PHYSICO-CHEMICAL STUDIES ON THE INTERACTION OF ORGANIC COMPOUNDS WITH CYANOGEN COMPLEXES WITH SPECIAL REFERENCE TO THEIR INTERACTION WITH NITROSOBENZENE, PYRIDINE, 8-HYDROXY-QUINOLINE 5-SULPHONIC ACID AND GLYCINE.

Thesis submiited for the award of the
Degree of Doctor of Philosophy
in Chemistry

by
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ROORKEE, U. P.
(INDIA)
Dec. 1966

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DECEMBER, 1966

CERTIFICATE

Certified that the thesis entitled "Physico-chemical studies on the interaction of cyanozen complexes with organic compounds, with special reference to their interaction with nitrosobenzene, pyridine 8-hydroxyquinoline 5-sulphonic acid and glycine", which is being submitted by Mr Hari Om for the award of the degree of doctors of philosophy in Chemistry of the University of Roorkee, Roorkee is a record of his own work under my supervision and guidance. 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 and three months at this University to perpare this thesis.

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ACKNOLEDGEMENT

I take this opportunity to express my deep and sincere gratitude to my teacher Dr. W.U. Malik, D.Sc., Ph.D., F.N.A.Sc., F.R.I.C. (London), Prof. and Head Chemistry Department, University of Roorkee, Roorkee for his benevolent help, keen interest and invaluable guiadance throughout the research work leading to the completion of thesis. I am greatly indebted to him for initiating me into research work and for his endearing and persistent efforts to inspire love and aptitude for the subject.

My thanks are also due to Dr. D.R. Gupta, Prof. and Head Chemistry Department, Pant Nagar University, Nainital, formerly Reader in Chemistry Department of Roorkee University for help and encouragement.

I am grateful to my fellow workers especially of Dr. S.P. Verma, Mr. C.L. Sharma, Mr. M.C. Jain, Mr. T.C. Sharma, Mr. Puran Chand, Mr. J.P.S. Arora and Mr. S.M. Saleem for sincere co-operation.

I shall be falling in my duty if I do not thank to the management and Principal of M.S. College, Saharanpur for providing study leave to carryout this work and to my colleagues of the college for encouragement.

Hari Om

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GENERAL INTRODUCTION

GENERAL INTRODUCTION

Complex metal cyanides of atleast twenty eight heavy metals (in between Ti (22) and U (92)) in their various oxidation states are reported in the existing literature (1). Majority of these compounds are hexa co-ordinated (octahedral), although quite a few exist as tetra co-ordinated (e.g., copper, zinc, palladium, nickel, mercury, platinum, gold etc.) cyanides (tetrahedral or square planar) or in the form of tricyano (planar) or dicyano (linear) complexes. Others of particular interest are cyano complexes of Mo, W and Re of co-ordination number eight (dodecahedral) with tendency to expand their co-ordinating sphere to ten and a series of 'mixed cyanide complexes', accomodating NO, OH, H_2O, CO, NH_3 etc. in the co-ordinating sphere, e.g., $Fe(CN)_5NO^{--}$, $KRe(CN)_2(CO)_4$, $W(CN)_7(H_2O)^{---}$, $CrO_4(CN)_2(NH_3)^{--}$.

Comprehensive investigations on the chemistry of metal cyanides have more or less remained limited to those of iron. Valuable information on the synthetic, thermodynamic, electrochemical, analytical and kinetic aspects is available on the basis of these investigations Similar approaches are being made towards the study of octacyano complexes in recent years.

Before introducing the problem it would be worthwhile to give a brief review of the work done on the complex cyanides of iron.

Synthetic:

Information on this aspect deals with the preparation of simple and mixed metal cyanides, salts of metal cyanides with organic bases and the characterisation of these compounds. Begining with the preparation of Iron blues. The synthetic aspects covered the preperation of such difficult compounds as the salts of hydroferrocyanic acid with a large number of organic bases, e.g., aniline, o-toluidine, dimethylaniline, pyridine, benzidine, isoquinoline etc. and basic dyestuffs, e.g. Bismark brown, auramine, malachite green, methyl violet, acriflavine etc.(2); mixed complex cyanides (3-10) of Fe(II): $Fe(CN)_5(H_2O)^{3-}$, $Fe(CN)_5\ (NO)^{2-}$, $Fe(CN)_5(NO_2)^{4-}$, $Fe(CN)_5(AsO_2)^{4-}$, $Fe(CN)_5(SO_3)^{5-}$, $Fe(CN)_5(CO)^{3-}$, $Fe(CN)_5(NSo_4)$, $Fe(CN)_5(NH_3)^{3-}$, $Fe(CN)_2(CH_3NC)_4$, $Fe(CN)_2(Phen)_2$, $Fe(CN)_2(dipy)_2$ $Fe(CN)_4(Phen)^{2-}$, $Fe(CN)_4(dipy)^{2-}$ and $Fe(CN)_2(CO_2)(Py)$ and Fe(III): $Fe(CN)_5\ H_2O^{2-}$, $Fe(CN)_5\ (NH_3)^{2-}$, $Fe(CN)_5(NO_2)^{3-}$ and $Fe(CN)_5(NO)^{3-}$.

Studies on the structure of these complexes date back to 1930 have been investigated. The constitution of Prussion and Turnbulls blues was studied by keggin and Mites (11) with the help of x-rays (more refined and accurate x-ray diffraction now makes it possible to make a distinction between the C and N attached to metal ion). These studies were extended by Weiser, Milligan and Bates (12) and later by Reganontic (13) to give useful information about the structure and chemical constants of a number of metal ferrocyanides. Investigations of the later author showed the existence of complex anions of the type $MFe(CN)_6^{--}$ with interstitial structures in thin films of copper ferrocyanide.

The techniques of absorption (visible, infra red and ultraviolet regions) spectra and magnetic susceptibility when applied to the dispersed precipitate of Iron blues lent support to the theory of super complex formation and formulae: $Fe\ Fe(FeCN_6)_2$ and $Fe\ Fe(FeCN_6)_3$ were assigned to Prussian and Turnbull blues respectively.

Recently magnetic (14), cryscopic (15) and polarographic (16-17) studies to investigate the structure of mixed complexes of Fe(II) and Fe(III) were employed.

<u>Colloidal properties:</u>

Investigations on this property can be divided under two sub-heads: one dealing with the properties of metal ferrocyanide colloids, the other dealing with the composition and stability of colloidal precipitates of some less familiar metal cyanogen complexes.

Viscosity data of Ghosh and Dhar (18), Malik and Bhattacharya (19) offered strong evidence for the adsorption of the reacting ions, Fe^{3+}, $FeCN_6^{4-}$, $FeCN_6^{---}$ on Prussian and Turnbulls blues. The latter authors also studied the composition, adsorptive, hydrolytic and colloidal properties of zinc, manganese, nickel and cobalt ferrocyanides. Other colloidal aspects studied were changes in conductivity, pH, zeta potential (20-21) of copper ferrocyanide, permeability(22-24) of metal ferrocyanide (cobalt, nickel, silver, chromium etc.) membranes and their sol-gel transformation. Malik (25) for the first time reported the existence of a number of soluble complexes of Cr(III); Be (II); Mo(III and VI), Ti(III and IV) etc. and studied their composition and stability by the spectrophotometric method (26-27). The Cr (III) and Cr(II) complexes were isolated and composition confirmed by chemical analysis.

Electrometric and analytical studies:

With the more frequent use of physico-chemical methods, especially the electrometric ones, precise information not only about the composition of these complexes but about the use of hexacyanoferrate (II and III) as analytical reagent was obtained. In this connection worth mentioning is the contributions of Kolthoff (28-29) who for the first time successfully employed conductometric and potentiometric methods in studying the metal cyanide reactions and, at the same time, demonstrated the importance of potassium ferrocyanide as a reagent for the estimation of metal ions, specially zinc (the use of conductivity titrations in precipitation analysis was employed). Kolthoff's work was followed by extensive investigations on the use of potassium ferro and ferricyanides in quantitative analysis by other workers and a number of papers on this aspect of the problem appeared from 1922 to 1929. These include the electrometric titrations of ferricyanide with titanous sulphate (30-31), Vanadate hydrosulphite (32) and ceric ions (33). The effect of alkali on the titrations of certain metal ions (Cd^{++}, Fe^{++}, Pb^{++} Ag^{+}, Mn^{++} etc.) with ferrocyanide (34) was discussed.

Extensive use of electrometric technique was made from 1946 onwards to study the compositions of the metal ferrocyanogen complexes. The complexes studied were cadmium ferrocyanide copper ferro and ferricyanides, Prussian and Turnbull blues, zinc ferricyanide, prussian green, mercuric and uranyl ferrocyanides, nickel ferricyanides (35-37).

The studies on metal ferrocyanogen complexes during this period was not limited to the use of conductometric and potentiometric methods alone. The comparatively new technique of amperometry was also employed for the elucidation of the composition of these complexes. Kolthoff (38) for the first time used amperometric titrations to show that the end point in the ferrocyanide titration of lead corresponded to the precipitation of Pb_2FeCN_6. Later on

Chounyk and Kleibs (39) Zuman (40) Khosla and Gaur (41) Amore (42) used amperometric titrations in studying copper ferrocyanide, ferric-ferro cyanides of manganese, cadmium and silver. Zolotavin and Kuznetova (43) carried out polarographic titrations with vanadyl sulphate.

Of the other recent techniques employed, besides amperometry and polarography are the coloumetric titrations and ion exchange methods. Hartley and Lingane (44) had described a method for the coloumetric titrations of Tl^+ in strongly alkaline solution by means of $Fe(CN)_6^{3-}$ generated by anodic oxidation of $Fe(CN)_6^{4-}$ at platinum anode. The accuracy of the method was found to be within 0.2 per cent.

In connection with the attempts to use hexacyanoferrate (II) as the analytical reagent it is worthwhile to mention the work of Deshmukh and Fujita. Deshmukh (46) carried out determination of ferrocynide with lead nitrate and also the volumetric determination of cadmium and cerium by potassium ferrocyanide. Cadmium and cerium were estimated by titrating excess of potassium ferrocyanide after the complete precipitation of the respective metal ferrocyanides, while in case of lead a saturated solution of diphenyl cabazone was used as an indicator. Fujita (47) estimated lead, silver manganese, nickel cobalt, cadmium and mercury volumetrically. He used starch-iodine (silver, manganese, nickel, cobalt), phenol red (lead) potassium chromate (mercury and cadmium) as internal indicators for the titrations of metal ions.

More recent studies of Boyland and Mery (48) reveal the possibility of using hexacyanoferrate (III) as a colorimetric reagent for the estimation of arylhydroxylamines and nitrones or its use as an oxidising agent for reducing sugars (49). Dolezal and Zyka (50) studied analytical use of hexacyanoferrate (III) in the determinations of quinones in presence of zinc salts as reaction accelerators.

Thermodynamics:

Thermodynamical measurements, which would include measurement of formation constants, enthalpies and entropies of formation in solutions, have been very little studied so far. Even for most stable complexes, e.g., $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ no stepwise formation constant has been successfully reported.

Hepler, Sweet (51) and Jesser had reported heat of solution in water of $K_3Fe(CN)_6$, $K_4Fe(CN)_6$ and the heat of oxidation of $Fe(CN)_6^{4-}$ by liquid Br_2.

Stephenson and Morrow (52) had measured the heat capacities of potassium ferricyanide and potassium cobalticyanide. These studies revealed a gradual transition, magnetic in nature, occuring at 131°K in the paramagnetic potassium ferricyanide.

Other investigations, worth mentioning, on thermodynamic properties are those of Asperger (53) Emschwiller (54) on the hydrolytic decomposition of hexacyanoferrate (II). More recent work in this direction is due to Breck (55) and Vernon (56) who investigated entropy differences between corresponding ferrate (III) and force constants and vibrations of, in relation to isostructural hexacyanoferrate (III).

Kinetic Studies:

Recent reviews (57,58) provided useful data on this aspects. These studies can be divided under the following sub-heads:

(a) Ligand Exchange

(b) Radio active metal exchange

(c) Redox Reaction

(d) Hydrolytic decomposition with dilute acids ultraviolet light and heavy metals.

(a) Ligand Exchange:

A great deal of work has already been done on the kinetics of radio cyanide exchange with the better known complex cyanides. It is unfortunate that almost always the exchange has been either immeasurably fast or slow. Little can be done with those reactions which are inconveniently slow but techniques could probably be developed for studying the very fast reactions. At present one can have no idea wether these immeasurably fast exchanges are really very fast or wether they are separation induced exchanges.

Another type of reaction which might be usefully investigated is the chemical exchange of ligands (this overlaps with the thermodynamic study of mixed complexes to some extent). Little kinetic work has been reported on this subject. Most of the work worth notable has been done on the exchange of the type (59,60) $Fe(phen)_3^{2+} + C\bar{N}$ and $Fe(CN)_6^{4-} + NO_2^-$. Very recently the use of hexacyanoferrate (III) has been reported for oxidation of sugars (D-glucose, D-galactose and D-fructose) by Nath, Singh (61) and Kasper (62). The former workers reported that the reaction rate of oxidation is independent of $Fe(CN)_6^{3-}$ concentration, and directly proportional to OH^- concentration and concentration of reducing sugars. The short induction period is due to dissolved oxygen in the reaction mixture which is considerably reduced by deaerating the solution with nitrogen. An enediol as the intermediate product is postulated. The reaction rates in decreasing order are D-fructose > D-glucose > D-galactose.

Kasper (62) investigated that the decrease in $K_3Fe(CN)_6$ concentration corresponded to first order reaction, activation constant $H = 1.41 \times 10^{13}$ activation energy $A = 22.2$ K.Cal/mole. The change in sodium hydroxide concentration also followed first order kinetics A= 21.625 K.cal/mole H = 7.961×10^{13}. The decrease of the D-glucose concentration followed second order kinetics A = 18.311 K.Cal/mole H= 3.352×10^{11}. The extensive studies on the oxidation of sulphite by means of hexacyanoferrate (III) have been carried out by Vepreksiska and Wagnerova (63). The oxidation of sulphite is a complex reaction in which sulphate is formed as the only product according to the over all scheme:

$$2\ Fe(CN)_6^{3-} + SO_3^{2-} + H_2O \ = \ 2\ Fe(CN)_6^{4-} + SO_4^{2-} + 2H^+.$$

The reaction is second order and the reaction rate is given by:

$$-\frac{dSO_3^{2-}}{dt} = K\left[Fe(CN)_6^{3-}\right]\left[SO_3^{2-}\right]$$

The rate constant decreased with decreasing pH of the solution and at pH about 3.5 the reaction practically does not take place. At a pH of 8.94 the temperature dependence of the rate constant is expressed by the equation $K = 1.41 \times 10^{-8}$ exp. (-14000/RT) mole/sec.

(b) Radio active exchange:

Radio active exchange of stable iron cyanogen complexes has been extensively studied by Staranks (64) and Lewis (65). The following exchange reactions have been studied.

$Fe(CN)_6^{4-} - \overset{*}{Fe}(aq)^{2+}$ No measurable exchange

$Fe(CN)_6^{4-}$ - $\overset{*}{CN}^-$	None at pH 10.3, $t_{1/2}$=c 35 h. at pH 3.5
$Fe(CN)_6^{3-}$ - $\overset{*}{Fe}(aq)^{3+}$	No exchange in six days
$Fe(CN)_6^{3-}$ - $\overset{*}{CN}^-$	No measurable exchange
$Fe(CN)_5(H_2O)^{3-}$ - $\overset{*}{CN}^-$	$t_{1/2}$=38 h at pH 10.0
$Fe(CN)_5(NO)^{2-}$ -$\overset{*}{CN}^-$	$t_{1/2}$=5.5 days at pH 10.3
$Fe(CN)_6^{3-}$ - $\overset{*}{Fe}(oxalate)_3^{3-}$	No exchange in 10 minutes at pH 1.2
$Fe(CN)_6^{4-}$ - $\overset{*}{Fe}(CN)_6^{3-}$	$K_2 = 3.5x10^2 M^{-1} sec^{-1}$ at 4°C

Korshunov and Lebedeva (66) investigated isotope exchange of iron in prussion blue. Adamson (67) established a general correlation between the rate of exchange of di and trivalent ions and their manganetic moments in the oxidation reduction reactions of hexacyanoferrate (II) ions in solutions.

(c) Redox reaction:

This field of research has a wide scope and overlaps section (a) and (b) in its wider interpretation. The following main redox reactions of iron cyanogen complexes were reported by Gordon (68), Czapski (69) and Sutin (70) are:

$Fe(CN)_6^{4-} + IrCl_6^{2-}$	K_2=1.2x10$^6 M^{-1} sec^{-1}$(in H_2O)
$Fe(CN)_6^{4-} + IrCl_6^{2-}$	K_2=4.1x10$^5 M^{-1} sec^{-1}$(in 0.5 M-$HClO_4$)
$Fe(CN)_6^{4-}$ + $Fe(phen)_3^{3+}$	K_2 10$^8 M^{-1} sec^{-1}$
$Fe(CN)_6^{4-}$ + $OS(dipy)_3^{3+}$	K_2 10$^8 M^{-1} sec^{-1}$
$Fe(CN)_6^{3-}$ + ferrohaemoglobin	K_2= x10$^4 M^{-1} sec^{-1}$

More recently the redox reaction of $Fe(CN)_6^{3-}$ + I^-, $Fe(CN)_6^{4-}$ + I_2 has also been studied by Indelli (71) and the oxidation reduction potential (E) of the $H_3Fe(CN)_6 \rightleftharpoons H_4Fe(CN)_6$ system was studied by Mohar and Papp (72). They reported the E^oC of the system as = 70.0xlogc + 692 mv., where c is the concentration expressed in moles/litre. The value of E_c^o was found to increase with increasing acidity according to E_{pH}^o =-94.5 pH + 691 mv. The temperature dependence of E^o is $\frac{dE}{dt}$ = 1.0 mv./°C.

(d) Hydrolytic decomposition:

The cyanogen complexes undergo hydrolytic decomposition. The problem regarding the possibility of the decomposition of cyanides by heavy metal ions was for the first time, explored by Pinter (73) who observed that Hg^{++} ions in slightly acid solution catalyse the formation of colloidal prussion blue from alkali ferrocyanide according to the following summarising equation:

$$8\ Fe(CN)_6^{4-} + 28H^- + 4K^- + O_2 =$$
$$4K\ Fe\ Fe(CN)_6 + 24\ HCN + 2H_2O$$

The studies on this intersting observation were extended after a period of ten years by Emschwiller (74) who initially carried out the studies on the dissociation of the ferrocyanide ions in aqueous solution by hydrogen ions. He observed that the rate of decomposition of $Fe(CN)_6^{4-}$

was of first order in lower concentration of hydrogen ions but was of zero order in the concentration of H^- at high acidities. Further the HCN formed during the dissociation retarded the decomposition especially at lower acidities. For 0.01M $K_4Fe(CN)_6$ and 2 to 5 N H^+ the reaction appeared homogeneous and could be followed by determining Fe^{++} or by using the violet colouration given by nitrosobenzene with $(Fe(CN)_5H_2O)$ for colorimetric estimation. The latter method gave enough evidence for stepwise dissociation first to $(Fe(CN)_5H_2O)^{3-}$ (K_1) and then Fe^{++} (rate constant about fifteen times K_1). This stepwise dissociation was also found to fit in the experimental results at 50°C for hetrogeneous decomposition to $K_2Fe\ Fe(CN)_6$. The following mechenism for the reaction was put forwarded:

$$Fe(CN)_6^{4-} + H_2O \longrightarrow Fe(CN)_5H_2O + CN^-$$

(slow reaction)

followed by the capture of CN^- by H^+.

Further extention on this espect was started with the effect of mercuric ions on the aqueous solution of potassium ferrocyanide by other workers, notably Asperger (75) who studied the kinetics of the reaction of potassium ferrocyanide and nitrosobenzene with special reference to the catalytic action of mercuric ions and ultraviolet light. He observed that the equilibrium of the reaction $Fe(CN)_6^{4-} + H_2O \rightleftharpoons (Fe(CN)_5H_2O)^{3-} + CN^-$ in the dark although shifts completely towards the left. The interaction between $(Fe\ (CN)_5H_2O)^{3-}$ and CN^- can be prevented by means of the relatively fast irreversible process $(Fe(CN)_5H_2O)^{3-} + C_6H_5NO$ —— $(Fe(CN)_5C_6H_5NO)^{3-} + H_2O$ thereby providing a means for determining the velocity which was found to depend on the concentration ($5x10^{-1}M$ to $5x10^{-4}M$) of potassium ferrocyanide and also on the concentration of nitrosobenzene (but only upto a concentration $1.4x10^{-2}M$). Addition of small amounts of mercuric chloride (order $10^{-5}M$) had the same influence as the ultraviolet light and the violet nitrosobenzene complex obtained was found to have the same absorption spectra in both cases. The velocity of the reaction of potassium ferrocyanide and nitrosobenzene in the presence of Hg^{++} ions depended on the pH, being maximum at pH 3.5. On carrying out absorption experiments at this pH with different concentration of mercuric ions, he found that the catalytic action of Hg^{++} ions was so large that it could be detected even at the concentration of $10^{-7}M$.

He put forward~~ed~~ the view that the reaction is strictly specific for Hg^{++} and a method can be employed for the determination of Hg^{++} ions in distilled water, other metal cations not interfering in the estimation. Based on this catalytic reaction he could also evolve a method for the diterminaiion of mercury vapours in atmosphere (76). The plot of log E_{30} against $\log(C_{Hg^{++}})$ gave a straight line upto concentration of 5×10^{-6} mole per litre of Hg^{++}, for higher concentration a linear relationship was not found to hold good.

More extensive and elaborated studies on the decomposition of potassium ferrocyanide by Hg^{++} ions was than taken up and he critically studied the influence of different mercurous and mercuric compounds including those with organic anions (O- and m-hydroxybenzoate, methylmercuric iodide, diphenyl mercury etc.). All other compounds showed catalytic activity besides diphenyl mercury where a catalytic action was not observed even at a concentration of 2×10^{-4}M.

Metal cyanides in biological systems:

Various porphyrin type iron complexes contain cyanide groups as a part of the co-ordination sphere. One form of vitamin B_{12} contains a cyanide group in the sixth co-ordination position of Co(III) though it is very liable to replacement by other groups. Dicyanide complexes of certain transitional metal phthalocyanines are also Known.

Poisoning by cyanide has been attributed to inhibition of a number of enzymes including the cytochrome oxidase system for oxygen stabilization in cells (77), in general, complex cyanides do not appear to have markedly poisonous properties unless one or more cyanide groups are easily removable from the co-ordination sphere. If however, it may be possible to prepare some derivatives of cyanogen complexes by replacing the easily removable cyanide groups by amino acids, then the mixed complexes may be of great biological importance.

The preceeding pages from the review of the literature, reveal the fact that investigations on cyanogen complexes have covered a wide and varigated field of study, ranging from the older concepts based on chemical analysis and physico chemical properties of the precipitates to the more recent ones, evolved on the basis of studies as the application of the modern electrochemical techniques (polarography, amperometry, coulometry exchange reactions etc.), the importance of the metal ferrocyanide reactions in analytical work and on the catalytic decomposition of iron cyanides by theoritical importance have been achieved by these studies. Many of these complexes still find use in the pigment industry (78), the facts remains that many interesting aspects of the problem have remained unexplored to these days. Many mixed complex cyanides with organic compounds existing in varying composition have not been studied so far on dropping mercury electrode. The concept of redox potential influencing the nature and composition of these compounds although put forward in early thirties, has not been fully worked out. Also, very little appears to have been done to study the kinetics, thermodynamics of the, photochemical redox and coloured reactions of metal cyanogen complexes with organic compounds employing various physico-chemical techniques. The work described in this thesis deals with such problems and includes the following studies.

(1) E^0 of the $Fe(CN)_5H_2O^{3-} \rightleftharpoons Fe(CN)_5H_2O^{2-} + e$ couple and the potentiometric estimation of potassium aquapentacyanoferrate (II).

(2) Polarographic studies on the kinetics of hydrolytic decomposition of potassium hexacyanoferrate (II). The anodic waves of hexacyanoferrate (II) and aquapentacyanoferrate (II).

(3) Spectrophotometric studies on the composition stability and kinetics of interaction of 8-hydroxyquinoline 5-sulphonic acid with potassium hexacyanoferrate (II).

(4) Paloregraphic studies on the reduction of the 8-hydroxyquinoline 5-sulphonate pentacyanoferrate (II) complex.

(5) Spectrophotometric and pH metric studies on the composition stability and kinetics of interaction of hexacyanoferrate (III) with nitrosobenzene.

(6) Reduction of nitrosobenzene pentacyanoferrate (II)

(II) complex at d.m.e.

(7) Amperometric titrations of (a) hexacyanoferrate (III) with Co (II) in ammonium citrate and glycine as complexing media. The reduction of resulting complexes at d.m.e. (b) hexacyanoferrate (III) with vitamine B_1 in alikaline medium.

(8) Spectrophotometric studies on the composition and stability of the product obtained by the interaction of pyridine with hexacyanoferrate (II).

(9) Reduction of bipyridine tetra-cyanoferrate (II) complex at d.m.e.

CHAPTER I

Standard electrode potential potential of aquapentacyanoferrate $^{3-} \rightleftharpoons$ aquapentacyanoferrate $^{2-}$ + e couple and polarographic studies on the hydrolytic decomposition of hexacyanoferrate (II).

(Part I)

E^0 of $(Fe^{II}Cy_5H_2O)^{---} \rightleftharpoons (Fe^{III}Cy_5H_2O)^{--} + e$ couple and the potentio-metric estimation of potassium aquapentacyanoferrate (II):

Several references (1-11) on the E^0 of the ferro-ferricyanide couple based on reactions with different oxidisable and reducible substances and simple ions are available in the existing literature. This couple in view of its high oxidation potential has successfully been employed in studying the oxidation of large number of organic compounds like sugars (12-14) vitamins (15) and modified proteins (16) etc.

Another oxidation couple falling under the category of ferrocyanogen couple is the $(Fe^{II}Cy_5H_2O)^{---} \rightleftharpoons (Fe^{III}(Cy)_5H_2O)^{--} + e$ which has not so far been investigated from the theoritical or applied stand point. It was therefore, considered worthwhile, to carry out investigations on its electrometric behaviour. In this part of the Chapter the following two aspects have been described.

(1) Estimation of potassium aquapentacyanoferrate (II) by oxidants-potassium permangnate, ceric sulphate and potassium dichromate.

(2) Determination of the standard electrode potential for the $(Fe^{II}(Cy_5)H_2O)^{---} \rightleftharpoons (Fe^{III}Cy_5H_2O)^{--} + e$ couple by potential mediator and Kolthoff's method.

EXPERIMENTAL

Potassium aquapentacyanoferrate (II) (was prepared vide Chapter I, Part I, page) and its solution was prepared by dissolving weighed quantity (assuming the formula $K_3FeCy_5H_2O$) in double distilled water. The aquapentacyanoferrate (III) was prepared by the oxidation of aquapentacyanoferrate (II) (17) and its solution was prepared by dissolving weighed quantity in double distilled water and strength was determined iodometrically. Potassium dichromate (A.R.) Potassium permanganate (A.R.) ceric sulphate (pure anhydrous) were used to prepare the respective solutions. Strengths were determined by usual methods.

Apparatus:

Pye portable potentiometer (type CAT No.7569 p) with lamp and scale arrangement was used for potentiometric measurements. The titration cell consisted of bright platinum and saturated calomel electrodes.

Estimation of aquapentacyanoferrate (II) was carried out using ceric sulphate, potassium permanganate and potassium dichromate as oxidants. Both direct (potassium aquapentacyanoferrate (II)} in the cell) and reverse (the oxidant in the cell) were carried out. Experiments were performed with the following concentration of reactants:

(1) 0.5M, 0.0166M, 0.0158M, potassium aquapentacyanoferrate (II) against 0.036M, 0.0847M, 0.00787M

ceric sulphate in direct titrations 0.0806M, 0.04M, 0.00849M and 0.05M potassium aquapentacyanoferrate (II) against 0.1M, 0.087M, 0.00787M and 0.00367M ceric sulphate respectively in reverse titrations (Fig.1,2).

(2) 0.04M, 0.0166M, 0.0155M, 0.00849M potassium aquapentacyanoferrate (II) against 0.05N, 0.1N, 0.0835N and 0.0099N potassium permanganate respectively in direct titrations (Fig.3).

(3) 0.04M, 0.0166M and 0.008M potassium aquapentacyanoferrate (II) against 0.05N potassium dichromate in direct titrations, 0.04M, 0.0806M potassium aquapentacyanoferrate (II) against 0.1N, 0.05N potassiu dictnmate in reverse titrations (Fig.4).

Initial volume in the cell in each case was 10 ml containing 4N sulphuric acid.

Some of the results are tabulated below:

TABLE No.1

Potentiometric titration of 0.05M potassium aquapentacyanoferrate (II) (in cell) against 0.036M ceric sulpha
Total volume 10.0 ml in 4N H_2SO_4.

Volume of ceric sulphate added	Pot. Vs S.C.E. volt	Volume of ceric sulphate added	Pot. Vs S.C.E. volt
0.0	0.280	6.5	0.513
0.6	0.352	6.6	0.540
1.0	0.368	6.7	0.550
1.5	0.380	6.8	0.885
2.0	0.390	6.9	0.981
3.0	0.409	7.0	1.008
4.0	0.425	8.0	1.080
5.0	0.444		
6.0	0.473		

Fig.1 curve 1

5.0 ml of 0.05M potassium aquapentacyanoferrate
(II) 6.8 ml of 0.036M of ceric sulphate.

TABLE No.2

Potentiometric titration of 5.0 ml of 0.1666M aquapentacyanoferrate (II) (in cell) against 0.0847M ceric sulphate. Total volume 10.0 ml in 4N sulphuric acid.

Volume of ceric sulphate added (in ml)	Pot. Vs S.C.E. volt	Volume of ceric sulphate added(in ml)	Pot. Vs S.C.E. volt
0.0	0.381	0.96	0.970
0.1	0.391	1.0	1.085
0.3	0.415	1.11	1.180
0.5	0.433	1.31	1.138
0.8	0.475	1.50	1.15
0.9	0.508		

Fig.1 curve II

5 ml of 0.01666M aquapentacyanoferrate (II)

0.96 ml of 0.0847 M ceric sulphate.

TABLE No.3

Potentiometric titration of 5.0 ml of 0.00158M hexacyanoferrate (II) (in cell) against 0.00787M ceric sulphate. Total voluem 10.0 ml in 4N sulpharic acid:

Volume of ceric sulphate added (in ml)	Pot. Vs S.C.E.	Volume of ceric sulphate added (in ml)	Potnsial Vs S.C.E.
0.0	0.437	10.0	0.740
1.0	0.442	10.1	0.856
2.0	0.455	10.1	0.856
4.0	0.462	10.2	0.960
6.0	0.491	10.5	1.044
8.0	0.497	11.0	1.090
9.0	0.515		

Fig.1 curve III

5.0 ml of 0.00158M aquapentacyanoferrate (II)
10.0ml of 0.00787M ceric sulphate.

The results of reverse titration (ceric sulphate in cell) against aquapentacyanoferrate (II) are shown in(Fig.2).

Potentiometric titration results for potassium permangnate atainst potassium hexacyanoferrate (II) (in cell) and for potassium dichromate direct titrations are shown in Fig.3 and Fig.4 respectively. Good results could not be obtained in reverse titrations.

TABLE No.4

Potential variation at the inflexion point for direct and reverse titrations *

Oxident	Concentration of $K_3FeCy_5H_2O$	Concentration of $K_3FeCy_5H_2O$	Observed potential at equivalence point	Remarks
Ce(iv)				
0.0367M	0.050M	0.050M	-0.8850V.	Theoretical potential (-1.203V.) not realised, an point was locate easily.
0.0847M	0.0166M	0.0165M	-0.870V.	
0.00787M	0.0158M	0.0159M	-0.8564V.	
Reverse titrations				
0.100M	0.0806M	0.0805M	-0.725V.	Theoretical potential (-1.203 V.) not realised.
0.0367M	0.050M	0.050M	-0.700V.	
0.0847M	0.040M	0.040M	-0.865V.	
0.00787M	0.00849M	0.00846M	-0.845V.	
Potassium permanganate				
0.050N	0.040M	0.040M	-0.858V.	Theoretical potential (-1.158V.) not realised end point was located easily.
0.10N	0.0166M	0.0165M	-0.739V.	
0.00835N	0.0155M	0.0156M	-0.853V.	
0.0099N	0.00849M	0.00848M	-0.980V.	
Potassium dichromate				
0.05N	0.04M	0.042M	-0.750V.	Theoritical potential (-1.191 V.) not realised results are not accurate.
	0.0166M	0.0160M	-0.735V.	
	0.008M	0.00788M	-0.731V.	
Reverse titrations:				
0.05N	0.04M	0.0367M	-0.750V.	Theoritical potential (-1.191V.) not realised results are unsatisfactory.
0.01N	0.0806M	0.077M	-0.725V.	
0.01N	0.05M	0.046M	-0.605V	

* The following values of oxidation potentials of the oxidants were taken in to consideration while making calculations, dichromate-1.33V., ceric-1.61V. permanganate 1.5V. and for aquapentacyanide-0.806 in 4N H_2SO_4.

$$E_e = \frac{bE_{o1} + aE_{o2}}{a+b},$$ where Ee is the potential at equivalence point E_{o1} and E_{o2} are the standard potentials of two couples involved in the system and a b are the number of electrons used in respective systems.

