was prepared in double distilled methyl alcohol. Stock solution of potassium hydroxide was prepared in double distilled water and its strength determined by titrating against standard oxalic acid solution.

Beckmann's model G-pH meter with extended electrode leads was used for pH measurements and conductance measurements were carried out with a Philips conductivity bridge. Bausch and Lomb spectronic '20' was used for absorption measurements.

Copper succinimide complex:

For investigating the composition and stability of copper-succinimide complex by Bjerrum's method, the procedure recommended by Calvin and Melchoir(loc.cit.) was adopted.

20 ml. of 0.5 M succinimide solution was mixed with varying amounts(0.0,0.4,0.7,1.0 ml.) of 0.1 M copper sulphate and 1.0 ml. of 0.01M, sulphuric acid, making the total volume to 25 ml. with double distilled watef. The mixtures were taken in the cell and nitrogen (free

from carbondioxide) was passed for maintaining inert atmosphere as well as for stirring the solution. All the measurements were performed at 30 ± 0.1°C using Towsen and Mercer water thermostat. 0.1 M potassium hydroxide solution(carbonate free) was added from an automatic micro burette for titrating the afore-said solutions. The results of the titrations are given in the following tables. The method adopted for calculating $\bar{n}$ and -log A (free ligand concentration) was the same as described earlier in Chapter I. The tables for calculations have been given along with titration tables.

pK value of succinimide used in these calculations is 9.29 as mentioned in Chapter I.

TABLE NO.1.

Titration of succinimide in absence of Copper sulphate.
20 ml. of 0.5 M succinimide-1.0 ml. of 0.01 M H_2SO_4 .
Total volume made upto 25 ml.by distilled water.

Vol.of KOH(ml.).	pH	Vol.of KOH(ml.)	pH
0.0	3.53	2.0	7.7
0.1	5.80	3.0	7.84
0.2	6.67	3.5	7.90
0.3	6.81	4.0	8.05
0.4	7.03	4.5	8.10
0.5	7.08	5.0	8.16
0.8	7.27	6.0	8.22
1.2	7.43	7.0	8.25
1.6	7.56	8.0	8.35

Fig. 1,Curve 1.

Titrations of succinimide in presence of $CuSO_4$:

Concentration of succinimide solution = 0.5 M.

Concentration of copper sulphate solution = 0.1 M.

Strength of H_2SO_4 solution = 0.01 M.

Strength of KOH solution = 0.1 M.

TABLE NO. 2.

20 ml. succinimide -0.4 ml. $CuSO_4$ - 1.0 ml. H_2SO_4 , total volume made upto 25 ml. by distilled water.

Vol. of KOH ml.	pH	Vol. of KOH ml.	pH
0.0	0.44	1.6	7.24
0.1	4.09	2.0	7.40
0.2	4.58	2.5	7.56
0.3	4.90	3.0	7.70
0.4	5.25	3.5	7.79
0.5	5.56	4.0	7.90
0.6	5.84	4.5	7.96
0.8	6.31	5.0	8.03
1.0	6.66	6.0	8.12
1.2	6.93	7.0	8.20
1.4	7.12	8.0	8.27

Fig.1, Curve 2.

TABLE NO. 2(A)

Calculations for formation curve.
For 0.4 ml. of 0.1 M $CuSO_4 \equiv 0.4 \times 10^{-4}$ moles.

pH	Δ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log succ.
4.0	0.08	0.08	0.145	5.6893
4.33	0.10	0.10	0.205	5.3567
4.67	0.17	0.17	0.408	5.0209
5.00	0.27	0.27	0.658	4.6926
5.33	0.35	0.35	0.832	4.3610
5.67	0.45	0.45	1.101	4.0257
6.00	0.57	0.57	1.412	3.6977
6.33	0.67	0.67	1.581	3.3664
6.67	0.80	0.80	1.882	3.0316
7.0	0.83	0.83	1.901	2.7021
7.33	0.83	0.83	1.960	2.3691
7.67	0.85	0.85	2.000	2.0325

Fig.2, Curve 1.

TABLE NO. 3.

20 ml. succinimide - 0.7 ml. $CuSO_4$ - 1.0 ml. H_2SO_4 , total volume made upto 25 ml. by distilled water.

Vol. of KOH ml.	pH	Vol. of KOH ml.	pH
0.0	3.45	2.8	7.50
0.1	3.93	3.2	7.60
0.2	4.34	3.6	7.70
0.3	4.64	4.0	7.78
0.5	5.05	4.5	7.85
0.7	5.44	5.0	7.93
1.0	5.98	6.0	8.05
1.2	6.29	7.0	8.16
1.6	6.80	8.0	8.24
2.0	7.12	9.0	8.32
2.4	7.33	-	-

Fig.1, Curve 3.

TABLE NO. 3 (A)

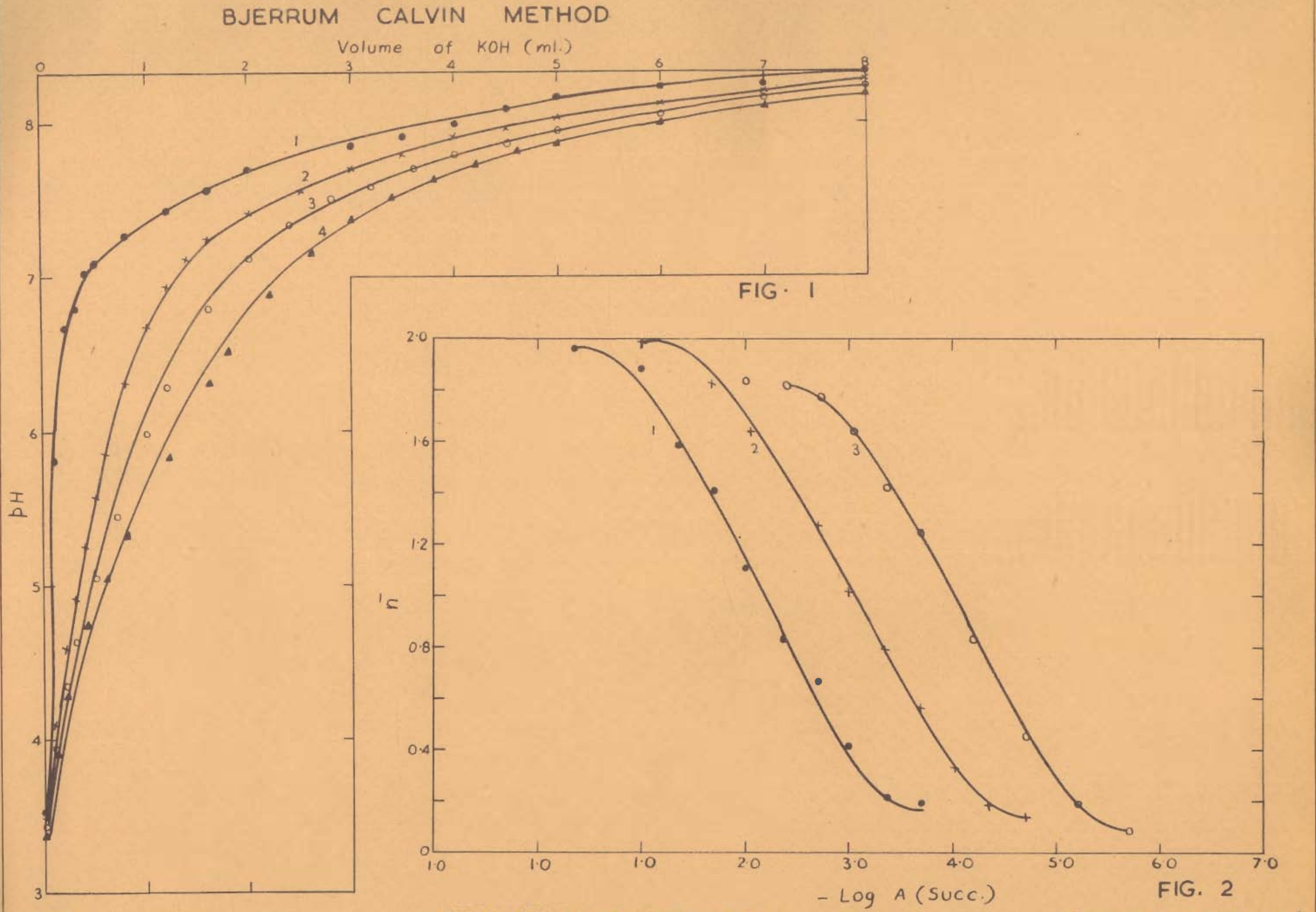
Calculations for formation curve.

For 0.7 ml. of 0.1 M $CuSO_4$ ≡ 0.7 x 10^{-4} moles.

pH	Δ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log succ.
4.0	0.100	0.100	0.143	5.6897
4.33	0.150	0.150	0.214	5.3573
4.67	0.250	0.250	0.356	5.0222
5.00	0.400	0.400	0.571	4.6948
5.33	0.575	0.575	0.821	4.3648
5.67	0.725	0.725	1.036	4.0304
6.0	0.900	0.900	1.286	3.7032
6.33	1.100	1.100	1.571	3.3736
6.67	1.250	1.250	1.786	3.0391
7.0	1.400	1.400	2.000	2.7116
7.33	1.400	1.400	2.000	2.3786
7.67	1.45	1.450	2.070	2.0424
8.0	1.45	1.45	2.070	1.7124

Fig.2, Curve 2.

BJERRUM CALVIN METHOD



FIG· 1

FIG. 2

FORMATION CURVES FOR Cu-SUCC. COMPLEX (AQUEOUS MEDIUM)

TABLE NO. 4.

20 ml. succinimide - 1.0 ml. $CuSO_4$ -1.0 ml. H_2SO_4 , total volume made upto 25 ml. by distilled water.

Vol. of KOH ml.	pH	Vol. of KOH ml.	pH
0.0	3.44	2.6	7.15
0.1	3.90	3.0	7.36
0.2	4.28	3.4	7.50
0.3	4.53	3.8	7.63
0.4	4.73	4.2	7.72
0.6	5.03	4.6	7.80
0.8	5.32	5.0	7.86
1.2	5.82	6.0	7.99
1.6	6.30	7.0	8.10
1.8	6.50	8.0	8.18
2.2	6.88	9.0	8.26

Fig. 1, Curve 4.

TABLE NO. 4 (A)

Calculations for formation curve.

For 1.0 ml. of 0.1 M $CuSO_4 \equiv 1.0 \times 10^{-4}$ moles.

pH	Δ KOH	Moles of KOH x 10^{-4}	$\bar{n}$	-log succ.
4.0	0.100	0.100	0.100	5.6897
4.5	0.225	0.225	0.225	5.1919
5.0	0.475	0.475	0.475	4.6961
5.5	0.850	0.850	0.850	4.2025
6.0	1.250	1.250	1.250	3.7092
6.33	1.500	1.500	1.500	3.3803
6.67	1.800	1.800	1.800	3.0482
7.0	1.95	1.95	1.95	2.7206
7.33	2.00	2.00	2.00	2.3884
7.67	2.00	2.00	2.00	2.0514
8.0	2.10	2.10	2.10	1.7230

Fig. 2, Curve 3.

For confirmation of the composition of copper-succinimide complex, copper sulphate alone and also in presence of succinimide solutions in proportions of 1:2 and 1:3 (Cu:Succinimide), were separately titrated against 0.1 M potassium hydroxide solution. Succinimide alone was also titrated against potassium hydroxide solution. Details of concentrations and volumes of the reactants used for this purpose are summarised below. Actual observations can be read from Fig.3.

TABLE NO.5.

Concentration of succinimide solution = 0.1 M

Concentration of copper sulphate solution = 0.1 M.

Strength of potassium hydroxide solution = 0.1 M.

Total volume in each set made upto 20 ml.

Vol. of $CuSO_4$ ml.	Vol. of succinimide ml.	$CuSO_4$: succinimide	Curve No.
0.0	15.0	-	1
5.0	0.0	-	2
5.0	10.0	1:2	3
5.0	15.0	1:3	4

Fig. 3

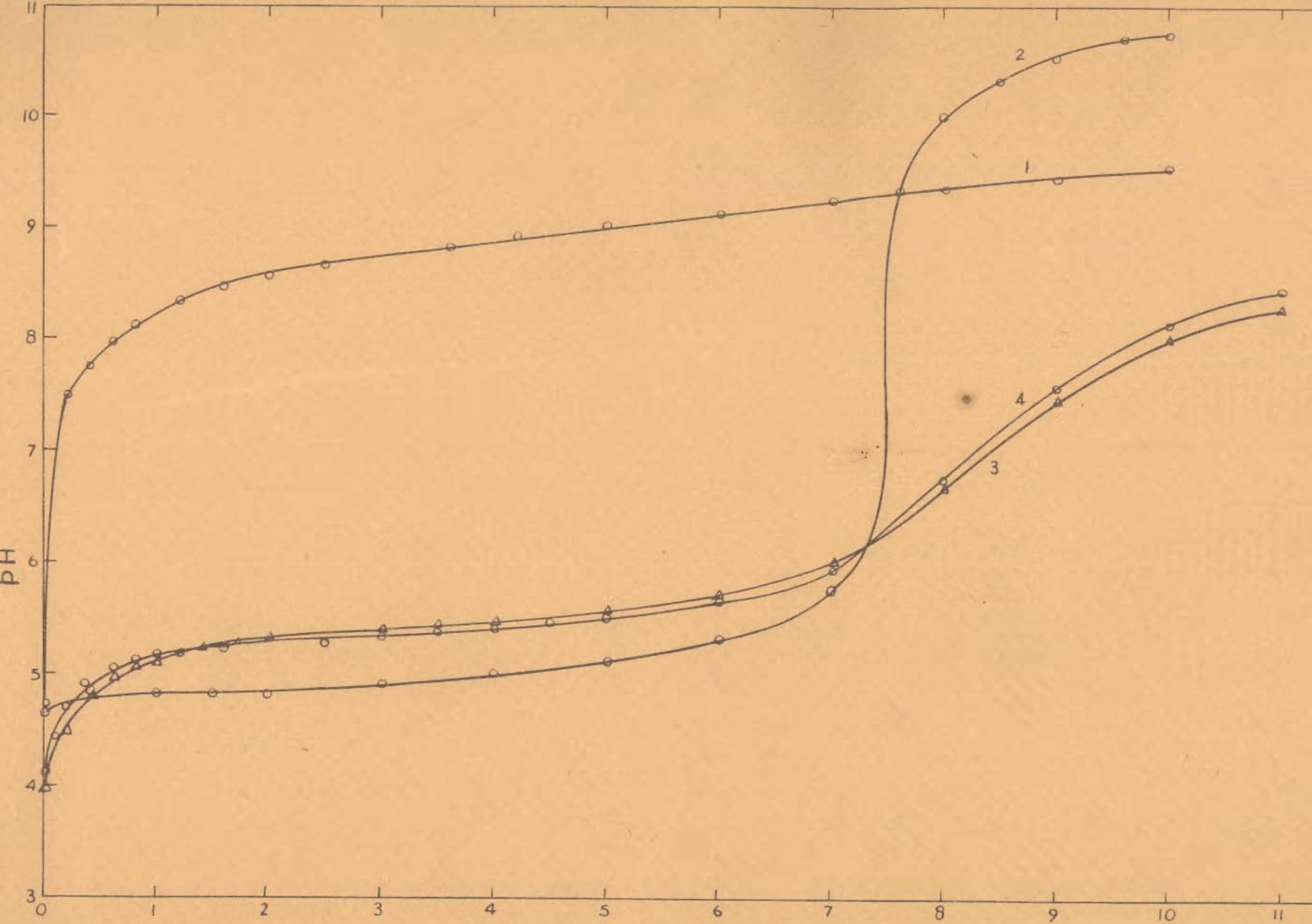


FIG. 3

Copper-saccharin complex, in methanolic medium

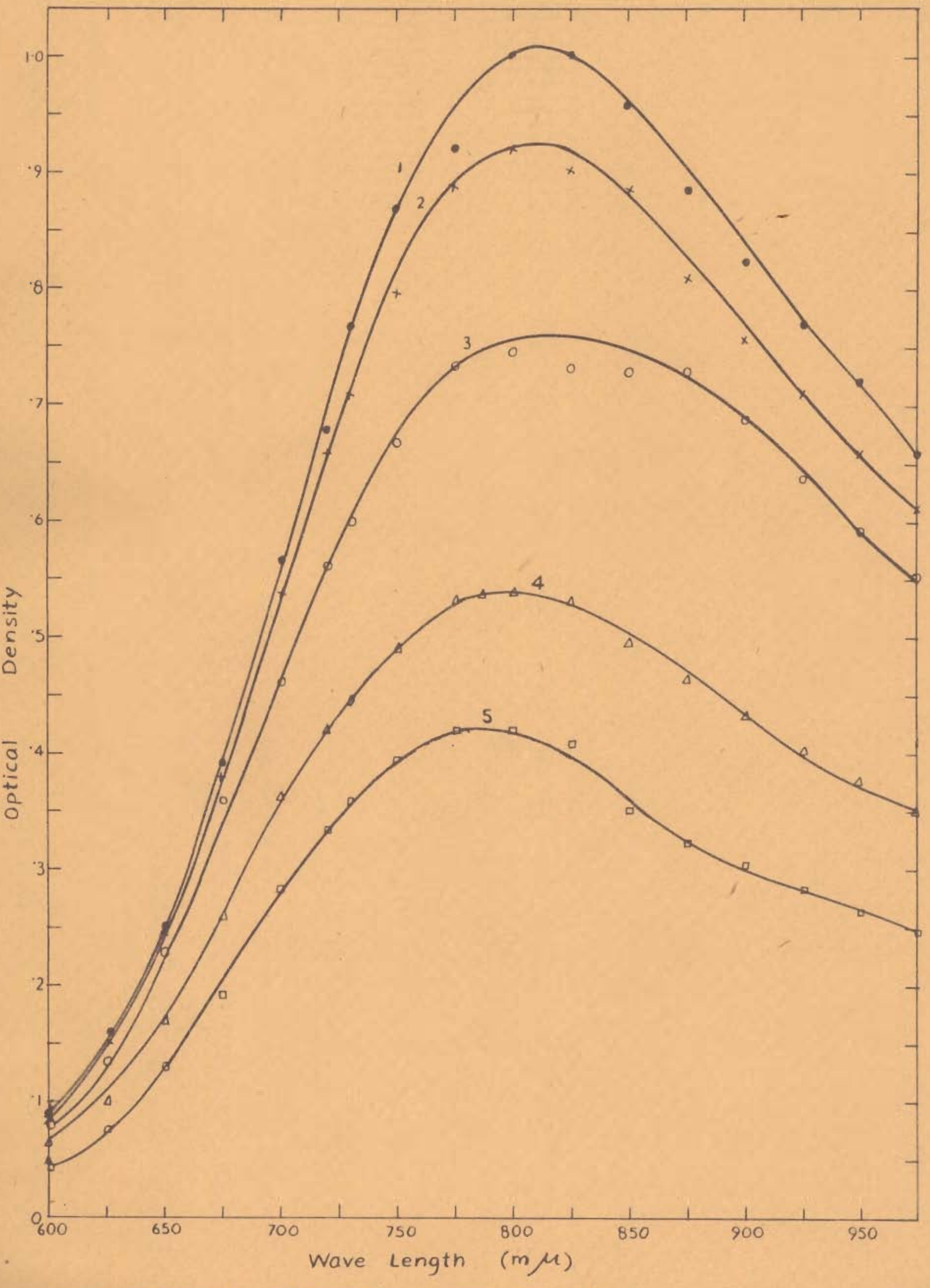
Spectrophotometric studies:- VosBurgh and Cooper's method (loc. cit.) was first of all employed to know the number of complexes formed by the interaction of copper sulphate with saccharin, in methanolic medium. The solutions of the reactants prepared in methanol (both of strength 0.04 M) were mixed in the ratios of copper sulphate to saccharin as 1:3, 1:2, 1:1, 2:1 and 3:1, by mixing 3.0, 4.0, 6.0, 8.0 and 9.0 ml. of copper sulphate to 9.0, 8.0, 6.0, 4.0 and 3.0 ml. of saccharin respectively. Optical density was measured at different wavelengths, ranging from 600 to 950 mu. All the mixtures gave maxima at 800 mu, showing thereby the formation of only one complex.

TABLE NO.6.

Concentration of the reactants = 0.04 M
Optical density of the mixtures prepared according to VosBurgh Cooper's method.

Wave length	Ratio of copper sulphate to saccharin				
mu	1:3	1:2	1:1	2:1	3:1
600	0.05	0.063	0.08	0.085	0.085
650	0.13	0.17	0.23	0.245	0.250
675	0.192	0.26	0.36	0.38	0.39
700	0.285	0.355	0.46	0.538	0.568
730	0.36	0.445	0.60	0.71	0.769
750	0.395	0.49	0.667	0.796	0.87
760	0.37	0.509	0.769	0.839	0.921
775	0.45	0.54	0.733	0.886	0.92
790	0.42	0.53	0.745	-	0.99
800	0.42	0.532	0.745	-	1.00
810	0.42	0.538	0.75	0.921	1.00
825	0.41	0.53	0.733	0.903	1.00
850	0.35	0.495	0.733	0.886	0.958
875	0.325	0.462	0.733	0.810	0.886
900	0.305	0.432	0.688	0.757	0.824
925	0.285	0.400	0.638	0.710	0.769
950	0.265	0.375	0.593	0.658	0.721

Fig.4



VOS BURGH COOPER'S METHOD (CU-SACCH. MIXTURES)

FIG · 4

VosBurgh Cooper's curves (Fig.4) gave the evidence for the existence of one complex only.

Job's method of continued variation:- Job's method was followed for determining the composition of the complex. Equimolar solutions of copper sulphate and saccharin, of concentrations, 0.0667 M, 0.05 M and 0.2 M, were mixed according to the method of continuous variation and O.D. measurements were carried out at wave lengths 660 and 710 mu. As the O.D. of copper sulphate was appreciable on the above wave lengths, the difference of O.D. of mixtures and copper sulphate, was plotted against the ratio, (Cu)/(Cu) + (Saccharin). The results are tabulated below:

TABLE NO. 7.

Concentration of saccharin = 0.0667 M

Concentration of copper sulphate = 0.0667 M.

Wave length 660 mu.

Vol. of $CuSO_4$ ml.	Vol. of saccharin. ml.	O.D. mixt.	O.D. $CuSO_4$	Difference
1.0	9.0	0.135	0.068	0.067
2.0	8.0	0.235	0.118	0.117
3.0	7.0	0.32	0.173	0.147
4.0	6.0	0.39	0.232	0.158
5.0	5.0	0.44	0.285	0.156
6.0	4.0	0.47	0.335	0.148
7.0	3.0	0.5157	0.38	0.136
8.0	2.0	0.523	0.435	0.088
9.0	1.0	0.53	0.48	0.05

Fig. 5, Curve 1.