For determining E^o by the potential mediator method ~~determining~~ potassium aquapentacyanoferrate (II) (10 ml., 0.0128M) was taken in the cell and the potential at the bright platinum electrode on adding gradually increasing amount of ceric sulphate (o.00171M), sufficient time being allowed to elapse after each addition for the attainment of steady potential, was measured. The titrations were carried out till the end point was reached as indicated by sudden change in potential. Experiments were performed employing different concentrations of sulphuric acid (range 0.5-7.0N). The value of E^o was calculated by the relation $E = E^o - \frac{RT}{nF} \log \frac{t}{t_c - t}$, where E is the electrode potential, t_c, the amount of titrant added at any particular stage during titration. The mean values of E^o as determined graphically (Fig.No.7) by plotting log $\frac{(Fe^{III}Cy_5H_2O)^{--}}{(Fe^{II}Cy_5H_2O)^{---}}$ against electrode potential in presence of sulphuric acid of concentrations

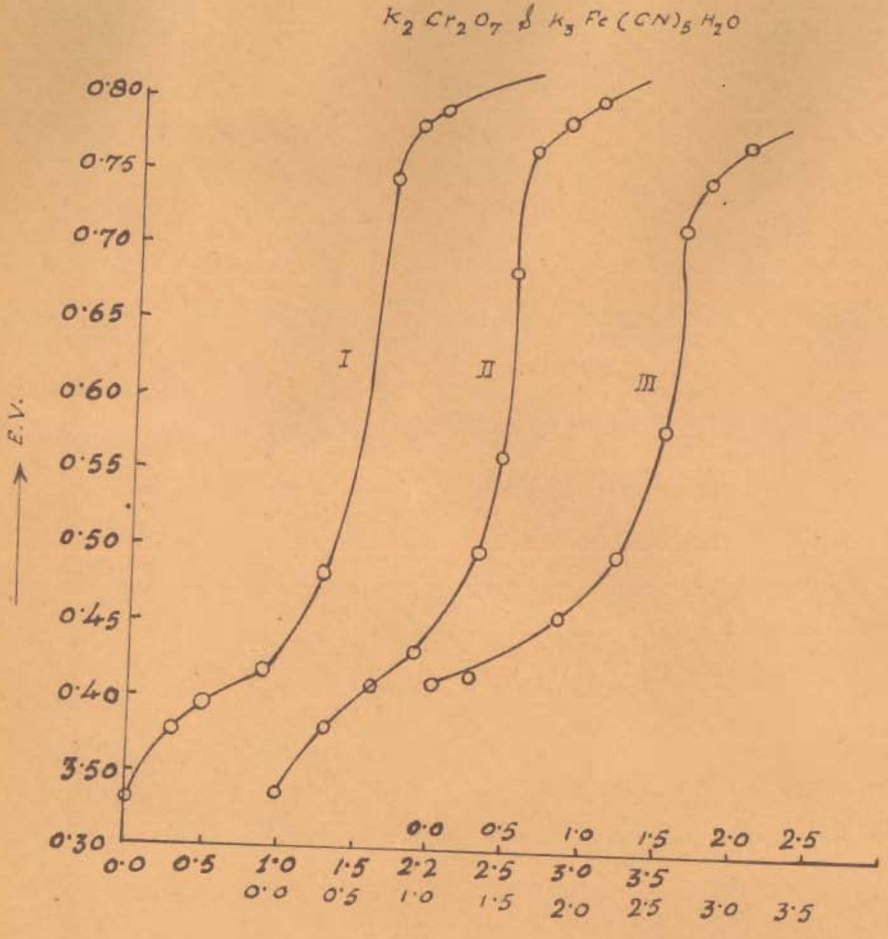

$K_2Cr_2O_7$ & $K_3Fe(CN)_5H_2O$
E.V.
0·80
0·75
0·70
0·65
0·60
0·55
0·50
0·45
0·40
3·50
0·30
I
II
III
0·0 0·5 1·0 1·5 2·2 2·5 3·0 3·5
0·0 0·5 1·0 1·5 2·0 2·5 3·0 3·5
0·0 0·5 1·0 1·5 2·0 2·5

FIG. 4

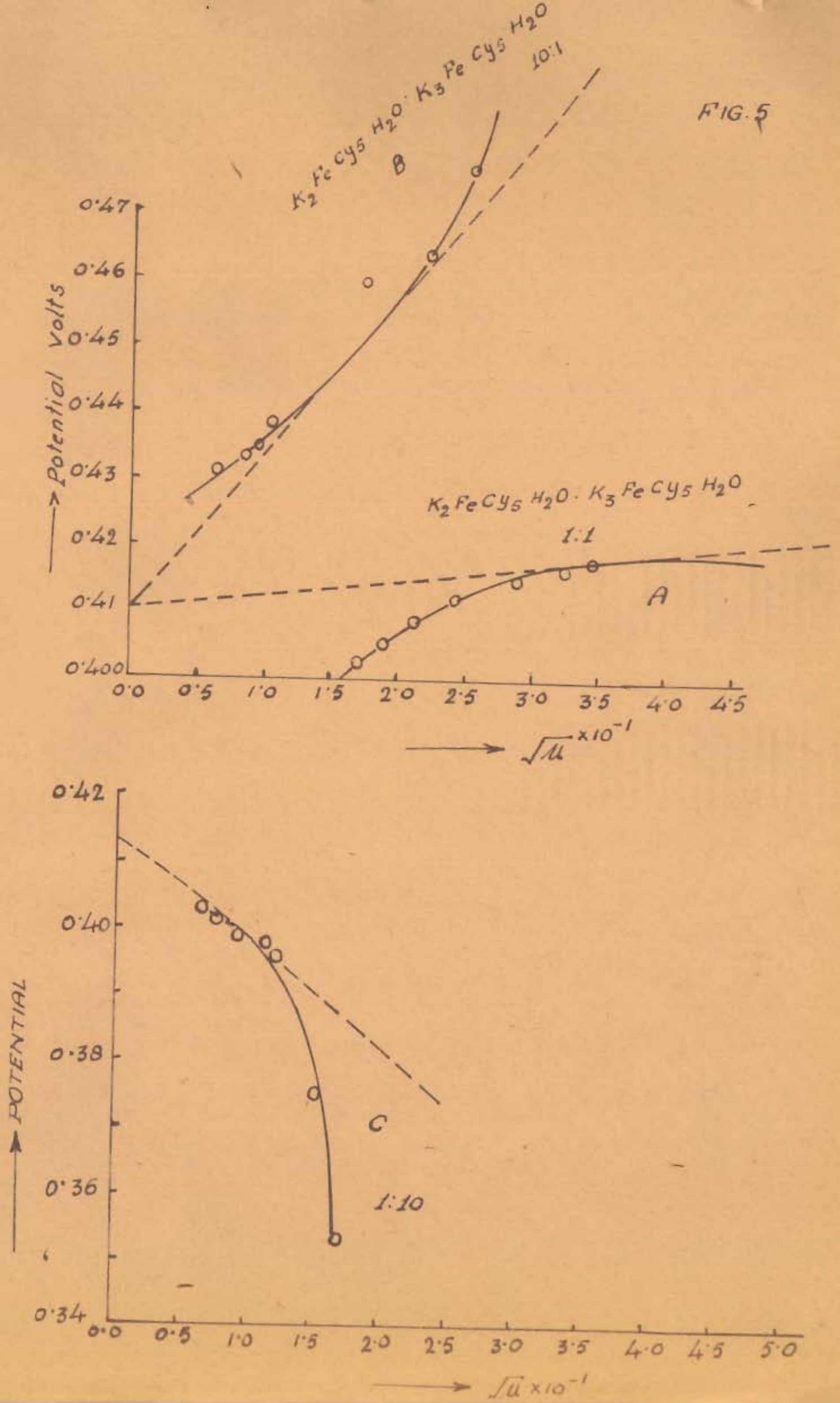

$K_2FeCy_5H_2O : K_3FeCy_5H_2O$
10:1
B
Potential Volts
0·47
0·46
0·45
0·44
0·43
0·42
0·41
0·400
$K_2FeCy_5H_2O \cdot K_3FeCy_5H_2O$
1:1
A
0·0 0·5 1·0 1·5 2·0 2·5 3·0 3·5 4·0 4·5
$\sqrt{\mu} \times 10^{-1}$
POTENTIAL
0·42
0·40
0·38
0·36
0·34
C
1:10
0·0 0·5 1·0 1·5 2·0 2·5 3·0 3·5 4·0 4·5 5·0
$\sqrt{\mu} \times 10^{-1}$

FIG. 5

FIG. 6.

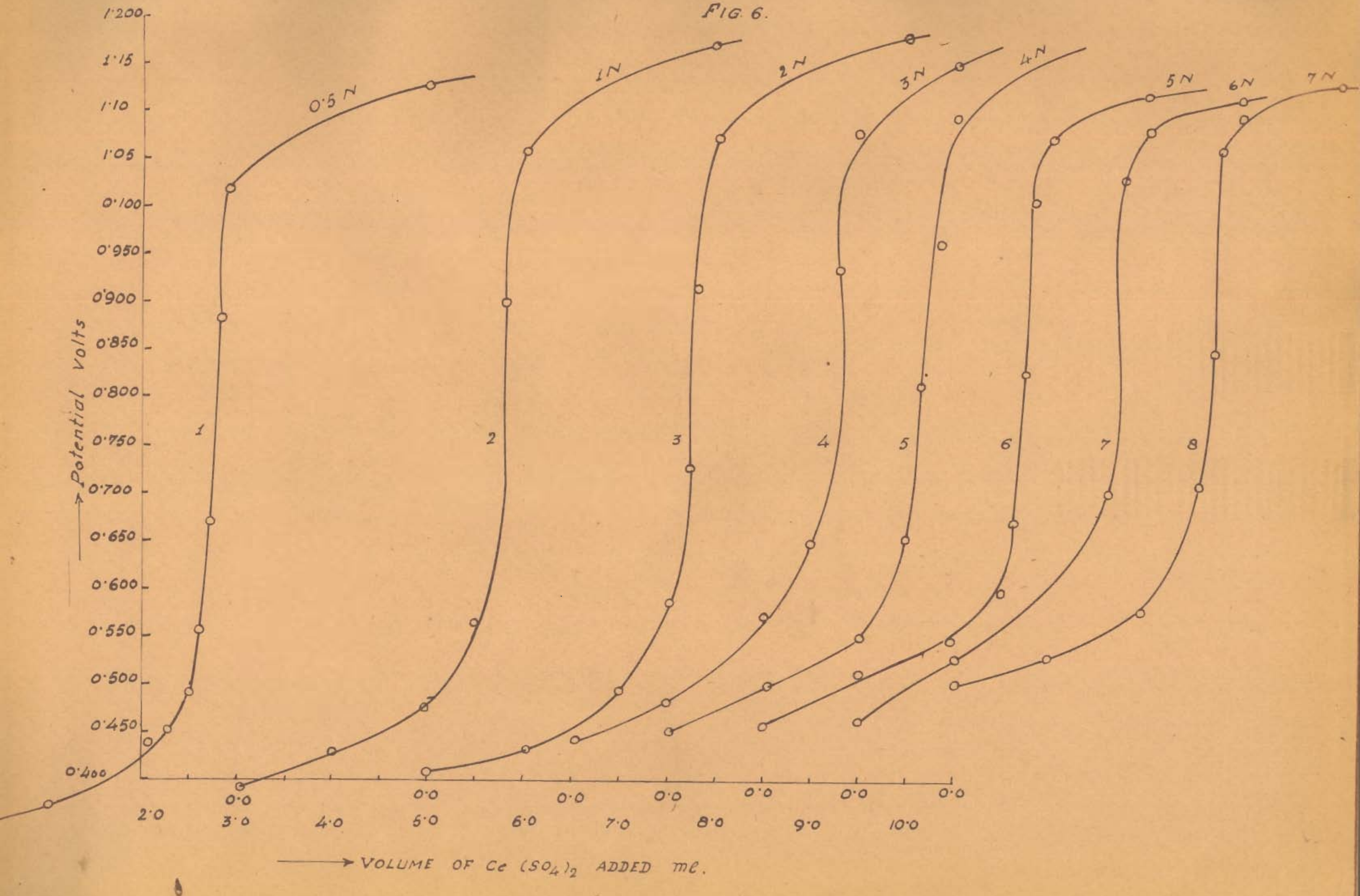

1·200
1·15
1·10
1·05
0·100
0·950
0·900
0·850
0·800
0·750
0·700
0·650
0·600
0·550
0·500
0·450
0·400
→ Potential volts
0·5 N
1 N
2 N
3 N
4 N
5 N
6 N
7 N
1
2
3
4
5
6
7
8
0·0
0·0
0·0
0·0
0·0
0·0
0·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10·0
→ VOLUME OF Ce $(SO_4)_2$ ADDED ml.

FIG. 7.

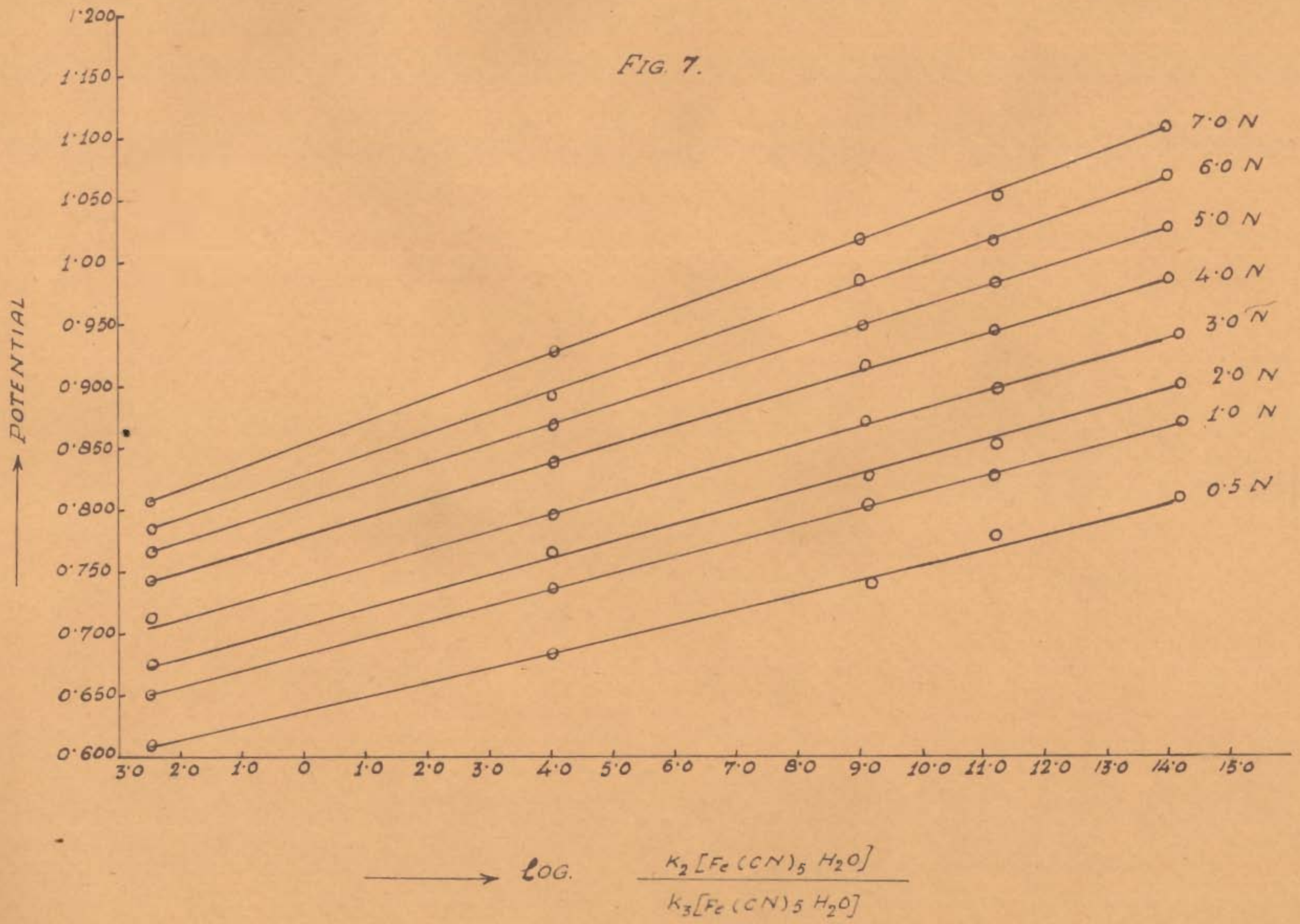

1·200
1·150
1·100
1·050
1·00
0·950
0·900
0·850
0·800
0·750
0·700
0·650
0·600
POTENTIAL
3·0
2·0
1·0
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10·0
11·0
12·0
13·0
14·0
15·0
7·0 N
6·0 N
5·0 N
4·0 N
3·0 N
2·0 N
1·0 N
0·5 N
$\log \frac{K_2[Fe(CN)_5H_2O]}{K_3[Fe(CN)_5H_2O]}$

TABLE No.1

pH	1.2	1.85	3.25	4.0	5.0	5.8	8.4	9.15	10.7	11.45
$E_{\frac{1}{2}}$ in volts Vs S.C.E. Hexacyanoferrate (II)	+0.15	+0.165	+0.182	+0.325	+0.29	+0.271	+0.271	+0.12	+0.10	-
Hydrolytic decomposition product.	+0.10	+0.10	+0.17	+0.15	+0.15	+0.16	+0.20	+0.12	+0.12	-
Aquapentacyanoferrate (II)	+0.11	0.11	0.160	0.15	0.15	0.16	0.16	0.115	0.12	-

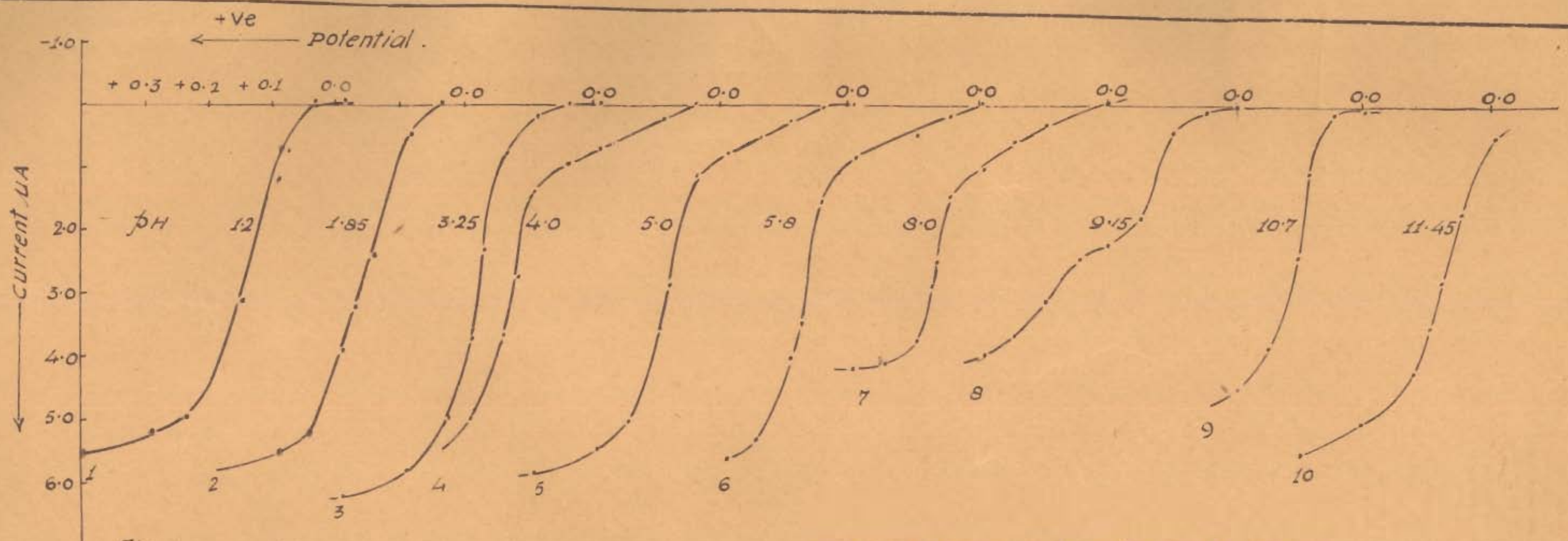


FIG. 1.A CURRENT VOLTAGE CURVES FOR HEXACYANOFERRATE (II) FROM pH 1.2 to (11.45)

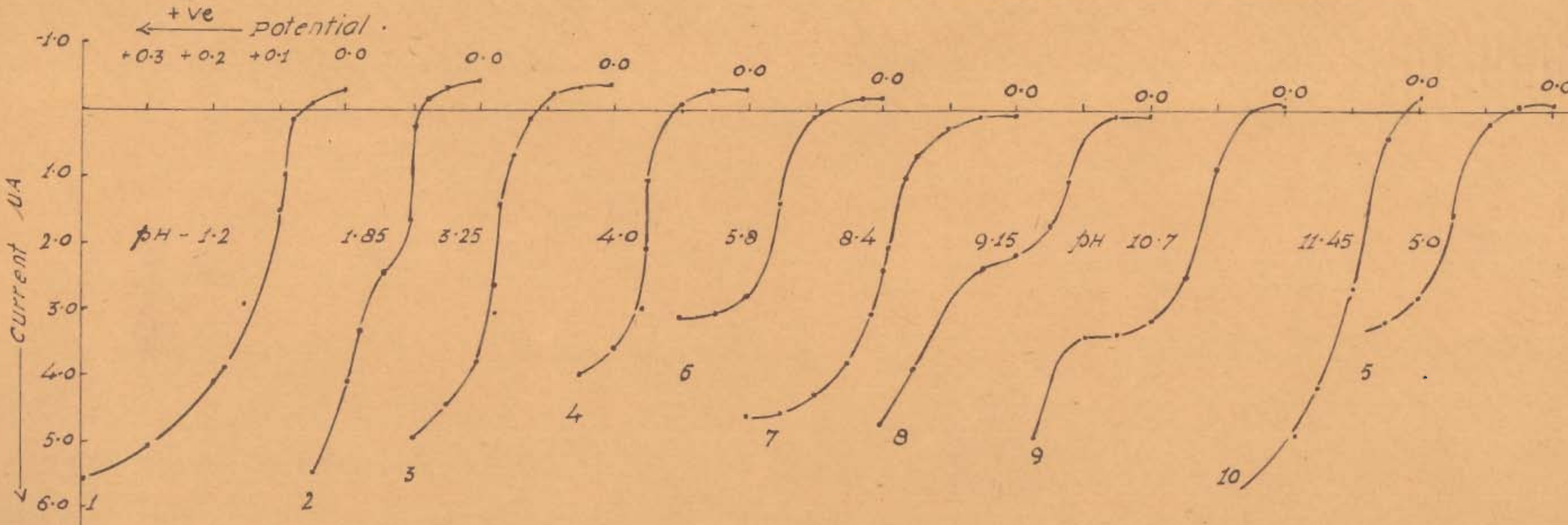


FIG. 1.B. CURRET VOLTAGE CURVES FOR HYDROLYTIC DECOMPOSITION PRODUCT OF HEXACYANOFERRATE (II) IN PRESENCE OF Hg^{++} IONS FROM pH 1.2 to 11.45.

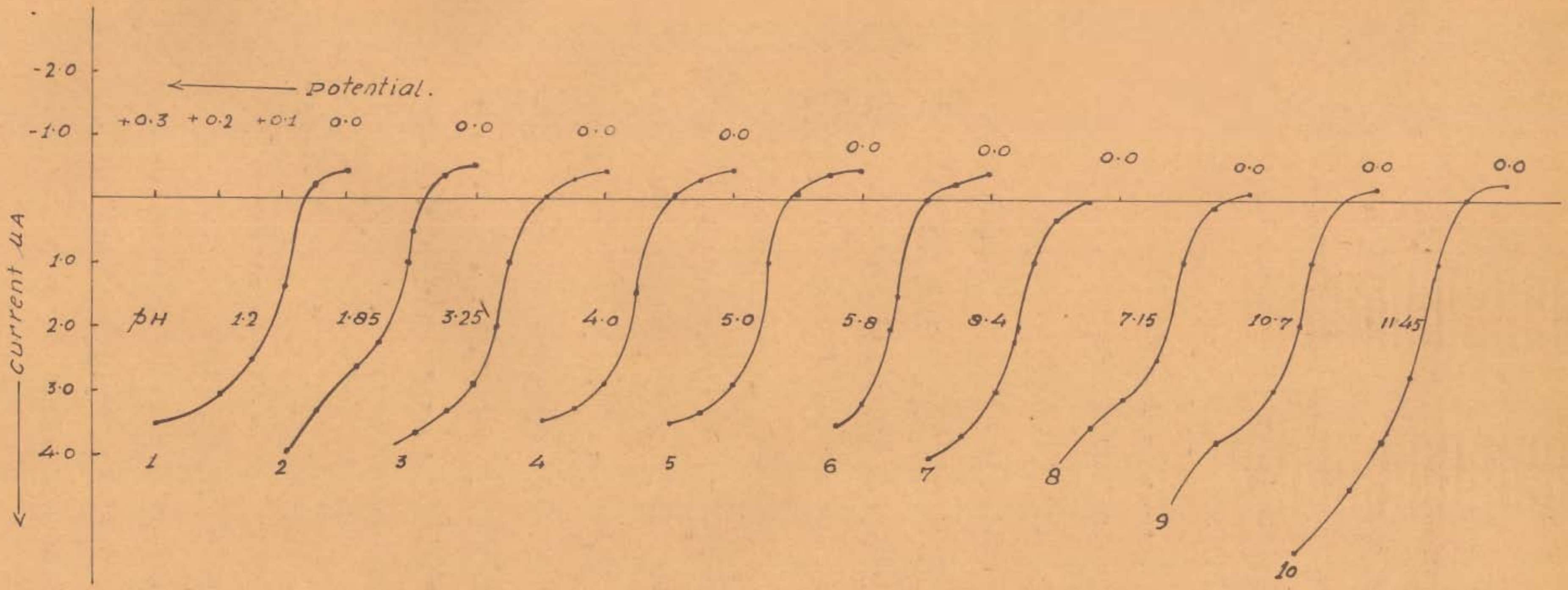


FIG. 1. c

current voltage curves for aqua pentacyanoferrate (II) from pH 1·2 to 11·45.

FIG. 2.A.

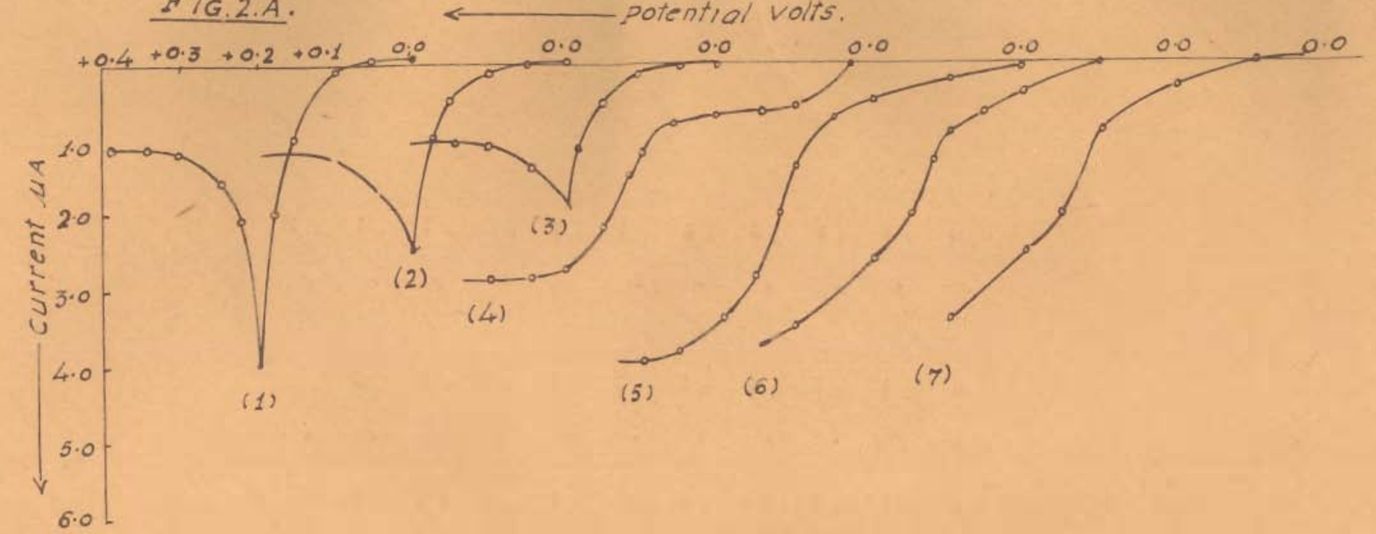
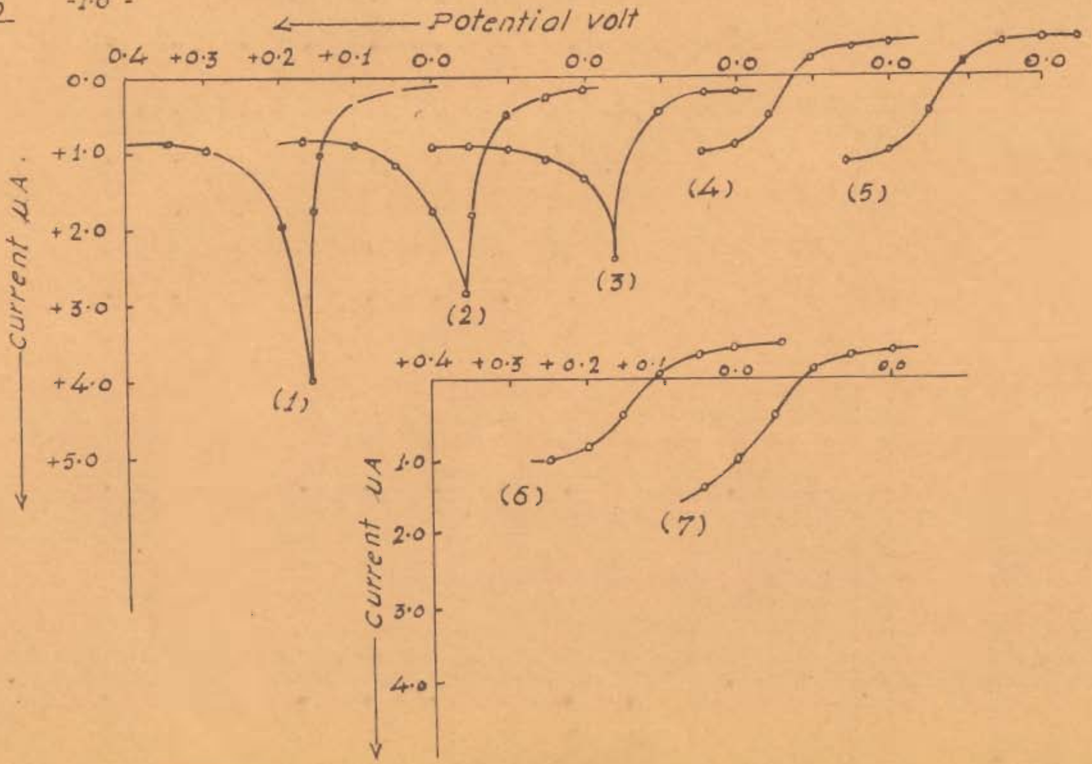

← potential volts.
+0.4 +0.3 +0.2 +0.1 0.0
0.0
0.0
0.0
0.0
0.0
0.0
← current µA
1.0
2.0
3.0
4.0
5.0
6.0
(1)
(2)
(3)
(4)
(5)
(6)
(7)

FIG. 2.b


-1.0 -
← potential volt
0.4 +0.3 +0.2 +0.1 0.0
0.0
0.0
0.0
0.0
0.0
← current µA.
+1.0
+2.0
+3.0
+4.0
+5.0
(1)
(2)
(3)
(4)
(5)
+0.4 +0.3 +0.2 +0.1 0.0
0.0
← current µA
1.0
2.0
3.0
4.0
(6)
(7)

0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0N were respectively 0.676, 0.749, 0.762, 0.806, 0.845, 0.866, 0.898 and 0.813 volt. Results are tabulated below:

TABLE No.5

E^{o} values at various concentrations of H_2SO_4 (potential mediator method) Volume and concentration of $K_3FeCy_5H_2O$ solution in the cell = 10.0 ml ; 0.0128M Normality of $Ce(SO_4)_2$ solution = 0.00171M. Value for S.C.E. at 30°C = 0.2397.

Conc. of H_2SO_4	Volume of $Ce(SO_4)_2$	Percentage of $(FeCy_5H_2O)^{--}$	Pot. Vs S.C.E.	Elect. Pot.	log $\frac{(FeCy_5H_2O)^{2-}}{(FeCy_5H_2O)^{3-}}$	E^{o} Calc.
0.5N	0.0	0.0	0.354	0.596	-	-
	1.0	35.71	0.367	0.607	-0.2553	0.622
	2.0	71.42	0.436	0.677	0.3988	0.654
	2.5	89.27	0.495	0.733	0.9201	0.678
	2.6	92.841	0.532	0.772	1.129	0.706
	2.7	96.412	0.667	0.807	1.4292	0.723
	2.8	100.00	0.882	0.922	-	-
1.0N	0.0	0.0	0.392	0.632	-	-
	1.0	35.71	0.420	0.660	-0.2553	0.675
	2.0	71.42	0.495	0.735	0.3988	0.711
	2.5	89.27	0.565	0.805	0.9201	0.750
	2.6	92.841	0.580	0.820	1.129	0.754
	2.7	96.412	0.625	0.865	1.4292	0.780
	2.8	100.00	0.900	1.124	-	-
2.0N	0.0	0.0=	0.409	0.649	-	-
	1.0	35.71	0.439	0.679	-0.2553	0.684
	2.0	71.42	0.520	0.760	0.3988	0.736
	2.5	89.72	0.585	0.825	0.9201	0.770
	2.6	92.841	0.605	0.845	1.129	0.779
	2.7	96.412	0.660	0.900	1.4292	0.780
	2.8	100.00	0.915	1.155	-	-
3.0N	0.0	0.0	0.446	0.686	-	-
	1.0	35.71	0.481	0.721	-0.2553	0.706
	2.0	71.42	0.550	0.790	0.3988	0.766
	2.5	89.72	0.630	0.870	0.9201	0.805
	2.6	92.841	0.660	0.900	1.129	0.634
	2.7	96.412	0.700	0.940	1.4292	0.855
	2.8	100.00	0.935	1.175	-	-

Table No.5 (continued)

Conc. of H_2SO_4	Volume of $Ce(SO_4)_2$	Percentage of $(FeCy_5H_2O)^{--}$	Pot. Vs S.C.E.	Elec. Pot.	log $\frac{(FeCy_5H_2O)^{2-}}{(FeCy_5H_2O)^{3-}}$	E^o Calc.
4.0N	0.0	0.0	0.450	0.690	-	-
	1.0	35.71	0.500	0.740	-0.2553	0.755
	2.0	71.42	0.596	0.835	0.3988	0.811
	2.5	89.72	0.675	0.915	0.9201	0.860
	2.6	92.841	0.700	0.940	1.129	0.874
	2.7	96.412	0.750	0.990	1.4292	0.905
	2.8	100.00	0.955	1.205	-	-
5.0N	0.0	0.0	0.453	0.693	-	-
	1.0	35.71	0.515	0.755	-0.2553	0.770
	2.0	71.42	0.620	0.860	0.3988	0.836
	2.5	89.72	0.700	0.940	0.9201	0.885
	2.6	92.841	0.735	0.975	1.129	0.909
	2.7	96.412	0.785	1.025	1.4292	0.940
	2.8	100.00	0.975	1.215	-	-
6.0N	0.0	0.0	0.465	0.705	-	-
	1.0	35.71	0.535	0.775	-0.2553	0.780
	2.0	71.42	0.620	0.860	0.3988	0.835
	2.5	89.72	0.720	0.960	0.9201	0.905
	2.6	92.841	0.780	1.020	1.129	0.954
	2.7	96.412	0.817	1.057	1.4292	0.972
	2.8	100.00	0.990	1.236.	-	-
7.0N	0.0	0.0	0.509	0.749	-	-
	1.0	35.71	0.565	0.804	-0.2553	0.819
	2.0	71.42	0.680	0.920	0.3988	0.895
	2.5	89.72	0.775	1.015	0.9201	0.960
	2.6	92.841	0.810	1.050	1.129	0.984
	2.7	96.412	0.860	1.100	1.4292	1.015
	2.8	100.00	1.060	1.300	-	-

Fig.6 curves 1,2,3,4,5,6,7 and 8 represent the potentiometric titration curves at 0.5, 1.2, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0M sulphuric acid respectively.

The value of E° in neutral medium was also determined employing Kolthoff's method (18) with only modification that measurements were carried out against a saturated calomel electrode instead of normal hydrogen or quin-hydron electrode. Since aquapentacyanoferrate (II) and aquapentacyanoferrate (III) behave like strong electrolytes, the oxidation potential should be greatly affected by a change of the ionic strengths of the solution. The purpose of study was to determine the potential of the aquapentacyanoferrate (II) and aquapentacyanoferrate (III) system at varying ionic strengths and to extrapolate the value to an ionic strength of zero; in other words to determine the normal potential of the system. In addition, the potential of a very dilute aquapentacyanoferrate (II) and ferrate (III) was determined in presence of neutral salts at varying ionic strengths, in order to test the Debye-Huckel equation.

At extremely small ionic strength, the relation between the activity coefficient of an anion and the ionic strength of the solution is given by the expression.

$$- \log f = AZ^2 \qquad (1)$$

where A is a constant for the solvent at the specific temperature and has a value of 0.514 for water at 30°C, and the ionic strength. The oxidation potential E of the system aquapentacyanoferrate (II) ferrate (III) at 30°C is then given by

$$E = E_0 + 0.06 \log \frac{{}^{a}FeCy_5H_2O^{2-}}{{}^{a}FeCy_5H_2O^{3-}} \qquad (2)$$

$$= E_0 + 0.60 \log \frac{C\ (FeCy_5H_2O)^{2-}}{C\ (FeCy_5H_2O)^{3-}} \ \frac{f_2}{f_3} \qquad (3)$$

The normal potential E^0 denotes the potential referred the normal hydrogen electrode in a system in which the activity of aquapentacyanoferrate (III) ${}^{a}(FeCy_5H_2O)^{3-}$ is equal to that of aquapentacyanoferrate (II) ${}^{a}(FeCy_5H_2O)^{3-}$ ${}^{C}(FeCy_5H_2O)^{3-}$ and ${}^{C}(FeCy_5H_2O)^{2-}$ represents the corresponding concentrations, where as f_2 and f_3 represent the activity coefficients of the aquapentacyanoferrate (III) and aquapentacyanoferrate (II) ions. If the limiting Debye-Huckel expression (equation 1) holds at extremely small ionic strengths and the system contains equimolecular amounts of potassium aquapentacyanoferrate (III) and potassium aquapentacyanoferrate (II), it is found from equation 1 and 3 that

$$E = E_0 + 0.60 \log f_2/f_3$$

$$= E_0 + 0.06 \times 3.5$$

Therefore, if the limiting Debye-Huckel expression holds, the measured potential E should be changed by 0.21 volt. for one unit change in the square root of the ionic strength.

For the experimental work three sets of measurements were performed.

(1) Equimolecular mixtures of potassium aquapentacyanoferrate (II) and potassium aquapentacyanoferrate (III) were taken and potential measured with respect to calomel electrode for concentration range 0.01 to 0.0002M. (corresponding to the ionic strength 0.12 to 0.0024).

(2) Mixtures prepared in the molar ratio {potassium aquapentacyanoferrate (II) to potassium aquapentacyanoferrate (III) 10:1}, the concentration range of aquapentacyanoferrate (II) solution being 0.01M to 0.000909M, (ionic strength 0.0660 to 0.00599) and:

(3) Mixture prepared in molar ratio (potassium aqupentacyanoferrate (II) to potassium aquapentacyanoferrate (III) 1:10) the concentration range of potassium aquapentacyanoferrate (II) solution being 0.001M to 0.000909M (total ionic strength 0.0660 to 0.005999).

The effect of univalent cations like Na^+ K^+ and H^+ was also observed in dilute equimolecular solutions of potassium aquapentacyanoferrate (II) and ferrate (III) (0.004M). The results are tabulated below:

TABLE No.6

Oxidation potential of equimolecular mixtures of $K_3Fe(Cy)_5H_2O$ and $K_2FeCy_5H_2O$.

M	μ	$\sqrt{\mu}$	Observed E.M.F (in volt)	E(in volt) against S.C.e
0.01	0.12	0.3464	0.177	0.417
0.0066	0.0792	0.2814	0.174	0.414
0.005	0.60	0.2449	0.171	0.412
0.004	0.048	0.2190	0.168	0.409
0.0033	0.0396	0.1989	0.167	0.407
0.0028	0.0336	0.1833	0.165	0.405
0.0075	00.300	0.1732	0.163	0.403

Fig.5(A)

TABLE No.7

Oxidation potential measured in a mixture containing $K_3Fe(Cy)_5$ H_2O and $K_2Fe\ Cy_5H_2O$ in the ratio 1:10.

$K_3FeCy_5H_2O$	$K_2FeCy_5H_2O$	Total μ	$\sqrt{\mu}$	E.M.F	Against S.C.E.	E^0 calculated
0.001	0.01	0.0660	0.2569	0.236	0.476	0.466
0.0008	0.008	0.0528	0.2297	0.223	0.463	0.453
0.00028	0.0028	0.0288	0.1697	0.219	0.459	0.449
0.00021	0.0021	0.01386	0.1174	0.202	0.442	0.432
0.000166	0.0016	0.01095	0.1095	0.198	0.438	0.478
0.000133	0.00133	0.008778	0.0932	0.200	0.440	0.425
0.0001056	0.001056	0.006969	0.0830	0.193	0.433	0.423
0.0000909	0.000909	0.005999	0.0760	0.191	0.431	0.421

Fig.5(B)

TABLE No.8

Oxidation potential measured in a mixture containing $K_3Fe(Cy)_5H_2O$ and $K_2Fe(Cy)_5H_2O$:

$K_3FeCy_5H_2O$	$K_2FeCy_5H_2O$	Total μ	$\sqrt{\mu}$	E.M.F.	Against S.C.E.	E^0 Calculated
0.001	0.01	0.0660	0.2569	0.122	0.362	0.372
0.0008	0.008	0.0528	0.2297	0.119	0.359	0.369
0.00028	0.0028	0.0288	0.1697	0.113	0.353	0.363
0.00021	0.0021	0.01386	0.1174	0.115	0.395	0.405
0.000166	0.0016	0.01045	0.1095	0.117	0.397	0.407
0.000133	0.00133	0.00877	0.0932	0.159	0.399	0.409
0.0001056	0.001056	0.00696	0.08306	0.161	0.401	0.411
0.0000909	0.000909	0.00599	0.07681	0.163	0.403	0.413

Fig. 5(c)

TABLE No.9

Oxidation potential measured in 0.004M $K_3Fe(Cy)_5H_2O$ and $K_2Fe(Cy)_5H_2O$: mixture in presence of acid and salts

Acid salt concentration	Total μ	$\sqrt{\mu}$	Observed potential					
			KCl	S.C.E	NaCl	S.C.E.	AlCl	S.C.E.
0.1M	0.1380	0.3615	0.195	0.435	0.193	0.432	0.350	0.590
0.2M	0.2380	0.4879	0.206	0.440	0.205	0.445	0.370	0.615
0.3M	0.3380	0.5714	0.225	0.465	0.213	0.453	0.390	0.631

The value of E^o was found by plotting the measured value of E of the three mixtures against $\sqrt{\mu}$ (Fig.5) and the extrapolating the straight line portion of the curve to zero ionic strength.

Ionic Strength which is a measure of the intensity of electrical field due to the ions in solutions, is defined as half the sum of the terms obtained by multiplying the molarity, or concentration of each ion present in the solution by the square of its valence:

DISCUSSION

The use of various oxidants for the estimation of equapentacyanide ion (in 4N sulphuric acid) lead to the following conclusion.

(1) Titrations between potassium permanganate and aquapentacyanide gave good results in wide concentration range. The rise in potential at the equivalence point 0.285V. and the value of $\frac{\Delta E}{\Delta V}$ by 2.85 V (Fig.3).

(2) Titrations between ceric sulphate and aquapentacyanoferrate (II) gave better results in comparision to potassium permanganate. The rise in potential at equivalence point is 0.45V. and change in value of $\frac{\Delta E}{\Delta V}$ 4.50V. (Fig.1,2).

(3) The results of potentiometric tetrations between potassium dichromate and aquapentacyanoferrate (II) could not be performed satisfactrily (error greater than 1 percent). The change in potential at equivalence point also not marked (0.104V) as compared for potassium permanganate (0.285V) and ceric sulphate (0.450)(Fig.4).

(4) Reverse titrations could only be carried out successfully with ceric sulphate.

(Various results are summarised in table No.4).

The potential mediator method using ceric sulphate as potential mediator gives quite high values 0.676, 0.7498, 0.762, 0.806, 0.845, 0.866, 0.898, 0.913V. in potassium aquapentacyanoferrate (II) solution containing 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0N sulphuric acid respectively (Fig.No.4). Natural salts exert a marked influence on the oxidation potential of the system. The values in hydrochloric acid and sulphuric acid was found much higher as compared to Kolthoff method, indicating the great hydrogen ion influence on the potential.

On plotting E^{o} against $\sqrt{\mu}$ and extrapolating to zero ionic strength the straight line portion of the curve a value of 0.4120V. is obtained with mixtures of equapentacyanoferrate (II) and potassium aquapentacyanoferrate (III) having the ratios 1:1 and 1:10 respectively. (Fig.5 curve A.B.). The value of E^{o} obtained by extrapolating the straight line portion of the curve to zero ionic strength for the mixtures of ratio 10:1 is slightly different as compared with other two (0.4130) (Fig.5 curve C).

CHAPTER I Part (II)

Polarographic studies on the Kinetics of hydrolytic decomposition of hexacyanoferrate (II). The anodic waves of hexacyanoferrate (II) and aquapentacyanoferrate (II):

Hexacyanoferrate (II) is not reducible at the dropping mercury electrode (1) but hexacyanoferrate (III) is reduced easily at this electrode giving fairly well defined diffusion waves. The hight of the wave is proportional to the hexacyanoferrate (III) concentration in neutral 0.1N potassium chloride (2). The potential of an equimolecular mixture of hexacyanoferrate (II) and ferrate (III) in 0.1N potassium chloride has been reported as +0.23V Vs S.C.E. Zuman (3) has carried detailed investigations on the polarographic behaviour of ferro-ferricyanide couple and reported it to be reversible even in 0.1M sulphuric acid. Mohai Papp and Nehar (4) has studied the effect of temperature and relative concentrations of the components on the oxidation reduction potential of hexacyanoferrate (II) ferrate (III) system and reported the values of temperature coefficient and dependence of the values of E^o on temperature and concentration. Kivalo (5) has carried out investigations on the polarographic maxima of hexacyanoferrate (III) in presence and absence of electrolytes (sodium perchlorate and potassium chloride).

Investigations has also been made by Rubin (6) on hexacyanoferrate (III) and ferrate (II) for the rate and diffusion system controlled currents at a plannar reversible electrode under applied potentials such that the reverse reaction makes an appreciable contribution to the over all process. Kachaturyan and Gorbachev (7) have studied the polarisation of reversible oxidation reduction system of ferri-ferrocyanide and reported the energy of activation for all cathodic and anodic processes. The limiting stage in the process was the diffusion of the materials to the electrode i.e. the concentration polarization. Meits (8) has utilized the diffusion constant ($i_d/cm^{2/3} t^{1/6}$) of hexacyanoferrate (III) to establish the relationship between diffusion current and capilliary characterstics for studying the electrode process.

The oxidation of hexacyanoferrate (II) at rotating platinum electrode has been reported by Klemenc (9) and Glasston (10). Investigations at cylindrical electrode, using a current generator, have been carried out by Margon and Chittenden (11). They measured the diffusion charge at +0.40 volts Vs S.C.E.

Some workers have reported the use of hexacyanoferrate (II) in amperometric titrations for the estimation of Zinc (II) (12), Chromium (II) (13), tungsten(VI) (14), vanadium (III) (15), chromium (III), Be (II), Cu(I), Ti (III), Ti (IV), Mn (III), Mo (IV) and MO (V) (16). But direct palorographic methods for the estimation of hexacyanoferrate (II) and aquapentacyanoferrate (II) have not been reported in the existing literature. The investigations described in this chapter deals with the following new aspects of the polarography of hexacyanoferrate (II).

(1) Polarographic reduction of hexacyanoferrate (II) and aquapentacyanoferrate (II) at d.m.e., carried out with the view to test the suitability of the method for the analytical work.

(2) Polarographic studies on the hydrolytic decomposition of hexacyanoferrate (II).

EXPERIMENTAL

Aquapentacyanoferrate (II) was prepared by the method described in Chapter II (p.). All the reagents used were of A.R. quality. The solutions of hexacyanoferrate (II) and aquapentacyanoferrate (II) were prepared by dissolving weighed quantities in distilled water. Their strengths were determined potentiometrically by titrating against potassium permangnate and ceric sulphate respectively (vide part I of this chapter).

Apparatus:

Heyrosvsky polarograph (LP 55A), operated manually in conjunction with Pye sclamp galvanometer in external circuit was used. Fisher capillary with droptime 4.2 sec. in open circuit was used.

Weight of one drop taken at a hieght of 50.0 cm of mercury column was 0.0035 gm. Polarographic cell together with S.C.E. was kept immersed in thermostatic bath maintained at 30 ± 0.1°C purified hydrogen was used for deaeration.

Beckman pH meter model H_2 was employed to adjust the pH values.

Buffers and supporting electrolytes:

All the buffers used were prepared in double distilled water. Walpole, potassium hydrogen phthalate, potassium dihydrogen phosphate, and borax buffers were used in pH range (1.0-2.0); (3.0-6.0); (7.0-8.6) and (9.0-11.5) respectively for maintaining the pH of the solutions. Solutions of the electrolytes lithium chloride, potassium chloride, sodium fluoride, potassium nitrate, potassium chlorate, sodium sulphate and barium chloride were prepared by dissolving weighed quantities in double distilled water.

Procedure:

The following experiments were performed to study the behaviour of hexacyano-ferrate (II) at d.m.e.

(1) The anodic waves of solutions containing 2.0 ml 10^{-2}M hexacyanoferrate (II), 18.0 ml of buffers pH values ranging from 1.2 to 11.6 were recorded at 1/30 senstivity of the polarograph in the potential region 0.4 to 0.0V.

(2) Mixtures containing 2.0 ml of 10^{-2}M hexacyanoferrate (II) and 1.0 ml of 1.0×10^{-4}M mercuric chloride was kept in dark to bring about the hydrolytic decomposition of hexacyanoferrate (II). Total volume was then made up to 20 ml by adding buffers of pH values ranging from 1.2 to 11.5. Anodic waves from +0.4 to 0.0V at 1/50 senstivity of the polarograph were recorded.

(3) Polarograms of the solution containing 2.0 ml of 10^{-2}M aquapentacyanoferrate (II) and 18.0 ml buffers of pH values 1.2 to 11.5 were recorded under conditions mentioned above.

(4) Polarograms of the buffers (17.0 ml or 18.0 ml diluted to 20.0 ml by water) were also recorded under similar condition.

The residual current corresponding to different buffers was substracted from the diffusion current recorded in experiments 1, 2 and 3.

Current voltage curves for hexacyanoferrate (II) its hydrolytic decomposition product and aquapentacyanoferrate (II) in pH range 1.2 to 11.45 are shown in Fig.(1a), (1b) and (1c) respectively. The $E_{1/2}$ values are tabulated below:

A marked difference in $E_{\frac{1}{2}}$ in the pH range 3.0 to 5.0 was observed between the waves of hexacyanoferrate (II) and its hydrolytic decomposition product. This could be confirmed from the $E_{\frac{1}{2}}$ values of the aquapentacyanoferrate (II) obtained under similar conditions (exp.No.3).

Since satisfactory data from these experiments were obtained in the pH range 3.0-5.0, pH 4.0 was chosen for detailed investigations. In order to study various aspects of the oxidation of hexacyanoferrate (II) and aquapentacyanoferrate (II) at d.m.e. the following sets solutions were prepared.

Set I.

Contained 8-solutions each with 2.0 ml, 0.01M hexacyanoferrate (II) and 2.0 ml of the electrolytes lethium chloride, sodium chloride, potassium chloride, sodium fluoride, potassium nitrate, potassium chlorate sodium sulphate and barium chloride (2.0, 2.0, 2.0, 1.0, 1.0, 0.5, 0.5 and 2.0M respectively in solutions 1 to 8). Total volume was made to 20.0 ml by buffer of pH 4.0.

Set II

Comprised of 8-solutions mentioned as above, in place of hexacyanoferrate (II), aquapentacyanoferrate (II) of similar concentration was used, so that the results of set(I)may be compared.

The residual current corresponding to the different buffers was substracted from the diffusion current, recorded for the solutions in Set I, II and III.

The results are tabulated below:

TABLE No.2

Oxidation of 1.0×10^{-3}M hexacyanoferrate (II) at pH 4.0 in various supporting electrolytes:

Potential	Current						
	Lithium chloride 0.1M	Pot. Chloride 0.1M	Sod. chloride 0.1M	Sod. fluoride 0.1M	Pot. Nitrate 0.05M	Pot. chlorate 0.05M	Sod. Sulphate 0.1M
+0.50	-	-	-	-	-	-	3.45
+0.40	1.15	1.2	1.1	2.85	3.35	2.60	2.65
+0.35	1.2	1.25	1.15	2.25	2.90	2.05	2.10
+0.30	1.25	1.4	1.2	1.35	1.45	1.00	0.90
+0.25	1.6	1.7	1.4	0.85	0.85	0.75	0.80
+0.20	4.0	2.4	1.9	0.80	0.55	0.55	0.50
+0.18	2.0	1.4	1.2	-	-	-	-
+0.15	1.0	0.5	0.5	0.75	0.20	-	-
0.10	+0.1	0.1	0.1	0.70	0.0	0.0	0.0
0.05	0.0	0.0	0.05	-	-	-	-
0.00	0.0	0.0	-	-	-	0.0	0.0
curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)

Fig.2A

TABLE No.3

Oxidation of 1.0×10^{-3}M hexacyanoferrate (II) aquapentacyanoferrate (II) at pH 4.0 in various supporting electrolytes:

Potential	Current μA						
V. Vs S.C.E	Lithium chloride 0.1M	Sodium chloride 0.1M	Potassium chloride 0.1M	Sodium fluoride 0.1M	Potassium nitrate 0.05M	Potassium chlorate 0.05M	Sodium sulphate 0.1M
+0.4	0.90	0.8	0.9	-	-	-	-
+0.35	0.95	0.9	0.95	-	-	-	-
0.30	1.0	1.0	1.0	-	-	-	-
0.25	1.2	1.2	1.1	1.0	1.1	1.5	1.45
0.20	2.0	1.8	1.4	0.9	1.0	0.9	1.0
0.16	4.0	2.9	2.4	-	-	-	-
0.15	-	-	-	0.5	0.5	0.4	0.5
0.10	0.40	0.5	0.4	-0.2	-0.10	0.0	-0.15
0.05	-	-	-	-0.3	-0.25	-0.3	-0.35
+0.0	0.20	0.20	0.2	-0.3	-0.35	-0.4	-0.40
Curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)

Fig.2(B)

Since reversible oxidation waves for the solutions in set I, II were obtained in 0.1M sodium fluoride as supporting electrolyte. The effect of concentration of aquapentacyanoferrate (II) and that of hexacyanoferrate (II) on their respective i_d values was studied by recording the polarograms of the following two sets of solutions.

Set I.

Comprised of 5-solutions, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of 1.0×10^{-2}M hexacyanoferrate (II) was mixed with 2.0 ml of 1.0M sodium fluoride and total volume was made up to 20.0 ml by adding the buffer of pH 4.0.

Set II

Again comprised of 5-solutions 1.0, 2.0, 3.0, 4.0 and 5.0 ml of aquapentacyanoferrate was added to 2.0 ml of sodium fluoride, total volume was made to 20.0 ml by adding buffer of pH 4.0.

The effect of mercury pressure to ascertain the nature of the electrode process was studied by recording the polarograms of solution No.2 at different heights. Drop time at+0.4V and the mean of maximum and minimum difflection was noted to plot curves between logi and logt. Results are tabulated below:

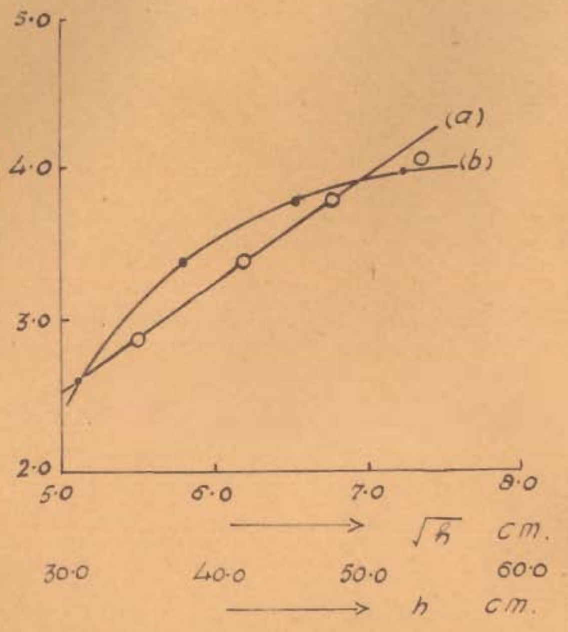


FIG. 3.A.
(a) Plot of id Vs √h.
(b) Plot of id Vs h.

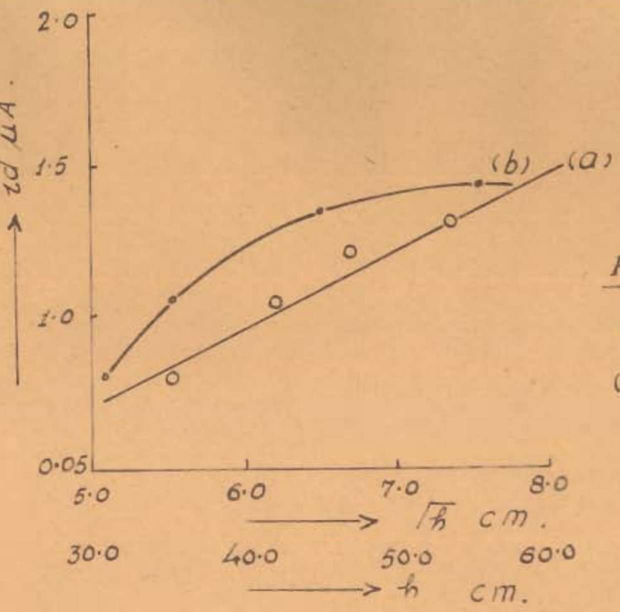


FIG. 3.B
(a) Plot of id Vs √h.
(b) Plot of id Vs h.

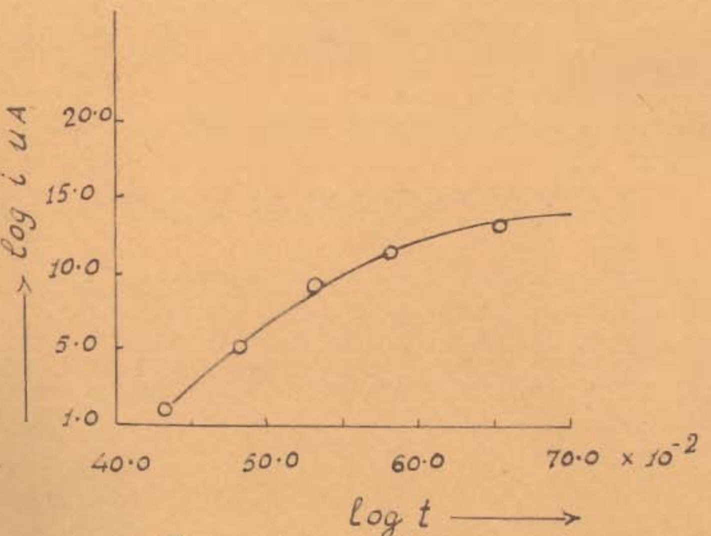


FIG. 5. A.

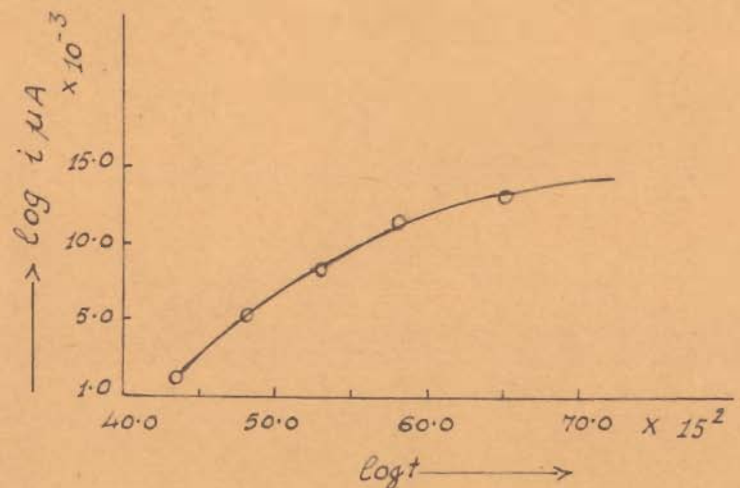


FIG 5.B.

TABLE No.4

Variation in current with potential for the various concentrations of hexacyanoferrate (II) (0.05x10^{-2}M to 0.25x10^{-2}M) at pH 4.0 in 0.1M sodium fluoride:

Potential	Current 1.1x10^{-6} A				
	Solution No.1	Solution No.2	Solution No.3	Solution No.4	Solution No.5
+0.40	1.42	2.84	4.10	5.75	7.15
+0.35	1.38	2.76	3.84	5.40	6.90
+0.30	0.90	1.35	1.35	1.36	1.36
+0.25	0.85	0.90	0.90	0.90	0.90
+0.20	0.85	0.90	0.85	0.85	0.90
+0.15	0.80	0.80	0.80	0.80	0.85
Curve	(1)	(2)	(3)	(4)	(5)

Fig.6(A)

TABLE No.5

Variation in current with potential for the various concentrations of aquapentacyanoferrat (II) (0.05x10^{-2}M to 0.25x10^{-2}M) at pH 4.0 in 0.1M sodium fluoride:

Potential	Current 1.1x10^{-6}A				
	Solution No.1	Solution No.2	Solution No.3	Solution No.4	Solution No.5
+0.25	0.50	1.1	1.45	1.98	2.4
+0.20	0.50	1.0	1.40	1.95	2.3
+0.15	0.0	0.5	0.80	1.3	1.50
+0.10	-0.20	-0.20	-0.20	-0.20	-0.20
+0.05	-0.30	-0.30	-0.30	-0.30	-0.30
+0.00	-0.35	-0.35	-0.35	-0.35	-0.35
Curve	(1)	(2)	(3)	(4)	(5)

Fig.6(B)

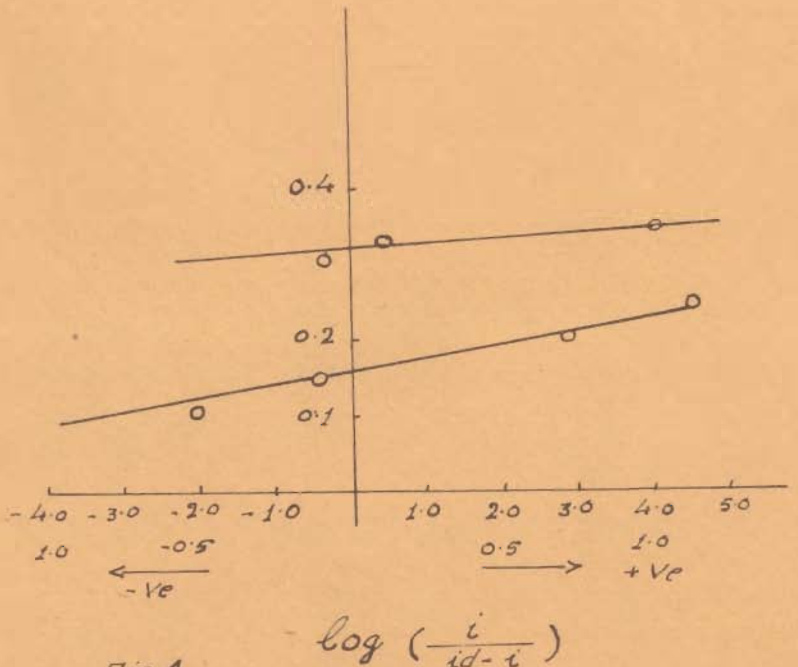


FIG 4.
Curve A scale I
" B " " II.

In order to see the possibility for the simultaneous determination of hexacyanoferrate (II) and aquapentacyanoferrate (II), the polarogram of the mixture containing 2.0 ml 10^{-2}M aquapentacyanoferrate (II), 2.0 ml 10^{-2}M hexacyanoferrate (II) 2.0 ml of Sodium fluoride and 14·0 ml of buffer of pH 4.0 (to make the total volume to 20.0 ml), was recorded. Results are tabulated below:

TABLE No.6

Variation in current with potential for the mixture of hexacyanoferrate (II) and aquapentacyanoferrate (II) (each 0.1×10^{-2}M at pH 4.0 in 0.1M sodium fluoride). Current due to medium was substracted:

Potential	Current 1.1×10^{-6}A Correct for the current of medium
+0.40	2.85
+0.35	2.75
0.30	1.35
0.25	0.90
0.20	0.90
0.15	0.50
0.10	-0.15
0.05	-0.30
0.00	-0.40

Fig.7

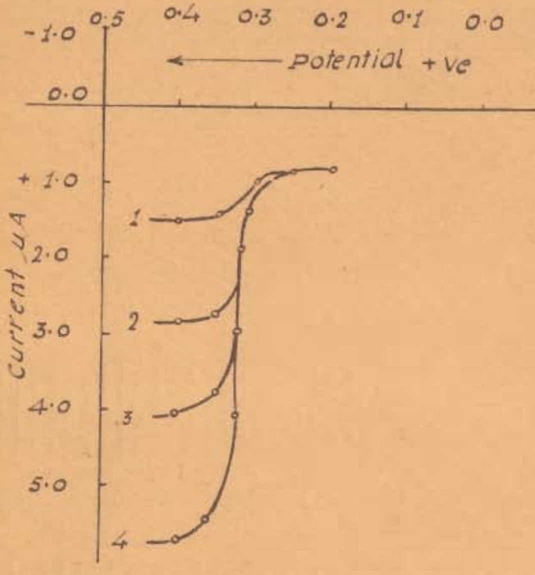


FIG. 6.(A).

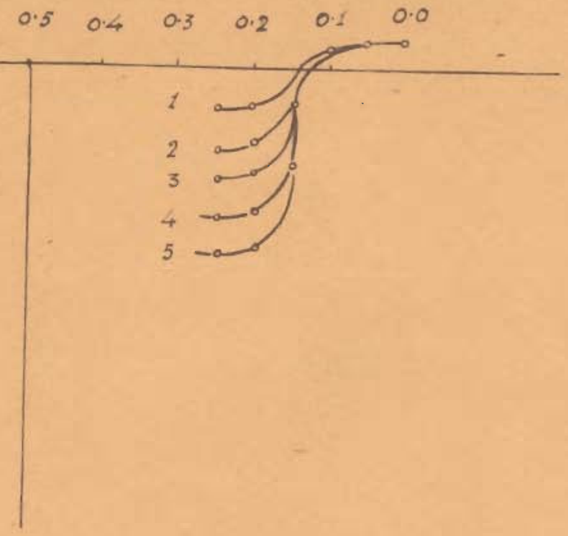


FIG 6(B)

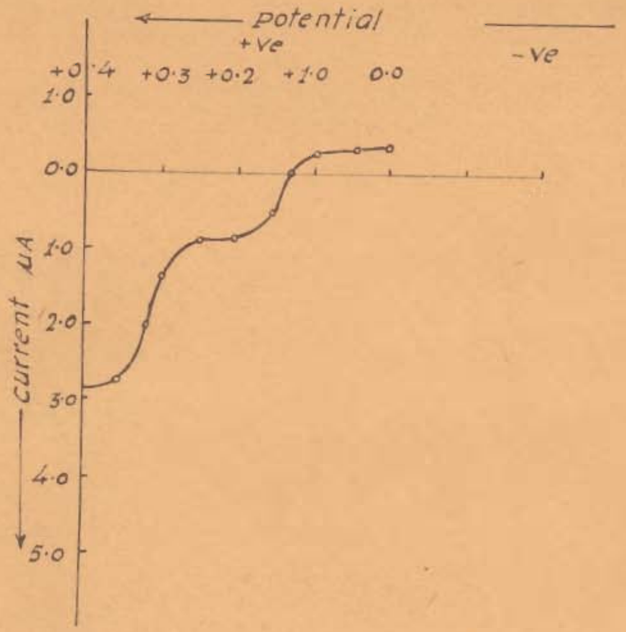


FIG. 7.