TABLE NO. 8.

Concentration of saccharin = 0.0667 M.

Concentration of $CuSO_4$ sulphate = 0.667 M.

Wave length 710 mu.

Vol. of $CuSO_4$ ml.	Vol. of saccharin ml.	O. D. mixt.	O. D. $CuSO_4$	Difference
1.0	9.0	0.240	0.135	0.105
2.0	8.0	0.438	0.250	0.188
3.0	7.0	0.602	0.370	0.232
4.0	6.0	0.745	0.495	0.250
5.0	5.0	0.854	0.600	0.254
6.0	4.0	0.943	0.699	0.244
7.0	3.0	1.046	0.800	0.228
8.0	2.0	1.097	0.939	0.158
9.0	1.0	1.125	1.046	0.079

Fig.6, Curve 1.

TABLE NO. 9.

Concentration of saccharin =0.05 M.

Concentration of copper sulphate =0.05 M.

Wave length 660 mu.

Vol. of $CuSO_4$ ml.	Vol. of saccharin ml.	O. D. mixt.	O. D. $CuSO_4$	Difference
1.0	9.0	0.095	0.053	0.042
2.0	8.0	0.177	0.088	0.089
3.0	7.0	0.237	0.130	0.107
4.0	6.0	0.290	0.168	0.122
5.0	5.0	0.330	0.210	0.120
6.0	4.0	0.360	0.245	0.115
7.0	3.0	0.380	0.282	0.098
8.0	2.0	0.390	0.320	0.070
9.0	1.0	0.400	0.355	0.045

Fig. 5, Curve 2.

TABLE NO. 10.

Concentration of saccharin = 0.05 M.

Concentration of copper sulphate = 0.05 M.

Wave length 710 mu.

Vol. of $CuSO_4$ ml.	Vol. of saccharin ml.	O. D. mixt.	O. D. $CuSO_4$	Difference
1.0	9.0	0.173	0.105	0.068
2.0	8.0	0.325	0.190	0.135
3.0	7.0	0.445	0.280	0.165
4.0	6.0	0.553	0.365	0.188
5.0	5.0	0.638	0.450	0.188
6.0	4.0	0.710	0.530	0.180
7.0	3.0	0.769	0.607	0.162
8.0	2.0	0.810	0.688	0.122
9.0	1.0	0.834	0.770	0.064

Fig.6, Curve 2.

TABLE NO. 11.

Concentration of saccharin = 0.02 M.

Concentration of copper sulphate = 0.02 M.

Wave length 660 mu.

Vol. of $CuSO_4$ ml.	Vol. of saccharin ml.	O. D. mixt.	O. D. $CuSO_4$	Difference
1.0	9.0	0.042	0.024	0.018
2.0	8.0	0.065	0.040	0.025
3.0	7.0	0.090	0.056	0.034
4.0	6.0	0.112	0.073	0.039
5.0	5.0	0.127	0.088	0.039
6.0	4.0	0.142	0.102	0.040
7.0	3.0	0.153	0.120	0.033
8.0	2.0	0.160	0.135	0.025
9.0	1.0	0.170	0.145	0.025

Fig. 5, Curve 3.

JOB'S METHOD

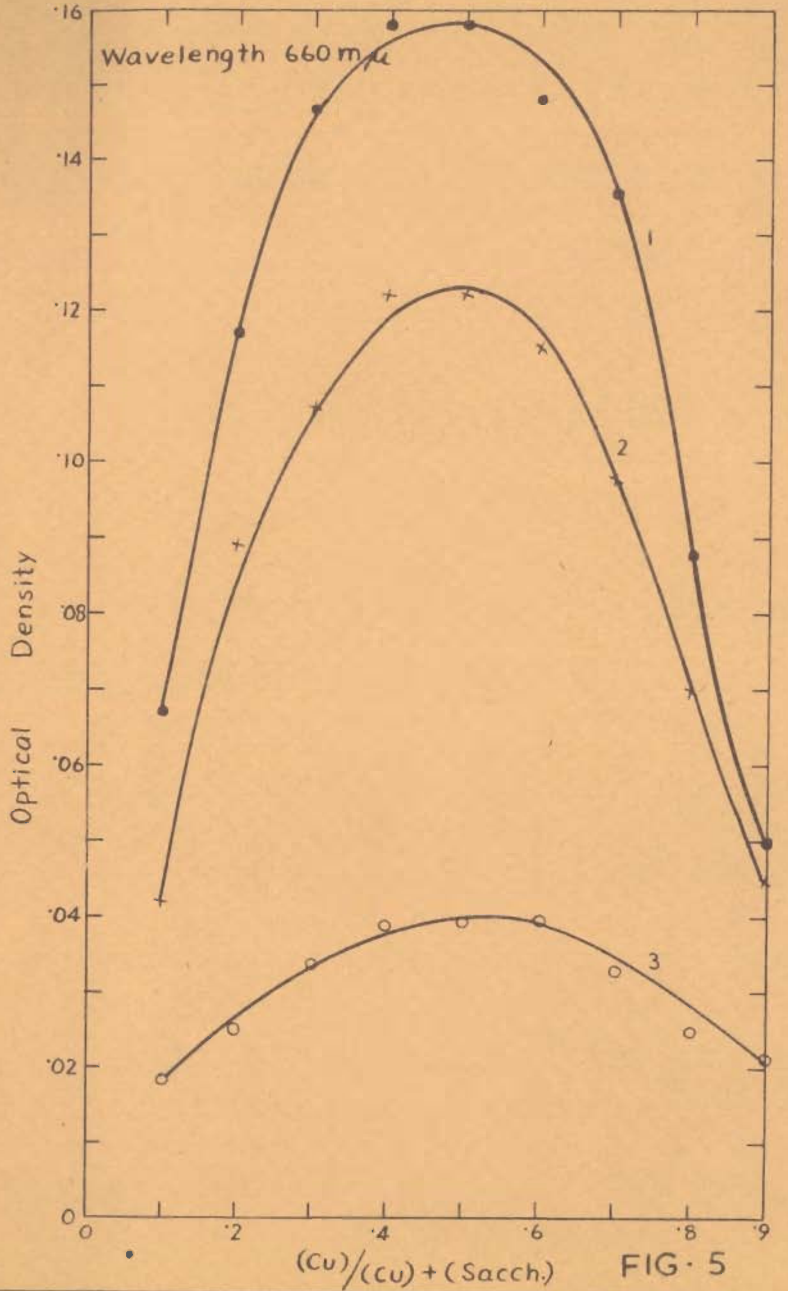


FIG · 5

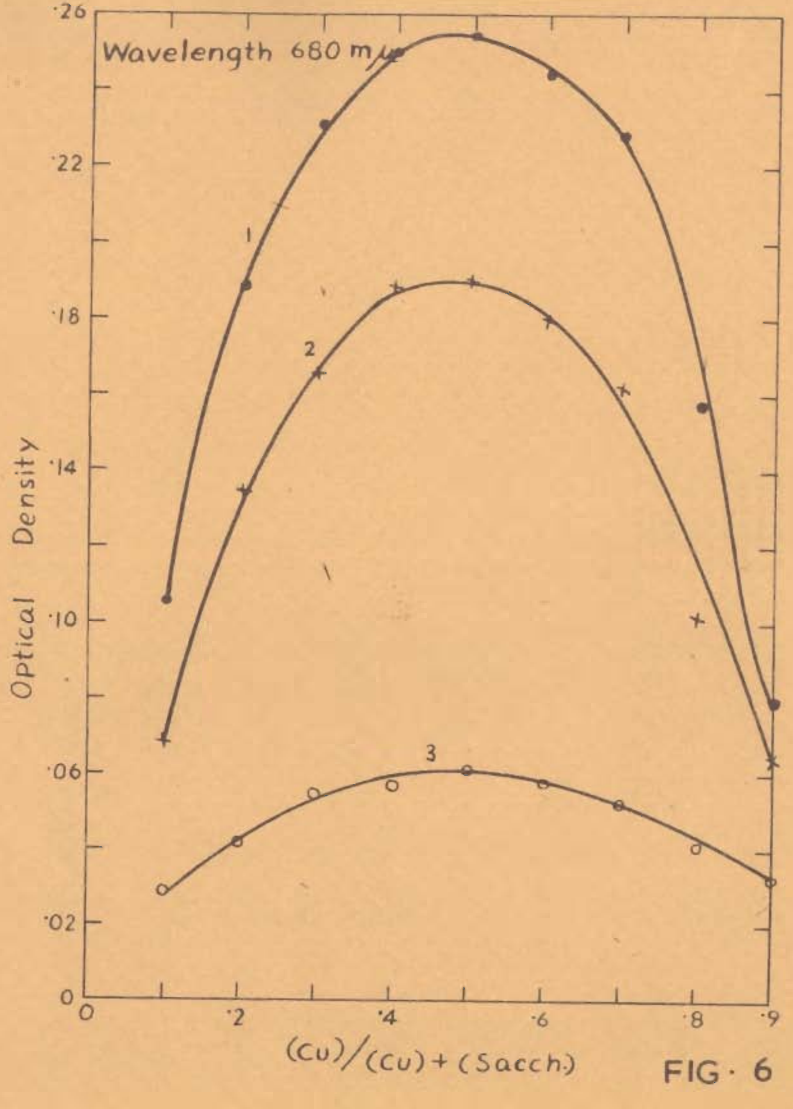


FIG · 6

TABLE NO. 12.

Wave length 710 mu.

Concentration of saccharin = 0.02 M.

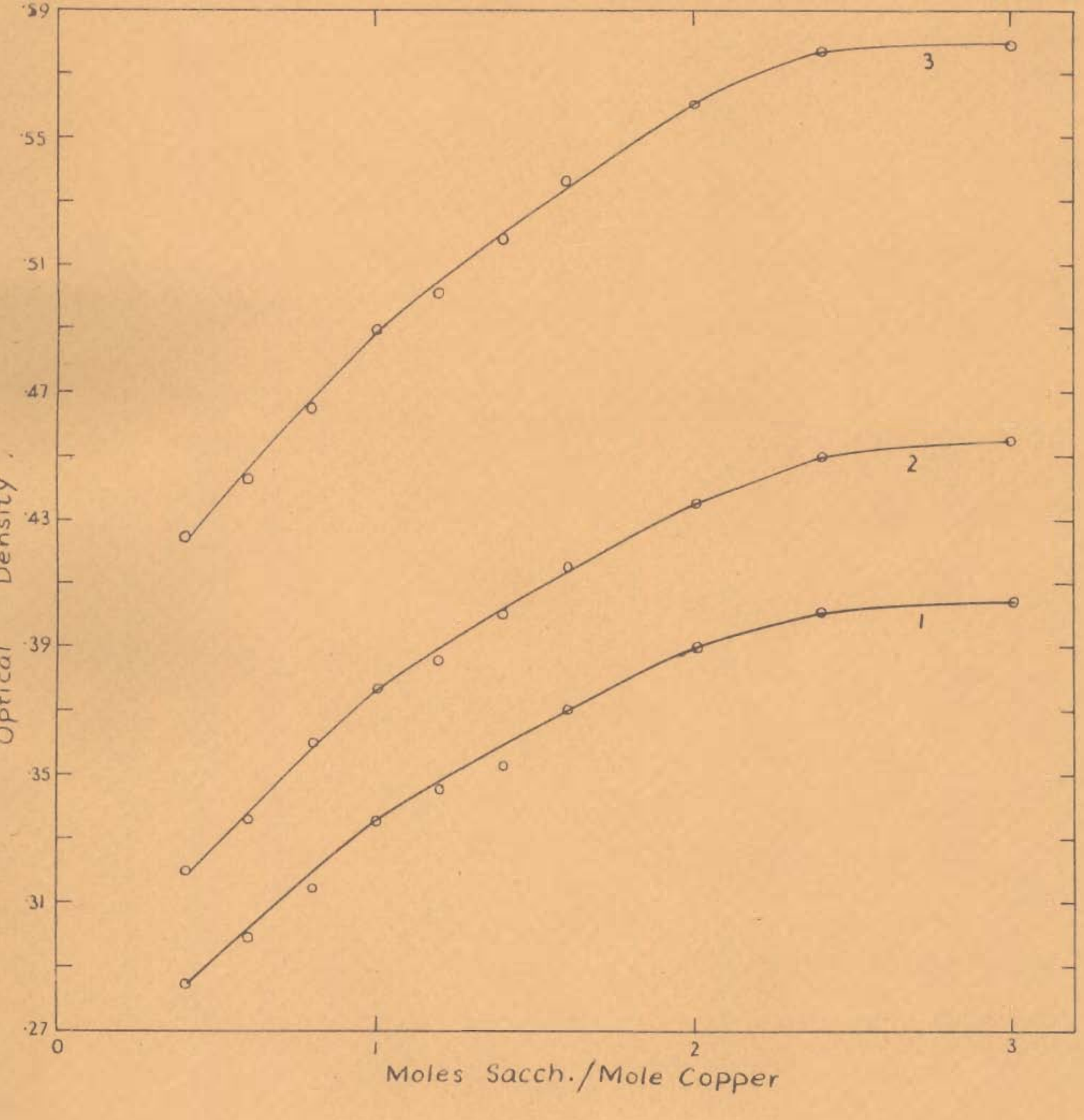
Concentration of copper sulphate = 0.02 M.

Vol. of $CuSO_4$ ml.	Vol. of Saccharin ml.	O. D. mixt.	O. D. $CuSO_4$	Difference
1.0	9.0	0.068	0.039	0.029
2.0	8.0	0.112	0.070	0.042
3.0	7.0	0.157	0.100	0.055
4.0	6.0	0.193	0.137	0.057
5.0	5.0	0.229	0.168	0.061
6.0	4.0	0.256	0.198	0.058
7.0	3.0	0.282	0.230	0.052
8.0	2.0	0.295	0.265	0.041
9.0	1.0	0.313	0.280	0.033

Fig.6, Curve 3.

Molar ratio method:

The results of Job's method were confirmed by molar ratio method. Solutions for this method were mixed keeping constant amount of copper and varying the concentration of saccharin. Experiments were performed at two concentrations of copper sulphate and O.D. measurements were made on different wave lengths. The results are given below:



MOLAR RATIO METHOD

FIG. 8

O.D.values of mixtures prepared according to the molar ratio method:

TABLE NO.13.

Volume of 0.04 M copper sulphate solution = 4.0 ml.

Concentration of saccharin solution = 0.08 M.

Total volume in each case was made upto 10 ml. by adding requisite volume of methyl alcohol.

Vol.of saccharin ml.	690 mu.	700 mu.	730 mu.	770 mu.	790 mu.	800 mu.
0.5	0.270	0.303	0.410	0.411	0.538	0.541
1.0	0.295	0.330	0.452	0.539	0.558	0.561
1.5	0.315	0.353	0.465	0.561	0.583	0.585
2.0	0.330	0.370	-	0.582	0.599	0.602
2.5	0.346	0.387	0.509	0.599	0.620	0.620
3.0	0.353	0.395	0.516	0.606	0.622	0.629
3.5	0.365	0.410	0.523	0.615	0.633	0.636
4.0	0.376	0.420	0.539	0.630	0.650	0.652
5.0	0.400	0.421	0.546	0.633	0.648	0.648
6.0	0.402	0.424	0.547	0.634	-	0.650
	Curve 1.	Curve 2.	Curve 3.	Curve 1.	Curve2.	Curve 3.
		Fig.7			Fig.9	

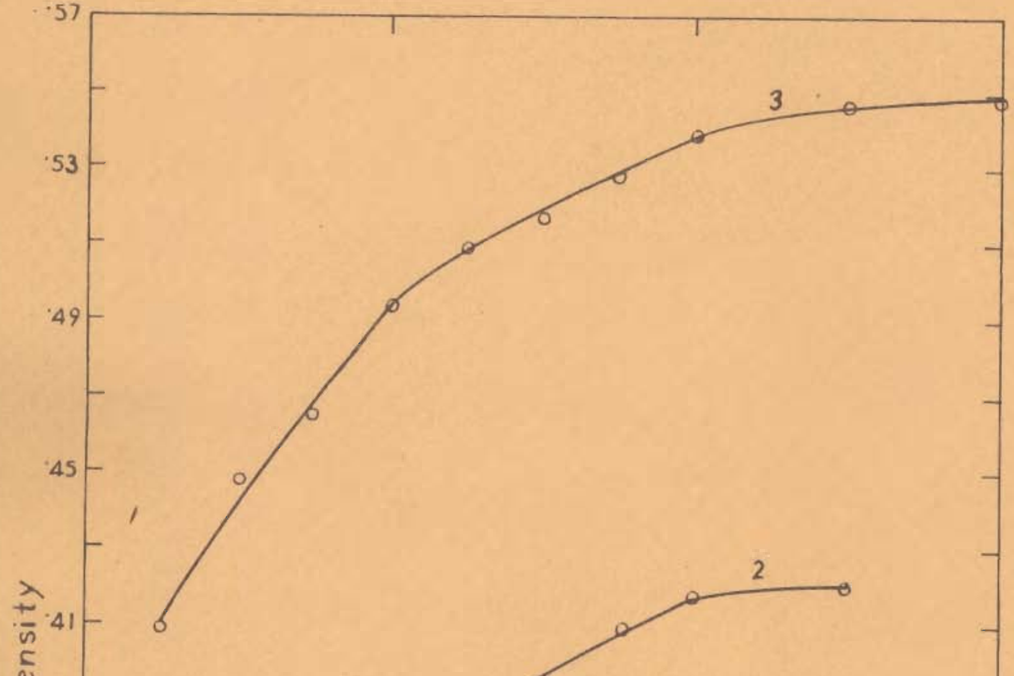
TABLE NO.14.

Volume of 0.04 M copper sulphate solution = 5.0 ml.

Concentration of saccharin solution = 0.08 M.

Total volume in each case was made upto 12 ml.by adding requisite volume of methyl alcohol.

Vol.of saccharin ml.	690 mu.	700 mu.	730 mu	770 mu.	800 mu.
1.0	0.285	0.320	0.425	0.523	0.545
1.5	0.299	0.335	0.442	0.533	0.559
2.0	0.314	0.360	0.465	0.561	0.583
2.5	0.335	0.380	0.490	0.586	0.607
3.0	0.345	0.385	0.500	0.597	0.620
3.5	0.352	0.400	0.519	0.614	0.634
4.0	0.370	0.415	0.538	0.634	0.654
5.0	0.390	0.435	0.560	0.653	0.675
6.0	0.400	0.450	0.577	0.668	0.684
7.0	0.403	0.455	0.578	0.700	0.680
	Curve 1.	Curve 2.	Curve 3.	Curve 1.	Curve 2.
		Fig. 8		Fig.11	



MOLAR RATIO METHOD

FIG· 7

Another method, which is in common with spectrophotometric methods, is the slope ratio method. This method not only provides a confirmation of the results of Job's and Molar ratio methods, but also helps in establishing the ratio of colour forming radicals to the metal ions. In the reaction $mA + nB = Am\,Bn$, if the concentration of B is constant and in sufficient excess to make dissociation negligible, the equilibrium concentration of the complex Am Bn will be essentially proportional to the analytical concentration of A, added in the reaction; so

$$(Am\,Bn) = C_A / m \quad ..... (1)$$

where the brackets refer to equilibrium concentration and C the analytical or total concentration. From Beer's law there is the relation $E = e\,d\,(Am\,Bn)$ ....(2), where E is the measured extinction, e the molecular extinction coefficient and d the thickness of the cell in cm.. Substituting the value of Am Bn from (1) and (2)

$$E = e\,d\ C_A / m \quad ....(3)$$

E is plotted against different analytical concentrations of A, keeping the concentration of B constant and in excess. Over the straight line portion of the curve, equation (3) is valid and this straight line will have a slope given by, $\text{Slope}_1 = e\,d / m$ .... (4)

Similarly if A is the component in constant excess and the concentration of B is varied,

$$Am\,Bn = C_B / n \quad ......(5)$$

If E is plotted against C_B, the slope of the straight line portion of the curve will be,

$$\text{Slope}_2 = e\,d / n \quad \ldots\ldots\ldots \quad (6)$$

The ratio of n to m in the complex may be determined by taking ratio of two slopes.

$$\text{Slope}_1 / \text{Slope}_2 = n/m$$

Further confirmation of the composition of copper saccharin complex was sought for. For this purpose slope ratio method was employed. Following two sets of experiments were performed.

Set I. Where the concentration of copper sulphate was kept constant and that of saccharin was varied. The results of the experiments performed for molar ratio method were used for plotting curves of this set also, vide Table No.13, Fig.9, Curve 1 to 3 ; and Table No.14, Fig.11, Curve 1 and 2.

Set 2. Concentration of saccharin constant, while that of copper sulphate varying. Here difference of O.D. of the mixtures and copper sulphate was plotted as the increase in O.D. was not due to complex ion formation only but also due to the presence of free copper sulphate. The results are tabulated in the following tables;

Concentration of saccharin solution = 0.04 M.

Strength of copper sulphate solution = 0.08 M.

Total volume made up = 10 ml.

TABLE NO. 15.

Wave length 770 mu.

Vol. of saccharin ml.	Vol. of $CuSO_4$ ml.	O.D. mixt.	O.D. $CuSO_4$	Difference
4.0	0.5	0.166	0.107	0.059
4.0	1.0	0.312	0.202	0.110
4.0	1.3	0.400	0.260	0.140
4.0	1.7	0.500	0.323	0.186
4.0	2.0	0.573	0.373	0.205

Fig. 10, Curve 1.

TABLE NO. 16.

Wave length 790 mu.

Vol. of saccharin ml.	Vol. of $CuSO_4$ ml.	O.D. mixt.	O.D. $CuSO_4$	Difference
4.0	0.5	0.168	0.112	0.056
4.0	1.0	0.320	0.216	0.104
4.0	1.3	0.405	0.275	0.130
4.0	1.7	0.526	0.345	0.181
4.0	2.0	0.594	0.395	0.199

Fig. 10, Curve 2.

TABLE NO. 17.

Wave length 800 mu.

Vol. of saccharin ml.	Vol. of $CuSO_4$ ml.	O.D. mixt.	O.D. $CuSO_4$	Difference
4.0	0.5	0.165	0.118	0.047
4.0	1.0	0.320	0.217	0.103
4.0	1.3	0.403	0.278	0.125
4.0	1.7	0.527	0.350	0.177
4.0	2.0	0.597	0.400	0.197

Fig. 10, Curve 3.

SLOPE RATIO METHOD : Cu-SACCHARIN COMPLEX

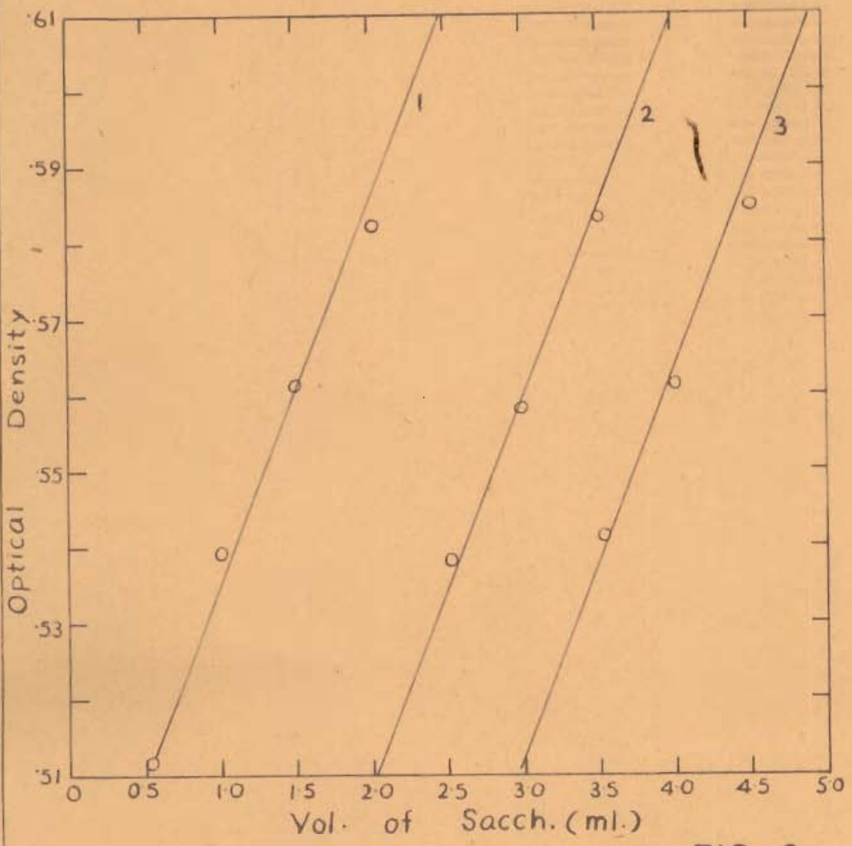


FIG. 9

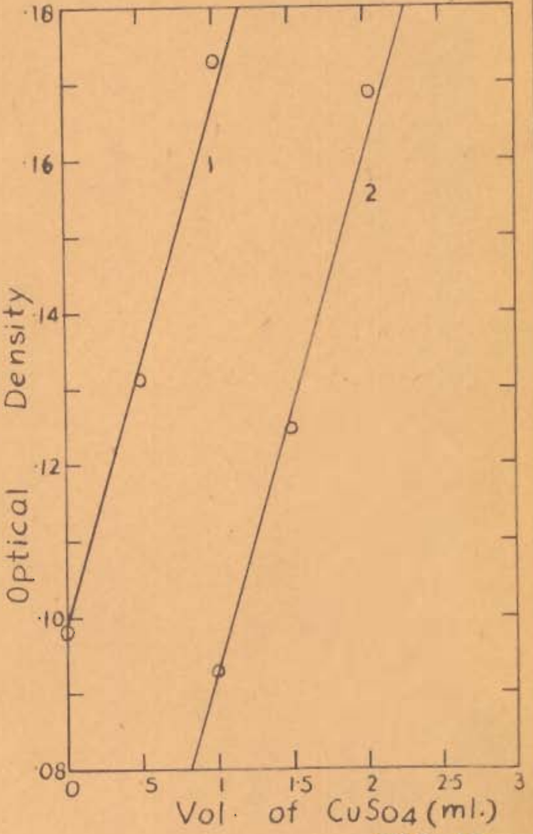


FIG. 12

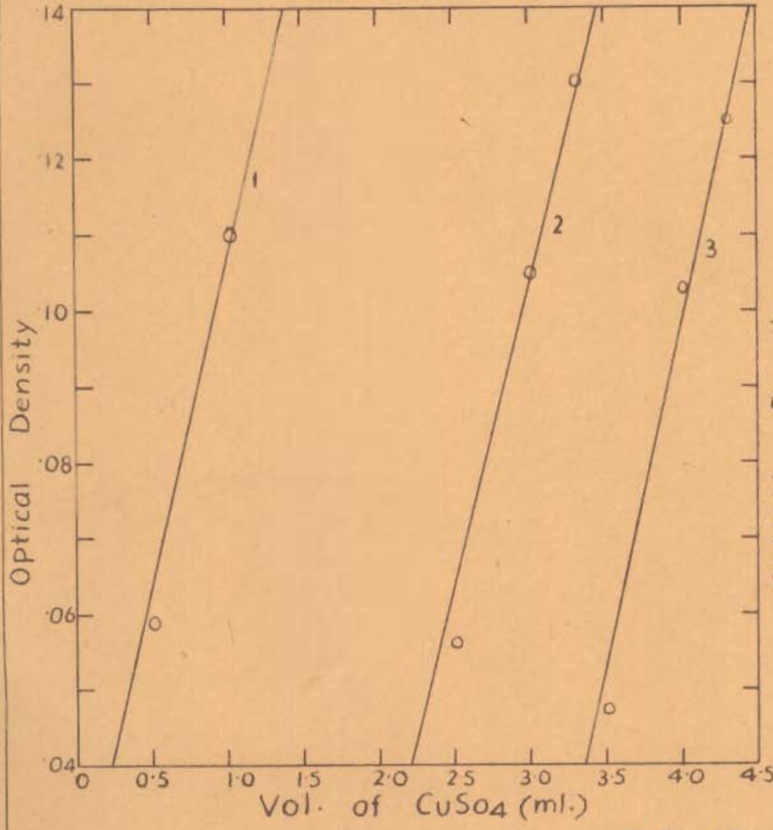


FIG. 10

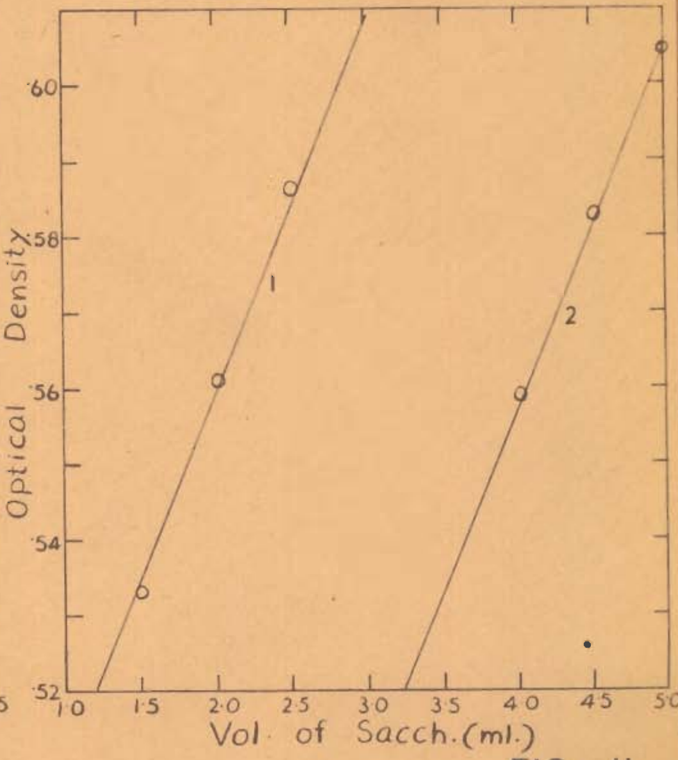


FIG. 11

Concentration of saccharin solution = 0.04 M.

Strength of copper sulphate solution = 0.08 M.

Total volume made up = 12 ml.

TABLE NO.18.

Wave length 770 mu.

Vol. of saccharin ml.	Vol. of $CuSO_4$ ml.	O. D. mixt.	O. D. $CuSO_4$	Difference
5.0	0.50	0.138	0.091	0.047
5.0	1.0	0.266	0.168	0.098
5.0	1.5	0.385	0.245	0.131
5.0	2.0	0.495	0.322	0.173
5.0	2.5	0.606	0.395	0.211

Fig.12, Curve 1.

TABLE NO.19.

Wave length 790 mu.

Vol. of saccharin ml.	Vol. of $CuSO_4$ ml.	O. D. mixt.	O. D. $CuSO_4$	Difference
5.0	0.5	0.140	0.095	0.045
5.0	1.0	0.272	0.179	0.093
5.0	1.5	0.395	0.270	0.125
5.0	2.0	0.511	0.342	0.169
5.0	2.5	0.623	0.415	0.208

Fig.12, Curve 2.

TABLE NO.20.

Wave length 800 mu.

Vol. of saccharin ml.	Vol. of $CuSO_4$ ml.	O. D. mixt.	O. D. $CuSO_4$	Difference
5.0	0.5	0.139	0.095	0.044
5.0	1.0	0.273	0.181	0.092
5.0	1.5	0.395	0.273	0.122
5.0	2.0	0.513	0.350	0.163
5.0	2.5	0.629	0.425	0.204

Fig. 12, Curve 3.

Stability constant of copper-saccharin complex:

For determining the stability constant of copper-saccharincomplex, two sets of mixtures were prepared by the method of continued variation. The optical density (not the difference) was plotted against the ratio(Cu)/(Cu)+ (saccharin According to Anderson's method, for 1:1 complex stability constant K is given by the equation,

$$K = \frac{X}{(a-X)(b-X)} \quad \text{when } X = \frac{a_1 b_1 - a_2 b_2}{(a_1 + b_1)-(a_2 + b_2)}$$

, a and b are having their usual significance(described in Chapter I)

TABLE NO. 21.

O.D. values for stability constant of copper saccharin complex.

Set I. Concentration of the reactants = 0.0667 M.

Set II. Concentration of the reactants = 0.05 M.

Vol. of $CuSO_4$ ml.	Vol. of saccharin ml.	O.D. set I.	O.D. Set II.
1.0	9.0	0.135	0.095
2.0	8.0	0.235	0.177
3.0	7.0	0.320	0.237
4.0	6.0	0.390	0.290
5.0	5.0	0.440	0.330
6.0	4.0	0.470	0.360
7.0	3.0	0.516	0.380
8.0	2.0	0.523	0.390
9.0	1.0	0.530	0.400
	Fig.13.	Curve 1.	Curve 2.

Conductometric titrations:

Conductometric titrations of saccharin against copper sulphate, in the methanolic medium, were carried out at four different concentrations in order to confirm the above results. Only direct titrations (metal ion as the titrant) could be possible. Volume correction, V + v / V was applied in order to minimise the dilution error(V and v having their usual significance). The readings for these titrations are tabulated below:

Readings for conductometric titrations: $CuSO_4$ in the cell.

TABLE NO. 22.

Vol. of copper sulphate solution = 10.0 ml.

Concentration of saccharin solution = 0.2 M

Strength of copper sulphate solution = 0.04 M.

Vol. of saccharin ml.	Corrected conductance (mhos x 10^{-3})	Volume of saccharin ml.	Corrected conductance (mhos x 10^{-3})
0.0	0.5076	2.3	1.493
0.3	0.7407	2.6	1.538
0.6	0.9434	3.0	1.587
0.9	1.0870	3.4	1.613
1.2	1.2200	3.8	1.695
1.5	1.3700	4.2	1.724
1.8	1.408	4.6	1.732
2.0	1.4490	5.0	1.754

Fig.14, Curve 1.

10 ml. of 0.04 M $CuSO_4$

≡ 1.9 ml. of 0.2 M saccharin≡ 8.5 ml. of 0.04 saccharin

Cu : saccharin = 1:0.85.

TABLE NO. 23.

Volume of copper sulphate solution =12 ml.

Concentration of saccharin solution =0.2 M.

Strength of copper sulphate solution =0.04 M.

Vol. of saccharin ml.	Corrected conductance (mhos x10^{-3})	Volume of saccharin ml.	Corrected conductance (mhos x 10^{-3})
0.0	0.6250	2.4	1.493
0.4	0.8547	2.8	1.515
0.8	1.031	3.2	1.562
1.2	1.176	3.6	1.684
1.6	1.266	4.0	1.724
2.0	1.370	-	-

Fig.14, Curve 2.

12 ml. of 0.04 M $CuSO_4$

≡ 2.4 ml. of 0.2 M saccharin ≡ 12.0 ml. of 0.04 M saccharin.

Cu : saccharin = 1:1

TABLE NO. 24.

Vol. ofcopper sulphate solution = 14 ml.

Concentration of saccharin solution = 0.2 M.

Strength of copper sulphate solution = 0.04 M.

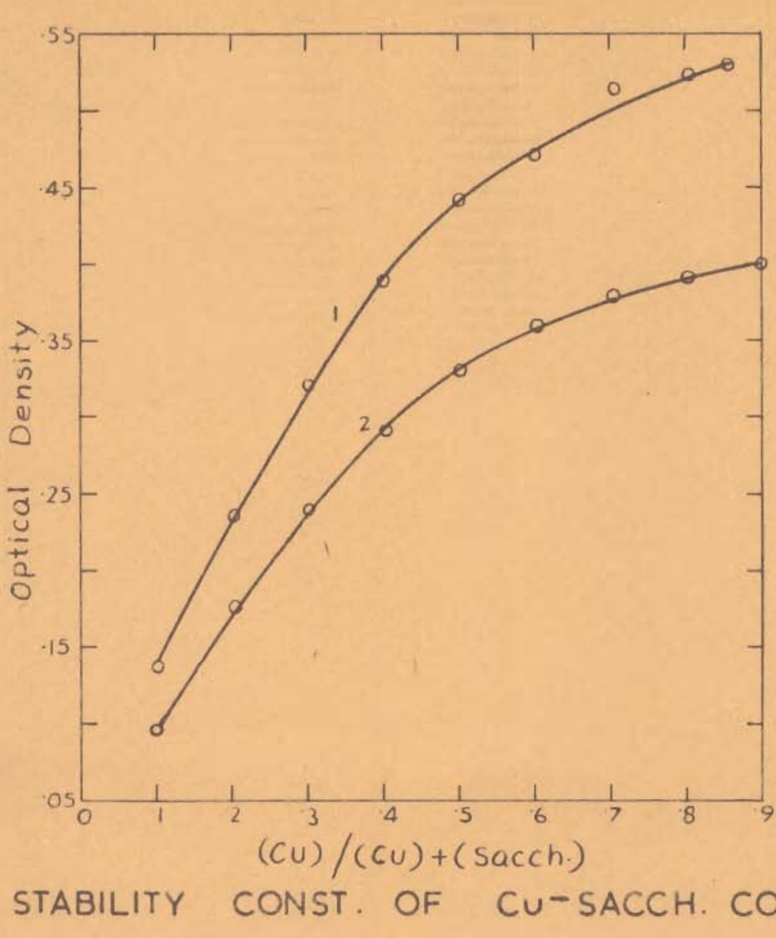
Vol. of saccharin ml.	Corrected conductance (mhos x 10^{-3})	Vol. of saccharin ml.	Corrected conductance (mhos x 10^{-3})
0.0	0.5780	2.8	1.471
0.5	0.7519	3.4	1.515
1.0	0.9346	4.0	1.587
1.5	1.1240	4.5	1.613
2.0	1.3160	5.0	1.695
2.4	1.4290	-	-

Fig.14, Curve 3.

14.0 ml. of 0.04 M $CuSO_4$

≡ 2.6 ml. of 0.2 M saccharin ≡ 13.0 ml. of 0.04 M saccharin

Cu : saccharin=1:0.93.



STABILITY CONST. OF Cu-SACCH. COMPLEX

FIG · 13

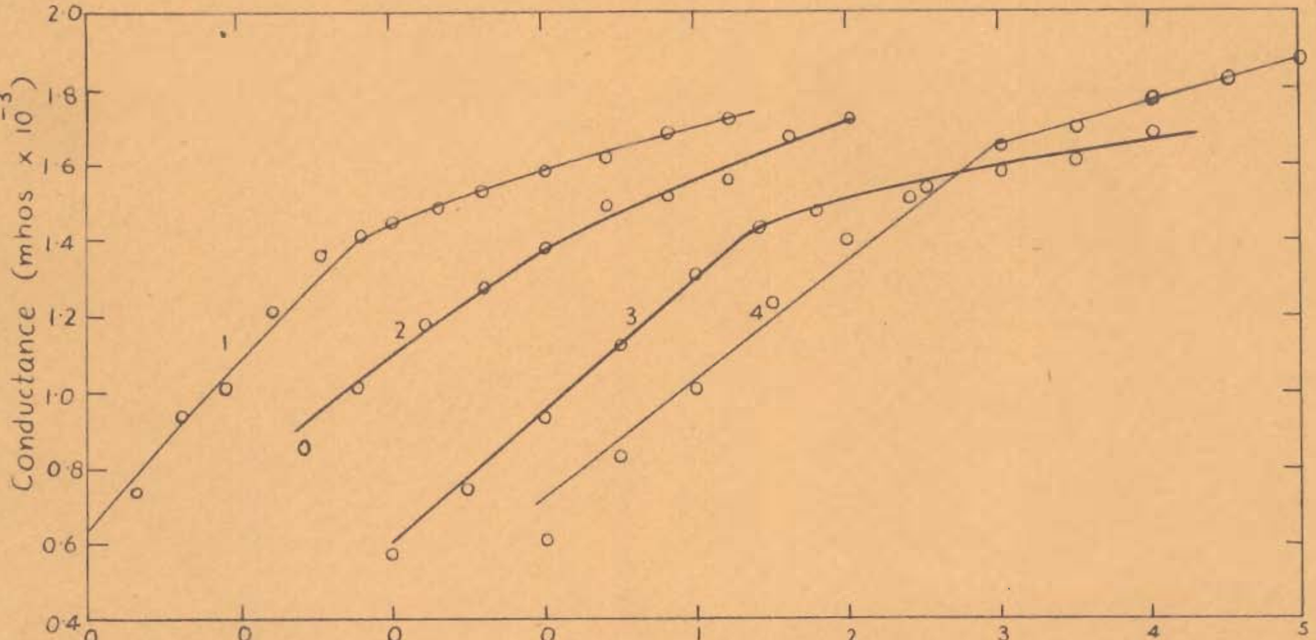


FIG · 14

TABLE NO. 25.

Volume of copper sulphate solution = 16 ml.

Concentration of saccharin solution = 0.2 M.

Strength of copper sulphate solution = 0.04 M.

Vol. of saccharin ml.	Corrected conductance (mhos x10^{-3})	Vol. of saccharin ml.	Corrected conductance (mhos x10^{-3})
0.0	0.6098	3.0	1.639
0.5	0.8333	3.5	1.695
1.0	1.0200	4.0	1.770
1.5	1.2350	4.5	1.818
2.0	1.3990	5.0	1.860
2.5	1.5380	-	-

Fig.14, Curve 4.

16 ml. of 0.04 M $CuSO_4$

≡ 3.1 ml. of 0.2 M saccharin ≡ 15.5 ml. of 0.04 M saccharin

Cu : saccharin = 1:0.97

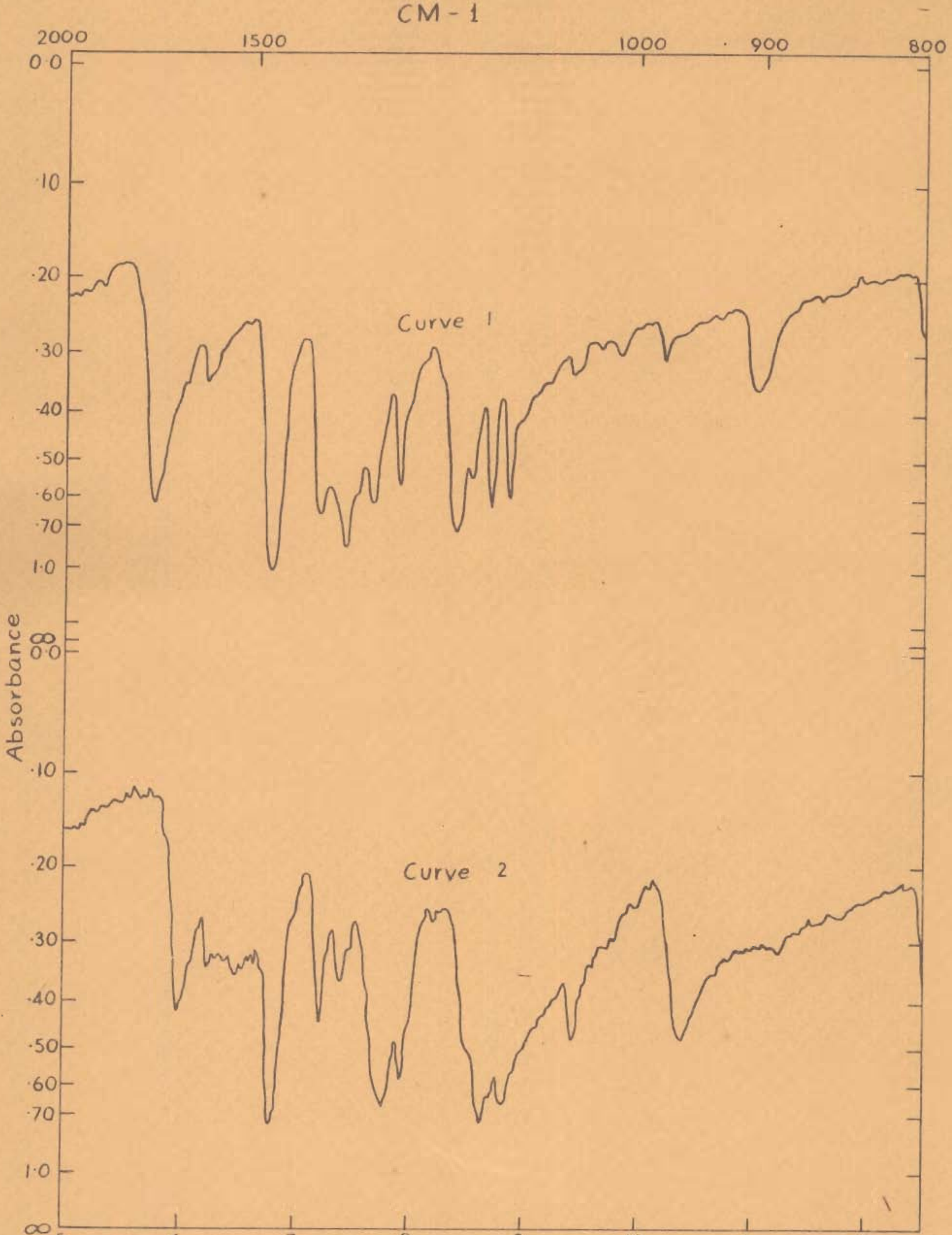
Isolation and chemical analysis:

200 ml. of 0.1 M copper sulphate solution was added to an equal volume of 0.1 M saccharin solution. The resulting mixture was concentrated by the method of evaporation under vacuum, when the blue coloured complex was obtained. Copper was estimated in the complex, gravimetrically as cuprous thiocynate and nitrogen by Kjeldahl's method. The results of the analysis are as follows:

Percentage of copper = 17.84

Percentage of nitrogen = 4.32

I.R. studies:- Infra-red spectra of the complex and saccharin were recorded by the method of fast scanning in nujol medium by Perkin and Elmer infra-cord. (Fig. 15)



Curve 1. Saccharin

Curve 2. Cu-Saccharin Complex

I. R. SPECTRA

FIG. 15

DISCUSSION

Soluble copper-succinimide complex, formed in aqueous medium:

From pH-metric studies typical titration curves were obtained, both with and without the presence of copper sulphate (Fig.1). The horizantal distance (excess of alkali consumed) between the two curves, at any value of pH, provided the amount of protons of succinimide liberated, by complexion i.e. the amount of ligand complexed. This value divided by the total metal ion in the system, afforded the value of $\bar{n}$. Thus at various values of pH a set of $\bar{n}$ values was determined and the concentration of free ligand (A^-) was calculated. This value of $\bar{n}$ was found to increase with pH and attained a maximum value of two suggesting thereby, formation of 1:2 complex. The values of $\bar{n}$ were plotted against the corresponding values of -log (A^-) (Fig.2). As a first approximation, the values of -log (A^-) at $\bar{n}$ = 0.5 and 1.5 were equal to log K_1 (4.65) and log K_2 (3.60) respectively. These temporary constants were corrected by Bjerrum's method of successive approximations. For this case spreading factor x, introduced by Bjerrum, is given by $K_1/K_2 = 4x^2$ and the formation function is given by,

$$\bar{n} = \frac{2\,x\,k\,(A^-) + 2\,k^2(A^-)^2}{1 + 2\,x\,k\,(A^-) + k^2(A^-)^2}$$

where k stands for average constant and is given by

$$k = (K_1K_2)^{1/2}$$

Corrected values of $\bar{n}$, obtained by solving equations for each corresponding value of (A^-), were then plotted against

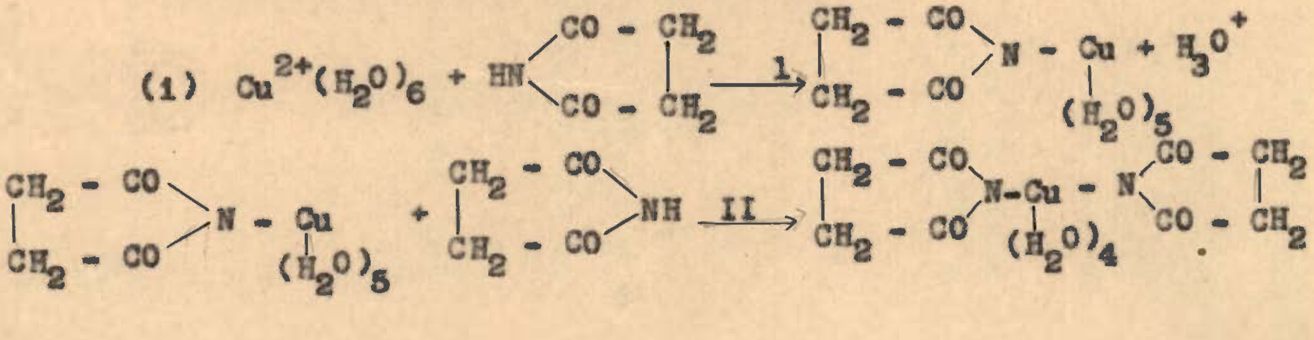
$-\log(A^-)$. The final values of $\log K_1$, $\log K_2$ and $\log K$ (over all stability constant) were 4.75, 3.41 and 8.17 respectively as shown below:

<u>Stepwise and over all stability constants</u>.

Curves	$\log K_1$ at $\bar{n}=0.5$	$\log K_2$ at $\bar{n}=1.5$	Over all stability constant $\log K=\log K_1+\log K_2$	Mean log K.
1	4.80	3.50	8.30	
2	4.75	3.40	8.15	8.17
3	4.70	3.35	8.05	

Fig. 2

Further confirmation of 1:2 (copper-succinimide) composition of the complex was afforded from the titration curves depicted in (Fig.3). Since a shift towards lower pH range was realised, it was concluded that hydrogen ions are definitely liberated due to complex ion formation. Moreover, since a inflexion, corresponding to the ratio of 2 moles of KOH : 1 mole of $CuSO_4$, was found to exist in the titration curves of copper sulphate-succinimide mixtures, it could be concluded that the number of molecules of succinimide involved in the reaction was also two. The reaction of succinimide and cupric ions below pH 8, may be represented by either of the following reactions,



higher pH range and precipitation of copper hydroxide took place.

VosBurgh and Cooper's method (Fig.4) suggested the formation of only one complex. The maximum peak appeared at 800 mu (methanolic solution of copper sulphate gave peak at 810 mu). Though the shift in the maximum was not very appreciable,yet change in absorbance on complexion was appreciable within the wavelength region 690 to 800 mu.

Keeping the above limitations in view Job's and other spectrophotometric studies were carried out in the wavelength region,690 to 800 mu.

From the Job's curves it could be seen that in each case the combining ratio of copper and saccharin comes out to be 1:1 (Figs.5 and 6).

Further support to the conclusions of Job's method was available from molar and slope ratio methods.Experiments carried out with different concentrations of the reactants gave typical molar ratio curves (Figs.7 and 8). The break in the curve and constancy in absorbance occurred at a higher molar ratio (copper : saccharin) than 1:1,which may be due to the dissociating nature of the complex. This method was,therefore,not expected to give a precise information about the composition of the complex.

Slope ratio method was also tried. First set (Figs.9 and 11) of experiments was carried out keeping metal concentration constant and varying the amount of saccharin . In the second set ,constant concentration of saccharin was mixed with varying amounts of copper sulphate. For this second set, the difference of optical density was plotted (Figs.10 and 12). This modification had to be made because on adding copper sulphate the increase in absorbance might not only be due to complexion but also due to free copper sulphate. The presence of free copper sulphate has been attributed to the dissociation of the complex. The above experiments gave parallel straight lines. From these results it could be precisely concluded that copper reacts with saccharin in 1:1 ratio.

Stability constant of complex:

The stability constant of 1:1 copper saccharin complex was determined by Anderson's method using equations 1 and 2, page 44(Fig.13). The value of the stability constant K was found to be, 3.015×10^2 .

Conductometric titrations:

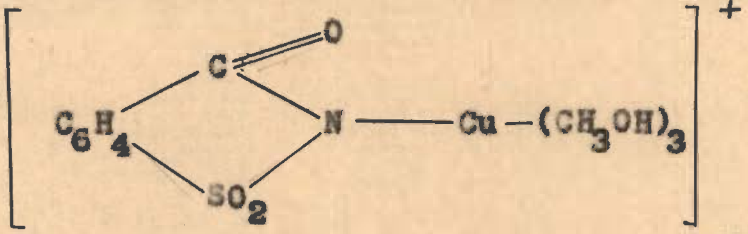
The titrations between copper sulphate and saccharin exhibited only one break for all concentrations of the reactants, confirming thereby the formation of 1:1 (copper-saccharin) complex(Fig.14, Curves 1-4).

I.R.Spectrum of the complex:

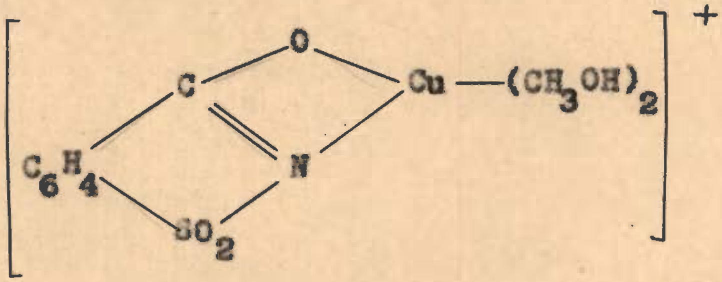
I.R.Spectra of saccharin and its 1:1 complex with copper (Fig.15) showed a decrease in the carbonyl frequency from 1735 to 1665 cm^{-1}, just as in case of succinimide and phthalimide complexes. The band due to SO_2 group at 1190 cm^{-1} is also shifted to lower frequency 1160 cm^{-1}. An OH stretching band is also shown in the spectrum probably due to the presence of methyl-alcohol in the complex.

On the basis of the above results, either of the following structures may be assigned to the complex,

(i)



(ii)



Preferably the first structure may be assigned to this complex, since results of chemical analysis are in better agreement with this formula.

CHAPTER V.

Cobalt complexes of succinimide and phthalimide (non biuret reaction mechanism).

INTRODUCTION

Cobalt complexes of biuret, peptides, proteins, diacid-imides and of related compounds are rarely reported in the literature on account of their unstable nature. Miller and Li (1) determined the configuration of the red species obtained on oxygenation of cobalt complexes of leucyl tyrosines(LT) employing magnetic, polarographic, pH metric and ion exchange studies. They showed that the structure was same as that of the corresponding glycyl-glycine complex. The postulated structure was$((LT)_2\ Co - (O_2) - (OH) - Co\ (LT)_2)$.

Magneto chemical studies of cobalt, nickel and copper with amides and imides were carried out by Cambi and Tremolada (2). In this work authors have dealt various classes of copper, nickel, and cobalt complexes, derived from amides and imides, which give the biuret reaction. But their studies were limited to chemical analysis of the complex and due consideration was not given to the various aspects controlling the stability of these complexes. This could have been possible if attempts were made to elucidate the nature and composition of these complexes by physico-chemical methods.

Preliminary investigations revealed that cobalt chloride did not undergo complex - ion with imides in aqueous medium, both in acidic and alkaline ranges. This reaction was therefore, tried in completely methanolic medium, so as to avoid hydrolytic and other decomposing influences of water. It was then observed that cobalt reacted with succinimide and phthalimide in presence of methanolic potassium hydroxide to give complexes, violet in colour, which gradually changed to pinkish violet on keeping.

The colour of the complexes was distinctly different from the colour of the turbid solution, obtained on adding caustic potash to the methanolic solution of cobalt chloride.

The interaction of cobalt with glutarimide and saccharin was also tried under conditions favourable for such complex-ion but unlike copper and nickel cobalt did not form complexes with these imides.

Another interesting point worth noting in study of these complexes was the strong solvation tendency of cobalt ions with methyl alcohol. Due consideration was given to this aspect also while describing the structure of these complexes. Z. Luz (3) showed that Co^{++} ions with Cl^- ions in methanol at temperatures between -60 and 80°C forms an octahedral monochloro complex ($Co(MeOH)_5\ Cl)^+$. Two kinds of cobalt (II) complexes which are easily distinguished by their colour are pink complexes that are six fold co-ordinated and have an octahedral structure and blue complexes that are four fold co-ordinated and have tetrahedral structure.

EXPERIMENTAL

Methods used for preparing methanolic solutions of succinimide, phthalimide and potassium hydroxide were the same as described earlier. Stock solution of cobalt(II) chloride was prepared by dissolving the reagent, B.D.H. (A.R.) in methanol and the metal estimated gravimetrically after precipitating as cobalt ammonium phosphate. For spectrophotometric and conductometric studies imide solutions were prepared in equivalent amount of potassium hydroxide.

Spectrophotometric studies were carried out with the help of Bausch and Lomb spectronic '20' after allowing sufficient warming up period.

pH measurements were made with a Cambridge bench type pH-meter in conjuction with Cambridge glass electrode and S.C.E.

Philips conductivity bridge was employed for performing conductrometric titrations.

Composition of cobalt (II) succinimide complex in methanolic medium by spectrophotometric methods:

First of all VosBurgh and Cooper's method was employed for determining the number of complexes formed and also for selecting suitable wavelengths for applying Job's and other spectrophotometric methods. Mixtures of solutions having different proportion(1:4,1:3,1:2,1:1) of cobalt and succinimide were prepared maintaining the sum of concentrations of cobalt and succinimide as 0.0333 M. Optical density measurements were made immediately after mixing the solutions.

TABLE NO. 1.

Optical density of methanolic solutions of coblat chloride.

Wave length	O.D. of $CoCl_2$ solutions of concentration.			
mu	0.008M	0.01M	0.012M	0.017M
325	0.007	0.008	0.015	0.016
330	0.009	0.005	0.013	0.020
335	0.008	0.008	0.012	0.018
340	0.009	0.005	0.010	0.016
345	0.007	0.003	0.010	0.015
350	0.006	0.006	0.009	0.012
360	0.007	0.004	0.010	0.010
380	0.009	0.005	0.012	0.013
400	0.007	0.008	0.010	0.018
425	0.012	0.012	0.020	0.030
440	0.025	0.027	0.036	0.054
450	0.031	0.042	0.052	0.075
460	0.045	0.055	0.073	0.105
470	0.056	0.070	0.093	0.135
480	0.079	0.085	0.108	0.165
500	0.090	0.114	0.145	0.210
520	0.100	0.130	0.162	0.240
525	0.100	0.126	0.159	0.237
540	0.080	0.105	0.135	0.198
560	0.048	0.062	0.078	0.119
580	0.021	0.028	0.037	0.060
600	0.012	0.013	0.017	0.028
625	0.008	0.007	0.010	0.018

Fig. 1.

One peak is obtained for cobalt chloride methanolic solution at 520 mu.

TABLE NO. 2.

Optical density of mixtures prepared according to VosBurgh and Cooper's method:

Concentration of cobalt chloride = 3.33×10^{-2} M.

Concentration of succinimide = 3.33×10^{-2} M.

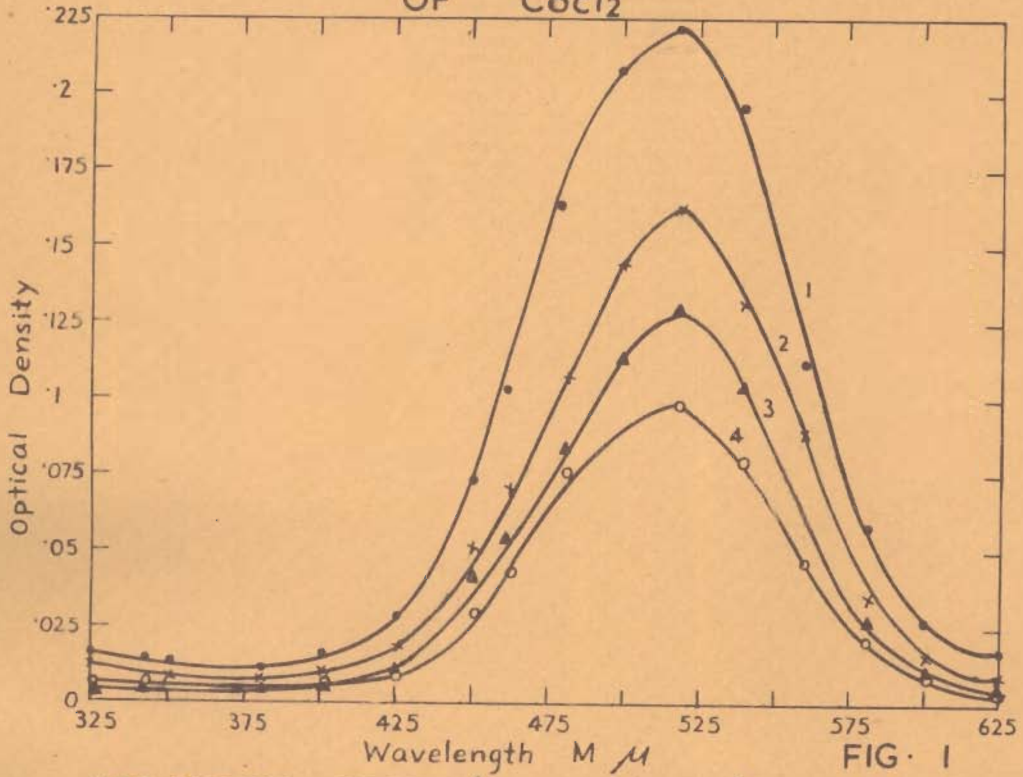
Wavelength	Ratio of cobalt chloride to succinimide.			
mu	1:4	1:3	1:2	1:1
325	0.185	0.202	0.232	0.155
340	0.115	0.125	0.140	0.090
350	0.083	0.083	0.097	0.065
375	0.043	0.043	0.050	0.038
400	0.033	0.031	0.035	0.037
425	0.038	0.042	0.050	0.055
450	0.067	0.080	0.100	0.131
475	0.097	0.115	0.163	0.212
500	0.108	0.135	0.195	0.270
520	0.115	0.145	0.200	0.285
530	0.112	0.140	0.190	0.270
550	0.100	0.127	0.152	0.212
575	0.087	0.091	0.097	0.130
600	0.060	0.068	0.067	0.080
625	0.040	0.047	0.045	0.051

Fig. 2.

Peak is obtained at 520 mu.

The above absorbance curves (Fig.1 and 2) suggested that the maxima in methanolic solution of cobalt chloride and its complex with succinimide occurred at the same wave-length (520 mu.).But the absorbance of cobalt-succinimide solutions was quite appreciable in the wave-length region 325-350 mu.,while absorbance of cobalt chloride solution was negligible in this region of wave-length. Therefore experiments for the composition of cobalt succinimide complex could be carried out in the

O.D. CURVES FOR METHANOLIC SOLUTION OF $CoCl_2$



FIG· 1

VOS BURGH COOPER'S METHOD (Co SUCC. MIXTURES)

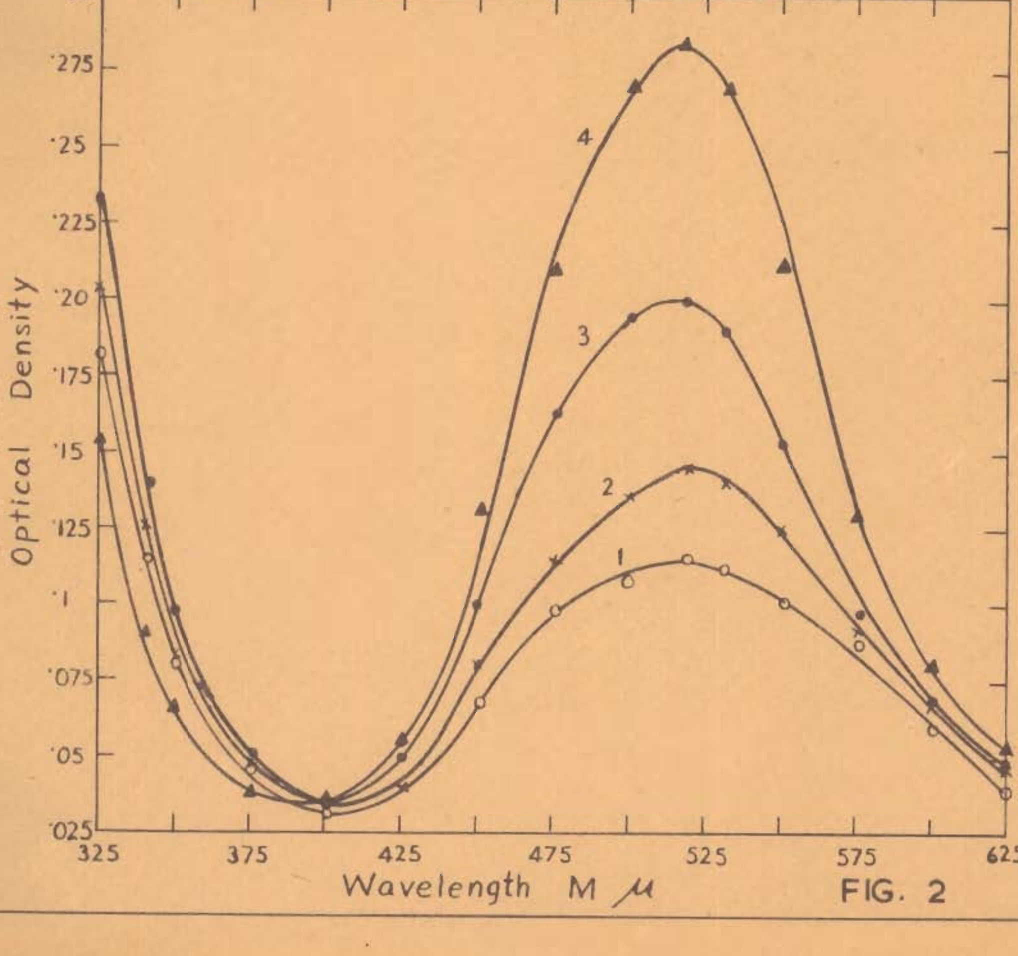


FIG. 2

above wave-length region.

Job's method of continued variation was followed for determining the composition of the complex. Equimolecular solutions of cobalt chloride and succinimide were mixed according to the method of continuous variation and optical density measurements were carried out at several wave-lengths. Experiments were performed at three concentrations of the reactants (0.04 M, 0.033 M and 0.0286 M) and optical density of the mixtures was plotted against the fraction (Co) / (Co) + (succinimide). The results are given below:

TABLE NO. 3.

Concentration of cobalt chloride = 0.04 M.

Concentration of succinimide = 0.04 M.

Vol. of $CoCl_2$ ml.	Vol. of succinimide. ml.	O. D. 325 mu	O. D. 330 mu	O. D. 335 mu	O. D. 340 mu.
0.5	9.5	0.078	0.070	0.062	0.057
1.0	9.0	0.135	0.122	0.108	0.093
1.5	8.5	0.165	0.142	0.135	0.115
2.0	8.0	0.213	0.183	0.155	0.140
2.5	7.5	0.235	0.208	0.175	0.150
3.0	7.0	0.265	0.232	0.200	0.168
3.5	6.5	0.280	0.250	0.205	0.178
4.0	6.0	0.240	0.212	0.178	0.145
5.0	5.0	0.153	0.128	0.102	0.085
6.0	4.0	0.120	0.100	0.080	0.068
7.0	3.0	0.098	0.080	0.067	0.052
8.0	2.0	0.075	0.067	0.060	0.050

Fig.3.

TABLE NO. 4.

Concentration of cobalt chloride = 0.0333 M.

Concentration of succinimide = 0.0333 M.