TABLE No.7

Effect of mercury pressure on the polarogram of 0.1×10^{-2}M hexacyanoferrate (II) in 0.1M sodium fluoride:

$h_{corr} = (h_{exp.} - h_{back})$, $h_{back} = 3.1/m^{1/3}t^{1/3}$

Height of mercury column h(corrected	h	Drop time	Limiting current 1.1×10^{-6}A	log t	log i
31.0 cm	5.52	4.55	2.6	0.6580	0.1343
38.8	6.22	3.90	3.35	0.5911	0.1250
45.7	6.76	3.42	3.7	0.5340	0.8543
55.5	7.45	3.03	3.95	0.4814	0.0556
60.0	7.74	2.72	4.0	0.4346	0.0213

Fig.3A Fig.5A

TABLE No.8

Effect of mercury pressure on the polarograms of aquapentacyanoferrate (II) 0.1×10^{-2}M in 0.1M sodium fluoride:

Height of mercury column h(corrected	$\sqrt{h}$	Drop time	Limiting current 1.1×10^{-6}A	log i	log t
31.0	5.52	4.50	0.56	0.1132	0.6532
38.0	6.22	3.88	1.1	0.1150	0.5800
45.7	6.76	3.40	1.7	0.0581	0.5316
55.5	7.45	3.03	1.8	0.0505	0.4800
60.0	7.74	2.70	1.9	0.0042	0.4314

Fig.3B Fig.3B

TABLE No.9

Loganthmic analysis for the polarogram of 0.1×10^{-2}M hexacyanoferrate (II) in 0.1M sodium fluoride at pH 4.0

Potential volts	Current μA	$\log \left(\frac{i}{i_d - i} \right)$
+0.4	2.85	-
0.35	2.80	+5.91
0.34	2.26	+4.015
0.33	2.30	+0.4170
0.30	1.40	-0.3665
0.25	0.90	-
0.20	0.80	-

Fig.(4A) Rk

TABLE No.10

Logarithmic analysis for the polarograms of 0.1×10^{-2}M aquapentacyanoferrate (II) in 0.1M sodium fluoride a pH 4.0.

Potential volts	Current μA	$\log \left(\frac{i}{i_d - i} \right)$
0.25	+1.0	+1.1139
0.20	+0.90	+0.7782
0.14	+0.40	-0.1249
0.10	-0.1	-0.5643
0.05	-0.3	-1.4313
0.00	-0.35	-

Fig.4B

Kinetics of hydrolytic decomposition of hexacyanoferrate (II):

Well defined diffusion controlled reversible steps of the oxidation of hexacyanoferrate (II) was obtained in 0.1M sodium fluoride at pH 4.0. The step height was found to be dependent on concentration and decreased continuously during its hydrolytic decomposition. Alongwith the decrease in the wave height of hexacyanoferrate (II) a new wave at less +ve potential due to the oxidation of the decomposition product (aquapentacyanoferrate (II)) appeared, whose height increased with time.

Since the plateau of hexacyanoferrate (II) wave was between the potential region +0.38 to 0.40V. the kinetics of decomposition were studied by measuring the decrease in current at different intervals at applied potential of +0.4V. Two solutions containing 8.0, 16.0 ml respectively of 0.01M hexacyanoferrate (II) were mixed with 8.0 ml of 1.0M sodium fluoride. Total volume was made to 8.00 ml by adding buffer of pH 4.0. These solutions were exposed to ultraviolet litht. Deacrease in current of solution No.1 and polarogram of solution No.2 at different intervals (to see the dissappearance of hexacyanofirrate (II) wave and subsequent appearance of the wave of aquapentacyanoferrate (II)) were recorded at 30 ± 0.1°C.

Experiment with solution No.1 (Set I above) were also performed under the action of white light or impresence of $0.1\times10^{-4}M$ mercuric chloride or chromic chloride to compare the catalytic activities of ultraviolet and white light. The results are tabulated below:

TABLE No.11

Current potential measurements for $0.1\times10^{-2}M$ hexacyanoferrate (II) in 0.1M sodium fluoride at pH 4.0 at different intervals under the action of ultraviolet light. Senstivity 1/25.

Potential volts	Current μA					
	Time in minutes					
	0.0	30.0	60.0	120.0	180.0	240.0
+0.45	5.9	5.3	4.9	4.42	3.7	3.4
+0.40	5.8	5.15	4.8	[illegible].21	3.6	3.2
+0.35	5.0	4.0	4.4	3.50	3.0	2.4
+0.30	2.0	1.8	1.9	1.9	1.9	2.1
+0.25	1.0	1.0	1.4	1.4	1.55	2.1
+0.20	0.8	0.75	1.0	1.2	1.3	1.7
+0.15	-	0.2	0.5	0.5	0.5	0.5
+0.10	-	-0.2	-0.1	-0.1	-0.2	-0.2
+0.05	-	-0.25	-0.3	-0.30	-0.30	-0.3
+0.0	-	-0.3	-0.35	-0.35	-0.35	-0.35
-0.10	-	+0.3	+0.35	+0.35	+0.35	+0.35
Curve	(1)	(2)	(3)	(4)	(5)	(60

Fig.8

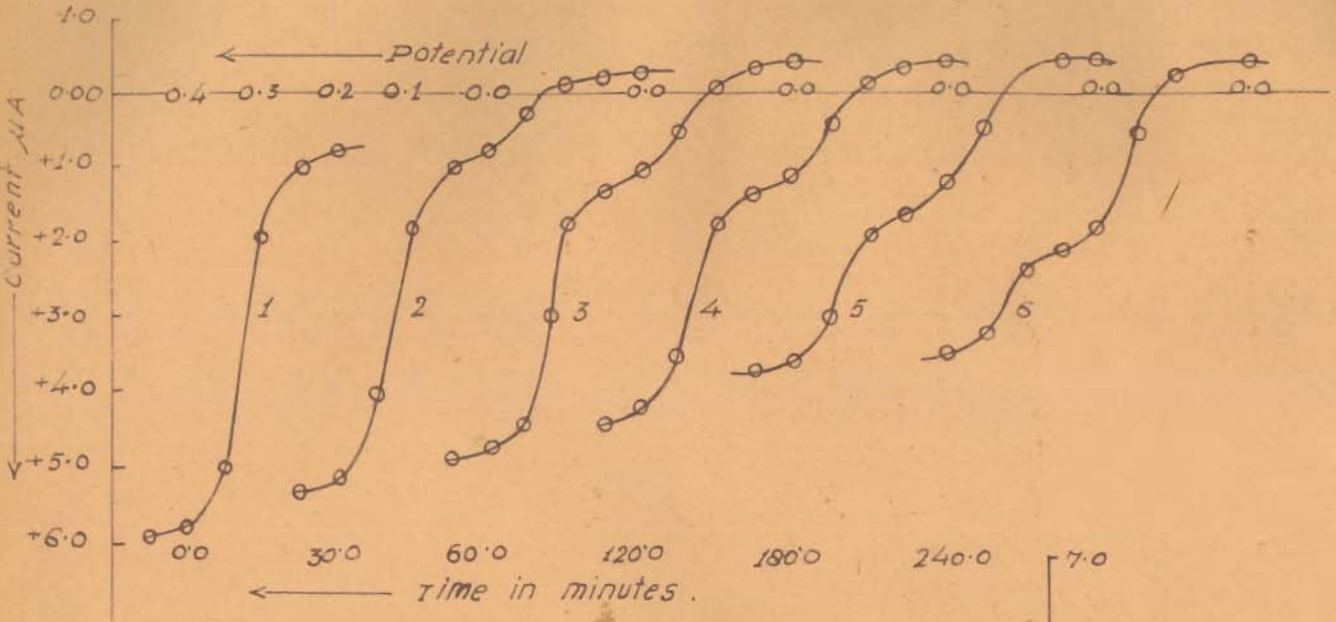


FIG. 8. Dissappearance of the wave of $K_4 Fe Cy_6$ and appearance of wave of $K_3 Fe Cy_5 H_2O$ during hydrolytic decomposition.

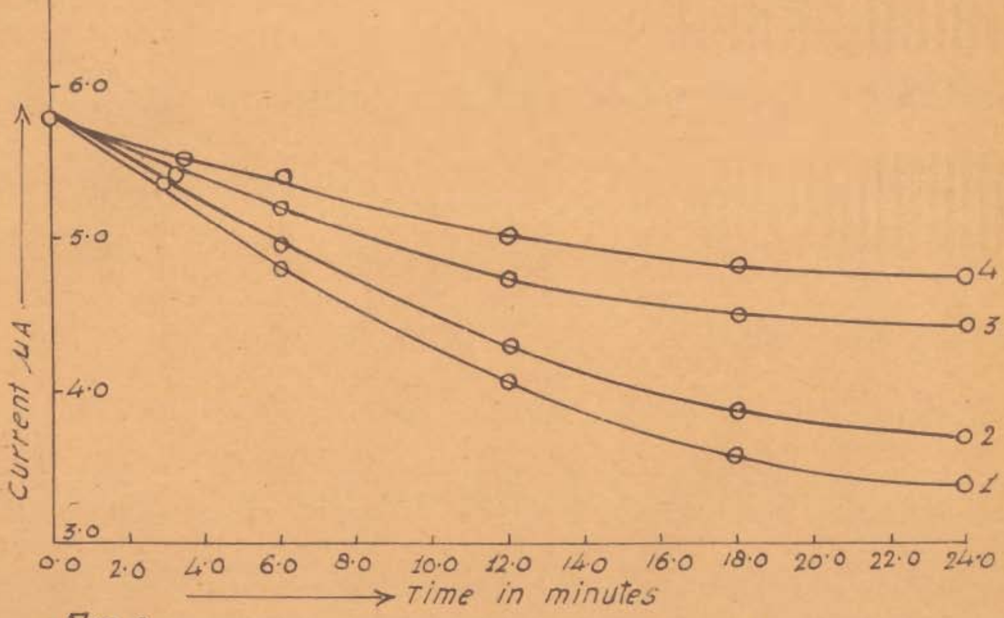


FIG. 9. Relative effect in the variation of current.

curve 1. ultra violet light
" 2. white light
" 3. 0.1×10^{-4} M murcuric chloride.
" 4. 0.1×10^{-4} M chromic chloride.

TABLE No.12

Comparative variation in current with time at applied potential of +0.4V, for the solution containing 0.1×10^{-2}M hexacyanoferrate (II) 0.1M sodium fluoride at pH 4.0, when it was exposed to ultraviolet light, white light or contained either 0.1×10^{-4}M Hg^{++} or Cr^{+++} ions.

Time in minutes	Current μA			
	Ultra-violet light	White light	Hg^{++}	Cr^{+++}
0.0	5.8	5.8	5.8	5.8
30.0	5.4	5.45	5.5	5.5
60.0	4.8	5.0	5.2	5.45
120.0	4.2	4.30	4.7	5.0
180.0	3.8	3.9	4.5	4.8
240.0	3.5	3.7	4.40	4.75
Curve	(1)	(2)	(3)	(4)

Fig.9

Order of reaction, temperature coefficient and energy of activation:

To determine these constants, current at different intervals at temperatures 30°C, 40°C and 50°C of the mixture containing 8.0 ml hexacyanoferrate (II), 8.0 ml 1.0×10^{-4}M mercuric chloride, 8.0 ml 1.0M sodium fluorided and 56.0 ml of buffer of pH 4.0 was measured.

The order of reaction at these temperatures was calculated from the slopes of the straight lines obtained by plotting log ($\frac{\Delta c}{\Delta t}$) against log $\bar{c}$. The value of rate constant K was determined employing the equation:

$$K = \frac{1}{c}\left(-\frac{\Delta c}{\Delta t}\right)$$

where Δc and $\bar{c}$ represent the change in concentration and mean concentration respectively during a small interval Δt.

Temperature coefficient and energy of activation were calculated by employing the relationship K_{t10}/k_t and equation $\log \frac{k_1}{k_2} = -E/2.303R\ (1/T_2 - 1/T_1)$ respectively. The results are tabulated below:

TABLE No.13

Variation in current with time at applied potential of +0.4V for the mixture containing 0.1×10^{-2}M hexacyanoferrate (II), 0.1M sodium fluoride and 0.1×10^{-4}M mercuric chloride.

Temperature $30^{\circ}C$ Senstivity 1/30

Time in minutes	Current μA	Δt	$-\Delta c$	$\frac{\Delta c}{\Delta t}$ $\times 10^{-4}$	$\log \frac{\Delta c}{\Delta t}$	$\bar{c}$ $\times 10^{-1}$	$\log \bar{c}$	$K = \frac{1}{c}\left(-\frac{\Delta c}{\Delta t}\right)$
0.0	5.8	-	-	-	-	-	-	-
30.0	5.4	30	0.26	87.0	1.9395	29.7	1.4728	2.92×10^{-3}
60.0	5.1							
120.0	4.75	60	0.30	50.01	1.6940	23.0	1.3617	2.30×10^{-3}
180.0	4.45							
240.0	4.2	60	0.10	17.00	1.2304	8.6	0.9063	2.0×10^{-3}
300.0	4.1							
24 hours	2.3							

Mean value of $K = 2.406 \times 10^{-3}$
Plot of current Vs time Fig.10 curve 1
$\log \frac{\Delta c}{\Delta t}$ Vs $\log \bar{c}$ Fig.11 curve 1 (slope = 1.21)

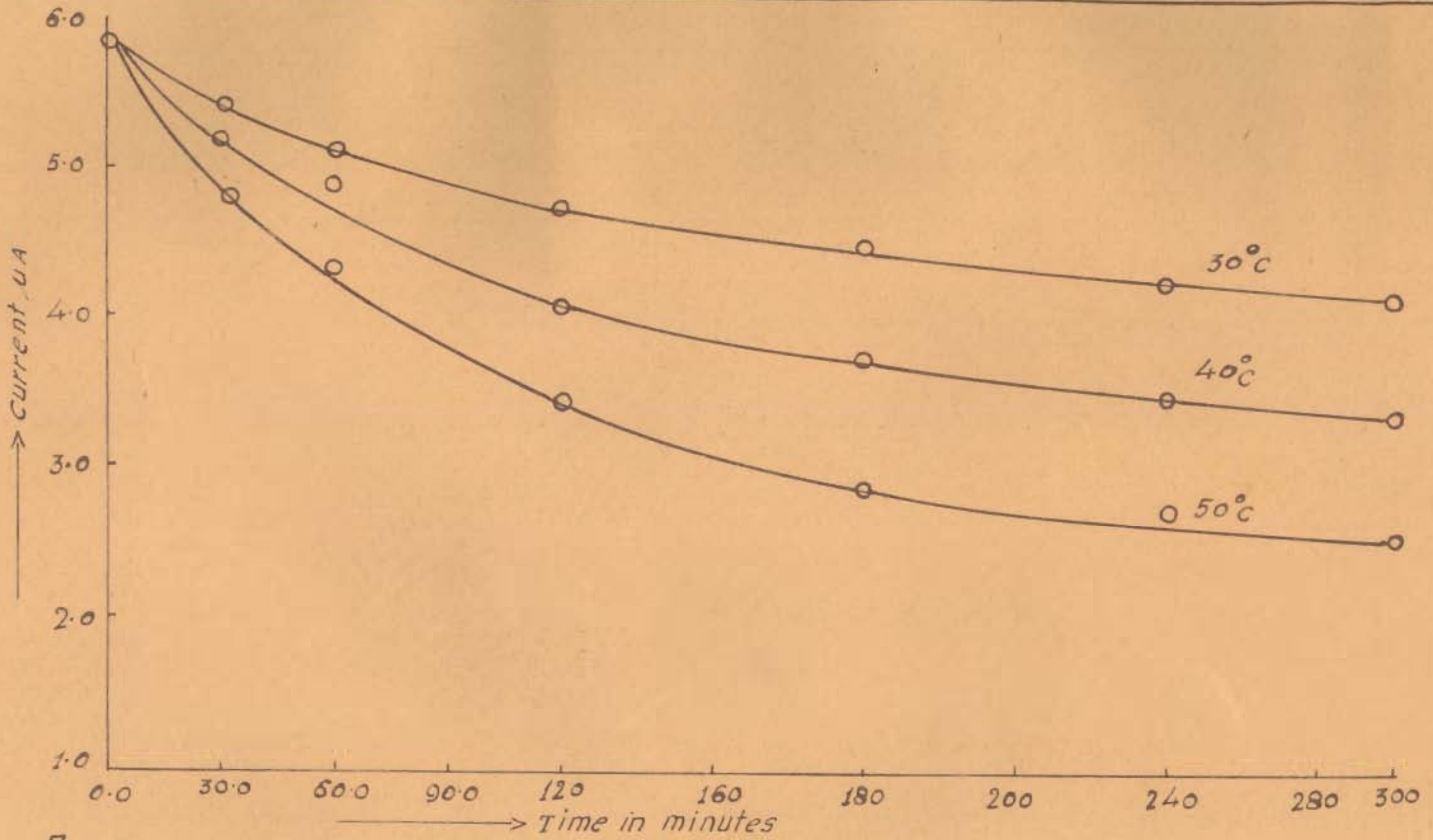


FIG. 10.
Effect of temp in the variation of current with time.

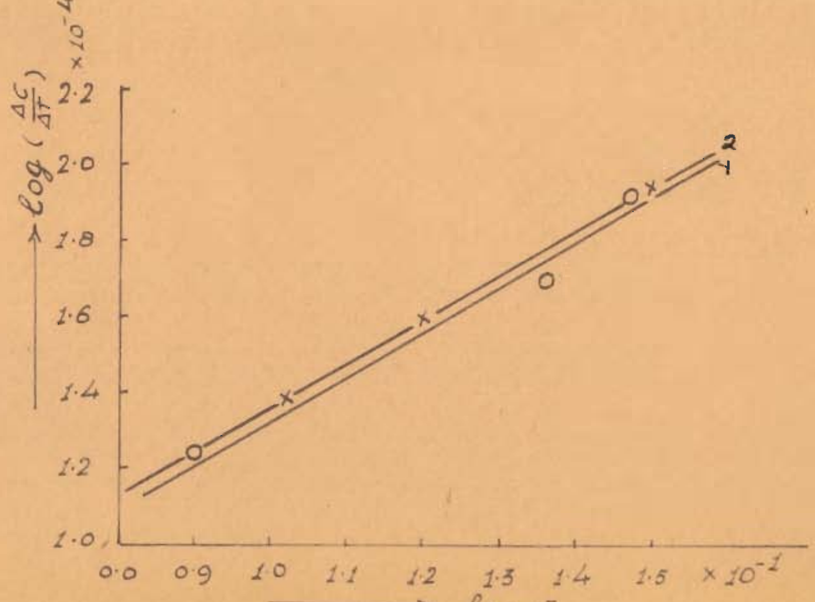


FIG. 11.(a)

TABLE No.14

Variations in current with time for the mixture containing 0.1×10^{-2}M hexacyanoferrate (II), 0.1M sodium fluoride and 0.1×10^{-4}M mercuric chloride at temp.40°C.

Time in minutes	Current A	Δt	$-\Delta C$	$-\frac{\Delta c}{\Delta t} \times 10^{-4}$	$\log \frac{\Delta c}{\Delta t}$	$\bar{c} \times 10^{-1}$	$\log \bar{c}$	$K = \frac{1}{\bar{c}}\left(\frac{\Delta c}{\Delta t}\right)$
0.0	5.80	-	-	-	-	-	-	-
30.0 60.0	5.2 4.95	30	0.25	83.3	1.9201	22.7	1.4425	3.67×10^{-3}
120.0 180.0	4.1 3.7	60	0.40	66.6	1.8235	16.0	1.2041	4.16×10^{-3}
240.0 300.0	3.45 3.3	60	0.15	25.0	1.3979	10.75	1.0294	2.32×10^{-3}
24 hours	2.3	-	-	-	-	-	-	-

Mean value of K = 3.376×10^{-3} min^{-1}

Plot of current Vs tim Fig.10 curve 2

Plot of $\log - \frac{\Delta c}{\Delta t}$ Vs $\log \bar{c}$ Fig.11 curve 2

(slope = 1.21)

TABLE No.15

Variations in current with time for the mixture containing 0.1×10^{-2}M hexacyanoferrate (II), 0.1M sodium fluoride and 0.1×10^{-4}M mercuric chloride at temp. 50°C.

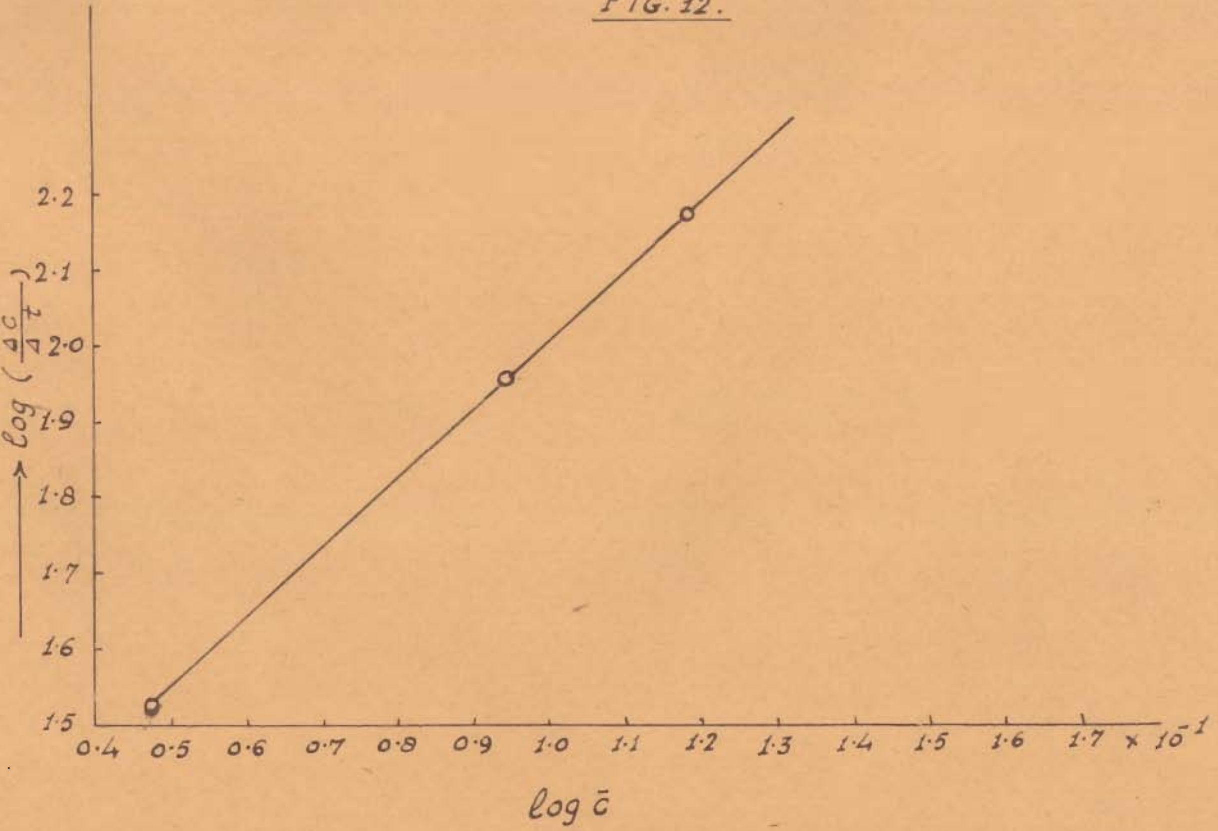
Time in minutes	Current µA	Δt	$-\Delta c$	$\frac{\Delta c}{\Delta t}$ x 10^{-4}	log $-\frac{\Delta c}{\Delta t}$	$\bar{c}$ x10^{-1}	log $\bar{c}$	$K = \frac{1}{\bar{c}}(-\frac{\Delta c}{\Delta t})$
0.0	5.75	-	-	-	-	-	-	-
30.0	4.75	30	0.45	150.0	2.1761	17.25	1.2370	8.69×10^{-3}
60.0	4.30							
120.0	3.45	60	0.55	91.67	1.9619	8.75	0.9420	10.46×10^{-3}
180.0	2.90							
240.0	2.7	60	0.20	33.33	1.5224	3.00	0.477	11.11×10^{-3}
300.0	2.5							
24 hours	2.3	-	-	-	-	-	-	-

Mean value of K = 10.086×10^{-3}

Plot of current Vs time Fig.10 curve 3

Plot log $-\frac{\Delta c}{\Delta t}$ Vs log $\bar{c}$ Fig.12 (slope = 0.93).

FIG. 12.



2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
$\log\left(\frac{\Delta c}{\Delta t}\right)$
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
$\times 10^{-1}$
$\log \bar{c}$

RESULTS AND DISCUSSION:

Results and Discussion Oxidation of hexacyanoferrate (II) and aquapentacyanoferrate (II):

From the current voltage curves drawn for 1.0×10^{-3}M hexacyanoferrate (II), its hydrolytic decomposition product (obtained in the presence of mercuric ions) at various pH values, it was found that there is a marked difference in $E_{\frac{1}{2}}$ values in the pH region 3.0 to 5.0 ml. Well defined steps could not be obtained either in lower or higher pH regions. The $E_{\frac{1}{2}}$ values of aquapentacyanoferrate (II) at pH 3.0 to 5.0 were found to be quite similar with the $E_{\frac{1}{2}}$ values of hydrolytic decomposition product of hexacyanoferrate (II) obtained in presence of mercuric ions. Similar type of results were obtained in presence of Cr^{+++} ions or on exposure of hexacyanoferrate (II) to ultraviolet or white light. The $E_{\frac{1}{2}}$ values for hexacyanoferrate (II) its hydrolytic decomposition product and aquapentacyanoferrate (II) are shown in table No.1 and the polarograms in Fig.1 A,B. and C curves (1-9).

Since the $E_{\frac{1}{2}}$ of hydrolytic decomposition product and that of aquapentacyanoferrate (II) was found to be same in the pH range 3.0 to 5.0 it may be concluded that presence of Hg^{++} or Cr^{+++} ions or the action of ultraviolet or white light decomposed hexacyanoferrate (II) to give similar products viz, the aquapentacyanoferrate (II):

In presence of 0.1M of either of the electrolytes, lithium chloride, potassium chloride or sodium chloride, 1.0×10^{-3}M hexacyanoferrate (II) gave a pronounded maxima (Fig.2 A curve 1,2 and 3) at +0.20V which could not be suppossed by the surface active agents like as cetyl trimethyl ammonium bromide, Nonidate p-40, gelatine and methyl red. In presence of 0.1M of sodium fluoride a reversible oxidation wave (Fig.2A curve 4 $E_{\frac{1}{2}} = + 0.32$V) was obtained. The electrode process was diffusion controlled as was verified by the effect of mercury pressure (Fig.4A) (Fig.3A) logarithmic analysis and by the plot of logi Vs log t. (slope of the curve = 0.163) (Fig.5A); (Table No.7,8). The step height was dependent on concentration studied in the range (0.05×10^{-2}M) to (0.25×10^{-2}M) Fig.6A. In 0.1M potassium nitrate 0.05M potassium at pH 4.0, 0.1×10^{-2}M hexacyanoferrate (II) oxidised giving irreversible waves, Fig.2A curves 5,6,7. No wave in barium chloride however, was obtained.

The behaviour of aquapentacyanoferrate (II) at d.m.e. was quite different/as compared with that of hexacyanoferrate(I and the $E_{\frac{1}{2}}$ values were also quite different (Table No.1). Although aquapentacyanoferrate (II) also gave pronounced maxima in 0.1M of alkali chlorides (Fig.2B curve 1,2 and 3) but its position shifted from 0.20 to 0.16V. Moreover its height decreased in passing from ~~sodium diboride~~ lithium chloride to potassium chloride. Here again the maxima could not be suppressed by the addition of surface active agents like cetyltrimethyl ammonium bromide, None date p-40 gelatine and methyl red.

Aquapenta-cyanoferrate (II) also got oxidised reversibly and diffusion controlled waves ($E_{\frac{1}{2}}$ = + 0.15V) were obtained in 0.1M sodium fluoride and potassium nitrate at pH 4.0 (Fig.2B curve 4,5). The logarithmic analysis (Fig.4B) mercury pressure (Fig.3B) and the plot oflogi Vs log t (Fig.5B slope of the curve = 0.162) gave evidence for the existence of reversible, diffusion controlled waves. The step height was dependent on concentration (Fig.6B in the range (0.05 to 0.25x10^{-2}M). The waves obtained in presence of 0.05M potassium chlorate, potassium sulphate were irreversible and ill defined, (Fig.2B, curve 6,7). No wave was realized in 0.1M barium chloride.

From the mixtures containing 0.1x10^{-2}M hexacyanoferrate (II) and aquapentacyanoferrate (II) in 0.1M sodium fluoride two distinct waves due to the oxidation of hexacyanoferrate (II) and aquapentacyanoferrate (II) respectively were realized (Fig.7).

Kinetics of the reaction:

Effect of Hg^{++}, Cr^{+++} ultraviolet and white light:

All these catalysts decomposed hexacyanoferrate (II) to the similar product (aquapentacyanoferrate (II)) which was easily ascertained because the behaviour of aquapentacyanoferrate (II) and decompositions product of hexacyanoferrate (II) at d.m.e. was quite similar.

During the course of decomposition the dissapearance of the wave of hexacyanoferrate (II) and the appearance of the wave of aquapentacyanide took place (Fig.8) curve 1,2,3,4,5 and 6 were recorded at 0.0, 30.0, 100.0, 120.0, 160.0 and 240th minutes respectively under the influence of vailet light.

From the plots of the current (measured at 0.4V) Vs the time (Fig.9) for the mixtures containing 0.1×10^{-2}M hexacyanoferrate (II), 0.1M sodium fluoride at pH 4.0 in presence of 0.1×10^{-4}M mercuric chloride or under the action of ultra violet or white light it was found that the effect of $Hg^{++} > Cr^{+++}$ on the hydrolytic decomposition of hexacyanoferrate (II). Similarly ultraviolet light was more effective in bringing about hydrolytic decomposition than white light. The current at 60th minute decreased to 17.25, 14.66, 10.35 and 6.90 per cent with ultraviolet, white light, mercuric chloride and chromic chloride respectively.

The hydrolytic decomposition of hexacyanoferrate (II) at pH 4.0 in presence of small amounts of mercuric chloride was found to be of first order because the values of the slopes of the curves (Fig.11 curve 1,2 and Fig.12) at temperatures 30°, 40° and 50°C were found to be 1.21, 1.21 and 0.93 (values very close to one). The mean values of rate constants at these temperatures were 2.406×10^{-3}, 3.376×10^{-3} and 10.086×10^{-3} min^{-1}. The temperature coefficient and energy of activation (Calculated with the rate constant values at 30° and 40°C) for the decomposition was found to be 1.403 and -6.411 K cal/mole.

These results are quite comparable with the studies carried out by Asperger (20) on the kinetics of interactions of hexacyanoferrate (II) with nitrosobenzene, and by Malik (21) on its interaction with Cr^{+++}, Be^{++} ions.

CHAPTER II

Interaction of nitrosobenzene with hexacyanoferrate (II) and ferrate (III).

(Part I)

The Reduction of Nitrosobenzene Complex with Aquapentacyanoferrate (II) at dropping mercury electrode.

The problem of hydrolytic decomposition of hexacyanoferrate (II) to agqapentacyanoferrate (II) was considered by a number of workers (1-6). Extensive studies on the kinetics of hydrolytic decomposition of hexacyanoferrate (II) in presence of small amounts of mercuric ions was carried out by S. Asperger (2,3) by determining the variations in the extinction with time of the violet complex $(FeCy_5C_6H_5NO)^{---}$ According to S. Asperger the equilibrium reaction $FeCy_6^{----} \underset{H_2O}{\rightleftharpoons} FeCy_5H_2O^{---} + CN^-$ (i) in dark shifted completely towards left but was prevented by relatively fast irreversible process:

$$FeCy_5H_2O+C_6H_5NO = FeCy_5C_6H_5NO+H_2O \qquad (ii)$$

It was then possible to measure the velocity of decomposition of potassium hexacyanoferrate (II) to aquapentacyanoferrate (II) by complexing the reaction product with nitrosobenzene. More recently Malik and Kaphley (7) carried out the decomposition of hexacyanoferrate (II) in presence of Be^{++} and Cr^{+++} ions. They studied the kinetics of interaction and the relatively fast irreversible process in presence of Be^{++} ions and reported second order reaction kinetics.

In this part of the chapter the results on the reduction of nitrosobenzene pentacyanoferrate (II) complex at dropping murcury electrode are reported. It may be mentioned that in the literature reduction of aliphatic and aromatic nitrosocompounds (8-11) (Nitrosobenzene, p-nitrosophenol, -nitroso-B-naphthol, and nitrosophenyl hydroxyl amine) have been reported. No references on the reduction of nitrosobenzene complex of the hydrolytic decomposition product of hexacyanoferrate (II) are available.

EXPERIMENTAL

SOLUTIONS:

Nitrosobenzene:

Nitrosobenzene was prepared by the method of Coleman et al (12). Its solution of required concentration was prepared in double distilled water containing 20 per cent alcohol and kept in freeze.

Composition of buffers:

All the buffers used were prepared in double distilled water. Clark and Lubs, potassium hydrogen phthalate, potassium dehydrogen phosphate, Borax and sodium dihydrogen phosphate buffers were used in pH range (1.0-2.0); (3.0-6.6), (7.0-8.6); (8.8-10.6 and (11.0-13.0) respectively for maintaining the pH of the solutions, under investigations.

Aquapentacyanoferrate (II):

Potassium aquapentacyanoferrate (II) was prepared employing Hoffman's method (13) with some modifications. In an ice cold dilute alkaline solution of potassium hexacyanoferrate (II) [potassium hexacyanoferrate (II) 10 gms potassium carbonate 1.0 gm in 200 ml double distilled water] chlorine was passed till the red colouration persisted. The solution was treated with oxygen free ice cold ethyl alcohol (4 folds). The yellow precipitate was collected in the atmosphere of hydrogen and dissolved in minimum quantity of water and treated with an ice-cold solution containing hydroxyl-amine hydrochloride and potassium carbonate (15 gms and 10 gms respectively dissolved in minimum quantity of double distilled water). Lemon yellow crystals were obtained with repeated crystalization of the above product from cold ethyl alcohol. The compound was dried in vacuum over sulphuric acid for 24 hours. The faint yellow aqueous solution did not show any turbidity even after several weeks.

Weighed quantity of aquapentacyanoferrate (II) was dissolved in double distilled water and its strength was determined potentiometrically against ceric sulphate.

Solution of potassium chloride of required concentration was prepared in double distilled water.

Apparatus:

A Toshniwal palarograph Type CLO-2 (India) was empolyed, using a Pye sclamp Galvanometer in the external circuit. The polarographic cell and the reference electrode (S.C.E.) were kept immersed in thermostatic bath maintained at 30 ± 0.1°C Purified hydrogen was used for de-aeration. A Fischer capillary with a drop time of 3.4 sec (ope circuit) was used for the d.m.e, the capillary constant $m^{2/3}\ t^{1/6}$ being 2.877. Potassium chloride and suitable buffers was used as the supporting electrolyte. Polarograms of the various mixtures in duplicate were taken after 24 hours of mixing the reactants. Mean of minimum and maximum diflection of galvanometer was recorded for each potential. No maximum suppressor was used in present studies. The following aspects were studied:

1-Mixtures containing 1.0 ml, 0.01M nitrosobenzene; 1.0 ml, 0.01M aquapentacyanoferrate (II); 1.0 ml, 1.0M potassium chloride were taken and total volume made up to 15.0 by adding requisite amount of the buffers, ranging from pH 1.15 to 12.5. Polarograms of nitrosobenzene alone in potassium chloride and various buffers were also taken for comparision.

The above studies were carried out to determine the influence of pH on the polarographic reduction of the violet complex. Results are tabulated below.

TABLE No.1

Current potential data for the reduction of Nitrosobenzene Pentacyanoferrate (II) complex:

Sensitivity 1/5 Current 1.1×10^{-8} ampers

pH	1.15	2.0	3.0	4.0	5.0
voltage	current	current	current	current	current
+0.08	+11.75	-0.15	-0.26	+0.35	+0.70
+0.06	-0.85	-0.80	-0.50	+0.15	+0.30
+0.04	-1.60	-1.15	-0.70	-0.05	+0.15
+0.02	-1.95	-1.35	-0.80	-0.20	+0.10
+0.00	-2.15	-1.40	-0.90	-0.32	+0.05
-0.00	+2.15	+1.40	+0.90	+0.32	-0.05
-0.02	+2.30	+1.60	+0.95	+0.45	+0.05
-0.04	+2.50	+1.70	+1.00	+0.52	+0.10
-0.06	+2.80	+1.95	+1.02	+0.57	+0.15
-0.08	+3.20	+2.15	+1.15	+0.62	+0.25
-0.10	+3.95	+2.65	+1.22	+0.67	+0.35
-0.15	+5.10	+4.50	+1.65	+0.72	-
-0.20	+5.40	+6.05	+3.00	+0.90	+0.55
-0.25	-	-	+5.25	+1.60	-
-0.30	+5.50	+6.45	+6.15	+3.57	+0.80
-0.35	-	-	-	-	+1.35
-0.40	+5.05	+0.55	+6.40	+6.35	+3.30
-0.45	-	-	-	-	+3.40
-0.50	+5.85	+6.60	+6.50	+6.60	+3.60
-0.60	+6.65	+6.75	+6.60	+6.65	+3.90
-0.70	+6.80	+7.20	+6.75	+6.85	+3.95
-0.80	+6.85	+7.55	+7.00	+6.95	+4.05
-0.90	+8.20	+7.55	+7.20	+7.00	+4.15
-1.00	+13.30	+7.75	+7.50	+7.10	+4.25
-1.10	-	+8.20	+7.70	+7.30	+4.30
-1.15	-	-	+7.90	+7.47	-
-1.20	-	+9.55	+10.75	+7.60	+4.45
-1.30	-	-	-	+12.50	+4.55
-1.40	-	-	-	-	+5.55
-1.50	-	-	-	-	-
Curve	(1)	(2)	(3)	(4)	(5)

Fig.1(a)

Current potential data for the reduction of Nitrosobenzene Pentacyanoferrate (II).

TABLE No.2

Current potential data for the reduction of Nitrosobenzene Pentacyanoferrate (II) complex:

Sensitivity 1/2 Current 1.1×10^{-8} amperes

pH	6.0	6.6	8.3	8.8
Voltage	Current	Current	Current	Current
+0.10	+4.65	+6.05	-	-
+0.08	+2.40	+4.60	+3.25	+4.10
+0.06	-	-	+0.65	+0.78
+0.04	+0.35	+0.45	+0.45	+0.56
+0.00	+0.25	+0.35	+0.35	+0.34
-0.00	-0.25	-0.35	-0.35	-0.34
-0.02	-0.20	-0.25	-	-
-0.04	-0.15	-0.25	-0.25	-0.25
-0.06	-0.05	-0.25	-	-
-0.08	+0.05	-0.20	-0.22	-0.15
-0.10	+0.15	-0.15	-0.15	-0.05
-0.15	+0.20	-0.10	-	-
-0.20	+0.55	-0.05	-0.05	+0.05
-0.30	+0.65	+0.12	+0.15	+0.34
-0.40	+0.80	+0.15	+0.25	+0.45
-0.45	+1.25	-	-	-
-0.50	+2.00	+0.45	+0.40	+0.55
-0.60	+2.10	+1.00	+0.78	+0.85
-0.70	+2.45	+1.20	+0.85	+1.00
-0.80	+2.50	+1.35	+0.85	+1.05
-0.90	+2.65	+1.40	+0.95	+1.15
-1.00	+2.80	+1.45	+0.95	+1.15
-1.10	+2.95	+1.50	+1.00	+1.25
-1.20	+2.05	+1.55	-	-
-1.30	+3.10	+1.60	-	-
-1.40	+3.15	+1.65	-	+1.45
-1.50	+3.25	+1.75	+1.25	+1.50
-1.60	+3.45	+1.85	+1.35	-
-1.70	+7.85	+1.95	-	+1.75
Curve	(6)	(7)	(8)	(9)

Fig.1 (a)

TABLE No.3

Current potential data for the reduction of Nitrosobenzene Pentacyanoferrate (II) complex:

Senstivity 1/2 Current 1.1×10^{-8} amperes

pH	9.6	10.6	11.4	12.4
Voltage	Current	Current	Current	Current
+0.10	+9.60	+12.85	-	-
+0.08	+4.95	+ 7.30	-	-
+0.06	+2.85	-	-	-
+0.04	+0.85	+ 1.65	Out of scale	-
+0.00	+0.45	+ 0.55	+5.35	-
-0.00	-0.45	- 0.55	-5.35	-
-0.04	-0.32	- 0.35	-0.75	-
-0.06	-0.25	-	-	-3.90
-0.08	-0.15	- 0.15	-0.35	-1.35
-0.10	-0.05	- 0.05	-0.25	-0.55
-0.20	+0.05	+ 0.15	+0.05	-0.12
-0.30	+0.40	+ 0.45	+0.35	-0.00
-0.40	+0.55	+ 0.55	-	+0.10
-0.50	+0.65	+ 0.65	+0.45	+0.20
-0.55	+0.77	-	-	-
-0.60	+1.15	+ 0.75	+0.55	+0.20
-0.70	+1.25	+ 1.30	+1.70	+0.40
-0.80	+1.55	+ 1.50	+2.45	+0.45
-0.90	+1.60	+ 1.60	+2.65	+0.67
-1.00	+1.60	+ 1.70	+2.90	+0.70
-1.10	+1.65	-	+3.00	-
-1.20	+1.75	+ 1.85	+3.10	+0.80
-1.30	+1.85	-	-	-
-1.40	+1.95	-	+3.30	-
-1.50	-	-	-	-
-1.60	+2.45	+ 2.15	+3.40	+1.20
Curve	(10)	(11)	(12)	(13)

Fig.1 (a)

TABLE No.4

Current potential data for the reduction of Nitrosobenzene

Senstivity 1/2 Current 1.1×10^{-8} amperes

pH Voltage	1.1 Current	2.0 Current	3.0 Current	4.0 Current	5.0 Current
+0.08	Out of scale	+4.00	+0.95	+0.75	+1.00
+0.06	+1.40	+1.75	+0.50	+0.30	+0.50
+0.04	+0.35	+0.60	+0.35	+0.00	+0.05
+0.02	-0.08	+0.25	+0.15	-0.175	-0.65
+0.00	-0.21	-0.15	-0.05	-0.275	-1.15
-0.00	+0.21	+0.15	+0.05	+0.275	+1.15
-0.02	+0.35	-	+0.05	+0.45	+1.40
-0.04	+0.40	+0.15	+0.10	+0.65	+1.55
-0.06	+0.50	+0.25	+0.20	+0.85	+1.70
-0.08	+0.55	+0.35	+0.35	+1.10	+1.80
-0.10	+0.60	+0.45	+0.40	+1.30	+2.00
-0.15	+0.70	+0.80	+0.65	-	+2.35
-0.20	+0.85	+1.05	+0.85	+3.45	+2.65
-0.30	+1.00	+1.40	+1.15	+7.60	+3.10
-0.40	+1.10	+1.70	+1.30	+9.85	+3.90
-0.50	+1.30	+2.10	+1.45	+10.15	+4.25
-0.60	+1.40	+2.65	+1.60	+10.30	+4.40
-0.70	+1.50	+3.00	+1.70	+10.55	+4.65
-0.80	+1.60	+3.30	+1.90	+11.00	+4.95
-0.90	+1.70	+3.60	+2.25	+12.15	+5.40
-1.00	+1.90	+5.00	+3.5	Out of scale	+6.05
-1.10	+2.70	+6.70	+4.45	-	+6.60
-1.20	+4.70	+9.90	Out of scale	-	+7.35
-1.30	Out of scale	Out of scale	-	-	+8.00
-1.40	-	-	-	-	+9.85
-1.50	-	-	-	-	Out of scale
-1.60	-	-	-	-	-
Curve	(1)	(2)	(3)	(4)	(5)

Fig.1(b)

TABLE No.5

Current potential data for the reduction of Nitrosobenzene

Senstivity 1/5 Current 1.1x10^{-8} amperes

pH	6.0	6.6	8.3	8.8
Voltage	Current	Current	Current	Current
+0.10	+2.50	+2.70	+2.85	+5.40
+0.08	+1.35	+1.55	+1.60	+2.05
+0.06	+0.95	+1.10	+1.10	+1.30
+0.04	+0.70	+0.90	+0.95	+1.00
+0.02	+0.06	+0.80	+0.80	+0.80
+0.00	+0.45	+0.60	+0.70	+0.55
-0.00	-0.45	-0.60	-0.70	-0.55
-0.02	-0.30	-0.42	-0.50	-0.30
-0.04	-0.10	-0.30	-0.35	+0.05
-0.06	+0.25	+0.05	-0.10	+0.35
-0.08	+0.70	+0.25	+0.35	+0.60
-0.10	+1.15	+0.70	+0.90	+0.80
-0.15	+2.05	+1.45	+1.85	+0.60
-0.20	+2.45	+2.15	+2.80	+1.35
-0.30	+2.75	+2.75	+3.20	+1.80
-0.40	+3.00	+2.95	+3.50	+2.00
-0.50	+3.35	+3.15	+3.75	+2.15
-0.60	+3.60	+3.45	+4.10	+2.25
-0.70	+4.00	+3.85	+4.35	+2.55
-0.80	+4.55	+4.40	+4.90	+2.85
-0.90	+5.20	+4.90	+5.50	+3.30
-1.00	+5.90	+5.55	+6.15	+3.70
-1.10	+6.65	+6.15	+6.55	+4.10
-1.20	+6.95	+6.60	+6.90	+4.30
-1.30	+7.15	+7.00	+7.10	+4.65
-1.40	+7.20	+7.55	+7.15	+4.70
-1.50	+7.50	+7.60	+7.15	+4.85
-1.60	Out of scale	+7.60	+7.15	+4.90
Curve	(6)	(7)	(8)	(9)

Fig.1(b)

TABLE No.6

Current potential data for the reduction of Nitrosobenzene

Senstivity 1/2 Current 1.1x10^{-8} amperes

pH	9.5	10.6	11.0	12.4
Voltage	Current	Current	Current	Current
+0.08	+8.70	-	-	-
+0.06	+2.00	+11.55	-	-
+0.04	+1.30	+3.70	-	-
+0.02	+1.00	+1.45	-	-
+0.00	+0.80	+0.90	-	-
-0.00	-0.80	-0.90	-11.45	-
-0.02	-0.60	-0.70	- 3.90	-
-0.04	-0.30	-0.50	- 1.45	-
-0.06	+0.05	-0.40	- 0.75	-10.05
-0.08	+0.45	-0.10	- 0.57	- 3.35
-0.10	+0.75	+0.30	- 0.48	- 1.55
-0.15	+1.10	+0.80	- 0.00	- 0.65
-0.20	+1.30	+1.05	+0.95	- 0.05
-0.25	+1.50	+1.25	+1.30	+ 0.15
-0.30	+1.60	+1.55	+1.60	+ 0.35
-0.40	+1.75	+1.80	+1.80	+ 0.45
-0.50	+1.95	+2.00	+1.90	+ 0.62
-0.60	+2.20	+2.30	+2.05	+ 0.75
-0.65	-	+3.00	+2.65	+ 1.35
-0.70	+2.55	+4.10	+3.90	+ 3.65
-0.80	+2.85	+4.75	+4.80	+ 5.20
-0.90	+3.30	+5.15	+5.40	+ 6.25
-1.00	+3.85	+5.60	-	+ 6.60
-1.10	+4.30	+5.95	+5.55	+ 6.80
-1.20	+4.55	+6.30	+5.95	+ 7.15
-1.30	+4.85	+6.30	+6.20	+ 7.50
-1.40	+5.00	+6.40	+6.30	+ 7.80
-1.50	+5.00	+6.50	+6.30	+ 8.00
-1.60	+5.15	-	-	-
Curve	(10)	(11)	(12)	(13)

Fig.1(b)

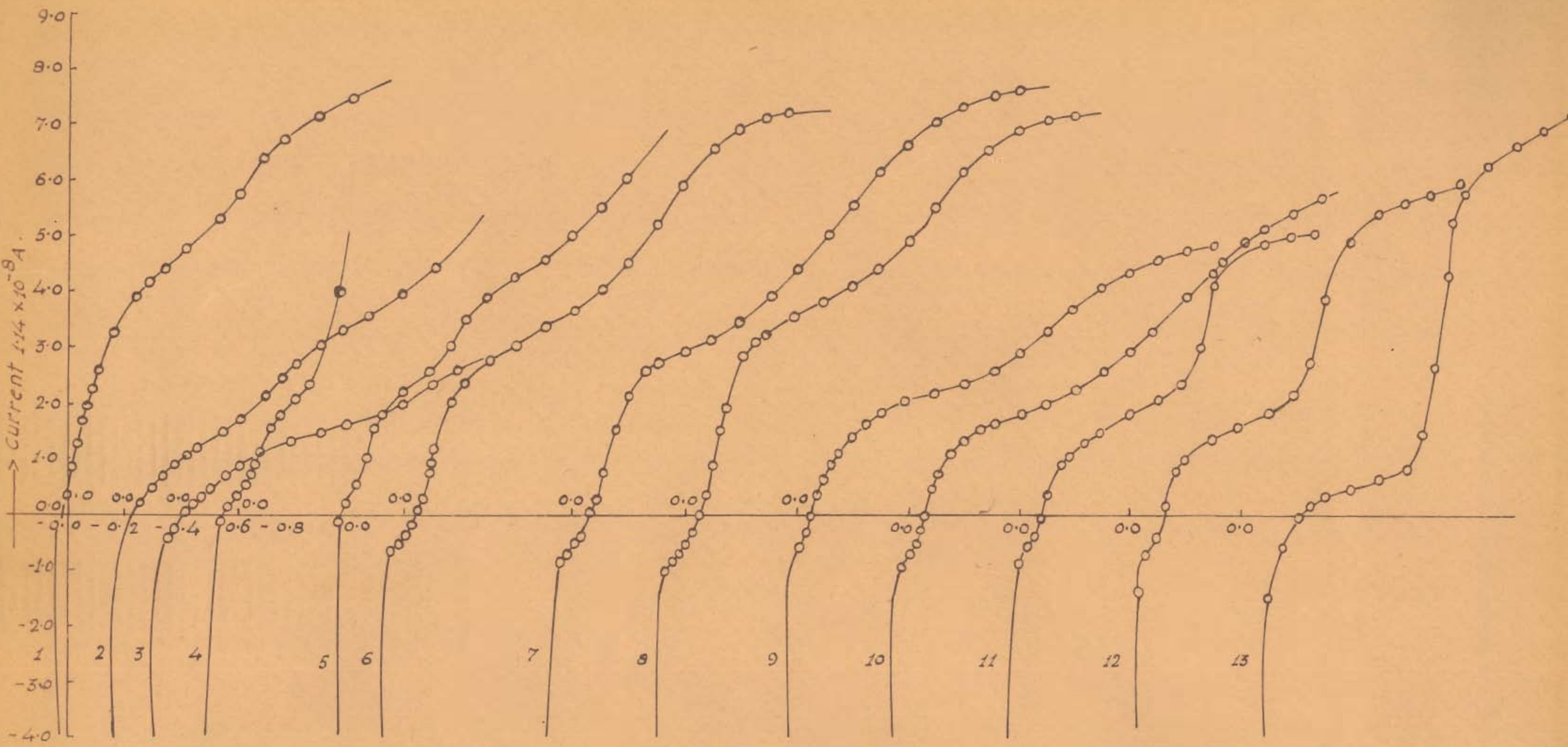


Fig. 1 (b)

Polarograms of nitrosobenzene at different pH values ①. 1·15, ② 2·0, ③ 3·0, ④ 4·0, ⑤ 5·0, ⑥ 6·0, ⑦ 6·6, ⑧ 8·3, ⑨ 8·85, ⑩ 9·5, ⑪ 10·6, ⑫ 11·0, ⑬ 12·4. 0·0 is the original for each curve.

2-Mixtures containing 3.0 ml of 0.01M nitrosobenzene and increasing amounts of (0.5, 1.0, 1.5, 2.0, 2.5, 3.0 ml) of 0.01M aquapentacyanoferrate (II); 1.0 ml, 1.0M potassium chloride, total volume made up to 15.0 ml by adding requisite amount of buffer of pH 4.0 (optimum pH from (I) above for the reduction of the complex) solutions were also prepared in reverse order, viz., using a constant volume of the aquapentacyanoferrate (II) (3.0 ml 0.01M aquapentacyanoferrate (II) and increasing amounts of nitrosobenzene (0.5, 1.0, 1.5, 2.0, 2.5 ml) and polarograms were recorded under similar conditions. Results are tabulated below:

TABLE No.7

Current potential data of the mixtures containing constant quantity of nitrosobenzene and increasing amounts of aquapentacyanoferrate(II).

pH 4.0 Current 1.1×10^{-8} amperes

Senstivity	1/5	1/5	1/5	1/10	1/10	1/10
Mixture	1	2	3	4	5	6
Voltage	Current	Current	Current	Current	Current	Current
+0.08	+0.10	+0.05	+1.15	+0.95	+1.15	+1.20
+0.06	-0.12	-0.40	-0.90	-0.25	+0.75	+0.20
+0.04	-0.30	-0.65	-1.10	-0.45	-0.35	-0.20
+0.02	-0.45	-0.85	-1.30	-0.60	-0.55	-0.50
+0.00	-0.50	-1.15	-1.40	-0.75	-0.75	-0.70
-0.00	+0.50	+1.15	+1.40	+0.75	+0.75	+0.70
-0.02	+0.60	+1.25	+1.52	+0.95	+0.85	-
-0.04	+0.70	+1.40	+1.52	+1.10	+1.05	+1.05
-0.06	+0.80	+1.45	+1.65	+1.22	+1.20	+1.20
-0.08	+0.90	+1.55	+1.70	+1.30	+1.25	+1.30
-0.10	+1.00	+1.65	+1.75	+1.40	+1.30	+1.40
-0.15	+1.20	+1.85	+1.90	+1.57	+1.40	+1.45
-0.20	+1.40	+2.10	+2.05	+1.75	+1.55	+1.55
-0.25	+1.80	+2.65	+2.70	-	+1.90	+1.85
-0.30	+2.72	+4.60	+4.80	+3.20	+3.20	+3.20
-0.35	+3.65	+7.60	+8.40	-	+5.45	+5.45
-0.40	+4.02	+9.40	+10.60	+6.90	+7.30	+7.30
-0.50	+4.10	+10.0	+11.55	+7.76	+8.40	+9.20
-0.60	+4.32	+10.3	+11.90	+8.07	+8.70	+9.50
-0.70	+4.50	+10.55	+12.25	+8.30	+9.05	+9.80
-0.80	+4.60	+10.70	+12.45	+8.40	+9.20	+10.00
-0.90	+4.80	+11.00	+12.65	+8.50	+9.35	+10.10
-1.00	+5.10	+11.50	+12.95	+8.80	+9.40	+10.20
-1.10	+5.50	+11.90	+13.30	+9.1	+9.65	-
-1.20	+5.80	+12.20	+13.50	+9.15	+9.65	-
-1.30	+9.65	+12.90	-	-	-	-
Curve	(1)	(2)	(3)	(4)	(5)	(6)
Diffusion Current	1.9	2.8	3.9	5.4	6.9	7.9

Fig.2(a)

Note: Curve 1,2,3 have been plotted from the reading of 1/10 senstivity (which are not given in the table).

3- In order to study the relationship between i_d and concentration of the complex, mixtures containing equimolecular (0.01M) quantities of the reactants (0.5 ml to 3.0 ml) were prepared using 1.0M potassium chloride and phthalate buffer of pH 4.0. Various results are recorded below:

TABLE No.8

Current potential data of the mixtures containing fixed amount of aquapentacyanoferrate (II) and increasing amounts of nitrosobenzene.

pH 4.0 Current 1.1×10^{-8} amperes

Senstivity	1/10	1/10	1/10	1/10	1/10
Mixture	1	2	3	4	5
Voltage	Current	Current	Current	Current	Current
+0.10	+1.85	+2.10	+2.10	+2.20	+2.30
+0.08	+0.25	+0.22	+1.25	+1.30	+1.30
+0.06	-0.70	-0.60	-0.05	-0.35	-0.40
+0.04	-0.90	-0.75	-0.57	-0.50	-0.55
+0.02	-1.00	-0.82	-0.72	-0.65	-0.70
+0.00	-1.20	-0.95	-0.95	-0.85	-0.90
-0.00	+1.20	+0.95	+0.95	+0.85	+0.90
-0.02	+1.30	+1.05	+1.03	+0.95	+0.95
-0.04	+1.35	+1.10	+1.10	+1.05	+1.05
-0.06	+1.40	+1.15	+1.13	+1.15	+1.20
-0.08	+1.40	+1.20	+1.17	+1.22	+1.30
-0.10	+1.47	+1.20	+1.20	+1.35	+1.40
-0.20	+1.65	+1.45	+1.30	+1.75	+1.78
-0.30	+2.32	+2.67	+2.75	+3.36	+3.40
-0.40	+3.62	+5.00	+5.90	+7.00	+7.85
-0.50	+3.80	+5.30	+6.30	+7.65	+9.15
-0.60	+3.90	+5.40	+6.45	+7.70	+9.55
-0.70	+3.90	+5.50	+6.55	+7.95	+9.85
-0.80	+4.00	+5.60	+6.60	+8.00	+10.00
-0.90	+4.01	+5.70	+6.65	+8.15	+10.10
-1.00	+4.22	+5.80	+6.75	+8.35	+10.27
-1.10	+4.25	+5.95	+6.80	+8.60	-
-1.20	+4.25	+6.00	+7.20	+6.30	+10.50
-1.30	+5.50	+6.70	-	-	-
-1.40	+7.80	+9.30	-	-	-
Curve	(7)	(8)	(9)	(10)	(11)
Diffusion Current	1.8	3.6	4.8	5.6	7.0

Fig.2(b)

TABLE No.9

i_d values obtained from the plots of current potential data for the mixtures containing (0.5, 1.0, 1.5, 2.0 2.5, 3.0 and 3.5 ml) of each of the reactants (0.01M)

pH 4.0 Current 1.10x10^{-8} amperes

Senstivity	1/5	1/5	1/5	1/5	1/5	1/5
Mixture	1	2	3	4	5	6
Concentration of complex x 10^{-2}M	0.333	0.666	1.000	1.333	1.666	2.000
Diffusion current i_{d} x 1.10x10^{-8} amperes	3.45	5.43	7.65	10.90	13.8	15.7

Fig.3

FIG.4.

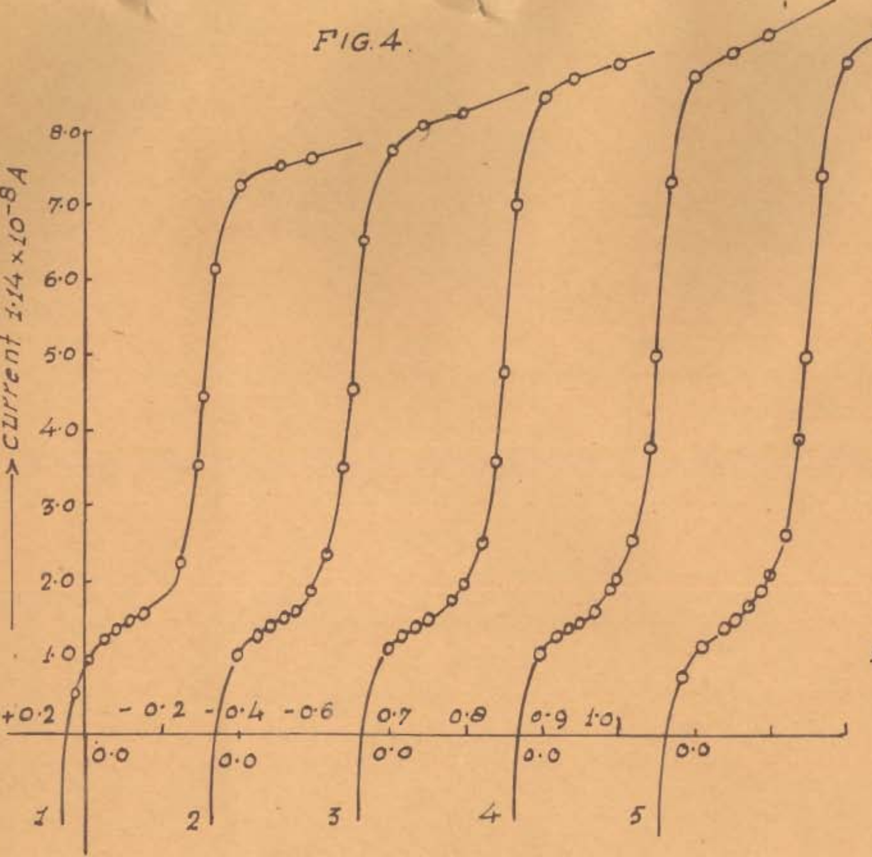
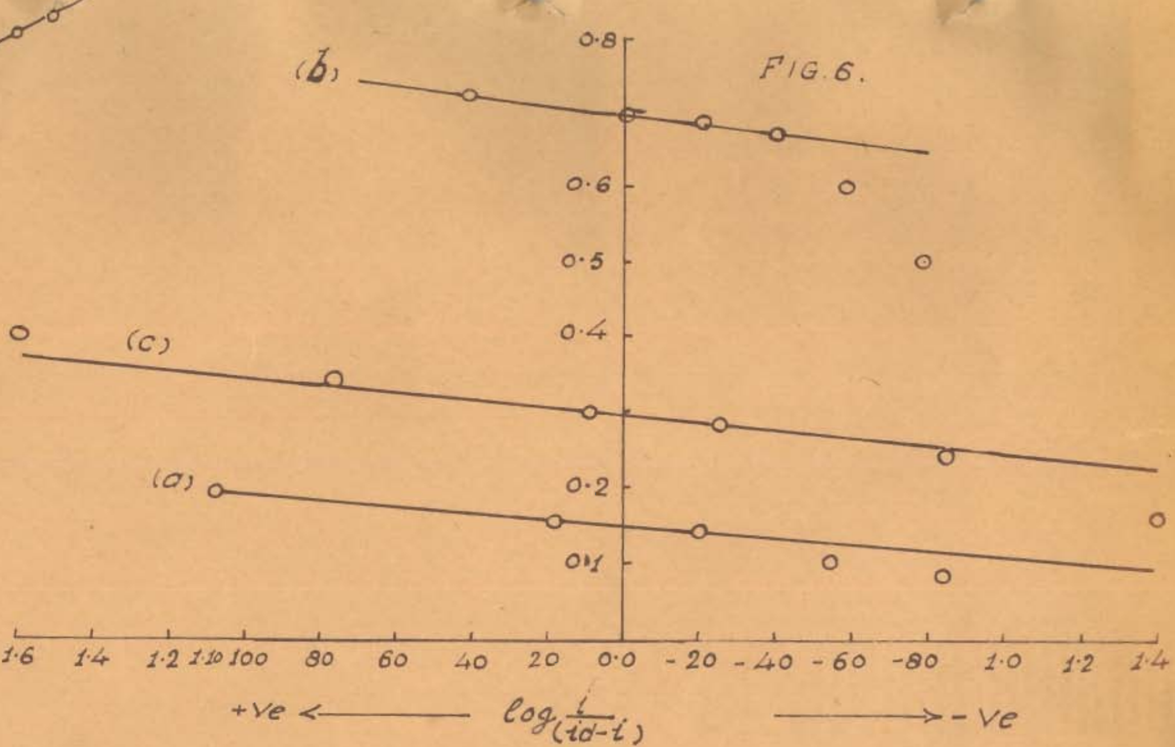
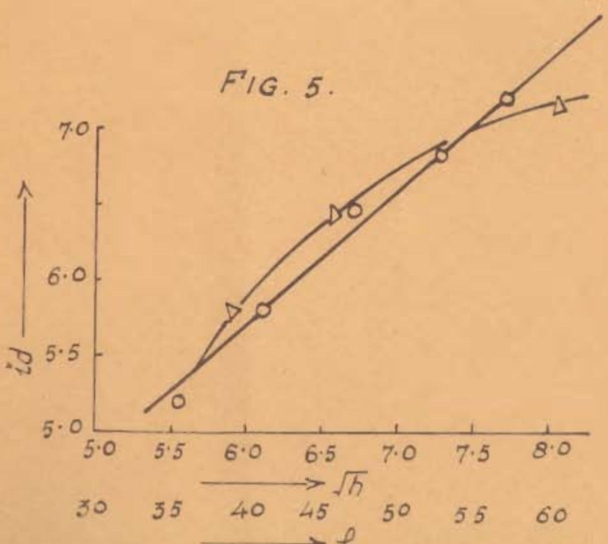


FIG.6.



(a) Plot of log $\left(\frac{i}{id-i}\right)$ at pH-2 for first wave.
(b) " " " " " " " second wave.
(c) " " " " " pH-4

FIG. 5.



(a) id vs √h. (b) id vs h.

FIG.3.

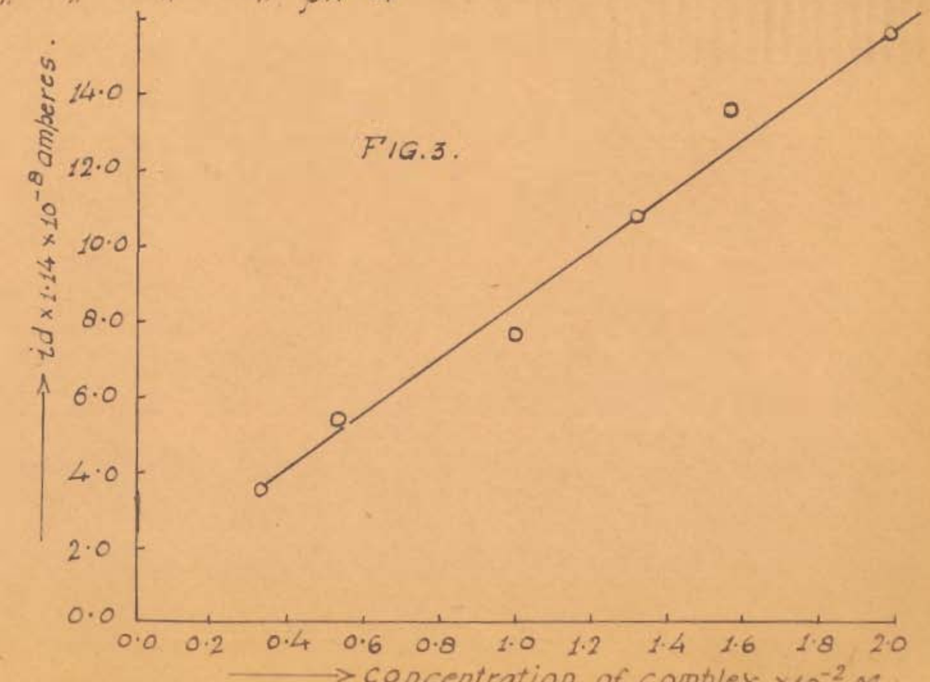


TABLE No.10

i_d Values obtained from the plots of current potential data, taken at different heights of the mercury column for the mixture containing 1.0 ml of each of the reactants (0.01M) in 15.0 ml of volume at pH 4.0.

Height ($h_{corr.}$)* of mercury column cm.	Diffusion current at 1/2 sensitivity $x1.40x10^{-8}$ A	Droptime Seconds
32.37	5.2	6.35
40.15	5.8	5.38
49.60	6.5	4.34
57.01	6.8	3.74
61.45	7.2	3.42

Fig.4

Plot of h and h. Vs i_d Fig.5

Plot of log $\frac{i}{i_d-i}$ Vs potential Fig.6

Plot of log i Vs log t Fig.7

* $h_{corr.} = h_{exp} - h_{back}$

and $h_{back} = \frac{3.1}{(5.6xm^{1/3}t^{1/3})}$

Results and discussions:

The reduction of the nitrosobenzene complex of potassium aquapentacyanoferrate (II) is dependent on pH of the medium. Three pH regions can be distinguished.

(1) From pH 1.0-4.0, reduction takes place in three waves. The first, rising directly from the dissolution of mercury decreases, as does the third most negative wave, where as the second increases. Total wave height remains practically constant (Fig.1 curve 1-4). The half wave potential of the second wave was shiffted from 0.10 V.at pH 1.15 to 0.30 V.at pH 4.0, where as that of third wave was shifted from 0.56 V.at pH 1.15 to 0.83 V.at pH 3.0.

(2) At pH >5, the height of the second wave decreases (Fig.1, curve 5-10). Another more positive wave appears at (0.06 V.at pH 5.0), the height of which is paractically pH dependent.

(3) At pH 10.6 the height of the second wave increases again, the half wave potential 0.7 V is identical with that of the free nitrosobenzene (Fig.1 curves 11-13) the results are summarised in table No.11.