Vol. of $CoCl_2$ ml.	Vol. of succinimide. ml.	O.D. 325 mu	O.D. 330 mu	O.D. 335 mu	O.D. 340 mu
1.0	9.0	0.105	0.093	0.077	0.064
1.5	8.5	0.143	0.125	0.108	0.087
2.0	8.0	0.180	0.162	0.135	0.112
3.0	7.0	0.227	0.200	0.165	0.140
3.5	6.5	0.232	0.200	0.168	0.145
4.0	6.0	0.200	0.175	0.148	0.120
5.0	5.0	0.158	0.135	0.112	0.092
5.5	4.5	0.130	0.115	0.093	0.073
6.0	4.0	0.121	0.099	0.081	0.071
7.0	3.0	0.091	0.083	0.070	0.060

Fig. 4.

TABLE NO. 5.

Concentration of cobalt chloride = 0.0286 M.

Concentration of succinimide = 0.0286 M.

Vol. of $CoCl_2$ ml.	Vol. of succinimide. ml.	O.D. 325 mu	O.D. 330 mu	O.D. 335 mu	O.D. 340 mu
1.0	9.0	0.084	0.077	0.060	0.050
1.5	8.5	0.110	0.098	0.078	0.062
2.0	8.0	0.130	0.108	0.087	0.069
2.5	7.5	0.160	0.133	0.102	0.085
3.0	7.0	0.179	0.148	0.121	0.100
4.0	6.0	0.143	0.115	0.093	0.072
5.0	5.0	0.095	0.078	0.062	0.045
6.0	4.0	0.071	0.058	0.042	0.030
7.0	3.0	0.045	0.037	0.024	0.018
8.0	2.0	0.029	0.022	0.013	0.006

Fig.5.

JOB'S METHOD

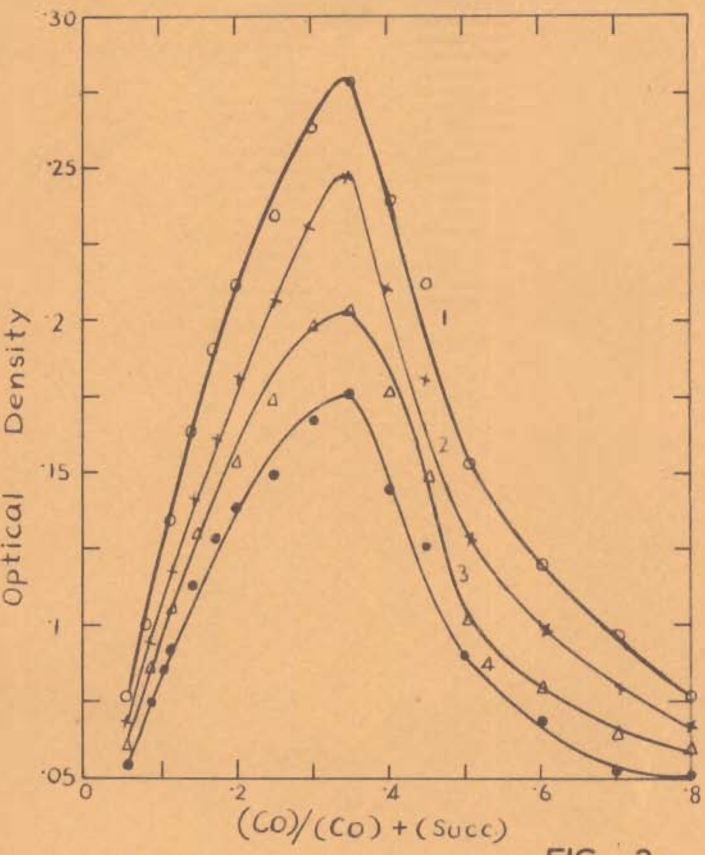


FIG. 3

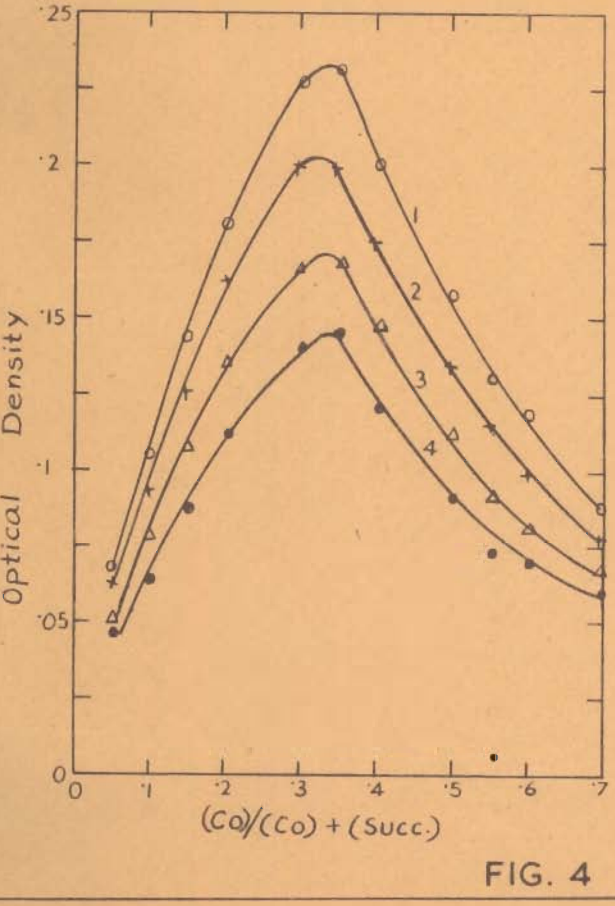


FIG. 4

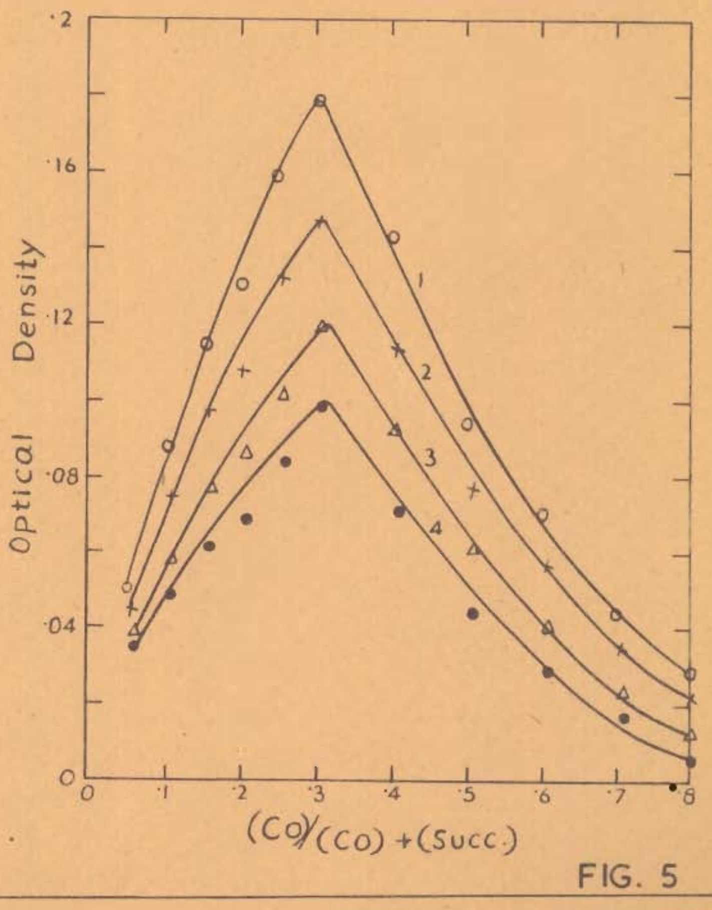


FIG. 5

Molar ratio method:- For obtaining confirmation of the results of Job's method, experiments employing molar ratio method were also performed. Solution were mixed according to the method described earlier(keeping constant amount of cobalt chloride and varying the concentration of succinimide. Here too three concentrations of metal ion were used for determining the composition of the complex. Following results were obtained:

TABLE NO. 6.

Volume of 0.0333 M cobalt chloride solution = 3 ml.

Concentration of succinimide solution = 0.0667 M.

Total volume made up by methyl alcohol = 8 ml.

Vol. of $CoCl_2$ ml.	Vol. of succinimide. ml.	O. D. 325 mu	O. D. 330 mu	O. D. 335 mu	O. D. 340 mu
3.0	0.5	0.176	0.163	0.150	0.140
3.0	1.0	0.186	0.176	0.158	0.146
3.0	1.5	0.206	0.187	0.170	0.151
3.0	2.0	0.227	0.208	0.182	0.162
3.0	2.5	0.261	0.238	0.205	0.173
3.0	3.0	0.300	0.270	0.230	0.195
3.0	3.5	0.305	0.272	0.231	0.198
3.0	4.0	0.310	0.275	0.231	0.198
3.0	4.0	0.310	0.277	0.230	0.200
3.0	5.0	0.301	0.276	0.231	0.192

Fig.6

TABLE NO. 7.

Volume of 0.0222 M cobalt chloride solution =5 ml.

Concentration of succinimide solution = 0.0667 M.

Total volume made up by methyl alcohol = 10 ml.

Vol. of $CoCl_2$ ml.	Vol. of succinimide, ml.	O.D. 325 mu	O.D. 330 mu	O.D. 335 mu	O.D. 340 mu
5.0	1.0	0.055	0.047	0.036	0.030
5.0	1.5	0.078	0.065	0.050	0.039
5.0	2.0	0.113	0.095	0.075	0.060
5.0	2.5	0.160	0.130	0.100	0.083
5.0	3.0	0.208	0.176	0.146	0.116
5.0	3.3	0.210	0.180	0.150	0.120
5.0	4.0	0.212	0.180	0.148	0.118
5.0	4.5	0.214	0.183	0.150	0.120
5.0	5.0	0.212	0.181	0.148	0.118

Fig. 7.

TABLE NO. 8.

Volume of 0.0222 M cobalt chloride solution = 3.0 ml.

Concentration of succinimide solution = 0.0667 M.

Total volume made up by methyl alcohol = 8 ml.

Vol. of $CoCl_2$ ml.	Vol. of succinimide, ml.	O.D. 325 mu	O.D. 330 mu	O.D. 335 mu	O.D. 340 mu
3.0	0.4	0.083	0.073	0.063	0.050
3.0	0.8	0.100	0.089	0.073	0.060
3.0	1.1	0.110	0.100	0.087	0.071
3.0	1.4	0.128	0.110	0.096	0.080
3.0	1.7	0.162	0.135	0.115	0.090
3.0	2.0	0.183	0.153	0.125	0.104
3.0	2.4	0.192	0.165	0.135	0.110
3.0	2.8	0.194	0.167	0.136	0.110
3.0	3.2	0.193	0.165	0.134	0.110

Fig. 8.

Stability constant of cobalt-succinimide complex:- Method of Anderson was used here also for calculating stability constant of the above complex. Two sets of mixtures of the reactants of concentrations 0.0333 M and 0.0286 M, were prepared according to the method of continuous variation. The optical density and not the difference was then plotted against the ratio (Co) /(Co) + (succinimide), at wave-length 325 mu. The equation for 1:2 (metal-ligand), complex described in Chapter I, was used for calculating stability constant, K.

TABLE NO. 9.

O.D. values for stability constant.

I Set. Concentration of the reactants= 0.0286 M.

II Set. Concentration of the reactants =0.0333 M.

Vol. of $CoCl_2$ ml.	Vol. of succinimide ml.	O.D. Set I.	O.D. Set II.
0.5	9.5	0.05	0.068
1.0	9.0	0.084	0.105
1.5	8.5	0.110	0.143
2.0	8.0	0.130	0.180
3.0	7.0	0.179	0.227
4.0	6.0	0.143	0.200
5.0	5.0	0.095	0.158
6.0	4.0	0.071	0.121
7.0	3.0	0.045	0.091

Fig. 9.

Spectrophotometric method could not be employed for determining the composition of cobalt-phthalimide complex due to its insoluble nature. However, the conductometric and pH metric methods could be successfully employed in this case.

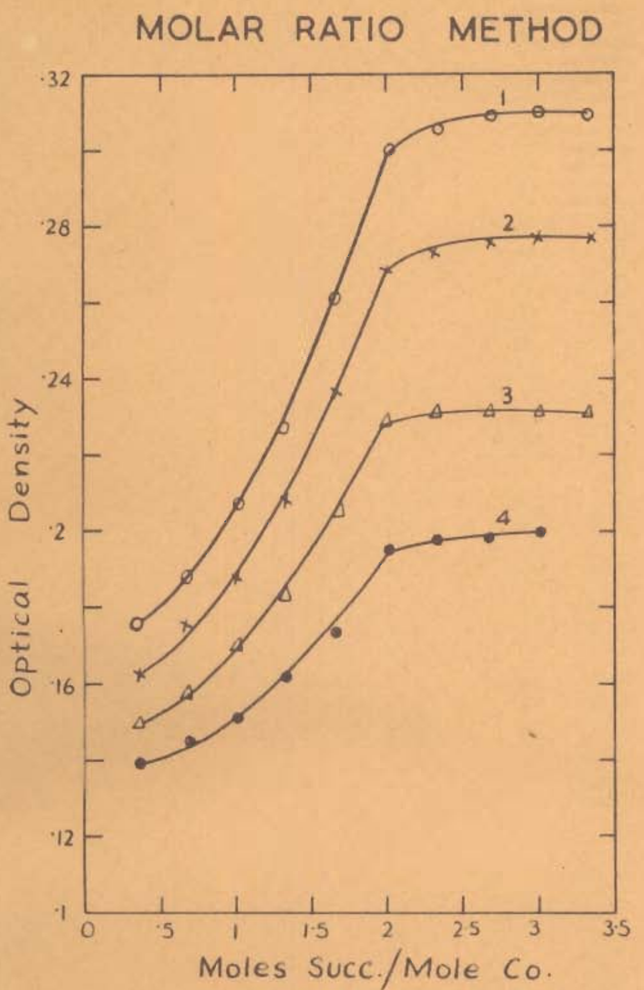

MOLAR RATIO METHOD

FIG. 6

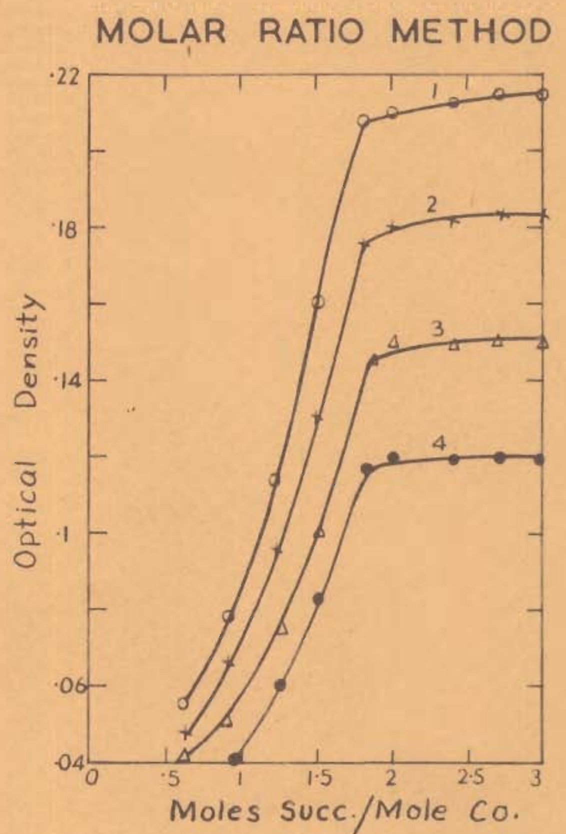

MOLAR RATIO METHOD

FIG. 7

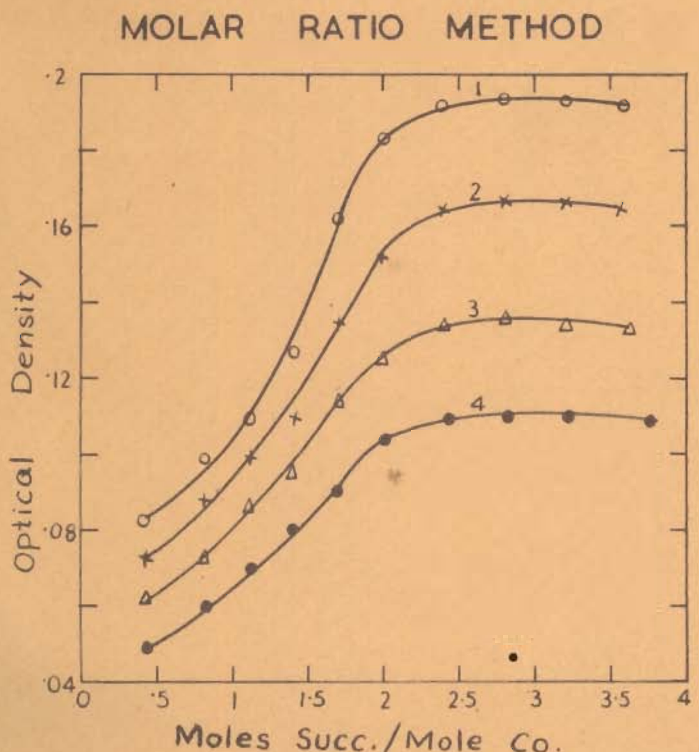

MOLAR RATIO METHOD

FIG. 8

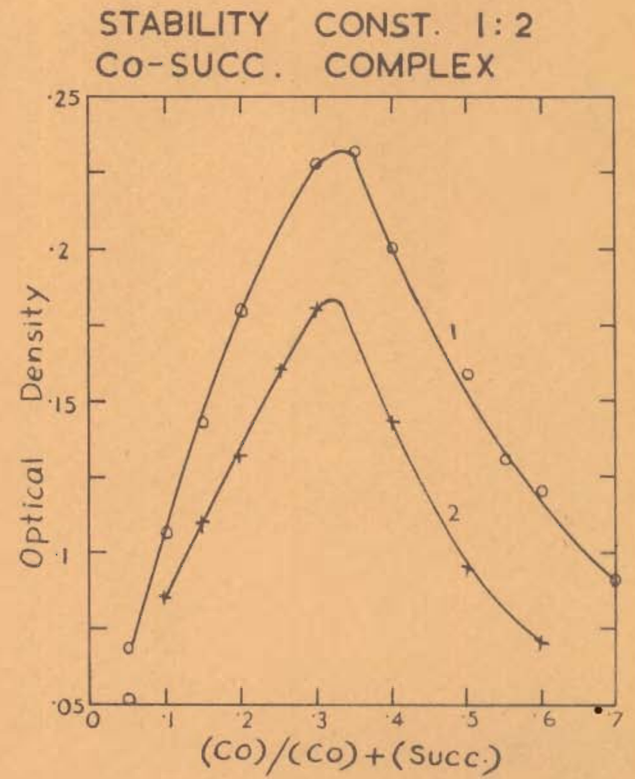

STABILITY CONST. 1:2
Co-SUCC. COMPLEX

FIG. 9

These two methods could also be conveniently employed in elucidating the composition of cobalt-succinimide complex. The results of the conductance and pH metric methods for both the complexes are described below.

Composition of cobalt complexes of succinimide and phthalimide by conductometric titrations method:

Conductometric titrations of succinimide and phthalimide solutions against cobalt chloride were carried out at several concentrations of the imide solutions (prepared in equivalent amount of potassium hydroxide). Only direct titrations (imides in the cell) could be performed. The effect of temperature on the conductance was minimised by putting the cell in a beaker of water. Volume correction was applied by multiplying the conductance value by a factor V + v / V, where V is the volume taken in the cell and v is the volume of the titrant added.

Readings for titrations: succinimide in the cell.

TABLE NO. 10

Concentration of succinimide solution = 0.05 M.

Strength of cobalt chloride solution = 0.25 M.

Volume of succinimide solution = 15 ml.

Vol. of $CoCl_2$ ml.	Corrected conductance (mhos $x10^{-2}$)	Vol. of $CoCl_2$ ml.	Corrected conductance (mhos $x10^{-2}$)
0.0	0.5464	2.0	0.5208
0.3	0.5369	2.5	0.5291
0.6	0.5291	2.8	0.5348
1.0	0.5208	3.0	0.5405
1.5	0.5181	-	-

Fig.10, Curve 1.

15 ml. of 0.05 M succinimide
≡ 1.5 ml. of 0.25 M $CoCl_2$ ≡ 7.4 ml. of 0.05 M $CoCl_2$

Co : succinimide = 1:2

TABLE NO. 11.

Concentration of succinimide solution = 0.04 M.

Strength of cobalt chloride solution = 0.25 M.

Volume of succinimide solution = 15 ml.

Vol. of $CoCl_2$ ml.	Corrected conductance (mhos x10^{-2})	Vol. of $CoCl_2$ ml.	Corrected conductance (mhos x10^{-2})
0.0	0.4444	1.5	0.4328
0.3	0.4405	1.8	0.4400
0.6	0.4367	2.1	0.4505
0.9	0.4329	2.4	0.4587
1.2	0.4305	2.6	0.4622

Fig. 10, Curve 2.

15 ml. of 0.04 M succinimide
≡1.25 ml. of 0.25 M. $CoCl_2$ ≡ 7.8 ml. of 0.04 M cobalt chloride
Co : succinimide = 1:1.92

TABLE NO. 12.

Concentration of succinimide solution = 0.0465 M.

Strength of cobalt chloride solution = 0.25 M.

Volume of succinimide solution = 15 ml.

Vol. of $CoCl_2$ ml.	Corrected conductance (mhos x 10^{-2})	Vol. of $CoCl_2$ ml.	Corrected conductance (mhos x10^{-2})
0.0	0.3655	2.4	0.3693
0.3	0.3636	2.6	0.3715
0.6	0.3625	2.8	0.3764
1.0	0.3597	3.0	0.3790
1.5	0.3584	3.3	0.3817
2.0	0.3679	3.6	0.3846

Fig. 10, Curve 3.

15 ml. of 0.0465 M succinimide
≡ 1.4 ml of 0.25 M $CoCl_2$ ≡ 7.6 ml. of 0.0465 M $CoCl_2$
Co : succinimide = 1:2

Readings for titrations: phthalimide in the cell.

TABLE NO. 13.

Concentration of phthalimide solution = 0.0223 M.

Strength of cobalt chloride solution = 0.25 M.

Volume of phthalimide solution = 15 ml.

Vol. of $CoCl_2$ ml.	Corrected conductance (mhos $\times 10^{-2}$)	Vol. of $CoCl_2$ ml.	Corrected conductance (mhos $\times 10^{-2}$)
0.0	0.2325	0.9	0.2272
0.1	0.2293	1.0	0.2427
0.2	0.2247	1.1	0.2538
0.3	0.2197	1.2	0.2681
0.4	0.2150	1.4	0.2833
0.5	0.2127	1.6	0.3003
0.6	0.2115	1.8	0.3145
0.7	0.2164	2.0	0.3322
0.8	0.2207	-	-

Fig. 11, Curve 1.