The simplest curve is observed at pH 4.0 where the limiting current of the single wave observed is diffusion controlled as verified by the effect of mercury pressure (Fig.4,5). Also the plot of logi against log t (Fig.7) providesevedence for a diffusion controlled two electron transfer process. The step height is also a linear function of the concentration of the complex (Fig.3).

The waves obtained with mixtures containing a fixed amount of the aquapentacyanoferrate (II) and varying amounts of nitrosobenzene and those of mixtures prepared in the reverse order, have i_d values that increase with the concentration of the reactants (Fig.2c) nitrosobenzene or aquapentacyanoferrate (II); but the values become constant at a combining ratio 1:1.

The following scheme for the formation and subsequent reduction of the violet complex is suggested.

$$Fe^{II}Cy_5H_2O + C_6H_5NO = Fe^{II}(Cy_5)C_6H_5NO + H_2O$$

$$Fe^{II}Cy_5C_6H_5NO + 2H^+ + 2e = Fe^{II}Cy_5C_6H_5NHOH \quad \text{(2nd wave)}$$

$$Fe^{II}Cy_5C_6H_5NHOH + 2H^+ + 2e = Fe^{II}Cy_5C_6H_5NH_2 \quad \text{(3rd wave)}$$

This scheme is in agreement with the reported polarographic reduction of nitrosobenzene (9) and N-phenyl hydroxyl-amine in this pH-range.

From the data obtained in the alkaline pH-range, it may be concluded that the complex starts decomposing beyond pH 6.0 and becomes quite un-stable at pH 11.0 $E_{\frac{1}{2}}$ and i_d values of nitrosobenzene aquapentacyanoferrate (II) complex and that of nitrosobenzene at different pH-values are shown in Table No.11.

TABLE No.11

$E_{\frac{1}{2}}$ and i_d values of nitrosobenzene aquapentacyanoferrate (II) complex and that of nitrosobenzene at different pH-Values: .

pH	1.1	2.0	3.0	4.0	5.0	6.0	6.6	8.3	8.8	9.5	10.6	11.0
Complex												
$(E_{\frac{1}{2}})_I$ (V.Vs S.C.E)	-0.10	-0.15	0.22	-0.30	-0.60	-0.10	-0.16	-0.24	-0.26	-0.26	-0.29	-
$(i_d)_I$	3.0	4.7	4.9	5.3	5.0	5.0	5.0	5.0	4.9	5.0	5.0	-
$(E_{\frac{1}{2}})_{II}$	-0.56	-0.70	-0.83	-	-0.83	-0.46	-0.56	-0.58	-0.59	-0.60	-0.65	-0.70
$(i_d)_{II}$	1.2	0.70	0.50	0.20	0.24	0.12	0.60	0.40	0.04	0.45	0.50	1.1
Nitrosobenzene												
$(E_{\frac{1}{2}})_I$	-0.63	-0.70	-0.82	-0.06	-0.08	-0.10	-0.12	-0.14	-0.10	-0.10	-0.10	-
$(E_{\frac{1}{2}})_{II}$	-	-	-	-	-	-0.36	-0.94	-1.0	-1.1	-1.1	-1.1	-0.7

Subscripts I and II refer to second and third steps respectively.

CHAPTER II (Part II)

Interaction of Nitrosobenzene with Hexacyanoferrate (III).

Several mixed complex cyanides with organic compounds of Fe(II) like $(FeCy_5NH_3)^{3-}$;(1) $FeCy_2(CH_3NC)_4$ (2), $FeCy_2(Phen)_2$, $Fe(Cy_2)$ $(dipy)_2$; $Fe(Cy)_4(Phen)^{2-}$; $FeCy_4(dipy)^{2-}$; $Fe(Cy)_2$ $(CO)_2$ (py) (3,4) and Fe(Cy) $(RCH_2NC)_5^{+(5)}$ and that of Fe(III) like $Fe(Cy_5)$ (NH_3)(6) and $FeCy_5(PhNO_2)^{3-}$(7) are available in the existing literature. Their synthesis and physico-chemical properties, although, present some interesting feature in the field of cyanogen complexes but very few references are available on the kinetics of interaction of organic compounds with cyanogen complexes. The notable contribution in this field is due to S. Asperger (8), who studied the effect mercuric ions on the reaction velocity, between hexacyanoferrate (II) and nitrosobenzene. The effect of gold compound ($AuCl_3$) on the rate of substitution reaction between Ph NO_2 and hexacyanoferrate (II) was studied by Yatsimerskii and Orlova (9). The reaction

$$AuCl_4^- + 4FeCy_6^{4-} + 2\ PhNO_2 \xrightarrow{H_2O} AuCy_2^+ + 2FeCy_6^{3-} + 2FeCy_5\ PhNO_2^{3-}$$

was first order with respect to the Au concentration and found to be independent of the $FeCy_5^{4-}$ concentration which was taken in excess. A machenism was proposed for this reaction to which the lowest stage of the reaction reported, was the formation of $FeCy_5H_2O^{3-}$.

Nothing has been so far reported in the

literature on the exchange reactions between the hydrolytic decomposition product of hexacyanoferrate (III) and organic compounds parallel to exchange reactions between hydrolytic decomposition product of hexacyanoferrate (II) and organic compounds. Therefore, it was thought worth while to study this aspect of reactions. However, we observed substitution reaction between hexacyanoferrate (III) and nitrosobenzene in presence of mercuric ions, in dilute solutions.

Priliminary observations revealed the following interesting facts.

(1) On keeping the mixtures of nitrosobenzene and hexacyanoferrate (III) in various proportions for several hours no change in colour was observed.

(2) In presence of small amounts of Hg^{++} ions a slow change in colour from yellow to light green, then bluish violet and finally a wine red or flesh colour; was developed. The change in light green colour realized in early stages was also observed when small quantity of Hg^{++} was added to hexacyanoferrate (III).

(3) The flesh colour on keeping for half an hour in sun light or under a bulb of white light or on heating for 10 minutes, slowly disappeared, but reappeared on keeping in dark for several hours. Prolonged action of sunlight or heat or white light brought about change in colour from flesh to green and then to light blue.

Keeping in view the above mentioned observations, the work described in this part of chapter carries the spectrophotometric and pH metric studies on the composition of the complex and kinetics of colour formation under different conditions.

EXPERIMENTAL

Prepration of solutions:

Hexacyanoferrate (III), rerystallized, was dissolved in double distilled water and its strength was determined volumetrically (10). Stock solution was kept in amber coloured bottle and the solutions of desired concentrations were prepared by diluting it.

Nitrosobenzene was prepared by the method of Coleman et al (11) and its solution was prepared in 80 per cent alcohol.

Solutions of mercuric chloride potassium chloride, potassium nitrate, potassium sulphate, potassium cyanide and different buffers were all prepared in double distilled water.

Apparatus:

Unicam SP-500 spectrophotometer was used for the measurements of optical density values (slit width 0.01 mm and silica cell of 1 cm thickness was used).

Backman pH-meter model H-2 was used for measuring the pH.

Vosburgh and Cooper's Method (12). Before carrying out actual spectrophotometric studies on the interaction of nitrosobenzene with hexacyanoferrate (III), absorption experiments were performed with the complex at different wavelengths in order to select suitable wavelength to workwith. Three solutions were prepared, each containing 10.0 ml of 10^{-4}M mercuric chloride, and No.1, 2.0 ml of 10^{-2}M hexacyanoferrate (III) No.2, 2.0 ml of 10^{-2}M nitrosobenzene No.3, 2.0 ml of 10^{-2}M hexacyanoferrate (III)and 2.0 ml of 10^{-2}M nitrosobenzene. Total volume in each case was made to 20.0 ml by adding requisit amount of water. Absorption measurements after keeping for 48 hours in dark were carried out in wavelength region 360 m$\mu$to 362 mμ(Table No.1) Vosbergh and coopers method was used to determine the number of complexes formed. Nitrosobenzene and hexacyanoferrate (III) of the concentration of 1.0x10^{-2}M were mixed in the ratios of hexacyanoferrate (III) to nitrosobenzene as 3:1, 2:1, 3:2, 4:3, 1:1, 3:4, 2:3, 1:2 and 1:3 keeping total volume to 12.0 ml. In each of the mixture was added 2.0 ml of 10^{-4}M mercuric chloride and 26.0 ml of buffer of pH-8.0 to make the total volume to 40.0 ml (it would be seen later on that the optimum pH for the reaction to attain completion). Kept in dark for 48 hours is 8.0 and optical density values were measured in the wavelength region 380 to 620 mμ. Results are tabulated below:

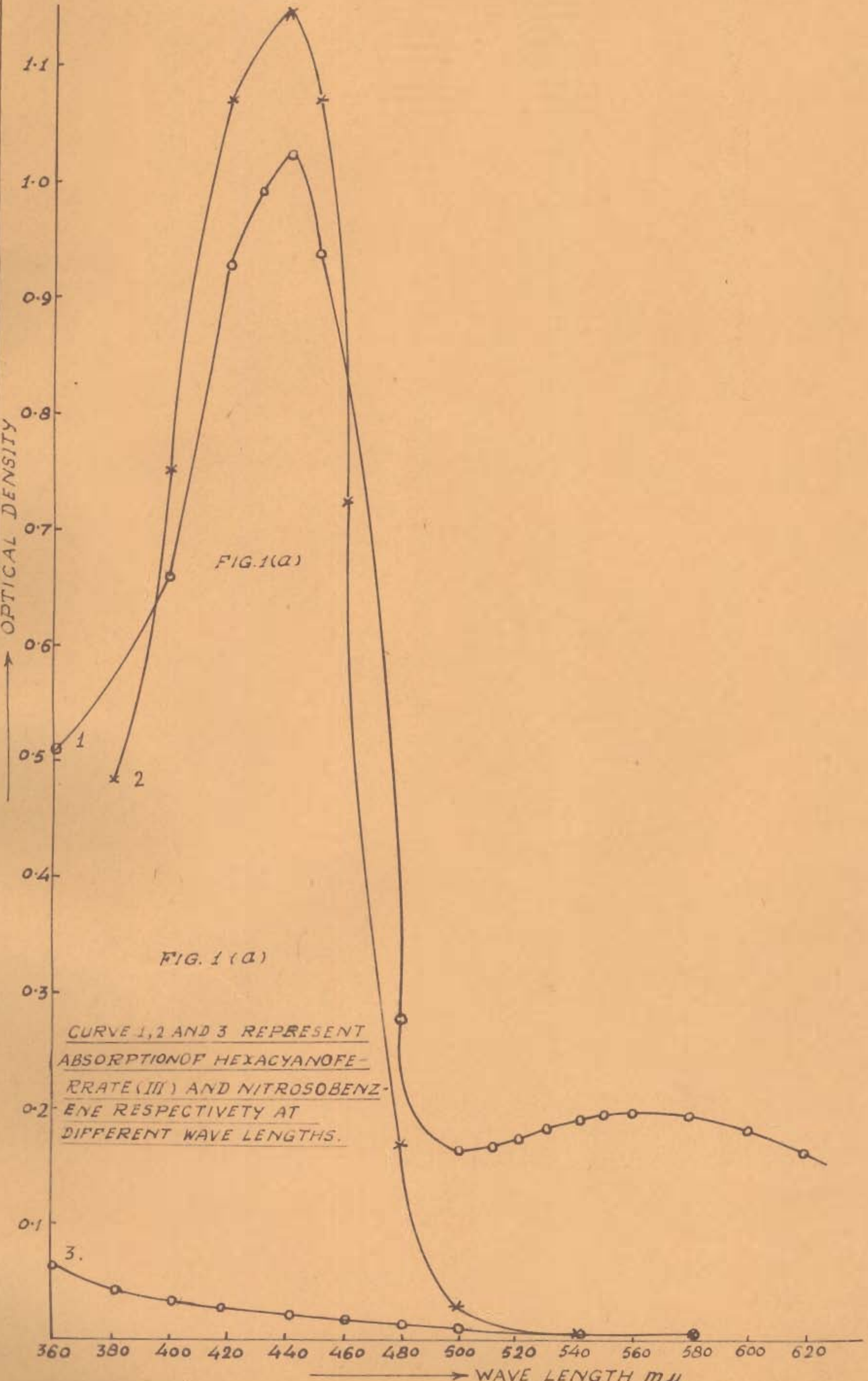


FIG. 1(a)

FIG. 1 (a)

CURVE 1,2 AND 3 REPRESENT ABSORPTIONOF HEXACYANOFERRATE(III) AND NITROSOBENZENE RESPECTIVETY AT DIFFERENT WAVE LENGTHS.

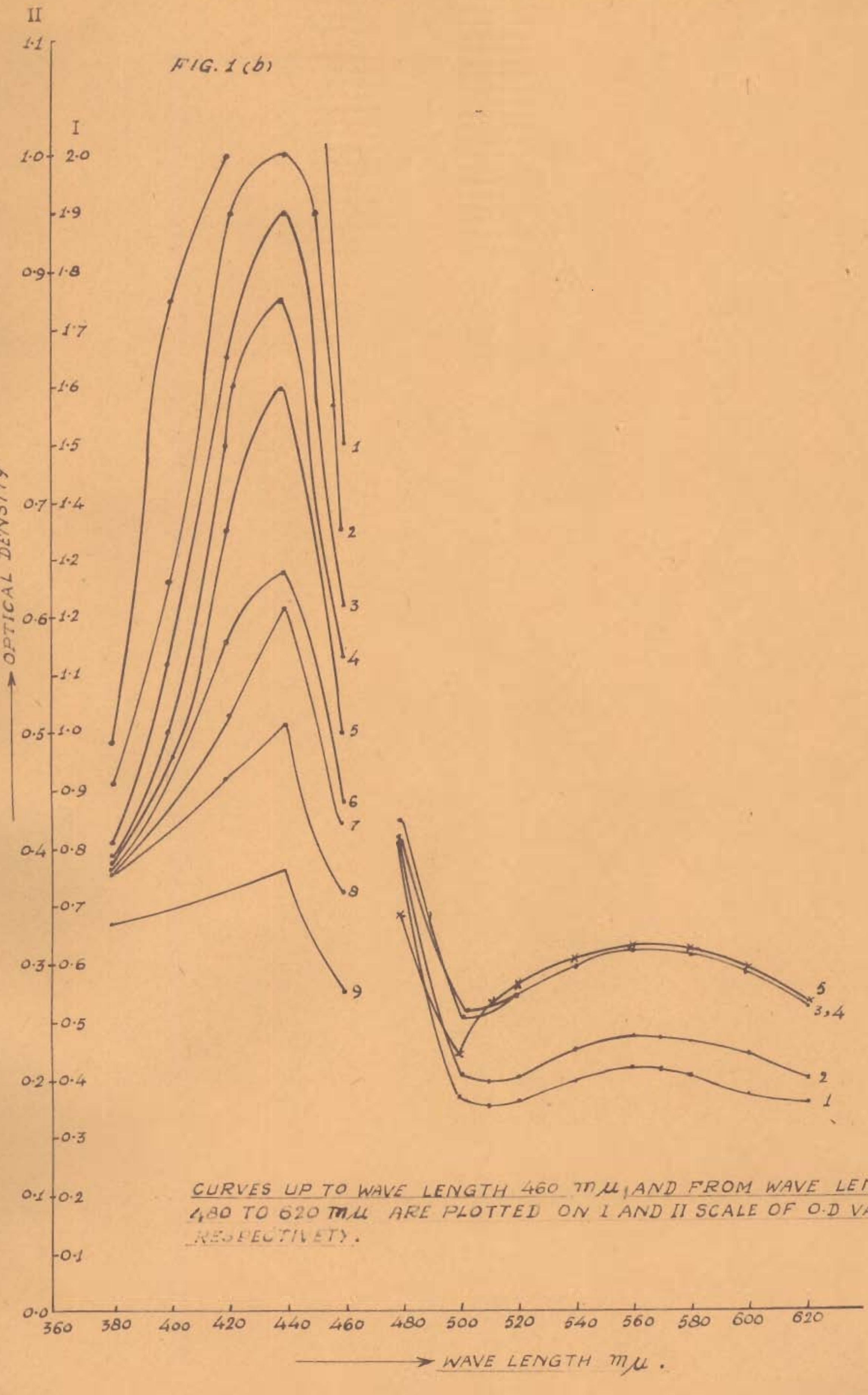
TABLE No.1

Concentration of Hexacyanoferrate (III) = 1.0×10^{-2}M
Concentration of Nitrosobenzene = 1.0×10^{-2}M
Concentration of mercuric chloride = 1.0×10^{-4}M

Wave length mμ	Optical density Values		
	Solution No.1	Solution No. 2	Solution No. 3
360	0.51	-	0.065
380	0.58	-	0.045
400	0.66	0.75	0.035
420	0.93	1.07	0.030
430	0.99	1.12	-
440	1.03	1.15	0.024
450	0.94	1.02	-
460	0.27	0.72	0.019
480	0.18	0.17	0.015
500	0.16	0.25	0.12
520	0.172	0.01	-
540	0.18	0.005	0.010
550	0.19	-	-
560	0.195	-	-
580	0.19	-	-
600	0.18	-	-
620	0.16	-	-
Curve	(1)	(2)	(3)

Fig.1(a)

FIG. 1 (b)



CURVES UP TO WAVE LENGTH 460 mμ, AND FROM WAVE LENGTH 480 TO 620 mμ ARE PLOTTED ON I AND II SCALE OF O.D VALUES, RESPECTIVELY.

TABLE No.2

Vosburgh Cooper's Method:

Concentration of hexacyanoferrate (III) = 1.0×10^{-2}M
Concentration of nitrosobenzene = 1.0×10^{-2}M
Concentation of mercuric chloride = 1.0×10^{-4}M

Wave length mμ	Optical density values								
	3:1	2:1	3:2	4:3	1:1	3:4	2:3	1:2	1:3
380	0.98	0.91	0.81	0.78	0.78	0.78	0.77	0.76	0.67
400	1.75	1.26	1.13	1.03	0.96	0.83	0.785	0.685	0.525
420	2.00	1.90	1.65	1.60	1.35	1.16	1.10	0.92	0.67
440	2.00	2.00	1.90	1.75	1.50	1.28	1.20	1.02	0.75
450	2.00	1.90	-	1.65	-	-	-	-	-
460	1.45	1.35	1.22	1.13	1.00	0.88	0.84	0.72	0.55
480	0.42	0.40	0.42	0.415	0.34	0.335	0.33	0.32	0.28
500	0.18	0.20	0.25	0.253	0.22	0.228	0.238	0.24	0.245
510	0.18	0.198	0.26	0.262	0.76	0.238	-	-	-
520	0.85	0.208	0.27	0.27	0.28	0.25	0.260	0.27	0.278
540	0.195	0.225	0.298	0.298	0.30	0.27	0.285	0.292	0.302
550	0.202	-	-	-	-	-	-	-	-
560	0.212	0.235	0.31	0.31	0.31	0.265	0.30	0.305	0.315
580	0.20	0.23	0.305	0.305	0.305	0.28	0.295	0.302	0.31
600	0.19	0.22	0.29	0.29	0.29	0.265	0.28	0.288	0.285
620	0.174	0.197	0.26	0.26	0.26	0.240	0.251	0.26	0.26
Curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)

Fig.1(b)

Job's Method (13)

For determining the complex ion formation by the interaction of nitrosobenzene and hexacyanoferrate (III) by Job's method of continued variation, the following four sets of solutions were prepared (1.0×10^{-2}M concentration of reactants for set I, II ; 0.5×10^{-2}M, 0.667×10^{-2}M concentrations of the reactants for set III and IV respectively). Set I was made up by mixing 4.5, 4.0, 3.5, 3.0, 2.5, 2.0 1.5 and 1.0 ml if hexacyanoferrate (III) with 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 ml of nitrosobenzene respectively. In each 1.0 ml of 10^{-4}M mercuric chloride was added and total volume was made to 25.0 ml by buffer pH 8.0. Set II, III and IV were also prepared exactly in the similar fashion with the only difference that the total volume was made to 20.0, 25.0 and 20.0 ml for IInd, IIIrd and IVth set respectively. Reaction mixture in each set were kept for 48 hours in dark and optical density values were measured at 560 mμ(the wavelength at which the maximum absorption for the complex took place). The curves were plotted between optical densities in different sets against the fraction nitrosobenzene/nitrosobenzene + hexacyanoferrate (III). The optical density values of reactants at the wavelength 560 mμwere almost neglible. Results are tabulated below:

TABLE No.3

Job's method of continued variation wavelength 560 mμ

Mixture	Optical density values			
	Set I	Set II	Set III	Set IV
1	0.075	0.12	0.04	0.155
2	0.083	0.20	0.65	0.190
3	0.125	0.24	0.85	0.245
4	0.155	0.275	0.95	0.290
5	0.180	0.385	0.13	0.345
6	0.173	0.370	0.12	0.340
7	0.165	0.36	0.11	0.335
8	0.160	0.345	0.10	0.330
9	0.148	0.30	0.095	0.300
Curve	(1)	(2)	(3)	(4)

Fig.2(a)

Molar ratio Method:

To determine the composition of the complex three sets of mixtures were prepared. In first set of mixtures 3.0 ml of 0.25×10^{-2}M hexacyanoferrate (III) was mixed with 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 ml of 0.25×10^{-2}M nitrosobenzene and to each mixture was added 1.0 ml of 1.0×10^{-4}M mercuric chloride. Total volume was made to 20.0 ml by buffer of pH 8.0. Other two sets of mixtures were also prepared in the similar fashion with 1.0×10^{-2}M and 0.5×10^{-2}M concent ratios of the reactants respectively.

Optical density measurements were carried out at 560 mμ after 48 hours of mixing. Curves for each set were plotted between the volume of nitrosobenzene added Vs the optical density. Results are tabulated below:

TABLE No.4

Molar ratio Method wave length = 560

Mixture	Optical density values		
	Set I	Set II	Set III
1	0.055	0.15	-
2	0.075	0.215	0.030
3	0.105	0.288	0.075
4	0.120	0.340	0.155
5	0.140	0.400	0.230
6	0.155	0.455	0.260
7	0.17	0.50	0.30
8	0.175	0.53	0.335
9	0.182	0.555	0.375
Curve	(1)	(2)	(3)

Fig.3

Formation constant of the complex:

The Job's method has been usefully employed for determining the formation constant of the complexes He and other authors (14-15) making the use of the relationship between the concentration and extinction coefficient colculated mathematically these constants for a number of complexes. Several modifications have been given by Harvey and Manning (16) based on spectrophotometric technique, but the method of Moore and Anderson is of wide applications. Recently Gupta and Sogani (18) used the method of Harvey and Manning for the calculation of dissociation constant of ferric triazine complexes.

Dey and Mukherji (19) have studied the composition and stability of lead alizarine sulphonate complex and derived the equation for the formation constant K for the general system

$$mA+nB = Am\ Bn$$

$$K = \frac{x}{(a-mx)(b-nx)} \qquad (1)$$

where x is the concentration of the complex and a,b are the initial concentrations of the reactants. Taking two concentrations a_1 and a_2; b_1 and b_2 of the reactants giving the same O.D. i.e. the same value of x, we can have from equation (1).

$$K = \frac{x}{(a_1-x)(b_1-x)} = \frac{x}{(a_2-x)(b_2-x)} \qquad (2)$$

when m=n=1 i.e. for 1:1 complex

$$x = \frac{a_1b_1 - a_2\,b_2}{(a_1+b_1) - (a_2+b_2)} \qquad (3)$$

Knowing the value of x from equation (3) K can be calculated from equation (2).

For determining the value of formation constant, two sets of the mixtures comprising of unequal concentrations of the reactants (0.1×10^{-2}M hexacyanoferrate (III) 0.05×10^{-2}M nitrosobenzene for first set and 0.1M hexacyanoferrate (III) and 0.667 M nitrosobenzene for second set) were prepared on the scheme of Job's method. Total volume in each set was made to 25.0 ml by buffer of pH 8.0. The ionic strength maintained at 0.4 by adding potassium chloride

$a_1 = 4.0 \times 10^{-4}$M, $a_2 = 7.33 \times 10^{-4}$M and
$b_1 = 11.8 \times 10^{-4}$M $b_2 = 9.0 \times 10^{-4}$M

For similar values of optical densities, Fig.2(b the value of x from egn (3) came out as 42.45×10^{-4}M and K was calculated as 3.611×10^{2}.

TABLE No.5

Job's method of continued variation to determine stability constant: Wavelength = 550 mμ

Mixture	Optical density values	
	Set I	Set II
1	0.095	0.10
2	0.096	0.125
3	0.095	0.15
4	0.125	0.165
5	0.16	0.20
6	0.18	0.245
7	0.22	0.265
8	0.20	0.240
9	0.16	0.225
Curve	(1)	(2)

Fig.2(b)

Kinetics of the Reaction:

Kinetics of the reaction were studied under the following sub-headings. The measurements of pH and O.D. values (at 575 mμ) were carried out at 25 ± 0.1°C by placing the different solutions in thermostatic both.

Variation in pH:

For studying the effect of fixed concentration of Hg^{++} ions in the variation in pH with time of nitrosobenzene, hexacyanoferrate (III) and their mixture the following three solutions were prepared.

No.1, contained 18.0 ml 10^{-2}M nitrosobenzene, 18.0 ml of water; No.2, comprised of 18.0 ml 10^{-2}M hexacyanoferrate (III) 18.0 ml of 50 per cent alcohol No.3, comprised 18.0 ml of 10^{-2}M hexacyanoferrate (III) and 18.0 ml of 10^{-2}M nitrosobenzene. Each of the solutions contained 4.0 ml of 10^{-4}M mercuric chloride. Results are tabulated below:

TABLE No.6

Variation in pH with time for nitrosobenzene, hexacyanoferrate (III) and their mixture in presence of constant amount Hg^{++}

Time in minutes	pH		
	Solution No.1	Solution No.2	Solution No.3
0.0	5.65	6.0	5.8
60.0	5.65	5.65	5.45
120.0	5.62	5.35	5.30
4.0 Hours	5.61	5.40	5.28
6.0 "	5.60	5.45	5.29
24.0 "	5.58	5.48	5.30
48.0 "	5.55	5.60	5.33
72.0 "	5.50	5.65	5.35
Curve	(3)	(1)	(2)

Fig.4

The effect of varing concentration of mercuric ions in the variation of pH of the reactants was studied by preparing two sets each of four solutions.

Set I:

3.0, 5.0, 7.0 and 9.0 ml of 10^{-4}M mercuric chloride was added to 2.0 ml of 10^{-2}M potassium hexacyanoferrate (III) the total volume was made to 20.0 ml.

Set II:

3.0, 5.0, 7.0, and 9.0 ml of 10^{-4}M mercuric chloride was added to 2.0 ml of 10^{-2}M nitrosobenzene the total volume was made to 20.0 ml (Table No.8). Results are tabulated below:

TABLE No.7

Set I: Effect of mercuric chloride concentration in the variation of pH with time of the solution of hexacyanoferrate (III).

Time in minutes	pH			
	Solution No.1	Solution No.2	Solution No.3	Solution No.4
0.0	4.8	4.8	4.7	4.65
20.0	4.45	4.3	4.2	4.15
60.0	4.05	3.9	3.85	3.75
120.0	3.95	3.85	3.65	3.60
180.0	3.95	3.85	3.68	3.50
18.0 hours	4.10	4.2	4.43	4.30
Curve	(1)	(2)	(3)	(4)

Fig.5(a)

TABLE No.8

Set II

Effect of mercuric ion concentration in the variation of pH with time of nitrosobenzene:

Time in minutes	pH			
	Solution No.1	Solution No.2	Solution No.3	Solution No.4
0.0	4.4	4.35	4.3	4.3
20.0	4.4	4.35	4.3	4.3
60.0	4.4	4.38	4.32	4.30
120.0	4.4	4.4	4.35	4.4
180.0	4.4	4.4	4.4	4.4
18 hours	4.35	4.4	4.5	4.5
Curve	(1)	(2)	(3)	(4)

Fig.5(b) Scale II

The effect of mercuric ions concentration in the variation of pH for the mixtures of hexacyanoferrate (III) and nitrosobenzene was studied by preparing a set of 5 solutions. Solution No.1 to 6 each contained 2.0 ml of 10^{-2}M nitrosobenzene. The increasing amounts 0.0, 1.0, 3.0, 5.0, 7.0, 9.0 ml of mercuric chloride was added in solution 1 to 6 respectively. Total volume was made to 20.0 ml by adding requisit amount of water. Results are tabulated below:

TABLE No.9

Effect of mercuric chloride concentration in the variation of pH with time of the nitrosobenzene and hexacyanoferrate (III) mixtures of equal concentrations:

Time in minutes	pH No.1	No.2	No.3	No.4	No.5	No.6
0.0	4.65	4.65	4.6	4.6	4.6	4.57
60.0	4.40	4.35	4.2	4.1	4.05	4.00
120.0	4.37	4.35	4.2	4.15	4.05	4.05
180.0	-	-	-	-	-	-
240.0	4.5	4.4	4.3	4.15	4.1	4.10
390.0	4.60	4.5	4.4	4.32	4.2	4.15
24 hours	4.70	4.8	4.7	4.6	4.5	4.5
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig.7(b)

The effect of reactants concentration (in presence of fixed amount of mercuric chloride) in the variation of pH with time was studied by preparing the follow to sets of solutions.

Set I.

0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 ml of 10^{-2}M nitrosobenzene was added to 2.0 ml of 10^{-2}M hexacyanoferrate (III) and 2.0 ml of 10^{-4}M mercuric chloride total volume was made to 30.0 ml by requisite amount of water.

Set II

This was prepared by mixing the solutions in reverse order of Set I. Results are tabulated below:

TABLE No.10

Effect of the increasing concentration of nitrosobenzene in the variation of pH with time for the mixtures containing fixed quantities of hexacyanoferrate (III) and mercuric chloride:

Time in minutes	pH							
	Solutions							
	1	2	3	4	5	6	7	8
0.0	6.20	6.25	6.25	6.30	6.40	6.40	6.40	6.40
60.0	6.10	6.15	6.20	6.20	6.20	6.30	6.33	6.36
120.0	6.07	6.13	6.20	6.20	6.22	6.30	6.25	6.30
300.0	6.00	6.10	6.20	6.25	6.27	6.40	6.45	6.45
420.0	6.10	6.20	6.30	6.35	6.38	4.45	6.50	6.50
24 hours	6.30	6.35	6.40	6.45	6.50	6.55	6.55	6.55

Curve (1) (2) (3) (4)

Fig.6(a)

TABLE No.11

Effect of the increasing concentration of hexacyanoferrate (III) in the variation of pH with time for the mixtures containing fixed quanitities of mercuric chloride and nitrosobenzene:

Time in minutes	pH							
	Solution Nos.							
	1	2	3	4	5	6	7	8
0.0	6.00	6.10	6.15	6.15	6.20	6.20	6.30	6.32
30.0	5.85	5.90	6.10	6.10	-	-	-	-
60.0	5.80	5.90	6.00	6.05	6.15	6.15	6.20	6.20
120.0	5.60	5.70	5.80	5.90	6.00	6.10	6.10	6.10
420.0	5.80	5.90	6.00	6.00	6.25	6.30	6.42	6.50
24 hours	6.00	6.12	6.21	6.25	6.34	6.35	6.40	6.60
48 hours	6.20	6.20	6.25	6.32	6.50	6.60	6.65	6.70
Curve	(1)	(2)	(3)	(4)				

Fig.6(b)

Variation in O.D.:

No variations in optical density values of hexacyanoferrate (II) and nitrosobenzene mixtures took place in absence of Hg^{++}ions. To study the effect of mercuric ion concentration in the variation of O.D with time for the mixture of hexacyanoferrate (III) and nitrosobenzene, following 6 solutions were prepared:

Solution No.1 to 6 each contained 2.0 ml 10^{-2}M hexacyanoferrate (III), 2.0 ml 10^{-2}M nitrosobenzene, increasing amount 0.0, 1.0, 3.0, 5.0, 7.0, 9.0 ml of mercuric chloride was added in solutions 1 to 6 respectively.

Total volume was made to 20.0 ml by adding requisite amount of water. Results are tabulated below:

TABLE No.12

Effect of mercuric chloride concentration in the variation of O.D. of hexacyanoferrate (III), and nitrosobenzene mixtures with time (unBuffered solutions):

Time in minutes	Optical density values					
	Mixture No.1	Mixture No.2	Mixture No.3	Mixture No.4	Mixture No.5	Mixture No.6
0.0	0.02	0.04	0.046	0.046	0.046	0.046
60.0	0.035	0.08	0.10	0.124	0.148	0.164
120.0	0.06	0.114	0.145	0.164	0.18	0.195
240.0	0.105	0.164	0.185	0.198	0.21	0.224
360.0	0.145	0.18	0.198	0.20	0.22	0.232
24 hours	0.16	0.20	0.23	0.23	0.24	0.25
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig.7(c)

Effect of pH:

The effect of pH on the reaction velocity was studied by measuring the optical density values at different intervals at 560 mμ(wave length for the maximum absorption of the complex). Here too seven solution each containing 2.0 ml of 10^{-2}M hexacyanoferrate (III), 2.0 ml of 10^{-2}M nitrosobenzene, were prepared. Solution 1 to 5 contained 1.0 ml of 10^{-4}M mercuric chloride and 15.0 ml of buffer of pH 4.9 to

9.0. Sixth solution contained 15.0 ml of water instead of buffer and seventh 16.0 ml of water with out mercuric chloride for comparison. Results are tabulated below:

TABLE No.13

Effect of pH in the variation of O.D. with time of the mixture containing fixed quantity of reactants and Hg^{++} ions. (Temp.25°C).

Time in minutes	Optical density values						
	pH						
	4.9	5.9	6.8	8.0	9.2	Without buffer pH 8.5	Without buffer & Hg^{++} pH 7.0
0.0	0.01	0.02	0.02	0.02	0.010	0.010	0.00
30.0	0.037	0.053	0.085	0.024	0.02	0.030	0.00
60.0	0.047	0.11	0.135	0.075	0.46	0.068	0.01
150.0	0.07	0.175	0.185	0.018	0.05	0.180	0.015
360.0	0.083	0.20	0.21	0.023	0.168	0.230	0.045
24 hours	0.0155	0.28	0.285	0.029	0.285	0.30	0.065
48 hours	0.20	0.305	0.318	0.33	0.290	0.288	0.070
70 hours	0.24	0.32	0.34	0.34	0.265	0.287	0.067
94 hours	0.24	0.325	0.34	0.34	0.236	0.280	0.065
116 "	0.23	0.32	0.31	0.32	0.216	0.255	0.06
138 "	0.22	0.30	0.31	0.31	0.205	0.25	0.06

Curve

Fig.7(a)

TABLE No.14

Optical density values at 130th minutes for the mixtures of the reactants of equal concentrations at different pH:

Wavelength 560 mμ Temp. 25°C

pH	5.0	6.0	7.0	8.0	8.5	9.2
O.D. 120 Minute	0.132	0.142	0.173	0.26	0.17	0.236

Fig.8

To study the effect of Hg^{++} ions on the reaction velocity at pH values 5.0, 6.0, 7.0 and 8.0 the O.D. values for the 4 sets of solutions were measured at 25°C, at 560 mμ at different intervals.

All the four solutions in each set contained 2.0 ml 10^{-2}M nitrosobenzene 2.0 ml 10^{-2}M hexacyanoferrate (III). In each set, increasing amounts 0.1, 1.0, 3.0, 5.0 ml of 10^{-4}M mercuric chloride was added in solutions 1, 2, 3, and 4 respectively. Total volume in each set was made to 20.0 ml by required amounts of buffers of pH values 5.0, 6.0, 7.0 and 8.0 for sets I, II, III and IV respectively. Results are tabulated below:

table No.15

Effect of mercuric chloride concentration in the variation of optical density with time for the mixtures of reactants of equal concentrations at pH 5.0 and 6.0:

Time in minutes	Optical density values Solution Nos.							
	1	2	3	4	5	6	7	8
0.0	0.03	0.034	0.04	0.04	0.035	0.035	0.35	0.35
30.0	0.06	0.095	0.15	0.195	0.055	0.12	0.162	0.20
60.0	0.074	0.115	0.185	0.238	0.078	0.132	0.182	0.255
120.0	0.084	0.132	0.14	0.26	0.085	0.142	0.21	0.27
15 hours	0.10	0.21	0.263	0.34	0.012	0.22	0.31	0.37
24 hours	0.123	0.21	0.263	0.34	0.09	0.21	0.36	0.37
48 hours	0.165	0.22	0.263	0.34	0.09	-	0.375	0.38
Curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)

Fig.9(a)

TABLE No.16

Effect of mercuric chloride at pH 7.0 and 8.0

Time in minutes	pH 7.0				pH 8.0			
	Optical density values							
	Mixture Nos.							
	1	2	3	4	5	6	7	8
0.0	0.04	0.45	0.05	0.06	0.043	0.047	0.05	0.05
30.0	0.06	0.13	0.202	0.245	0.05	0.125	0.17	0.73
60.0	0.06	0.15	0.23	0.27	0.06	0.165	0.23	0.255
120.0	0.065	0.137	0.25	0.30	0.06	0.205	0.26	0.30
hours								
5.0	0.65	0.205	0.30	0.338	0.07	0.275	0.324	0.37
7.0	0.07	0.23	0.34	0.365	0.075	0.31	0.355	0.425
24.0	0.08	0.30	0.51	0.485	0.08	0.37	0.39	0.56
30.0	0.09	0.30	0.51	0.52	0.095	0.39	0.40	0.59
Curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)

Fig.9(b)

Effect of concentration of reactants on the reaction velocity:

The effect of reactants concentration on the reaction velocity was studied measuring optical density values of two sets of mixtures at 25°C at pH 8.0 (the optimum pH of the reaction).

Set I.

0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 ml 10^{-2}M nitrosobenzene was added to 2.0 ml of 10^{-2}M hexacyanoferrate (III) and 2.0 ml of 10^{-4}M mercuric chloride total volume was made to 30.0 ml by requisite amount of buffer of pH 8.0.

Set II.

This was prepared in reverse order of Set I nitrosobenzene was kept constant. Results are tabulated below:

TABLE No.17

Effect of nitrosobenzene concentration in the variation of the O.D. with time for the mixtures containing fixed amount of hexacyanoferrate (II) and mercuric chloride at pH 8.0

Time in minutes	Optical density values								
	Mixture Nos.								
	1	2	3	4	5	6	7	8	9
0.0	0.01	0.013	0.035	0.042	0.05	0.050	0.050	0.050	0.050
60.0	0.012	0.025	0.05	0.06	0.07	0.075	0.80	0.084	0.094
140.0	0.013	0.032	0.058	0.074	0.09	0.104	0.118	0.13	0.14
Hours									
10.0	0.013	0.048	0.014	0.126	0.148	0.20	0.246	0.29	0.32
19.0	0.014	0.085	0.014	0.18	0.25	0.29	0.338	0.41	0.42
44.0	0.014	0.115	0.205	0.235	0.35	0.39	0.435	0.52	0.52
68.0	0.014	0.145	0.235	0.26	0.39	0.435	0.485	0.58	0.58
92.0	0.014	0.135	0.230	0.248	0.40	0.44	0.495	0.61	0.61
Curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)

Fig.10(a)

TABLE No.18

Effect of hexacyanoferrate (III) concentration in the variation of the optical density with time for the mixtures containing fixed amount of nitrosobenzene and mercuric chloride at pH 8.0

Time in minutes	Optical density Values								
	Mixture Nos.								
	1	2	3	4	5	6	7	8	9
0.0	0.014	0.016	0.016	0.016	0.016	0.016	0.017	0.018	0.019
60.0	0.14	0.033	0.038	0.040	0.041	0.044	0.048	0.050	0.056
120.0	0.014	0.042	0.048	0.052	0.054	0.055	0.060	0.072	0.075
180.0	0.014	0.048	0.056	0.063	0.064	0.076	0.080	0.088	0.084
hours									
10.0	0.14	0.070	0.088	0.11	0.128	0.14	0.015	0.016	0.172
18.0	0.03	0.13	0.138	0.145	0.15	0.155	0.17	-	0.198
42.0	0.03	0.155	0.15	0.157	0.172	0.183	0.195	-	0.24
Curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)

Fig.10(b)

Effect of Electrolytes:

To study the effect of electrolytes on the reaction velocity, measurements of optical densities were followed at different intervals at pH 8.0 for the following four solutions:

Each solution contained 2.0 ml of 10^{-2}M hexacyanoferrate (III), 2.0 ml of 10^{-2}M nitrosobenzene, 2.0 ml of 10^{-4}M mercuric chloride and 0.0, 0.5, 1.0 ml of potassium chloride (2.0M), potassium nitrate (1.0M) potassium cyanide (1.0M) in solution No.2,3 and 4 respectively. Total volume in each case was made to 25.0 ml by buffer of pH 8.0. Results are tabulated below:

TABLE No.19

Effect of electrolytes, in the variation of optical density with time for the mixtures of the equal concentration of the reactants and constant concentration of mercuric chloride at pH 8.0

Time in minutes	Optical density values			
	Without electrolyte Mixture (1)	KCl Mixture No.2	KNO_3 Mixture No.3	KCN Mixture No.4
0.0	0.030	0.027	0.028	0.030
60.0	0.047	0.036	0.045	0.030
120.0	0.580	0.045	0.050	0.030
hours				
5.0	0.085	0.073	0.078	0.030
7.0	0.10	0.092	0.97	0.030
24.0	0.17	0.165	0.166	0.030
96.0	0.151	0.016	0.155	0.035
Curve	(1)	(2)	(3)	(4)

Fig.11

Effect of Temperature:

Temperature effect was studied by measuring O.D. values at temperatures 20°C, 25°C, 30°C and 35°C at different intervals for the solution comprising of 4.0 ml 0.05×10^{-2}M hexacyanoferrate (III) 4.0 ml of 0.05×10^{-2}M nitrosobenzene, 2.0 ml of 1.0×10^{-4}M mercuric chloride and 30.0 ml of buffer of pH 8.0. Results are tabulated below:

TABLE No.20

Effect of temperature in the variation of optical density with time for the mixtures of equal concentration of the reactants containing same amount of mercuric chloride at pH 8.0

Time in minutes	Optical density values			
	20°C	25°C	30°C	35°C
0.0	0.015	0.015	0.020	0.020
60.0	0.028	0.032	0.038	0.040
120.0	0.037	0.044	0.050	0.056
180.0	0.044	0.051	0.059	0.070
240.0	0.048	0.058	0.066	0.076
300.0	0.054	0.060	0.070	0.080
360.0	0.058	0.065	0.074	0.086
420.0	0.060	0.070	0.079	0.090
Curve	(1)	(2)	(3)	(4)

Fig.12

TABLE No.21

Optical density at 120th minute:

Temp.°C	20	25	30	35
$O.D._{120}$	0.037	0.042	0.050	0.060
$1/T\times10^{-3}$	3.41	3.35	3.33	3.25
$\log O.D._{120}$	-1.4318	-1.3565	-1.3010	-1.2518

Fig.13

Results and Discussion:

Absorption of hexacyanoferrate (III) Nitrosobenzene and complex:

Maximum absorption for 1.0×10^{-3}M hexacyanoferrate (III) took place at 440 mμ. No maximum was realized in the case of nitrosobenzene (1.0×10^{-3}M). The optical density was found to diminish continuously from 360 mμ onwards Fig.1(a) curve 1,2 and 3). Maximum absorption for the flesh coloured complex (obtained by mixing 1.0×10^{-2}M of reactants in the ratios of hexacyanoferrate (III) to nitrosobenzene as 3:1, 2:1, 3:2, 4:3, 1:1, 3:4, 2:3, 1:2 and 1:3 (at pH 8.0) took place at 560 mμ(Fig.1(b) curve 1-9). As is evident from (Fig.1(a) curve 1,2,3) the absorption of nitrosobenzene and hexacyanoferrate (III) is almost negligible at 560 mμ. Existance of one peak suggested the formation of only one complex. (Fig.1(b)).

Composition and formation constant of the complex:

The plots of O.D. Vs the ratio $C_6H_5NO/K_3FeCy_6+C_6H_5NO$ (Fig.2 a curves 1,2,3 and 4) for Job's method of continued variation indicated the formation of 1:1 complex. The results of the plots of molar ratios method (Fig.3 curves 1,2,3) also confirmed the existance of 1:1 complex. The formation constant K of the complex employing method due to Dey and Mukherjee utilizing the curves 1,2 Fig.2(b) came out as 3.611×10^2.

Variation in pH of hexacyanoferrate (III), Nitrosobenzene and their mixture in presence of Hg^{++} ions:

As is evident from Fig.4 curve 1 that the pH of hexacyanoferrate (III) in presence of mercuric ions first decreased and then increased slowly and finally become constant after 48 hours. The variation in pH of nitrosobenzene under similar conditions is almost negligible (Fig.4 curve 2). During the interaction of nitrosobenzene with hexacyanoferrate (III) in presence of mercuric ions the pH first decreased then increases slowly and finally become constant as the reaction proceeded to completion. The rate of decrease of pH was relatively higher than the rate of increase.

From Fig.5(a) it is evident that with heigher concentration of mercuric ions more pronounced decrease in pH is realised. But with lapse of time pH increases and becomes almost constant after 48 hours. No effect of mercuric chloride concentration is observed in the variation of pH of nitrosobenzene Fig.5(b).

The variation in pH with time in presence of increasing amounts of nitrosobenzene (0.025×10^{-2}M to 0.2×10^{-2}M) of hexacyanoferrate (III) (0.1×10^{-2}M); containing fixed amount of mercuric chloride (0.5×10^{-4}M) was followed first with a decrease and then slight increase as in previous cases achieved. The same course of variation in pH was observed for mixtures containing fixed amount of nitrosobenzene but varying concentration of hexacyanoferrate (III) (0.025×10^{-2}M to 0.2×10^{-2}M) in presence of 0.5×10^{-4}M mercuric chloride. But the effect of nitrosobenzene concentration was more pronounced as compared to the concentration of hexacyanoferrate (III). Fig.6(a),(b).

The variation in pH with time in presence of varying amounts of mercuric chloride (0.05×10^{-4}M to 0.45×10^{-4}M), of the mixtures of nitrosobenzene and hexacyanoferrate (III) (each concentration of 0.1×10^{-2}M) followed the same behaviour as in the above two cases Fig.7(b).

Effect of pH:

From the curves Fig.7(a) obtained by plotting O.D. of the mixtures at different intervals for solutions containing 0.1×10^{-2}M nitrosobenzene, 0.1×10^{-2}M hexacyanoferrate (III) and 0.05×10^{-4}M mercuric chloride at pH values 4.9, 5.9, 6.8, 8.0, and 9.2 it is evident that the velocity of the reaction is maximum at pH 8.0. The plot between pH and O.D. (measured at 120th minutes O.D. 120) give peak at pH 8.0.

The effect of mercuric chloride concentration ranging from 0.005×10^{-4} to 0.25×10^{-4}M on reaction mixtures prepared by 0.1×10^{-2}M hexacyanoferrate (III) and nitrosobenzene at pH values 5.0, 6.0, 7,0 and 8.0 is dipicted in Fig.9(a),(b). It is evident that increase in the concentration of mercuric ions increases the velocity of the reaction, but the maximum effect was observed at pH 8.0. Therefore, it may be very safely concluded that both mercuric ions and pH of the medium play important role during the progress of the reaction.

Effect of reactants concentration at pH 8.0:

From curves obtained by plotting O.D. values (measured at different intervals at 25°C) for the mixtures containing 0.08×10^{-2}M hexacyanoferrate (III) and 0.08×10^{-2}M mercuric chloride, varying concentration of nitrosobenzene (from 0.04×10^{-2}M to 0.32×10^{-2}M), (setl); it is evident that the reaction velocity is dependent upon the concentration of nitrosobenzene.

Similarly from the optical densities for mixtures containing fixed concentration of nitrosobenzene and mercuric chloride and varying concentrations of hexacyanoferrate (III), it is found that the reaction velocity is dependent upon the concentration of hexacyanoferrate (III). However the effect of nitrosobenzene is more pronounced than of hexacyanoferrate (III).

Effect of electrolytes:

The curves obtained by plotting optical density values against time in presence of different electrolytes (potassium nitrate, potassium chloride, and potassium cyanide each 0.04M in mixtures containing 0.08×10^{-2}M each of the hexacyanoferrate (III) and nitrosobenzene and 0.08×10^{-4}M mercuric chloride indicated that the reaction velocity is appreciably decreased in presence of electrolytes. The effect of potassium chloride was greater than that of potassium nitrate. In presence of potassium cyanide the reaction velocity was completely stopped. This indicated that cyanide ions were evolved during the course of reaction (Fig.11).

Influence of Temperature:

The influence of temperature was studied with mixtures containing 0.1×10^{-2}M hexacyanoferrate (III), 0.1×10^{-2}M nitrosobenzene 0.05×10^{-4}M mercuric chloride. The reaction velocity was found to be temperature dependent. The complex obtained at 20°C slowly decomposed at 40°C. The plot of log of optical density measured at 120th minute ($\log_{10}O.D._{120}$) against 1/T resulted in a straight line, whose slope corresponded to an energy of activation = 5.45k.Cal/molecule.

On the basis of above mentioned facts, the reaction may be assumed to take the following course.

(1) $Hg^{++} + FeCy_6^{---} + H_2O \rightleftharpoons$

$FeCy_5(OH)^{---} + \underline{Hg\ (CN)}^{+} + \underline{H}^{+}$

(2) $FeCy_5\ (OH)^{---} + C_6H_5NO \rightleftharpoons$

$FeCy_5(C_6H_5NO)^{--} + OH^{-}$

Following the catalytic decomposition of hexacyanoferrate (III)

(3) $Hg(CN)^{+} + FeCy_6^{---} + H_2O \rightleftharpoons$

$Hg(CN)_2 + FeCy_5(OH)^{---} + H^{+}$

(4) $OH^{-} + H^{+} \rightleftharpoons H_2O$

(5) $Hg(CN)_2 + 2H_2O \rightleftharpoons Hg^{++} + 2HCN + 2OH^{-}$

Of these reaction (I) was a slow reaction and followed with a increase in pH and was dependent upon both the concentration of Hg^{++} and hexacyanoferrate (III). (2) is fast reaction representing the formation of the complex $(Fe^{III}Cy_5\ C_6H_5NO)$. Reaction (3) represents the catalytic decompositions of $FeCy_6^{---}$ by the cation $Hg(CN)^{+}$ and should be dependent upon the concentration of $FeCy_6^{---}$. Since the variation in O.D. was less marked with varying amount of hexacyanoferrate (III). This reaction should be slow than reaction (1); reaction (4) represents the removal of H^{+} ions and reaction (5) takes place due to the hydrolysis of potassium cyanide.

It appears quite probable that H^{+} ions which liberated as shown in equation (1) were immediately removed by the presence of OH^{-} ions in the moderately alkaline solutions and therefore, the reaction velocity was maximum at pH 8.0. In alkaline solutions above pH 9.5. The reaction velocity, completely stopped because the liberation of H^+ ions was completely prevented in excess of OH^- ions. Moreover in unbuffered solutions in the intermediate stages of the reaction probably a competion between H and OH^- to entre in the reaction took place and pH increased only due to the hydrolysis of cyanide ions liberated during the course of reaction.

CHAPTER III

Interaction of 8-hydroxyquinoline 5-sulphonic acid with hexacyanoferrate (II).

(Part I)

Spectrophotometric studies on the composition of the complex formed, and kinetics of the reaction between 8-hydroxyquinoline 5-sulphonic acid and hexacyanoferrate (II).

The hydrolytic decomposition of hexacyanoferrate (II) and the subsequent replacement of one of the cyanide groups by ammonia, nitro or nitrosogroups under the influence of heat, light and dilute acids or in presence of small amounts of Cr^{+++}, Hg^{++} and Be^{++} has been reported by a number of workers (1-10). Thus nitrosobenzene can be introduced to aquapentacyanoferrate (II) by replacing the water molecule to give a violet coloured complex.

We have observed similar type of exchange reaction between the hydrolytic decomposition product of hexacyanoferrate (II) obtained in presence of Hg^{++}ions and 8-hydroxyquinoline 5-sulphonic acid (potassium salt). This complex olive green in colour was studied spectrophotometrically and pH metrically.

Priliminary experiments provided the following information:

(1) At room temperature (25°C) no reaction between 8-hydroxyquinoline 5-sulphonic acid and hexacyanoferrate (II) appeared to be possible when the reactants were mixed as such. But when mixed at the pH maintained between 3.5 to 4.5. Slow variations in optical densities were observed and it took several days for the appearance of olive green colour.

(2) In presence of small amounts of Hg^{++}, Cr^{+++} and Be^{++} the reaction was found to be catalysed at room temperature. After a lapse of few hours an olive green complex was obtained.

(3) The above reaction was found to be dependent on temperature, attained equilibrium (30 minutes) when heated on a water bath.

(4) The Reaction was found to be pH dependent, the catalytic activity of Cr^{+++}, Be^{++} and Hg^{++} completely stopped in alkaline range.

(5) No change in colour in the mixture of hexacyanoferrate (II) and 8-hydroxyquinoline 5-sulphonic acid with and without catalysing ion in presence of small amount of potassium cyanide took place.

On the basis of the above information provided by the above studies the following aspects of the reaction were investigated:

(i) Spectrophotometric studies in order to determine the composition and stability.

(ii) Spectrophotometric and pH-meric studies on the kinetics of their interaction in presence of Cr^{+++}, Be^{++} and Hg^{++} ions.

EXPERIMENTAL

APPARATUS:

Baush and Lomb Spectronic 20' was used to determine the composition and stability of the complex. Unichem SP-500 spectrophotometer was used to study the kinetics of the reaction (Slit width 0.01 mm, silica cell of 1.0 cm thickness was used.

pH of the solutions were measured by Beckmann pH meter Model H_2.

Solutions:

8-hydroxyquinoline 5-sulphonic acid:

Requisit quantity of recrystalized 8-hydroxyquinoline 5-sulphonic acid A.R. was dissolved as potassium salt in double distilled water.

Hexacyanoferrate (II)

Hexacyanoferrate (II) A.R. quality was dissolved in double distilled water and its strength determined by the usual method. pH of 0.01M hexacyanoferrate (II) solution varied from 6.5 to 7.5 during the course of one week. The solution was kept well corked in amber coloured vessels.

VosBurgh and Cooper's Method:

Before starting the actual experimentation on the interaction of 8-hydroxyquinoline 5-sulphonic acid with hexacyanoferrate (II) by spectrophotometric methods absorption experiments were performed with the reactants and the complex at different wave lengths, in order to select suitable wave length to work with, the following four sets of solutions were prepared:

Set No.I Consisted of two solutions:

No.1 Contained 1.0 ml of 10^{-2}M hexacyanoferrate (II) 1.0 ml of 10^{-4}M mercuric chloride; total volume was made to 100 ml.

Set No.II.

No.2 Contained 1.0 ml of 0.5×10^{-2}M hexacyanoferrate (II) 1.0 ml of 0.5×10^{-4}M mercuric chloride, total volume was made to 50.0 ml.

Set II Again consisted of two solution. No.I contained 1.0 ml of 10^{-3}M 8-hydroxyquinoline 5-sulphonic acid, 1.0 ml of 10^{-4}M mercuric chloride total volume was made to 10 ml. No.2~~II~~ contained similar quantities of 8-hydroxyquinoline 5-sulphonic acid and mercuric chloride as given above but total volume was made to 40.0 ml.

Optical density values of both the sets were measured in ultravoilet and visible region.

Set No.III.

Nine solutions consisted of hexacyanoferrate (II) and 8-hydroxyquinoline 5-sulphonic acid of concentration 1.0×10^{-2}M; mixed in the ratios of hexacyanoferrate (II) to 8-hydroxyquinoline 5-sulphonic acid as 3:1, 2:1, 3:2, 4:3, 1:1, 3:4, 2:3, 1:2 and 1:3 keeping the volume 12.0 ml. In each of the mixtures was added 1.0 ml of 10^{-4}M mercuric chloride and total volume was made to 30 ml. The optical densities of the solutions were measured on keeping the mixtures for 24 hours in dark, in wave length region 325 to 625 m .

Set No.IV

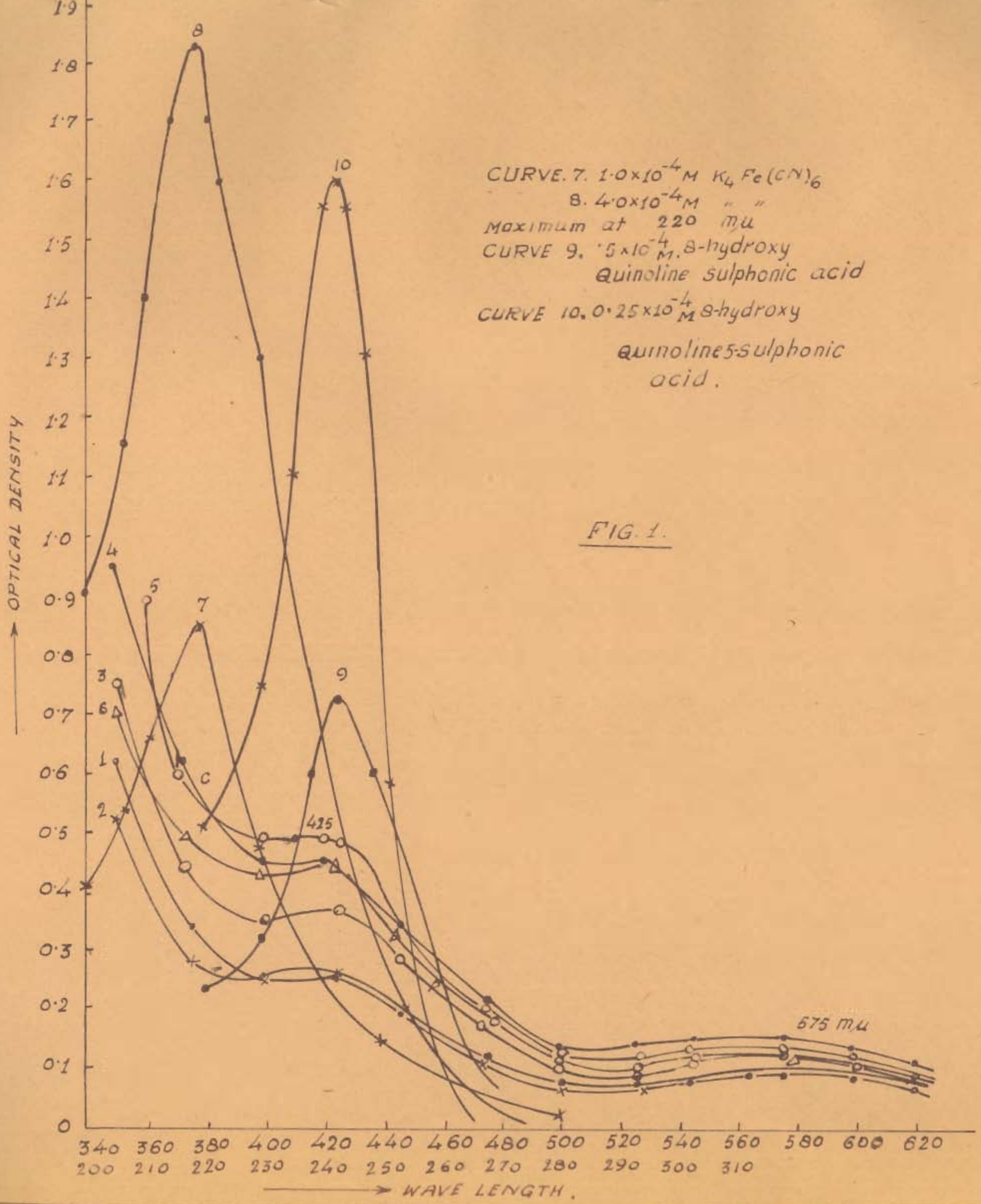
Consisted of seven solutions prepared with 0.2×10^{-2} M concentrations of the reactants in the ratio of hexacyanoferrate (II) and 8-hydroxyquinoline 5-sulphonic acid as 2:1, 3:2, 4:3, 1:1, 3:4, 2:3 and 1:2 keeping the total volume 12.0 ml. To each was added 1.0 ml of 10^{-4} M mercuric chloride and the total volume was made to 30.0 ml by adding buffer of pH 4.0 the optimum pH of the reaction.

TABLE No.1

Optical density values of hexacyanoferrate (II) and 8-hydroxyquinoline 5-sulphonic acid at different wave lengths:

Wave length mμ	Optical density			
	Hexacyanoferrate (II) Set I		8-hydroxyquinoline 5-sulphonic acid, Set II	
	Solution No.1	Solution No.2	Solution No.1	Solution No.2
200	0.41	0.88	-	-
206	0.53	1.15	-	-
210	0.65	1.40	-	-
215	0.77	1.70	-	-
218	0.85	1.90	-	-
220	0.85	1.90	0.236	0.51
222	-	1.85	-	-
225	0.74	1.65	0.240	0.55
230	0.45	1.30	0.320	0.74
240	0.25	0.70	0.680	1.55
245	-	-	0.715	1.60
250	0.15	0.36	0.700	1.54
260	0.09	0.22	0.275	0.58
270	-	-	0.075	0.19
280	0.04	0.16	-	-
300	0.01	0.38	-	-
Curve	(7)	(8)	(9)	(10)

Fig.1



CURVE. 7. $1{\cdot}0\times10^{-4}$M $K_4Fe(CN)_6$
8. $4{\cdot}0\times10^{-4}$M " "
Maximum at 220 mμ
CURVE 9. $\cdot5\times10^{-4}$M. 8-hydroxy
Quinoline sulphonic acid
CURVE 10. $0{\cdot}25\times10^{-4}$M 8-hydroxy
quinoline 5-sulphonic
acid.

FIG. 1.

Ratio of $K_3Fe(CN)_6$ and 8-Hydroxy-quinoline 5-sulphonic acid.

Curve 1. 3:1 ×
2. 2:1 •
3. 4:3 ⊙
4. 3:2 ●
5. 1:1 ○
6. 2:3 △

TABLE No.2

VasBurgh and Cooper's Method

Optical density values of the mixtures of the reactants (1.0×10^{-2}M) in different ratios at various wave length (un-buffered solutions) Set III.

Wave length mμ	Optical density								
	3:1	2:1	3:2	4:3	1:1	3:4	2:3	1:2	1:3
325	-	-	-	-	1.30	1.30	-	-	-
350	0.62	0.52	0.75	0.95	0.90	0.75	0.70	0.66	0.60
375	0.34	0.28	0.44	0.62	0.60	0.49	0.44	0.43	0.41
400	0.25	0.25	0.35	0.45	0.47	0.43	0.39	0.41	0.39
425	0.26	0.26	0.36	0.44	0.47	0.45	0.41	0.44	0.42
450	0.19	0.20	0.28	0.35	0.35	0.35	0.32	0.34	0.33
475	0.12	0.12	0.17	0.22	0.21	0.20	0.17	0.19	0.18
500	0.70	0.07	0.10	0.14	0.13	0.11	0.09	0.09	0.08
525	0.70	0.07	0.09	0.15	0.12	0.10	0.07	0.75	0.07
550	0.80	0.07	0.11	0.15	0.13	0.10	0.08	0.07	0.07
575	0.85	0.85	0.12	0.16	0.14	0.11	0.08	0.07	0.07
600	0.80	0.07	0.10	0.14	0.12	0.09	0.07	0.07	0.06
620	0.70	0.07	0.08	0.12	0.11	0.07	0.65	0.06	0.06
Curve	(1)	(2)	(3)	(4)	(5)	(6)			

Fig.1

TABLE No.3

Optical density values of the mixtures of the reactants (0.5x10^{-2}M) in different ratios at pH 4.0 at various wave lengths (Set IV).

Wave length mμ	Optical density						
	2:1	3:2	4:3	1:1	3:4	2:3	1:2
325	-	-	-	-	-	-	-
350	-	-	-	-	0.95	0.775	0.95
375	-	0.85	0.90	0.85	0.77	0.775	0.80
400	0.85	0.74	0.80	0.80	0.75	0.760	0.75
410	0.85	-	-	-	-	-	-
425	0.90	0.75	0.85	0.82	0.78	0.770	0.76
435	0.90	-	-	-	-	-	-
450	0.80	0.60	0.70	0.60	0.47	0.500	0.45
475	0.60	0.42	0.49	0.42	0.31	0.330	0.29
500	0.53	0.36	0.42	0.36	0.27	0.280	0.25
525	0.56	0.39	0.47	0.39	0.29	0.310	0.28
550	0.60	0.43	0.52	0.44	0.33	0.360	0.33
575	0.62	0.44	0.54	0.45	0.36	0.360	0.38
600	0.58	0.40	0.51	0.43	0.36	0.380	0.43
625	0.49	0.34	0.44	0.38	0.35	0.370	0.47

Job's Method:

The following sets of mixtures were prepared.

Set I

4.0, 3.5, 3.0, 2.5, 2.0, 1.5, and 1.0 ml of 1.0×10^{-2}M hexacyanoferrate (II) was mixed with 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 ml of 8-hydroxyquinoline 5-sulphonic acid. To each mixture was added 1.0 ml of 10^{-4}M mercuric chloride (and 2.0 ml of 2.0 M KCl was added to maintainionic strength constant) and 32.0 ml of buffer of pH-4 (the optimum pH of the reaction) to make the total volume to 40.0 Set II was also prepared exactly in the same way as above with the 0.666×10^{-2} concentration of the reactants at pH 4.0.

Both the sets were kept in dark for 48 hours and optical density values were measured at wave lengths 425 and 575 mμ(the wave lengths found by vosBurgh and cooper's Method). The curves were plotted between the optical density values for the various mixtures against the fraction, 8-hydroxyquinoline 5-sulphonic acid/8-hydroxy-quinoline 5-sulphonic acid + hexacyanoferrate (II) at wave length 575 mμ(the absorbtion of the reactants was negligible at 575 mμ). The difference of optical density values of the complex and reactantants against the mole fraction mentioned above were plotted at 425 m (since the optical densities for both the reactants at this wave length were appreciable).

TABLE No.4

Job's method of continued variation

Mixture No.	Optical density values			
	Set I		Set II	
	Wave length * 425 mμ	Wave length 575 mμ	Wave length * 425 mμ	Wave length 575 mμ
1	0.33	0.43	0.22	0.29
2	0.42	0.52	0.27	0.35
3	0.46	0.63	0.30	0.42
4	0.50	0.67	0.38	0.46
5	0.48	0.63	0.35	0.43
6	0.44	0.59	0.28	0.40
7	0.38	0.52	0.26	0.35
Curve	(1)	(2)	(3)	(4)

Fig.2

* At wave length 425 the differences between optical densities of reactants and complex have been noted.

Molar Ratio method-(loc cit)

The composition of the complex by molar ratio method was determined by preparing two sets of solutions:

Set I:

1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 ml of 10^{-2}M 8-hydroxyquinoline 5-sulphonic acid was added

FIG. 2

Job's Method.

Q = 8-hydroxy quinoline 5-sulphonic acid.