15 ml. of 0.0223 M phthalimide
≡ 0.65 ml. of 0.256 M of $CoCl_2$ ≡ 7.3 ml. of 0.0223 M $CoCl_2$
Co : phthalimide = 1:2.06

TABLE NO. 14.

Concentration of phthalimide solution = 0.03 M.

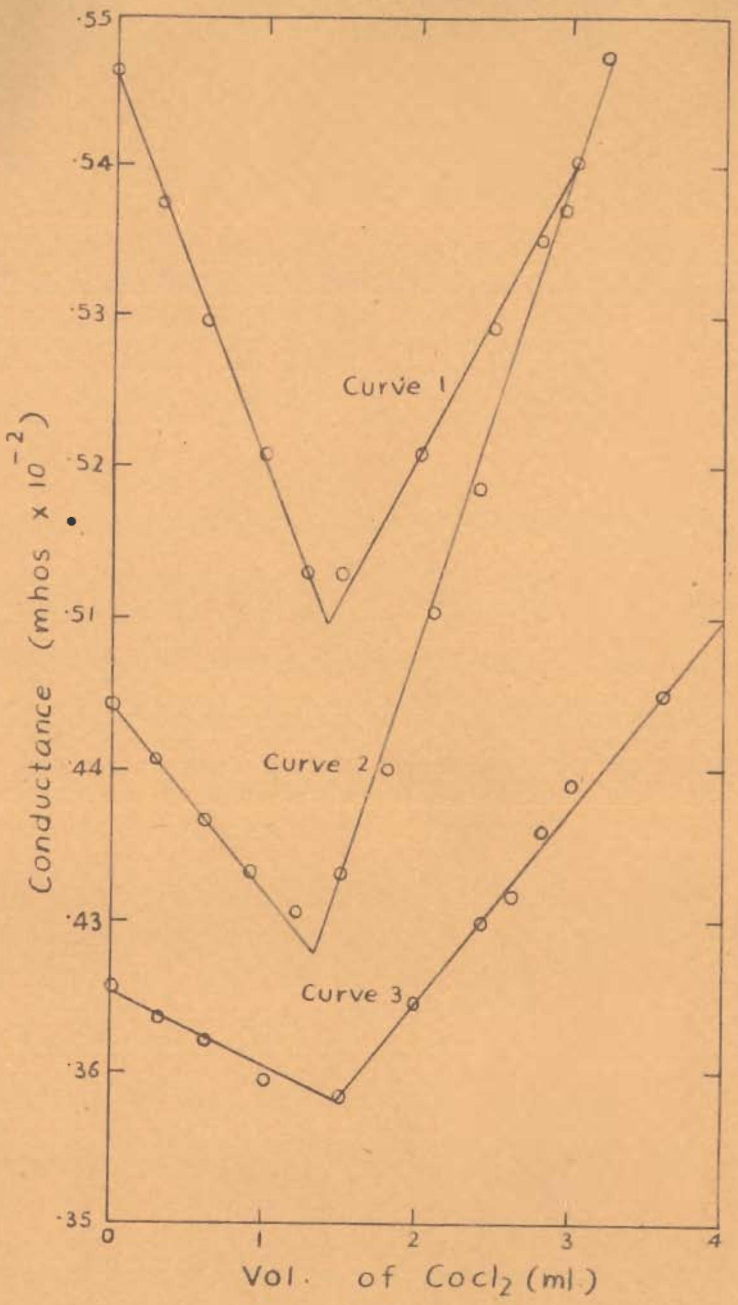
Strength of cobalt chloride solution = 0.25 M.

Volume of phthalimide solution =

Vol. of $CoCl_2$ ml.	Corrected conductance (mhos $\times 10^{-2}$)	Vol. of $CoCl_2$ ml.	Corrected conductance (mhos $\times 10^{-2}$)
0.0	0.2638	0.8	0.2314
0.1	0.2604	0.9	0.2358
0.2	0.2544	1.0	0.2433
0.3	0.2500	1.1	0.2597
0.4	0.2445	1.3	0.2825
0.5	0.2398	1.5	0.3049
0.6	0.2364	1.7	0.3268
0.7	0.2331	1.9	0.3436

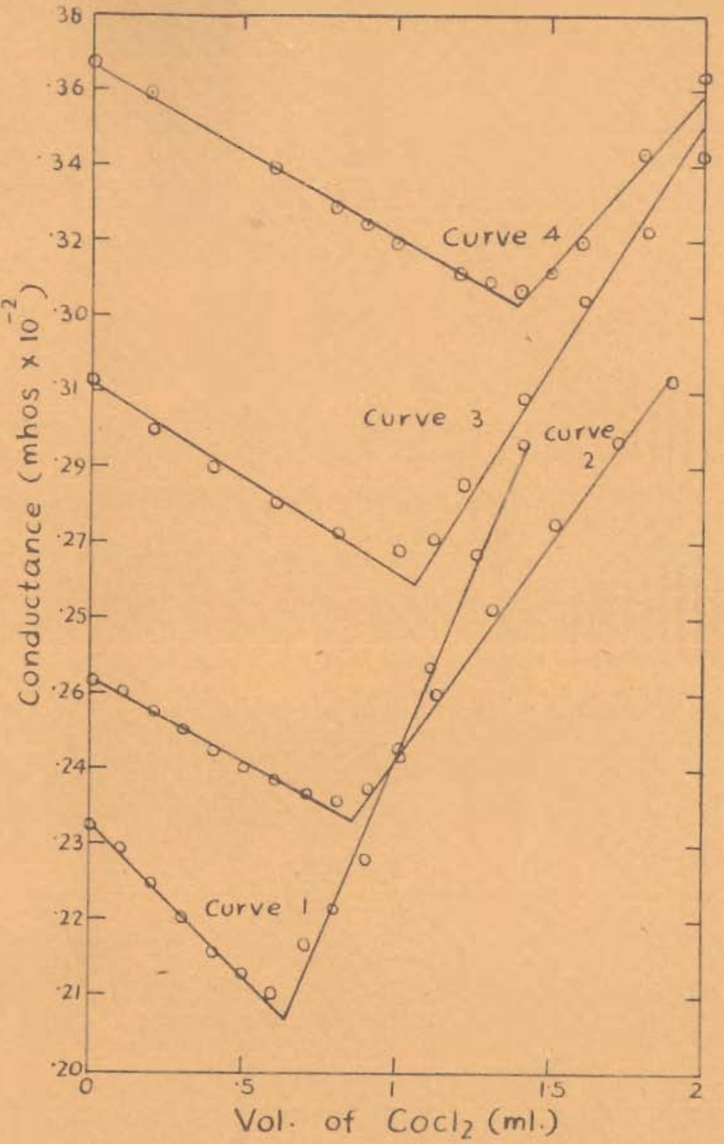
Fig. 11, Curve 2.

15 ml. of 0.03 M phthalimide
≡ 0.9 ml of 0.25 M $CoCl_2$ ≡ 7.6 ml. of 0.03M $CoCl_2$
Co : phthalimide = 1:1.98



Co-SUCC. COMPLEX

FIG. 10



Co - PHTH. COMPLEX

FIG. 11

TABLE NO. 15.

Concentration of phthalimide solution = 0.035 M.

Strength of cobalt chloride solution =0.25 M.

Volume of phthalimide solution = 15 ml.

Vol. of $CoCl_2$ ml.	Corrected conductance (mhos $x10^{-2}$)	Vol. of $CoCl_2$ ml.	Corrected conductance (mhos $x10^{-2}$)
0.0	0.3125	1.2	0.2841
0.2	0.2994	1.4	0.3077
0.4	0.2898	1.6	0.3338
0.6	0.2800	1.8	0.3524
0.8	0.2725	2.0	0.3731
1.0	0.2681	2.2	0.3876
1.1	0.2717	2.4	0.4030

Fig. 11, Curve 3.

15 ml. of 0.035 M phthalimide
≡ 1.1 ml. of 0.25 M $CoCl_2$ ≡ 7.65 ml. of 0.036 M of $CoCl_2$
Co : phthalimide = 1:1.96

TABLE NO. 16.

Concentration of phthalimide solution = 0.048 M

Strength of cobalt chloride solution = 0.25 M

Volume of phthalimide solution = 15 ml.

Vol. of $CoCl_2$ ml.	Corrected conductance (mhos $x10^{-2}$)	Volof $CoCl_2$ ml.	Corrected conductance (mhos $x10^{-2}$)
0.0	0.3676	1.5	0.3115
0.2	0.3597	1.6	0.3195
0.4	0.3472	1.8	0.3436
0.6	0.3390	2.0	0.3636
0.8	0.3289	2.2	0.3817
1.0	0.3195	2.4	0.3968
1.2	0.3115	2.6	0.4132
1.3	0.3086	2.8	0.4255
1.4	0.3067	3.0	0.4356

Fig. 11, Curve 4.

15 ml. of 0.048 M phthalimide
≡ 1.45 ml. of 0.25 M $CoCl_2$ ≡ 7.5 ml. of 0.048 M $CoCl_2$
Co : phthalimide = 1:2

pH metric studies on cobalt complexes of succinimide and phthalimide:

For obtaining further confirmation of the compositions and also to ascertain the nature of cobalt complexes of succinimide and phthalimide, pH metric titrations were performed hezm also according to the method recommended by Calvin and Melchoir. Typical titration curves were obtained in both the cases of succinimide and phthalimide. The values of $\bar{n}$ and - log A (free ligand concentration) were calculated by the method described earlier. Tables showing calculations for formation curve have been given along with titration tables for both the imides. pK values of succinimide and phthalimide, used for calculations are 9.74 and 9.50 respectively (as determined in Chapter I and II).

Cobalt-succinimide complex:

TABLE NO. 17.

Titration of succinimide solution in absence of cobalt chloride.

10.0 ml. of 0.5 M succinimide - 1.0 ml. of 0.01 M HCl, total volume made up to 15 ml. by methyl alcohol, titrated against 0.1 M KOH.

Vol. of KOH. ml.	pH	Vol. of KOH. ml.	pH
0.0	1.91	1.5	9.46
0.1	7.55	2.0	9.53
0.2	8.42	2.5	9.58
0.3	8.76	3.0	9.61
0.4	8.94	3.8	9.66
0.6	9.14	4.2	9.68
0.8	9.27	4.6	9.69
1.1	9.37	5.0	9.71

Fig. 12, Curve 1.

Titrations of succinimide in presence of cobalt chloride:

Concentration of succinimide = 0.5 M

Strength of cobalt chloride solution = 0.125 ml.

Strength of hydrochloric acid solution= 0.01 M.

Strength of potassium hydroxide solution = 0.1 M.

TABLE NO.18.

10 ml. of succinimide -0.5 ml. of cobalt chloride-1.0 ml. of hydrochloric acid, total volume made upto 15 ml. by methyl alcohol.

Vol. of KOH. ml.	pH	Vol. of KOH. ml.	pH
0.0	1.96	1.5	8.69
0.1	4.61	1.81	8.97
0.2	5.28	2.2	9.17
0.3	5.66	2.6	9.29
0.4	5.96	3.0	9.37
0.6	6.60	3.5	9.44
0.8	7.42	4.0	9.48
1.0	7.90	4.5	9.52
1.2	8.24	5.0	9.56

Fig.12, Curve 2.

TABLE NO.18(A)

Calculations for formation curve.

For 0.5 ml. of 0.125 M $CoCl_2$ = 0.625×10^{-4} moles.

pH	ΔKOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log succ.
5.5	0.200	0.200	0.32	4.7230
6.0	0.325	0.325	0.52	4.2264
6.5	0.500	0.500	0.80	3.7314
7.0	0.625	0.625	1.00	3.2349
7.5	0.850	0.850	1.36	2.7411
8.0	0.925	0.925	1.48	2.2431
8.5	1.150	1.150	1.84	1.7492
9.0	1.425	1.425	2.28	1.2566
9.25	1.500	1.500	2.40	1.0085

Fig.13, Curve 1.

TABLE NO. 19.

10 ml. of succinimide-0.7 ml. of cobalt chloride-1.0 ml. of hydrochloric acid, total volume made upto 15 ml. by methyl alcohol.

Vol. of KOH. ml.	pH	Vol. of KOH. ml.	pH
0.0	2.10	1.6	8.20
0.1	4.80	1.8	8.44
0.2	5.33	2.0	8.65
0.4	5.87	2.3	8.87
0.6	6.25	2.6	9.03
0.8	6.69	3.0	9.16
1.0	7.28	3.5	9.25
1.2	7.67	4.0	9.32
1.4	7.94	4.5	9.36

Fig. 12, Curve 3.

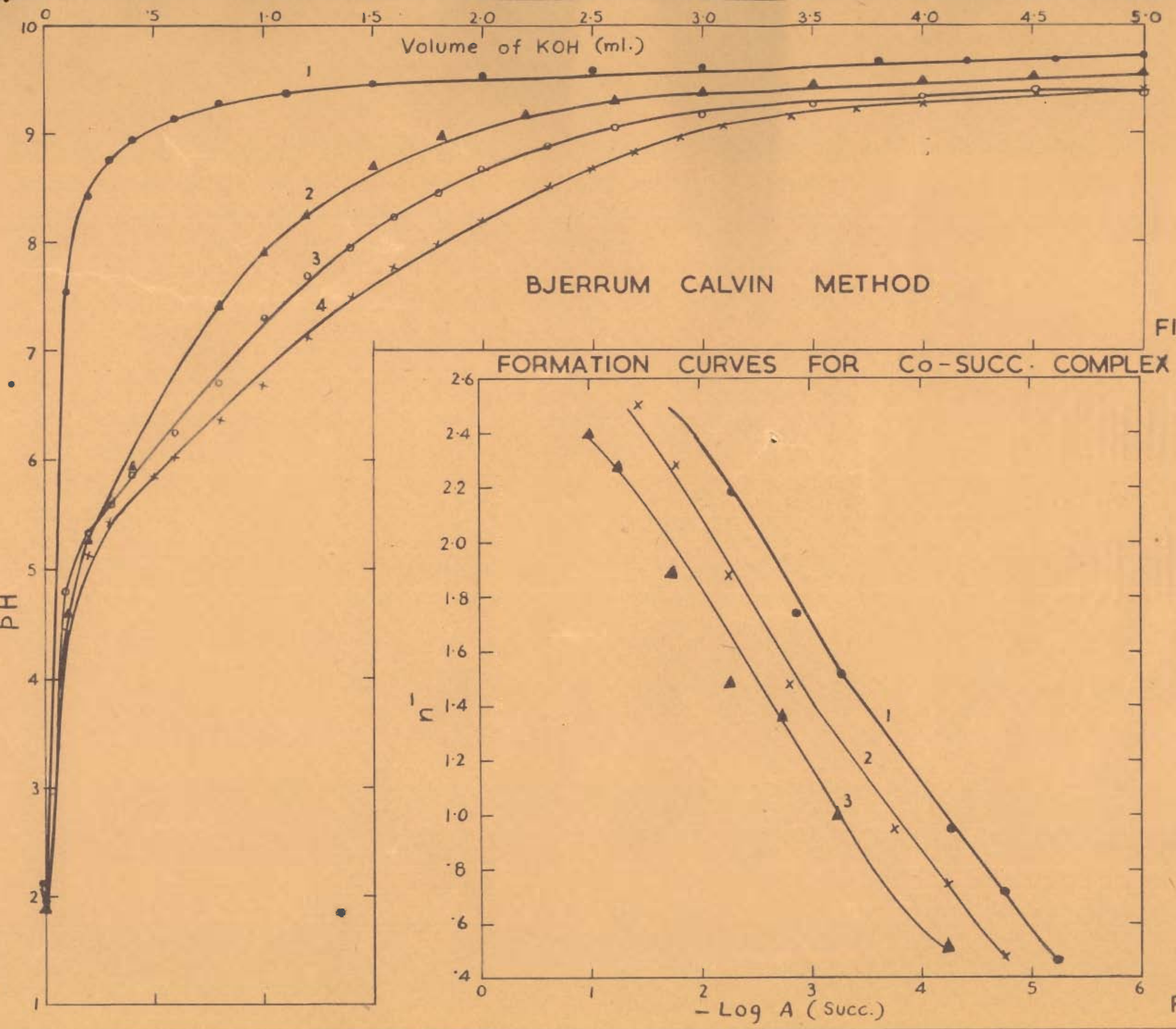
TABLE NO. 19(A)

Calculations for formation curve.

For 0.7 ml. of 0.125 M. $CoCl_2 \equiv 0.875 \times 10^{-4}$ moles

pH	△ KOH	Moles of KOH. $\times 10^{-4}$	$\bar{n}$	-log succ.
5.5	0.225	0.225	0.257	4.7235
6.0	0.425	0.425	0.486	4.2292
6.5	0.650	0.650	0.743	3.7355
7.0	0.825	0.825	0.942	3.2404
7.5	1.000	1.000	1.142	2.7451
8.0	1.300	1.300	1.485	2.2532
8.5	1.650	1.650	1.880	1.7624
9.0	2.000	2.000	2.280	1.2715
9.25	2.160	2.160	2.380	1.0266

Fig. 13, Curve 2.



BJERRUM CALVIN METHOD

FIG. 12

FORMATION CURVES FOR Co-SUCC. COMPLEX

FIG. 13

TABLE NO.20.

10 ml. of succinimide-0.9 ml. of cobalt chloride -1.0 ml. of hydrochloric acid, total volume made upto 15 ml. by methyl-alcohol.

Vol. of KOH. ml.	pH	Vol. of KOH. ml.	pH
0.0	2.00	2.0	8.18
0.1	4.45	2.3	8.47
0.2	5.12	2.5	8.66
0.3	5.44	2.7	8.83
0.5	5.84	2.9	8.95
0.6	6.02	3.1	9.05
0.8	6.36	3.4	9.15
1.0	6.68	3.7	9.22
1.2	7.11	4.0	9.28
1.4	7.49	4.5	9.36
1.6	7.76	5.0	9.42
1.8	7.96	-	-

Fig. 12, Curve 4.

TABLE NO.20(A)

Calculations for formation curve.

For 0.9 ml. of 0.125 M. $CoCl_2 \equiv 1.125 \times 10^{-4}$ moles.

pH	Δ KOH	Moles of KOH. $\times 10^{-4}$	$\bar{n}$	-log succ.
5.5	0.275	0.275	0.244	4.7250
6.0	0.525	0.525	0.466	4.2321
6.5	0.825	0.825	0.733	3.7504
7.0	1.075	1.075	0.955	3.2472
7.5	1.300	1.300	1.155	2.7532
8.0	1.700	1.700	1.511	2.2637
8.5	2.050	2.050	1.733	1.7728
9.0	2.450	2.450	2.177	1.2828
9.25	2.650	2.650	2.355	0.9378

Fig. 13, Curve 3.

<u>Cobalt-phthalimide complex:</u>

Concentration of phthalimide = 0.05 M.

Strength of $CoCl_2$ solution = 0.05 M.

Strength of potassium hydroxide solution. = 0.1 M.

TABLE NO. 21.

Titration of phthalimide solution in absence of cobalt chloride.

15.0 ml. phthalimide solution diluted to 20.0 ml. by methyl-alcohol, titrated against 0.1 M KOH.

Vol. of KOH. ml.	pH	Vol. of KOH. ml.	pH
0.0	8.85	2.0	10.80
0.1	9.65	2.5	10.90
0.2	9.93	3.0	11.00
0.3	10.10	4.0	11.15
0.4	10.20	5.0	11.33
0.6	10.35	6.0	11.50
0.8	10.48	7.0	11.63
1.2	10.62	8.0	11.78

Fig. 14, Curve 1.

Titrations of phthalimide in presence of cobalt chloride:

TABLE NO. 22.

15.0 ml. of phthalimide-0.2 ml. of cobalt chloride, total volume made upto 20 ml. by methyl alcohol, titrated against KOH.

Vol. of KOH.ml.	pH	Vol. of KOH.ml.	pH
0.0	5.80	1.8	10.85
0.2	9.20	2.5	11.00
0.4	10.04	3.0	11.10
0.6	10.30	3.5	11.20
0.8	10.45	4.0	11.30
1.0	10.56	4.5	11.39
1.4	10.73	5.0	11.48

Fig. 14, Curve 2.

TABLE NO. 22(A)

Calculations for formation curve.

For 0.2 ml. of 0.05 M $CoCl_2$ ≡ 0.1×10^{-4} moles.

pH	Δ KOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log phth.
6.5	0.0375	0.0375	0.375	4.4267
7.0	0.050	0.0500	0.500	3.9270
7.5	0.075	0.075	0.750	3.4276
8.0	0.100	0.100	1.000	2.9281
8.5	0.150	0.150	1.500	2.4292
9.0	0.175	0.175	1.750	1.9298
9.5	0.200	0.200	2.000	1.4303
10.0	0.190	0.190	1.900	0.9300
10.25	0.175	0.175	1.850	0.6798

Fig. 15, Curve 1.

TABLE NO. 23.

15.0 ml. of phthalimide-0.4 ml. of cobalt chloride, total volume made upto 20 ml. by methyl alcohol, titrated against KOH.

Vol. of KOH. ml.	pH	Vol. of KOH. ml.	pH
0.0	5.80	1.4	10.63
0.1	6.97	1.8	10.80
0.2	7.90	2.5	10.98
0.3	8.60	3.0	11.08
0.4	9.40	3.5	11.15
0.5	9.75	4.0	11.24
0.6	10.00	4.5	11.35
0.8	10.28	5.0	11.44
1.1	10.48	-	-

Fig. 14, Curve 3.

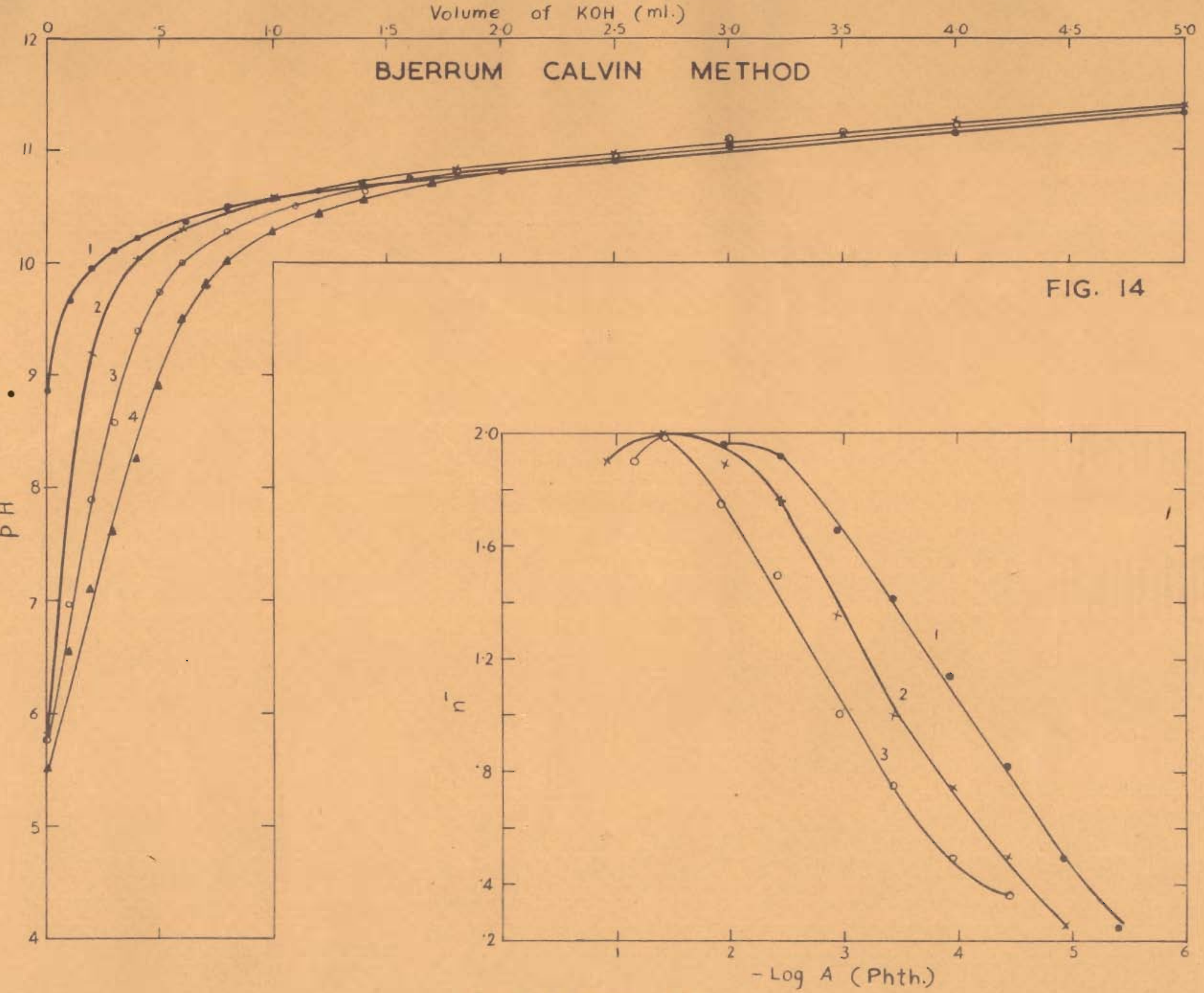
TABLE NO. 23(A).

Calculations for formation curve.

For 0.4 ml. of 0.05 M $CoCl_2$ ≡ 0.2×10^{-4} moles.

pH	△ KOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log phth.
6.5	0.050	0.050	0.250	4.4270
7.0	0.100	0.100	0.500	3.9281
7.5	0.150	0.150	0.750	3.4292
8.0	0.200	0.200	1.000	2.9303
8.5	0.275	0.275	1.375	2.4320
9.0	0.350	0.350	1.750	1.9335
9.5	0.375	0.375	1.875	1.4341
10.0	0.400	0.400	2.000	0.9345
10.25	0.380	0.380	1.900	0.6841

Fig. 15, Curve 2.



BJERRUM CALVIN METHOD

FIG. 14

FORMATION CURVES FOR Co-PHTH COMPLEX

FIG · 15

TABLE NO. 24.

15.0 ml. of phthalimide - 0.6 ml. of cobalt chloride, total volume made upto 20 ml. by methyl-alcohol, titrated against KOH.

Vol. of KOH. ml.	pH	Vol. of KOH. ml.	pH
0.0	5.51	1.2	10.43
0.1	6.55	1.4	10.55
0.2	7.10	1.7	10.70
0.3	7.60	2.0	10.80
0.4	8.26	2.5	10.95
0.5	8.90	3.0	11.03
0.6	9.48	3.5	11.12
0.7	9.80	4.0	11.22
0.8	10.00	4.5	11.33
1.0	10.28	5.0	11.42

Fig. 14, Curve 4.

TABLE NO. 24 (A)

Calculations for formation curve.

For 0.6 ml. of 0.05 M $CoCl_2$ ≡ 0.3×10^{-4} moles.

pH	$\triangle$ KOH	Moles of KOH $\times 10^{-4}$	$\bar{n}$	-log phth.
6.5	0.080	0.080	0.266	4.4276
7.0	0.150	0.150	0.500	3.9292
7.5	0.250	0.250	0.833	3.4314
8.0	0.350	0.350	1.166	2.9335
8.5	0.425	0.425	1.416	2.4351
9.0	0.500	0.500	1.666	1.9367
9.5	0.575	0.575	1.916	1.4380
10.0	0.575	0.575	1.916	0.9380
10.25	0.550	0.550	1.833	0.6878

Fig. 15, Curve 3.

DISCUSSION

It was observed that in methanolic medium cobalt-chloride reacted with succinimide and phthalimide in presence of methanolic potassium hydroxide, to give, a soluble violet complex with succinimide and a insoluble violet complex with phthalimide. The composition and stability constant of cobalt-succinimide complex were established by spectrophotometric, conductometric and pH-metric studies. Isolation of the complex could not be possible as any attempt for its isolation resulted in the precipitation of cobalt hydroxide.

The composition of cobalt-phthalimide complex was established by conductometric and pH-metric methods. Spectrophotometric studies could not be performed in view of the insoluble nature of the complex.

Cobalt-succinimide complex:

On applying VosBurgh and Cooper's method evidence for the formation of only one complex was forthcoming. However, it was interesting to note that the curves obtained did not resemble with those obtained in the case of nickel-imide complexes, where two peaks were realised. The maxima for methanolic solutions of cobalt chloride, and its complex with succinimide occurred at the same wavelength, 520 mu (Figs.1 and 2). But the absorbance for cobalt-succinimide mixtures was quite large in the wavelength region, 325 - 350 mu, while the absorbance of cobalt chloride was negligible in this region of wavelength. Therefore experiments for composition of the complex were performed in this region.

From Job's method of continued variation, where experiments were performed in the wavelength range of 325 to 340 mu, the plots of optical density of equimolar solution against ratio $(Co^{2+})/(Co^{2+}) + (Succinimide)$, suggested the formation of 1:2 (Co-succinimide) complex (Figs.3 and 5).

Confirmation of the results of Job's method was available from molar ratio method. The break in the curves again corresponded to 1:2 metal-imide ratio (Figs.7 and 8).

The stability constant of the complex was calculated from Anderson's method using equations 3 and 5, pages 44 and 45. Thus from Fig.9, taking the values of a_1 , b_1 and a_2 , b_2 as .667 x 10^{-2}, 2.667 x 10^{-2} and .828 x 10^{-2}, 2.03 x 10^{-2}M respectively, the value of K, stability constant of the complex was found to be, 3.35 x 10^{4}.

The conductometric titrations of succinimide (in the cell) against cobalt chloride confirmed the formation of 1:2 (cobalt: succinimide) complex (Fig.10, Curves 1-3). Blank titrations performed between imide and KOH on the one hand and between metal and imide on the other, showed non-interference with the above results.

During pH-metric studies, it was indicated that the value of $\bar{n}$, average number of ligand moles bound per metal ion, gradually increased with increase of pH and attained a maximum value of two, showing thereby the formation of 1:2 complex (Fig.12). The plots of $\bar{n}$ and -log A were used to determine the apparent stability constant of the complex. The value of apparent over-all stability constant as calculated from average stability constant is shown below:

Cobalt-succinimide complex: (Apparent stability constant).

Curves	Average stability constant log k=-log A at $\bar{n}$=1.0	Over all stability constant log K=2 log k	Mean logK
1	3.20	6.40	
2	3.25	6.50	6.45
3	3.225	6.45	

Fig.13

Cobalt-phthalimide complex:

From the break in conductometric titrations between phthalimide and cobalt chloride, it is evident that cobalt interacts with the phthalimide in the ratio 1:2. Here too blank titrations performed as in case of succinimide, did not interfere with the results on composition of the complex.

As in the case of copper-imide insoluble complexes, Bjerrum's method could be used here also upto the pH range in which the precipitation was not set-up. As with cobalt-succinimide complex, it was observed that the maximum value of $\bar{n}$ was two. The increase in $\bar{n}$ with pH suggested that the anionic form of phthalimide was taking part during complexion(Fig.14). The plots of $\bar{n}$ values against -log A (free ligand concentration) gave the formation curves (Fig.15). The value of over all apparent stability constant obtained from formation curves is tabulated below:

Cobalt-phthalimide complex(Apparent stability constant).

Curves	Average stability constant log k=-log A at $\bar{n}$=1.0	Over all stability constant log K=2 log k	Mean log K
1	3.0	6.0	
2	3.0	6.0	6.05
3	3.05	6.1	

Fig.15

Structure of the complexes:

1:2, Co(II)-succinimide complex:- This complex is formed by non-biuret reaction as only two basic nitrogen atoms are involved therein. Since cobalt exhibits the property of solvation in methanol(3) therefore the structure may represented,

$$(C_4H_4O_2N)_2 \ Co \ (CH_3OH)_4$$

1:2,Co(II)-phthalimide complex:- This complex also cannot be considered to be formed by biuret reaction as it fails to fulfil the essential condition of involvement of four basic nitrogen atoms. The structure of the complex may, therefore,be represented as,

$$(C_8H_4O_2N)_2 \ Co \ (CH_3OH)_4$$

RESUME

RESUME

Amongst the nitrogen bearing ligands, offering sites simultaneously for salt formation and co-ordination, diacid-imides, both aliphatic and aromatic, deserve special mention. This class of compounds, known for their tendency to form hydrolysable metal complexes, has attracted little attention as a complexing agent.

The original concept of the biuret reaction (development of a reddish violet colour on the addition of copper sulphate to biuret in an alkaline medium) has been greatly modified and extended so as to include(i) different basic media, like barium and calcium hydroxides, magnesium oxide, sodium carbonate, ammonia, piperidine etc. (ii) metal ions other than copper, viz., nickel and cobalt (iii) complexing agents other than biuret, viz., amino acid-amides, peptides, proteins, acid-amides and imides.

The biuret reaction of acid imides has not been studied fully. Schiff (1) in his generalisation of the groups responsible for the biuret reaction did not include these compounds. Tschugaeff (2) reported the reaction in the ammonical, aqueous ethanolic, and pyridine media.

But for few passing references of Ley and Werner(3), and Rising and Johnson (4), nothing worth mentioning exists in the literature and much remains to be done to elucidate the nature of the biuret and non biuret reactions, involved in the case of metal-imide complexes.

A systematic and comparative study of the products formed in aqueous and non-aqueous media by the interaction of heavy metal ions with complexing agents containing imide groups was therefore, considered worth undertaking.

Both soluble and insoluble metal complexes of imides were studied in aqueous as well as in methanolic media. The metal ions used in these studies were nickel(II), copper(II), and cobalt (II); imides used as complexing agents were, succinimide, phthalimide, glutarimide and saccharin. Electrometric methods viz., potentiometric, conductometric, amperometric and pH metric titrations, and spectrophotometric methods were employed for studying the nature and composition of the complexes. The composition of the complexes was also confirmed by the method of chemical analysis in cases where isolation was possible. The nature of the complexes was further investigated by I.R. studies. Stability constants of the complexes were calculated by spectrophotometric and Bjerrum's method (as extended by Calvin and Melchior) depending upon the suitability of the method for a particular complex. Since the pH scale set for water is not strictly applicable in case of methanolic medium, the stability constants calculated from Bjerrum's method were not considered to give absolute value. The constants derived in methanolic medium by pH-metric studies, were designated as apparent stability constants.

1. Nickel-succinimide complexes (biuret and non biuret reaction mechanisms:

Two complexes, one yellow and the other green were formed by the interaction of methanolic solutions of nickel chloride and succinimide in presence of methanolic potassium hydroxide. The yellow complex was not very stable and got decomposed by moisture. The green variety was obtained with excess of the metal salt. It was also possible to decompose the yellow complex into the green one by adding gradually increasing amount of nickel chloride. In the aqueous medium the behaviour was different. The complex obtained in presence of excess of succinimide, was green in colour while in excess of metal ion precipitation of the hydroxide took place. The combining ratio for the yellow complex was found by spectrophotometric, conductometric and pH-metric methods. The green complex (formed in the higher proportions of nickel ions) could only be studied spectrophotometrically since the conductometric method failed to give sharp inflexion points while the Bjerrum's method could not be employed due to the limited concentration range in which the studies were possible.

The green complex obtained in the aqueous medium could be studied by Bjerrum's method employing the procedure of Calvin and Melchior. Other methods, viz., spectrophotometric, conductometric etc., could not be successfully employed due to the precipitation of nickel hydroxide in presence of excess of the metal salt.

Composition and stability of the complexes:

VosBurgh and Cooper's method when applied to study the yellow complex, not only provided necessary information for the number of complexes formed, and the suitable wave-lengths to work with but helped immensely in indicating that two complexes, with absorption ranges fairly wide apart are formed depending on the relative amounts of the reactants present in the reaction mixture. From the curves (Chapter I, Fig. 2) it would be seen that the mixtures with higher proportions of succinimide showed appreciable absorption in the range 430 to 480 mu, while mixtures having lower proportion of succinimide showed very little absorption in the above wave-length region. Hence the stoichiometry of the yellow complex, formed in excess of succinimide could be safely studied spectrophotometrically in the wave-length region 430 to 480 mu. On the other hand, a suitable wave-length for investigating the green complex could be selected from the maximum appearing in the higher wave-length side of O.D. curves.

On applying Job's method on the wave-lengths 440, 450 and 460 mu, peaks were obtained at the molar ratio 1:4 (Ni-succinimide), thereby showing the existence of the complex $(C_4H_4O_2N)_4Ni$, (Chapter I, Figs. 3-5). The results found further confirmation by the molar ratio method (Chapter I, Figs. 6-8). The stability constant of the complex as determined by mole ratio method was found to be $K = 2.869 \times 10^5$, (Chapter I, Fig. 6, Curve 2).

Direct conductometric titrations with methanolic succinimide (prepared in equivalent amount of KOH) in the cell, gave sharp inflexion points confirming the formation of 1:4 complex(Fig.16, Curve 1-4). The reverse titrations (nickel chloride in the cell) deserve a special mention. During the course of the titrations it looked as if the precipitation of nickel hydroxide in presence of four equivalents of methanolic potassium hydroxide, would interfere with the titrations. But interestingly enough it was found that the presence of freshly precipitated hydroxide did not interfere with the titrations due to its stepwise decomposition into the yellow complex. The titrations under these conditions were quite successful, again giving sharp indication of the existence of 1:4, nickel-succinimide complex (Fig.17, Curve 1,2 and 3).

pH-metric studies employing Calvin and Melchior procedure clearly provided evidence for the fact that hydrogen ions are liberated during the course of the reaction and the anionic form of succinimide was taking part during complex-ion. The value of $\bar{n}$, average number of ligand moles added per metal ion had increased gradually with increase of pH and attained a limiting value of four(Fig.19-21). The value of apparent stability constant, calculated by pH-metric method came out to be, log K = 7.93 ,(Table P.75).

Chemical analysis of the isolated yellow complex also confirmed 1:4, Ni-succinimide complex.

The I.R. spectra of succinimide and its 1:4 complex with nickel(Fig.25) gave the following information:

The main feature of the spectrum was a marked shift in the carbonyl stretching frequency from 1750 cm^{-1} (succinimide) to 1660 cm^{-1} (complex), pointing towards metal oxygen binding in the complex. This may be true for the isolated complex which may change its nature on heating and drying, but is not possible for the complex in solution where both chemical evidence and pH-metric data gave strong indication of co-ordination through nitrogen. Moreover the complex showed interesting splitting of the band of the type shown by the parent imides due to vibrational coupling. Another interesting features of the complex was to lower the frequencies of 1180 cm^{-1} band, which may have a strong component of the C-N vibrational stretching band. Further duplet around 830 cm^{-1} (probably due to ring vibration) also shifts to lower frequency on complex-ion.

The composition of the green complex formed in non-aqueous medium, was established by Job's and mole ratio methods. The peak was obtained corresponding to 1:2, Ni-succinimide composition by Job's curves (Chapter 1, Figs. 9-11). The results of the Job's method were confirmed by mole ratio method, when the inflexion again corresponded to 1:2 (Ni-succinimide) complex (Chapter I, Figs. 12-14). But the nature of the curves was slightly different from those of the typical molar ratio curves. The O.D. values instead of remaining constant, were found to decrease, after the stoichiometric ratio had been realised. This decrease could be explained due to formation of 1:4 (Ni-succinimide) yellow complex, in presence of excess of succinimide. This was also evident from the fact that the absorption of yellow complex was much less than that of the green variety in wave-length region of 630-670 mu (Chapter I, Fig.2).

The stability constant K of this complex was determined by the method of Anderson and coworkers and was found to be, $K = 6.14 \times 10^4$ (Chapter I, Fig.15).

Nickel-succinimide complex, in aqueous medium:

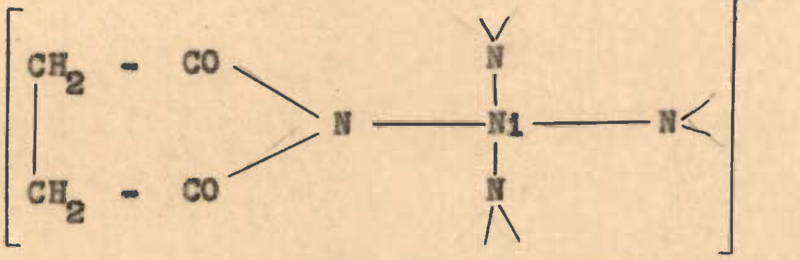
Unlike the complexes formed in non-aqueous medium, the one in the aqueous medium was stable only in presence of excess of succinimide. As stated earlier, experimental limitations could allow only the use of pH metric method to study the composition and stability of the complex in the aqueous medium.

Typical titration curves were obtained when succinimide was titrated, against potassium hydroxide with and without the presence of nickel ions (Chapter 1, Fig.23). The value of $\bar{n}$ (average number of ligand moles added per metal ion) was found to increase with pH and attained a constant value in the range of one at pH 7.5, suggesting thereby 1:1 (Ni-succinimide) composition of the complex (Fig.24). The mean value of log K, stability constant, as calculated by Bjerrum's method came out to be log K = 3.025.

Mechanism of the reaction between nickel chloride and succinimide in aqueous and methanolic media:

(i) 1:4 nickel succinimide complex(yellow in colour) formed in methyl-alcohol.

This reaction is essentially a biuret reaction for the reason that four basic nitrogen atoms are involved in co-ordination with nickel atom. A similar mechanism was proposed by Rising and Yang (5) for the amide complexes of copper involving co-ordination with four basic nitrogen, accompanied by the splitting of four hydrogen atoms from two amide molecules. The structure of 1:4 complex may be represented as,

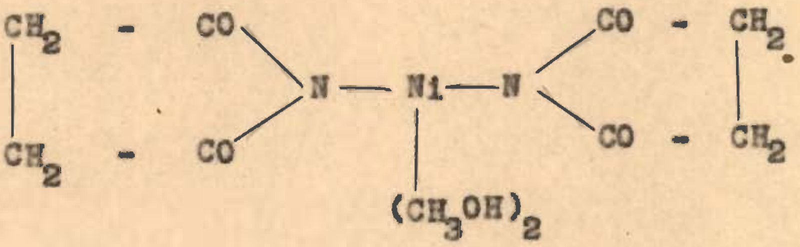


Chemical evidence and pH-metric data gave strong evidence of co-ordination through nitrogen, for the complex in solution. I.R. spectra of the isolated complex did not give clear indication for the binding through nitrogen, probably due to change in the nature of the complex on heating and drying.

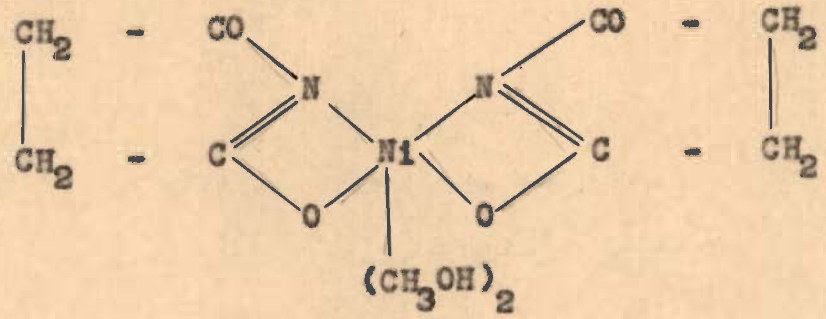
(ii) 1:2 nickel succinimide complex (green in colour) formed in methyl-alcohol.

The following structures may be assigned for 1:2 complex:

(i)



(ii)



However in view of lack of evidence in favour of any one of the two, the composition of this complex can be formulated as $((C_4H_4O_2N)_2\ Ni\ (CH_3OH)_2)$, the co-ordination number of nickel is completed by two molecules of methyl-alcohol. The formation of this green complex involves co-ordination with two basic nitrogen instead of four. The biuret reaction mechanism cannot, therefore, be put forward here.

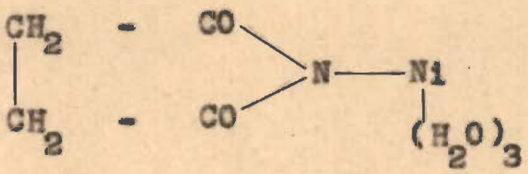
(iii) 1:1 nickel succinimide complex (green in colour) formed in aqueous medium.

The reaction between succinimide and nickel in aqueous medium, below pH 8 may be represented by the following mechanism,

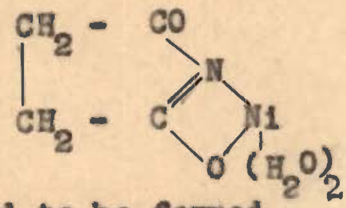
$$Ni^{2+}(H_2O)_4 + (C_4H_4O_2NH) \longrightarrow (C_4H_4O_2N)\ Ni^{+}\ (H_2O)_3$$

The structure of the above complex may be represented by either of the following two formulae,

(i)



(ii)



This complex also can-not be considered to be formed by biuret'reaction mechanism.

II. Nickel complexes of phthalimide and glutarimide (biuret and non biuret reaction mechanisms).

By the interaction of phthalimide with nickel, in methanolic medium, evidence for the existence of two soluble complexes, a yellow one formed with excess of phthalimide and a green one in excess of metal ion, was forthcoming. Both the complexes were highly sensitive towards moisture. Moreover, just like the nickel-succinimide complex, the yellow complex got changed into a green one on the addition of excess of nickel(II).

Unlike nickel-succinimide,interaction of phthalimide with nickel could not be studied in aqueous medium,on account of the extremely low solubility of phthalimide in water. Composition and stability of the yellow complex have been established by spectrophotometric,conductometric and pH metric methods. The results have been further confirmed from chemical analysis of the isolated product and also from its I.R. spectrum. As regards the green complex,only spectrophotometric method could be employed to study its composition and stability due to the restrictions similar to succinimide complex.

The interaction of nickel with glutarimide was studied to examine the effect of nature of the ring of imides on the complexes formed(glutarimide is a six membered ring compound compared as against a five membered ring present in phthalimide and succinimide). Here too,the preliminary studies revealed that the corresponding green complex was stable only in non aqueous medium. However,unlike nickel-phthalimide, no yellow complex was obtained with excess of the complexing agent,but only a green product was obtained irrespective of the metal-glutarimide ratio. This complex could be studied by pH metric method only, and the same difficulty as metwith in case of nickel-succinimide complex in aqueous medium, was encountered here.

Composition and stability of the complexes:

Nickel-phthalimide complexes: - VosBurgh and Cooper's curves (Fig.1) obtained, were similar to those obtained with succinimide. The mixtures having higher proportions of phthalimide showed appreciable absorption in the wave-length region 425 to 480 mu, while the mixtures with low proportions absorbed very little in the above wave-length region. The two maxima, occurred at 360 and 650 mu(while in case of succinimide, the first maximum occurred at 400 mu).

The plots for Job's method in the wave-length region of 425 to 480 mu, gave peaks corresponding to 1:4 (nickel-phthalimide) ratio, for the yellow complex(Figs.2-4). The mole ratio method also confirmed the results of Job's method of continued variation(Fig.5 and 6). A slightly modified version of the molar ratio method was also employed, by keeping phthalimide (colourless)constant and varying the concentration of nickel chloride(coloured). This method, besides providing information about the composition of the complex, also furnished difinite evidence for the decomposition of the yellow complex in presence of the excess of nickel (Fig.7 and 8). It was further observed that optical density values beyond the inflexion point, showed, gradual decrease instead of remaining constant. This decrease might be due to the formation of green complex which, as already stated, showed much lesser absorption on the wave-length 440 and 460 mu.. The stability constant of the yellow complex as determined by the mole ratio method came out to be $K = 3.89 \times 10^6$ (Fig.6, Curve 1). Conductometric titrations, both direct (phthalimide in presence of equivalent KOH, in the cell) and reverse (nickel chloride with four equivalents of KOH in the cell), provided definite evidence for 1:4 (Ni-phthalimide) complex (Fig.16-18, 20 and 21). pH-metric studies (Calvin and Melchior method) also gave evidence of the fact that four anionic molecules of phthalimide co-ordinated with one atom of nickel. The apparent stability constant calculated by this method was found to be $\log K = 13.9$ (Fig.23-25).

Chemical analysis of the yellow coloured nickel phthalimide complex confirmed the existence of 1:4 Ni-phthalimide complex. The I.R. spectra of phthalimide and its 1:4 nickel complex (Fig.29), revealed a marked shift in the carbonyl stretching frequency, from 1750 cm^{-1} to 1660 cm^{-1}. Since the pH titrations and other chemical evidence seems to indicate that the co-ordination is through nitrogen, the decrease in carbonyl frequency could be interpreted due to the mass effect of the heavy metal atoms, which must have some perturbation in these ring compounds. Furthermore some of the decomposed metal in the isolated product, might react with carbonyl group resulting a decrease in its frequency.

The composition of the green complex was established by Job's and molar ratio, methods. The maxima obtained in the Job's method (Fig.9-11) and the inflexion in molar ratio method (Fig.12-14) pointed towards the formation of 1:2 (Ni-phthalimide) complex. Here again molar ratio curves deviated from the normal behaviour (O.D. after the inflexion point, instead of remaining constant showed a decrease), due to the formation of yellow complex in excess of phthalimide. The stability constant of the green complex was determined by Anderson's method using the equation derived in Chapter I, for 1:2 complex and the value of K was found = 9.61×10^4 (Fig.15).

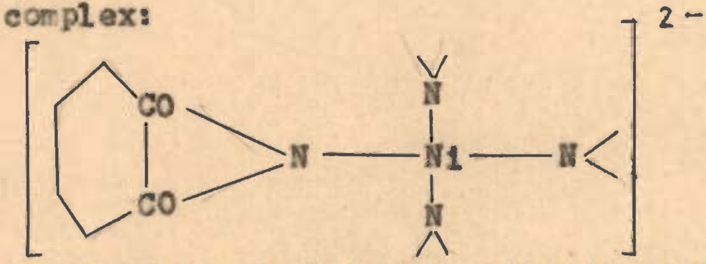
Nickel-glutarimide complex:- Interaction of nickel with glutarimide was studied by pH-metric method only, since conductometric and spectrophotometric methods could not be employed due to limitations similar to those encountered in case of nickel-succinimide complex in aqueous medium. The shape of pH-metric curves (Fig.26) was in accordance with the typical curves of Bjerrum's method. The value of $\bar{n}$, average number of ligand moles added per metal ion, was found to increase with pH and attained a constant value at $\bar{n} = 2$, indicating the formation of 1:2, nickel-glutarimide complex (Fig.27). The apparent value of the over all stability constant as determined from the formation curves came out to be, log K = 9.033.

Further confirmation of the composition of 1:2 , nickel-glutarimide complex was obtained from pH titrations curves obtained for solutions containing nickel chloride mixed with glutarimide in different proportions(Fig.28). A gradual shift of curves towards the lower pH range was observed till the combining ratio of nickel:glutarimide, approached 1:2. Beyond this the pH curves showed overlapping indicating that the maximum shift in pH is realised on displacement of two hydrogen ions of glutarimide by a metal ion.

Structure of the complexes:

(i) 1:4 nickel-phthalimide complex(yellow in colour formed in methyl-alcohol.

This complex is formed by a biuret reaction mechanism,since four basic nitrogen atoms are involved in co-ordination with nickel(already discussed in Ni-succinimide complex). The following structure may be assigned to the complex:



I.R.spectrum of the isolated complex does not confirm binding through nitrogen,but in solution the complex is bound through nitrogen. Different physico-chemical methods give evidence in favour of the above structure.

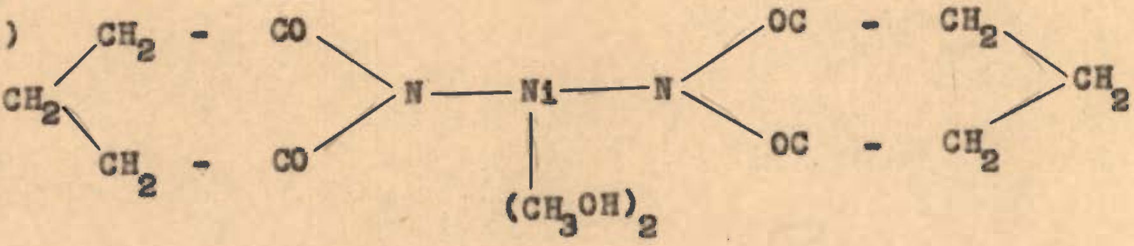
(ii) 1:2 nickel-phthalimide complex(green in colour)formed in methyl-alcohol.

Assuming that two molecules of methyl-alcohol are associated with one atom of nickel in the methanolic solution (6), formula of 1:2 (nickel phthalimide)complex may be represented as $(C_8H_4O_2N)_2$ Ni $(CH_3OH)_2$,the co-ordination number of nickel being completed by two molecules of methyl-alcohol. The possibility of chelation also exists in this complex,similar to 1:2 nickel-succinimide complex,since co-ordination through both nitrogen and oxygen is also possible. The formation of this green complex involves co-ordination with two basic nitrogen instead of four,the biuret reaction mechanism cannot therefore,be put forward here.

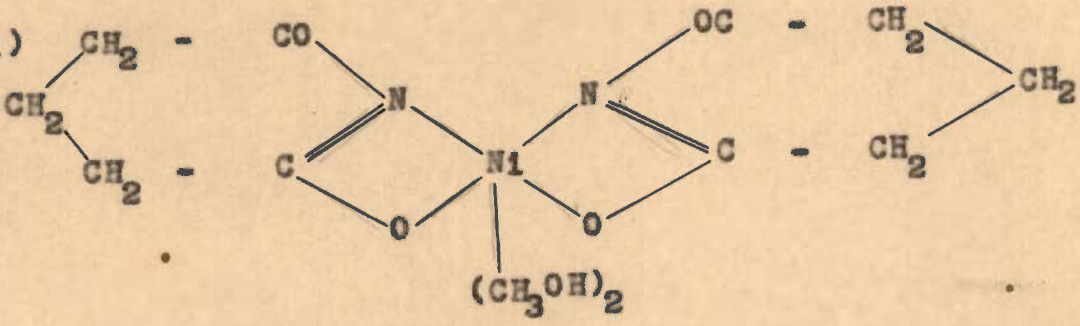
(iii) 1:2 nickel-glutarimide complex(green in colour)formed in methyl-alcohol.

The structure of 1:2,nickel-glutarimide complex may be represented by the following formulae,

(i)



(ii)



However,for lack of evidence in favour of any of the two structures, the complex may be represented as,

$$(C_5H_6O_2N)_2\ Ni\ (CH_3OH)_2$$

This complex again is not formed by biuret reaction mechanism since only two nitrogen atoms are involved in complex-ion.

III. Insoluble copper complexes of imides(succinimide, phthalimide and glutarimide) involving biuret reaction mechanism:

Preliminary investigations performed in aqueous medium revealed that copper got precipitated as hydroxide on mixing with alkaline solutions of imides. However, on carrying out the reaction in methanolic medium, complex-ion was possible to realise. It was thus observed that bluish violet insoluble complex was obtained, on mixing methanolic potassium hydroxide to a metal-imide mixture. This bluish violet precipitate was highly sensitive towards moisture. Moreover, like nickel-imide complexes, these copper-imide complexes also got decomposed in excess of copper sulphate.

The composition of in-soluble copper complexes of succinimide, phthalimide and glutarimide, formed in methanolic medium, were studied employing conductometric, potentiometric, amperometric, and pH-metric methods. The results of the above studies were further confirmed by chemical analysis of the isolated products and I.R. spectra.

Conductometric studies:- In both direct (imides prepared in equivalent amount of KOH, in the cell) and reverse (copper sulphate along with four equivalents of KOH, in the cell), titrations the combining ratio of copper-imide came out to be 1:4 (Figs.1-4,9-12 and 17-20 for direct titrations). During the course of reverse titrations, on gradual addition of the titrant(imide), the copper hydroxide precipitate decomposed and got converted into the bluish violet complex completely, when imide corresponding to the equivalence point was added(Figs.5-8,13-16 and 21-23). The latter experiments offer possibilities of carrying out conductometric titrations with freshly prepared precipitates or suspensions which can interact with the titrant.

Potentiometric titrations:- For potentiometric titrations in the methanolic medium, it was found that a redox indicator electrode could be developed if a platinum wire electrode was dipped in a solution of cupric ions, containing extremely small amounts of cuprous ions($-Cu^{2+} : -Cu^{+}$). By employing the above device, both direct(copper sulphate in the cell) and reverse (imides in the cell) titrations were performed successfully. From the inflexion points, precise information about the binding ratio 1 Cu:4 imide, was obtained (Figs. 24-45).

Amperometric titrations:- The amperometric titrations confirmed the results of other studies. Heretoo, the combining ratio of 1:4 (copper : imide) was realised for all the three imides. However, typical curves were not obtained (Figs. 46-54). Attempt has been made to explain the nature of the curves in terms of kinetic and adsorption currents.

pH-metric studies:- Bjerrum's method is normally employed to determine the composition and stability of soluble complexes. It was observed that the experimental procedure of this method could be used to determine the composition and stability of complexes showing tendency to exist as colloidal precipitate. Since the complexes remained in highly dispersed form in excess of the ligand, and flocculation sets in, only in the higher pH range, average stability constants could be computed from the curves (with and without the metal ions) in the range of pH where precipitation is not started.

In all the three cases the value of $\bar{n}$ was found to increase regularly with increase of pH and attained a constant value of approximately four (Figs.55-61), confirming the existence of 1:4 (metal-imide) complexes. The values of apparent stability constants as calculated from the average stability constants are tabulted below:

	Average stability constant, $\log k = -\log A$ at $\bar{n} = 2$.	Over all stability constant, $\log K = 4 \log k$.
Cu-succinimide complex.	2.833	11.333
Cu-phthalimide complex.	3.45	13.80
Cu-glutarimide complex.	3.483	13.933

The pH metric titrations performed with copper alone and with different proportions of imides, 1:1, 1:2, 1:3, 1:4 and 1:5 (Cu:imide) (Figs.62-64) exhibited a continuous shift towards lower pH region till a metal-imide ratio of 1:4 is reached. Beyond this ratio the curve obtained over lapped the curve for 1:4 proportion showing thereby that a maximum of four protons can be liberated from four imide molecues per metal ion. Chemical analysis of the isolated complexes also confirmed 1:4 (metal-imide) combining ratio.

I.R. studies: - The I.R.spectra of imides and their 1:4 complexes with copper revealed a marked shift in carbonyl stretching frequency (Figs.65-66) pointing towards oxygen-metal binding. Since the pH-metric, conductometric and other chemical evidence seems to indicate that the co-ordination is through nitrogen, the decrease in carbonyl frequency could be interpreted due to the mass effect of the heavy metal atoms, which would definitely have some perturbation in these ring compounds. The NH vibration frequency could not be examined due to the interference from the OH absorption bands of methanol, which probably is present in the complex.

In view of the results, structure of copper complexes of succinimide, phthalimide and glutarimide may be represented by the formulae given below:

Cu-succinimide $((C_4H_4O_2N)_4 \quad Cu \quad (CH_3OH)_2)^{2-}$

Cu-phthalimide $((C_8H_4O_2N)_4 \quad Cu \quad (CH_3OH)_2)^{2-}$

Cu-glutarimide $((C_5H_6O_2N)_4 \quad Cu \quad (CH_3OH)_2)^{2-}$

The solvation of metal ions with methanol is not unusual as has also been reported in the literature(6)

Evidence for this is also available from I.R.spectra where OH absorption bands of methanol occurred.

The most interesting aspect of these studies, however, is that all the three complexes inspite of their insoluble nature are formed by biuret reaction mechanism since four basic nitrogen are involved in the reaction.

IV. Soluble copper complexes of succinimide and saccharin, (non biuret reaction mechanism):

Preliminary experiments in the aqueous medium revealed the formation of a bluish coloured copper-succinimide complex in the lower pH range (pH $<$ 8), stable only in excess of succinimide. This complex could be studied successfully by Bjerrum's method only. The conductometric method failed to give any inflexion point in view of the originally high conductance of succinimide solution. So was the case with spectrophotometric methods, since mixtures containing excess of copper sulphate got precipitated not allowing the use of wide concentration range for spectrophotometric studies.

Formation of another soluble copper-imide complex was observed when copper sulphate was mixed with saccharin in methanolic medium. Owing to the hydrolytic nature of this complex, probably no attempt has been made so far to study its nature. Unlike the copper succinimide complex described above, the spectrophotometric as well as the conductometric methods could be employed to determine its composition. The pH-metric method could, however, not be employed, since this reaction did not take place in alkaline medium.

Copper-succinimide complex:- Typical pH-metric titration curves were obtained both with and without the presence of copper sulphate(Figs. 1), when succinimide was titrated against potassium hydroxide solution. The value of $\bar{n}$ was found to increase with pH and attained a maximum value of two, indicating the formation of 1:2 (Cu-succinimide) complex. From the formation curves (Fig.2) the values of log K_1 , log K_2 (step-wise constants) and log K (over all stability constant), were found to be 4.75, 3.41 and 8.17 respectively. Further confirmation of 1:2 composition of the complex was obtained from the potentiometric curves (Fig.3). In these curves, since an inflexion corresponding to the ratio of two moles of KOH : one mole of copper sulphate was found to exist, it could be concluded that the number of molecules of succinimide involved in the reaction was also two.

This 1:2 (Cu-succinimide) complex formed in aqueous medium may be assigned two structures as possibility of chelation also exists in this complex (vide under discussion Chapter IV). Since there is no definite evidence in favour of any one of the two structures, the composition of the complex, may be formulated as $(C_4H_4O_2N)_2\ Cu\ (H_2O)_4$.

The behaviour in this pH range in aqueous medium is quite diffèrent from that of the biuret complex of copper-succinimide in methanolic medium.

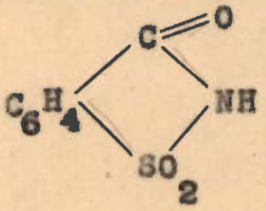
Copper-saccharin complex:- VosBurgh and Cooper's method suggested the formation of one complex only (Fig.4). Though the shift in maximum peak was not appreciable yet change in absorbance on complex-ion was quite large in the wave-length region 690 to 750 mu. The peaks obtained by Job's method corresponded to 1:1 (Cu-saccharin)ratio (Figs.5 and 6). The results of Job's method were further confirmed by molar ratio and slope ratio methods(Figs.7 and 8). In slope ratio,for the case when saccharin was kept constant,and copper was varied,the difference of O.D. was plotted,since the increase in O.D.was not only due to complex-ion,but also due to the free copper sulphate(Figs. 10-12).

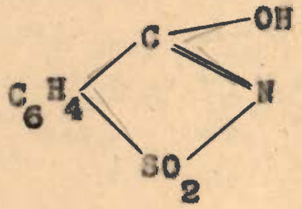
Conductometric titrations were also quite successful,inspite of the fact that it was not a precipitation reaction,giving sharp breaks corresponding to 1:1(Cu-saccharin) ratio(Fig.14,Curves 1-4).

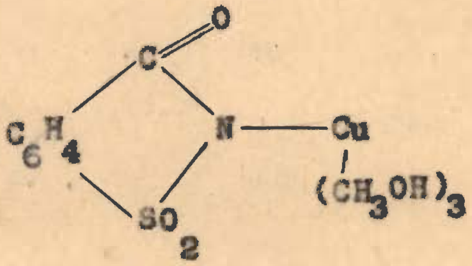
The formation constant of the complex was calculated by Anderson's method using equations 1 and 2, Page 44, Chapter I. The value of formation constant K was found to be 3.015×10^2 .

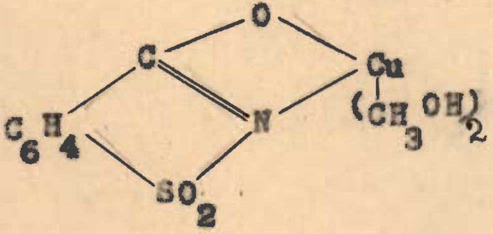
I.R.spectra of copper-saccharin complex showed a decrease in the carbonyl frequency from 1735 to 1665 cm^{-1}. (Fig.15). The band due to SO_2 group at 1190 cm^{-1} was also shifted to lower frequency 1160 cm^{-1}. An OH stretching band was also observed in the spectrum due to the presence of methyl-alcohol in the complex.

On the basis of the above results either of the following structures may be assigned to the complex, corresponding to the following two structures of saccharin.









V. Cobalt complexes of succinimide and phthalimide (non biuret reaction):

Cobalt chloride did not undergo complex-ion with imides in aqueous medium, both in acidic and alkaline ranges. However, it was observed that in methanolic medium, cobalt chloride reacted with succinimide and phthalimide in the higher pH range, to give, a soluble violet complex with succinimide and a insoluble violet coloured complex with phthalimide. The interaction of cobalt with glutarimide and saccharin was also tried under conditions favourable for such complex-ion, but unlike copper and nickel, cobalt did not form complexes with these imides. While studying these complexes, the strong solvation tendency of cobalt ions with methyl-alcohol was given due consideration(7).

The composition and stability of cobalt-succinimide complex were established by spectrophotometric, conductometric and pH-metric studies. Isolation of the complex could not be possible, as any attempt for its isolation resulted in the precipitation of cobalt hydroxide. The composition of cobalt-phthalimide complex was established by conductometric and pH-metric studies only. Spectrophotometric studies could not be made in view of the insoluble nature of the complex.

Cobalt-succinimide complex: - Here VosBurgh and Cooper's absorbance curves, suggested that the maxima in methanolic solutions of cobalt chloride and its complex with succinimide occurred at the same wave-length (520 mu.) (Fig. 2). But the absorbance for cobalt-succinimide mixtures was quite large in the wave-length region 325-350 mu., while absorbance of cobalt chloride solutions was negligible in this region of wave-length. Therefore experiments for composition, of the complex were performed in this region of wave-lengths. From Job's method of continued variation (Figs. 3-5) as well as from molar ratio method (Figs. 6-8), evidence for 1:2 (cobalt-succinimide) ratio was obtained. The stability constant of the complex was calculated from Anderson's method employing equations 3 and 5, Pages 44 and 45. The value of stability constant, K was found to be 3.35×10^4.

Conductometric titrations (succinimide in the cell) confirmed the formation of 1:2 complex (Figs. 10, Curves 1-3). During pH-metric studies it was indicated that the value of $\bar{n}$ increased with increase of pH, and attained a maximum value of two showing the formation of 1:2 complex. The value of apparent over all stability constant as computed from average stability constant was found to be ,log K = 6.45.

Cobalt-phthalimide complex:- Conductometric titrations(Fig.1 between cobalt chloride and phthalimide(in the cell),gave sharp break corresponding to 1:2 combining ratio of cobalt-phthalimide. In pH-metric studies variations in pH were similar to those as observed in cobalt-succinimide complex. On the basis of these studies the existence of a 1:2 complex was envisaged. As in the case of copper-imide complexes in methyl-alcohol,Bjerrum's method could be used in the pH range upto which precipitation was not set up. The value of over all apparent stability constant as calculated from average stability constant came out to be, log K = 6.05 (Figs.14 and 15).

Structure of the complexes:

(i) 1:2 cobalt-succinimide complex(violet in colour)formed in methyl-alcohol.

This complex is formed by non biuret reaction mechanism since only two basic nitrogen atoms are involved in the complex-ion. Since cobalt exhibits the property of solvation in methanol(7),the structure of the complex may be represented as, $(C_4H_4O_2N)_2$ Co $(CH_3OH)_4$.

(ii) 1:2 cobalt-phthalimide complex(violet in colour)formed in methyl-alcohol.

According to the similar considerations as involved in cobalt-succinimide complex,structure of 1:2,cobalt-phthalimide complex may be represented as:

$$(C_8H_4O_2N)_2\ Co\ (CH_3OH)_4$$

Biuret reaction mechanism cannot be put forward here also since only two basic nitrogen atoms are involved in the structure.

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