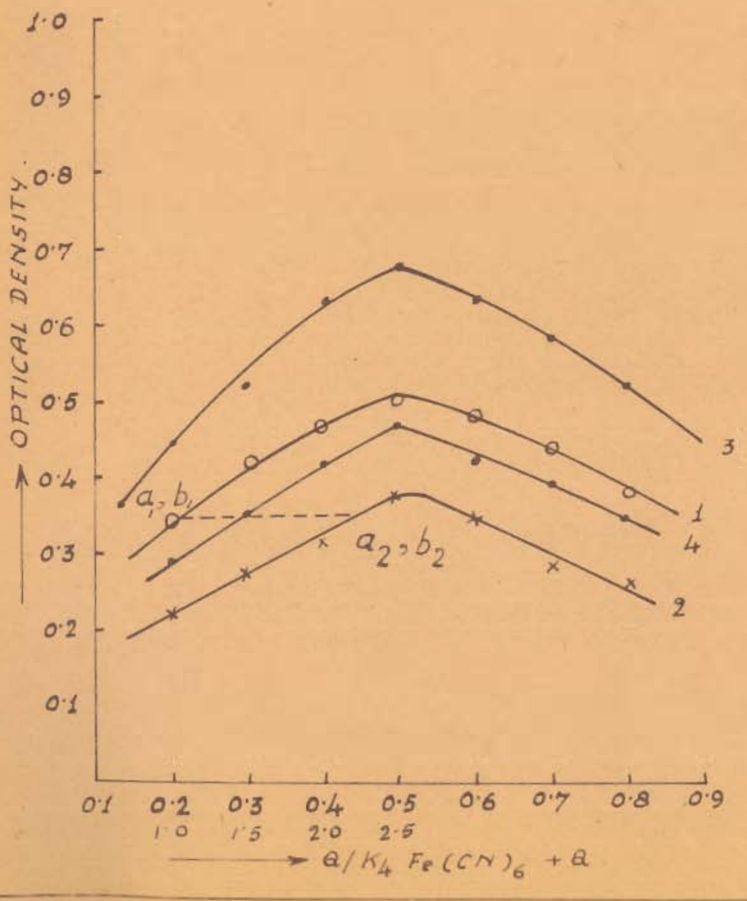
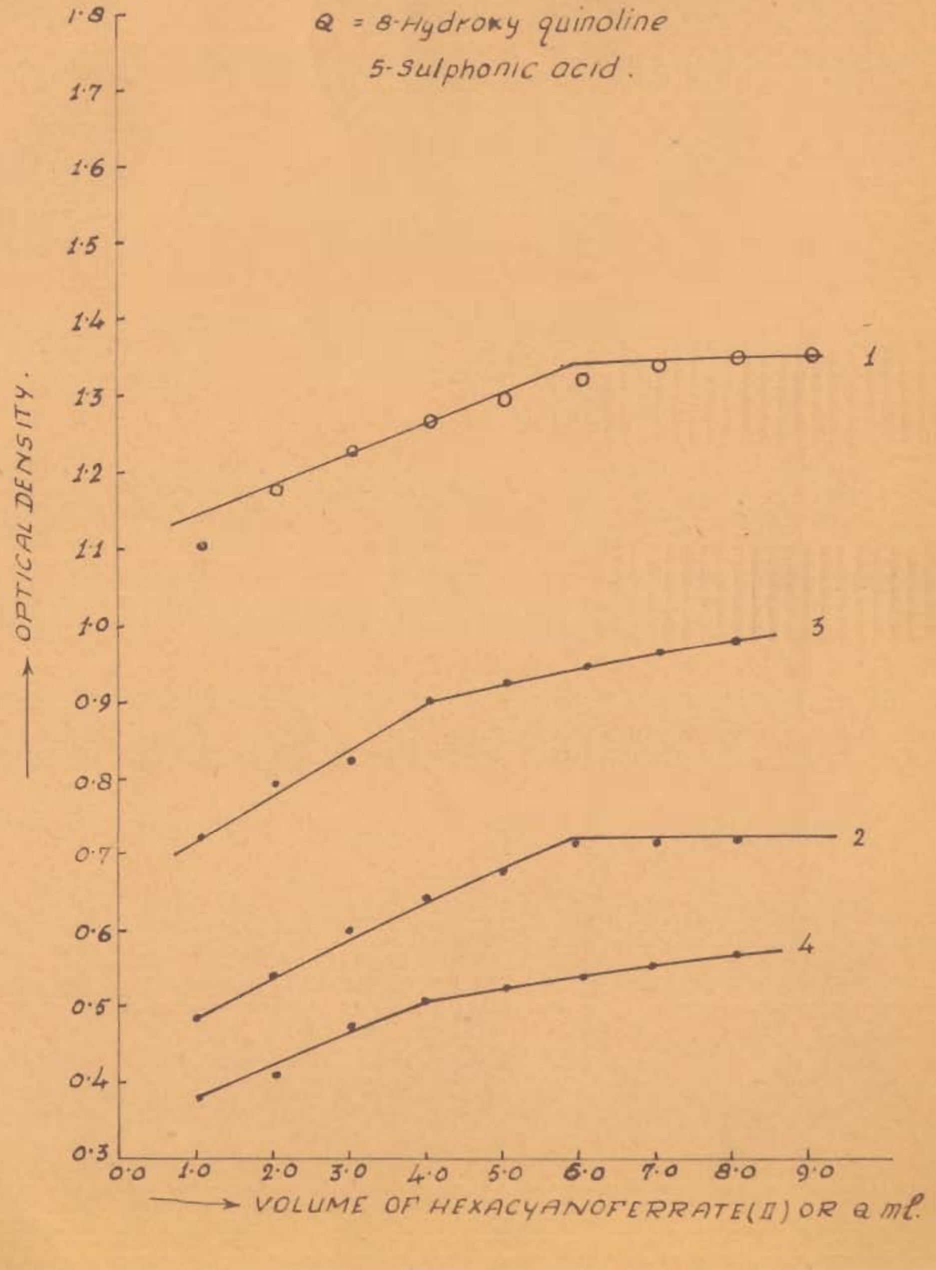


FIG. 3.

Molar Ratio Method

Q = 8-Hydroxy quinoline 5-Sulphonic acid.



to 6.0 ml of 10^{-2}M of hexacyanoferrate (II). To each was added 1.0 ml of 10^{-4}M mercuric chloride total volume was made to 30.0 ml by adding requisite amount of buffer of pH-4.0.

Set II:

1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 ml of $1.0\text{x}10^{-2}$M 8-hydroxyquinoline 5-sulphonic acid was mixed with 4.0 ml of 10^{-2}M hexacyanoferrate (II) To each was added 1.0 ml of 10^{-4}M mercuric chloride and total volume was made to 30.0 ml by adding requisite amount of buffer of pH-4.0.

Optical density values were measured at 425 m and 575 mμ. Graphs for each set were plotted between the volume of either of the reactant Vs the optical density. Results are tabulated below

TABLE No.5

Molar Ratio method

Mixture No.	Optical density values			
	Set I		Set II	
	425 mμ	575 mμ	425 mμ	575 mμ
1	1.10	0.48	0.72	0.37
2	1.18	0.54	0.79	0.41
3	1.23	0.60	0.82	0.47
4	1.27	0.64	0.90	0.50
5	1.30	0.68	0.92	0.53
6.	1.32	0.70	0.95	0.54
7	1.34	0.72	0.97	0.55
8	1.35	0.72	0.98	0.57
Curve	(1)	(2)	(3)	(4)

Fig.3

FIG. 4

SLOPE RATIO METHOD.

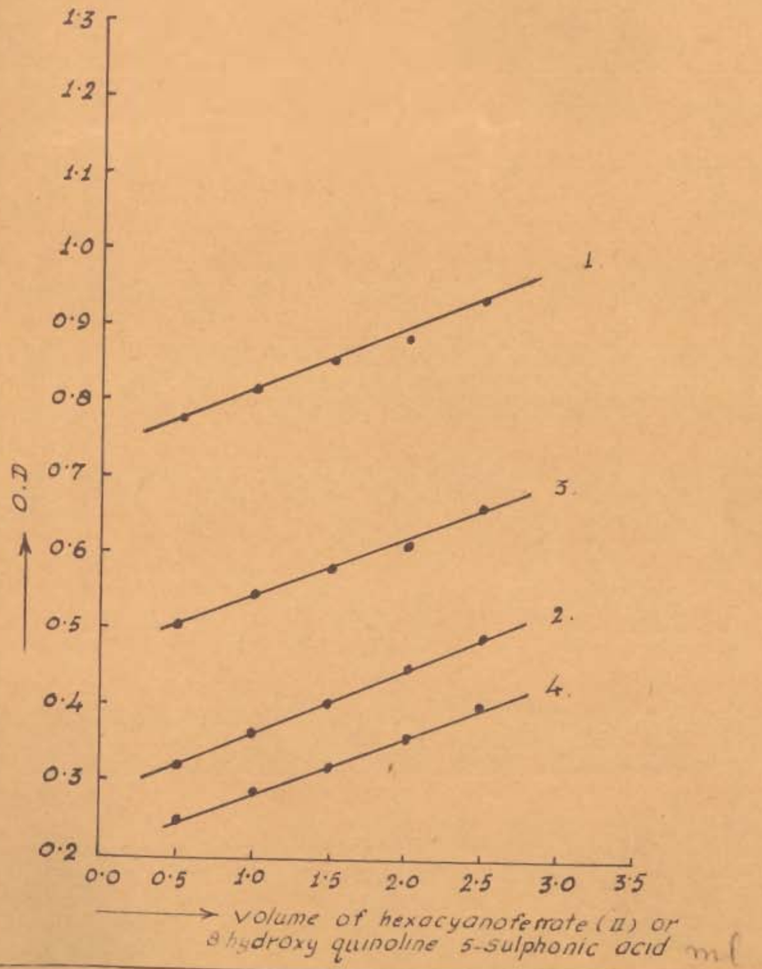
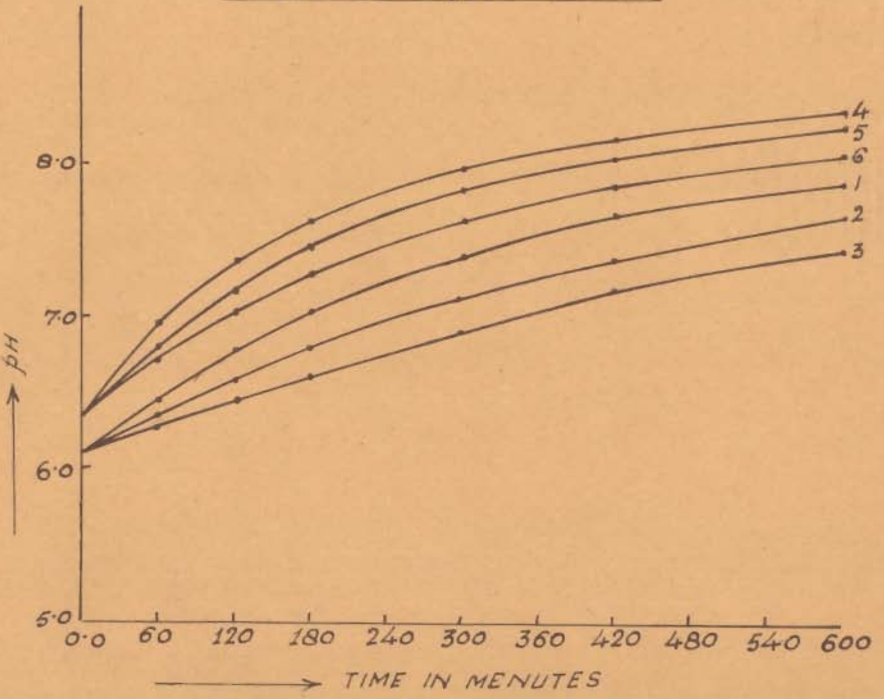


FIG. 5.

VARIATION OF pH WITH TIME.



Slope ratio method:

To determine the composition of the complex by slope ratio methods, two sets of solutions were prepared.

Set I

0.5, 1.0, 1.5, 2.0, 2.5 ml of 10^{-2}M hexacyanoferrate (III) mixed with 6.0 ml of 10^{-2}M 8-hydroxyquinoline 5-sulphonic acid. To each was added 1.0 ml of 10^{-4}M mercuric chloride and total volume was made upto 40.0 ml by buffer of pH 4.0.

Set II.

was m$\overset{a}{o}$de up of solutions mixed in reverse order.

Optical density values for both the sets were measured after 48 hours at 425 mμ and 575 mμ curves were plotted between the volume of varying reactant Vs the corresponding optical density values. Results are tabulated below:

TABLE No.6

Slope Ratio Method

Mixture No.	Optical density			
	Set I		Set II	
	425 mμ	575 mμ	425 mμ	575 mμ
1	0.78	0.32	0.50	0.24
2	0.81	0.36	0.54	0.28
3	0.85	0.40	0.57	0.32
4	0.88	0.45	0.60	0.35
5	0.93	0.49	0.65	0.40
Curve	(1)	(2)	(3)	(4)

Fig.4

Stability constant:

Stability constant of the complex was determined at pH-4.0 and constant ionic strength 0.2 $\overset{\mu}{\cancel{m}}$ by utilizing the equation

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

The details are given (in chapter II page 94-95).

Utilizing the curves (1) and (2) of Fig.2 the values of a_1, a_2; b_1 and b_2 were found to be 2.625, 3.663, 9.875 and 4.662×10^{-4}M respectively for similar optical density values. The value of x came out to be 2.118×10^{-4} and K was found to be $2.5.307 \times 10^{3}$.

Kinetics of Reaction:

Reaction between hexacyanoferrate (II) and 8-hydroxyquinoline 5-sulphonic acid was extremly slow and was found to be catalysed by small amounts of Hg^{++}, Cr^{+++} and Be^{++} at room temperature. The reaction velocity was dependent on pH and increased with increase in temperature, concentration of the reactants and the catyst.

Reaction kinetics were studied at wave length (575 mμ) at which the adsorption of the reactants was negligible. The studies were carried out in thermostatic bath maintained at 20±0.1°C. The reactants before mixing were kept for about half an hour in the both so as to attain the temperature of the both. Optical density values were measured at different intervals during the course of reaction.

To study the effect of temperature on the reaction velocity 2.0 ml of the solution from the reaction mixture at different intervals, at different temperatures was with drawn in a ice cold 8.0 ml of water and optical density values were measured at 575 mμ.

The following aspects of the kinetics of the reaction were studied.

Variation in pH:

First of all the effect of Hg^{++}, Cr^{+++} and Be^{++}ions on the variation in pH with time for hexacyanoferrate (II), 8-hydroxyquinoline 5-sulphonic acid and their mixtures was studied. The following sets were prepared.

Set I:

Solution No.1 to 3 contained 1.0 ml of 10^{-2}M hexacyanoferrate, 1.0 ml of 10^{-4}M mercuric chloride chromic chloride and berrylium nitrate in No.1,2 and 3 respectively. Total volume was made to 20.0 ml by adding requisite amount of water.

Set II.

Solution No.1 to 3 were prepared as above. 8-hydroxyquinoline 5-sulphonic acid was used in place of hexacyanoferrate (II).

Set III

Solution No.1 to 3 each contained 1.0 ml 1.0×10^{-2}M hexacyanoferrate (II), 1.0 ml 1.0×10^{-2}M

8-hydroxyquinoline 5-sulphonic acid and 1.0 ml of 10^{-4}M mercuric chloride, chromic chloride and berrylium nitrate was then added to these solutions. Total volume was made to 20.0 ml by water.

pH values of all the three sets were measured at different intervals. Results are tabulated below:

TABLE No.7

Variation in pH

Time in minutes	pH					
	Set I			Set III		
	Solution 1	Solution 2	Solution 3	Solution 1	Solution 2	Soluti 3
0.0	6.10	6.10	6.10	6.40	6.40	6.4
60.0	6.45	6.35	6.30	7.00	6.80	6.7
120.0	6.80	6.60	6.45	7.40	7.20	7.0
180.0	7.10	6.75	6.60	7.65	7.45	7.3
300.0	7.45	7.10	6.90	8.00	7.80	7.6
360.0	-	-	-	-	-	-
420.0	7.70	7.40	7.20	8.20	8.05	7.8
480.0	-	-	-	-	-	-
540.0	-	-	-	-	-	-
600.0	7.90	7.80	7.70	8.30	8.15	8.05
24 hours	7.95	7.90	7.90	8.40	8.40	8.35
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig.5

After comparing the catalytic activity of the ions mentioned above (it was maximum for mercuric chloride) variation in pH with time of mixture containing varying quantities of either of the reactants was studied. The following sets of solutions were prepared.

<u>Set I</u>

1.0, 2.0, 3.0, 4.0, 5.0, 6.0 of 10^{-2}M hexacyanoferrate (II) was added to 3.0 ml of 10^{-2}M 8-hydroxyquinoline 5-sulphonic acid. To each was added 1.0 ml of 10^{-4}M mercuric chloride and total volume was made to 20.0 ml by water.

<u>Set II</u>

Consisted of solutions, mixed in the reverse order of Set I.

FIG. 6(b)

EFFECT OF REACTANTS CONCENTRATION

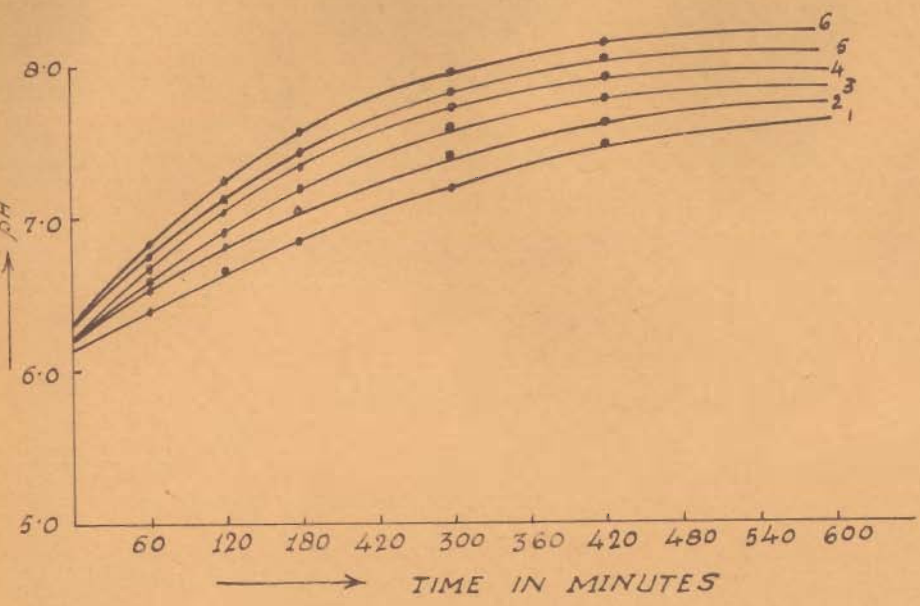


FIG. 6(a)

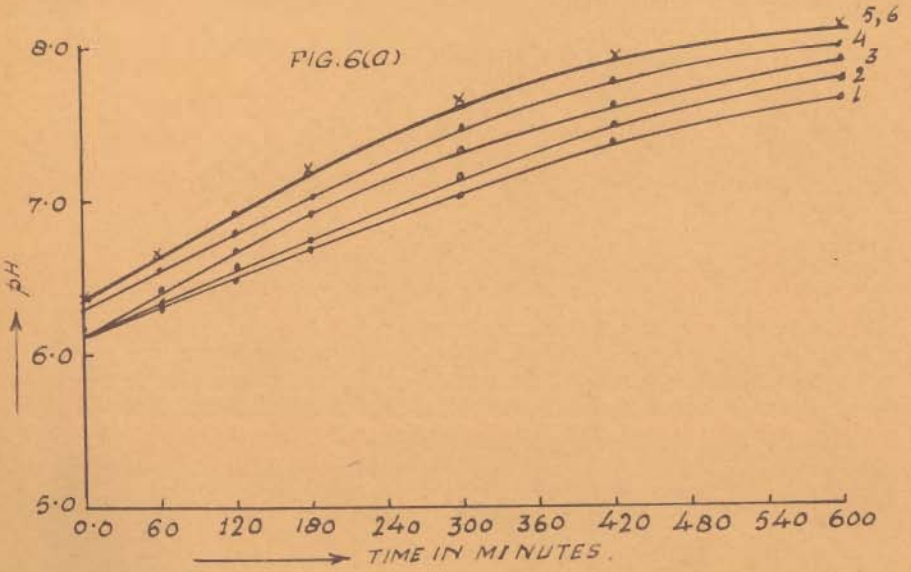
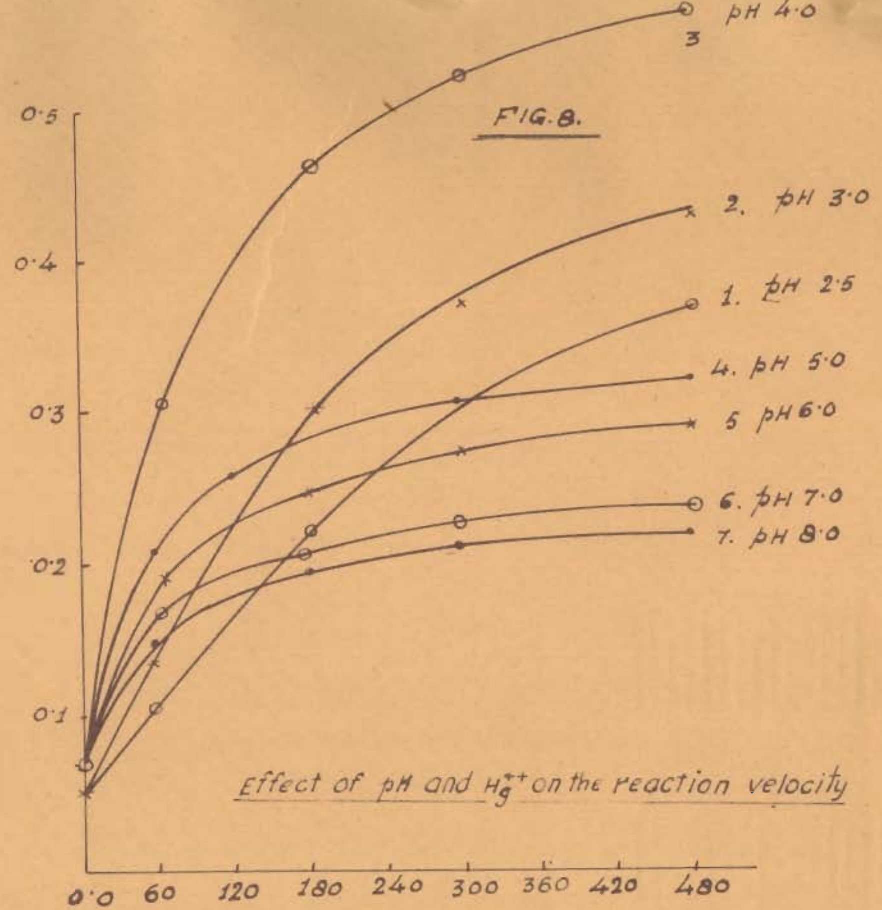


FIG. 8.



Effect of pH and Hg^{++} on the reaction velocity

FIG. 7.

Effect of pH on the reaction velocity.

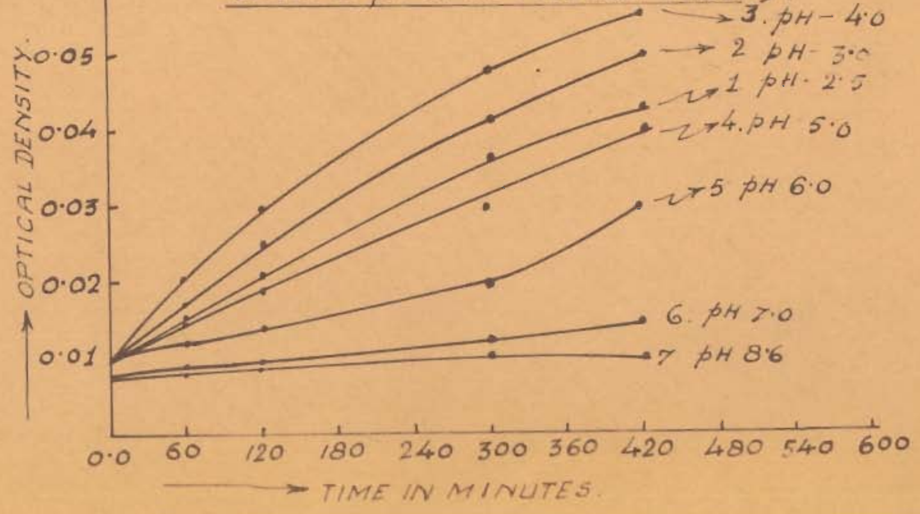


TABLE No.8

Effect of concentration of the reactants in the Variation of pH with time, 8-hydroxyquinoline 5-sulphonic acid fixed:

Time in minutes	pH					
	Set I					
	Solution No.1	Solution No.2	Solution No.3	Solution No.4	Solution No.5	Solutio No.6
0.0	6.1	6.1	6.1	6.2	6.3	6.35
60.0	6.3	6.35	6.45	6.55	6.65	6.70
120.0	6.45	6.55	6.65	6.8	7.0	7.04
180.0	6.65	6.75	6.9	7.0	7.2	7.22
240.0	-	-	-	-	-	-
300.0	7.0	7.15	7.3	7.5	7.65	7.70
360.0	-	-	-	-	-	-
420.0	7.35	7.5	7.6	7.8	7.9	7.9
480.0	-	-	-	-	-	-
540.0	-	-	-	-	-	-
600.0	7.65	7.7	7.9	8.0	8.0	8.05
24 hours	7.7	7.75	7.95	8.0	8.0	8.1
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig. 6(a)

TABLE No.9

Effect of concentration of the reactants in the variation of pH with time (hexacyanoferrate (II) fixed):

Time in minutes	pH Set II					
	Solution No.1	Solution No.2	Solution No.3	Solution No.4	Solution No.5	Solution No.6
0.0	6.15	6.2	6.2	6.25	6.3	6.3
60.0	6.35	6.5	6.62	6.70	6.8	6.82
120.0	6.65	6.8	6.86	7.05	7.2	7.25
180.0	6.82	7.05	7.24	7.40	7.45	7.55
300.0	7.15	7.35	7.55	7.70	7.83	7.95
420.0	7.50	7.60	7.80	7.90	8.05	8.10
600.0	7.65	7.75	7.85	7.95	8.10	8.20
24 hours	8.00	8.05	8.10	8.15	8.15	8.20
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig. 6(b)

Effect of pH on Reaction Velocity (Absence of catalysing ions):

The effect of pH on the velocity of reaction was studied by measuring the optical density values at 30 ± 0.1°C at wave length 575mμ for a set of seven solutions containing 4.0 ml each of the reactants of concentration 1.0×10^{-2}M. Total volume was made to 20.0 ml by adding requisite quantity of the buffer of pH values 2.7, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.6 in solutions No.1,2,3,4,5,6 and 7 respectively.

TABLE No.10

Effect of pH on the variation of O.D. with time

Time in minutes	Optical density values						
	pH						
	2.7	3.0	4.0	5.0	6.0	7.0	8.6
0.0	0.01	0.01	0.01	0.01	0.01	0.007	0.007
60.0	0.016	0.017	0.020	0.014	0.012	0.008	0.008
120.0	0.021	0.025	0.030	0.018	0.014	0.009	0.008
300.0	0.036	0.041	0.048	0.030	0.020	0.011	0.009
360.0	-	-	-	-	-	-	-
420	0.043	0.050	0.055	0.040	0.030	0.013	0.011
Curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)

Fig.7

Effect of pH on the catalysed Reaction:

It was studied by measuring the optical density values at different intervals for a ~~density values~~ set of seven solutions, containing 4.0 ml of the reactants., each of concentration of $1.0x10^{-2}$M 1.0 ml 10^{-4}M mercuric chloride (because the catalytic activity of mercuric chloride was maximum). Total volume was made to 20.0 ml by adding requisite quantity of buffer of pH 2.5, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 in solutions 1,2,3,4,5,6 and 7 respectively. The results are tabulated below:

TABLE No.11

Effect of Hg^{++} ions and pH on the variation of optical density with time:

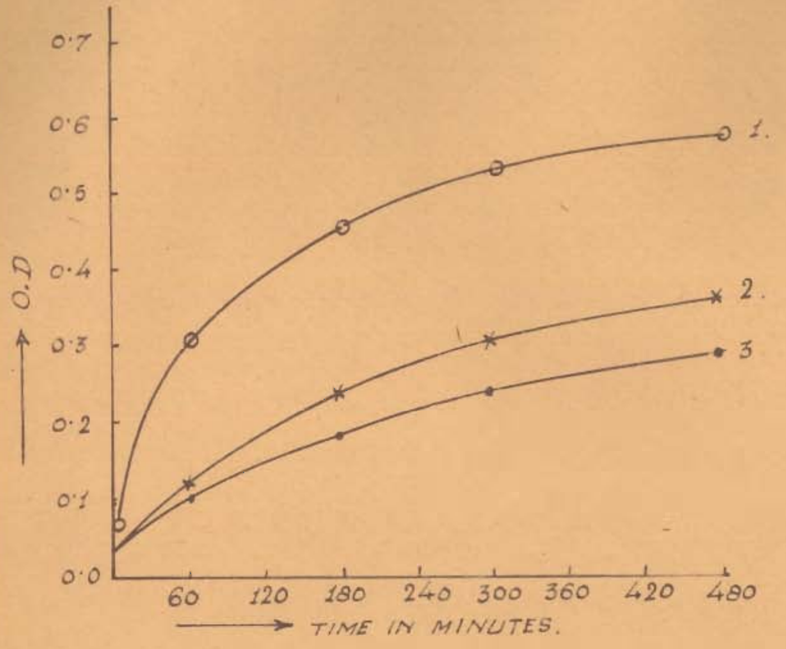
Time in minutes	Optical density values						
	pH						
	2.5	3.0	4.0	5.0	6.0	7.0	8.0
0.0	0.05	0.05	0.07	0.07	0.07	0.07	0.07
60.0	0.10	0.135	0.30	0.21	0.19	0.17	0.15
180.0	0.24	0.30	0.46	0.28	0.245	0.20	0.19
300.0	0.30	0.37	0.525	0.305	0.27	0.225	0.21
480.0	0.365	0.425	0.56	0.32	0.29	0.245	0.22
24 hours	0.49	0.55	0.65	0.36	0.30	0.28	0.24
Curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)

Fig.8

From the above experiment it was found that the optimum pH for the catalysed and uncatalysed reaction was 4.0. To study comparative effect of catalysist at this pH a set of three solutions, each containing $4.0x10^{-2}$M hexacyanoferrate (II) and 8-hydroxyquinoline 5-sulphonic acid; 1.0 ml $1.0x10^{-4}$ mercuric chloride, chromic chloride and berrylium nitrate in solution 1,2 and 3 respectively were prepared. Total volume was made to 20.0 ml by buffer of pH 4.0. The results are tabulated below:

FIG. 9.

COMPARATIVE EFFECT OF Hg^{++} Cr^{+++} AND Be^{++} ON THE REACTION VELOCITY AT pH 4.0



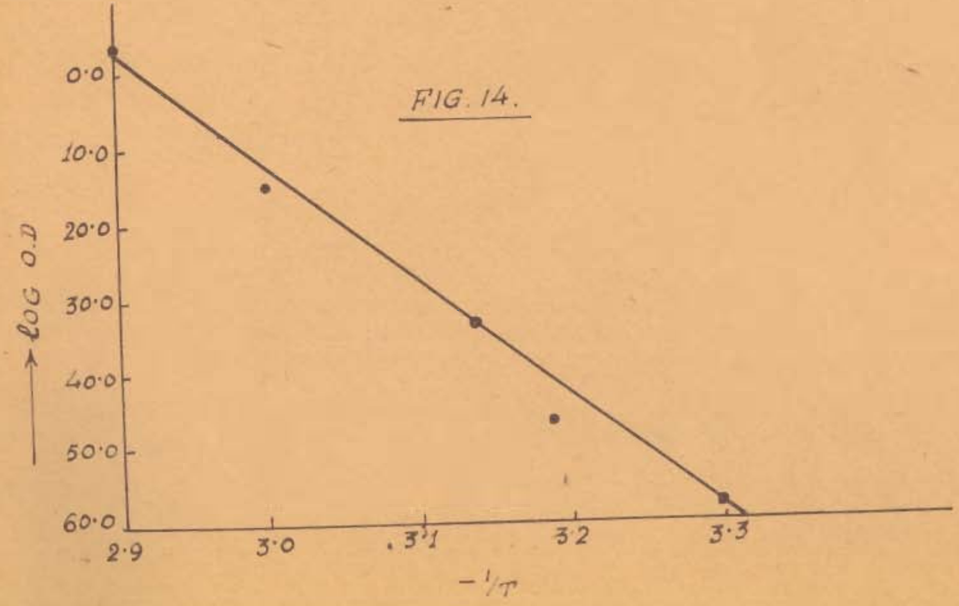


FIG. 14.

FIG. 10.

Dependence of the velocity of reaction (curve I in presence of Hg^{++} ions, curve (II) in absence of Hg^{++} ions) on pH. For curve I graph between O.D measured at 60th minute and for curve (II) measured at 420th minute vs pH have been plotted. concentration of reactants $0{\cdot}5 \times 10^{-3}$ M concn of Hg $0{\cdot}1 \times 10^{-4}$ M, temp 30°c.

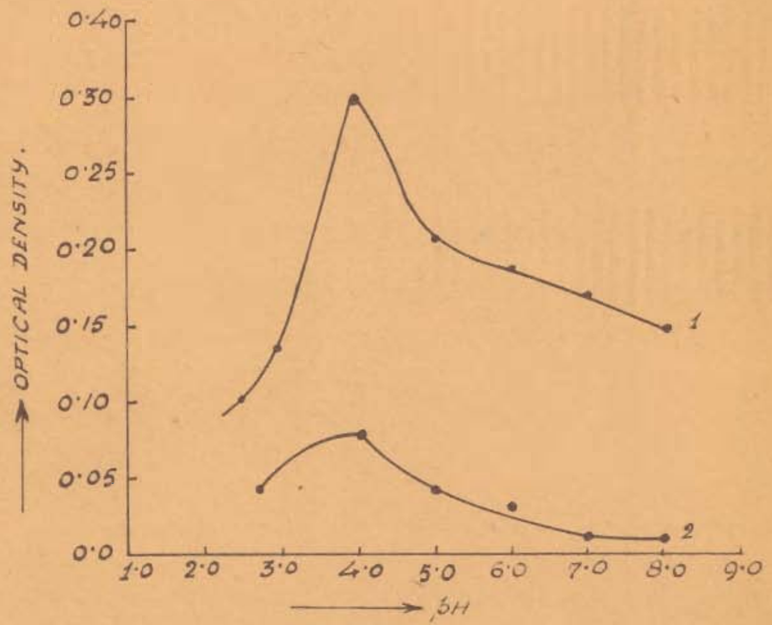


TABLE No.12

Comparative effect of Hg^{++}, Cr^{+++} and Be^{++}ions on the reaction velocity pH (4.0)

Time in minutes	Optical density values		
	Solution No.1	Solution No.2	Solution No.3
0.0	0.07	0.06	0.06
60.0	0.30	0.11	0.09
180.0	0.45	0.23	0.17
300.0	0.52	0.30	0.24
480.0	0.57	0.336	0.29
Curve	(1)	(2)	(3)

Fig.9

Effect of concentration of the reactants:

The effect of concentration of the reactants on the velocity of the reaction at pH 4.0 was studied by measuring optical density values at different intervals for the following sets of mixtures.

Set I.

1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 ml of 10^{-2}M 8-hydroxyquinoline 5-sulphonic acid was added to 4.0 ml of 10^{-2}M hexacyanoferrate (II). To each was added 1.0 ml of 10^{-4}M mercuric chloride and total volume was made to 25.0 ml by buffer of pH 4.0

Set II.

Solutions were prepared in reverse order.

FIG. 11 (a)

EFFECT OF 8-HYDROXY QUINOLINE 5-SULPHONIC ACID. CONCENTRATION

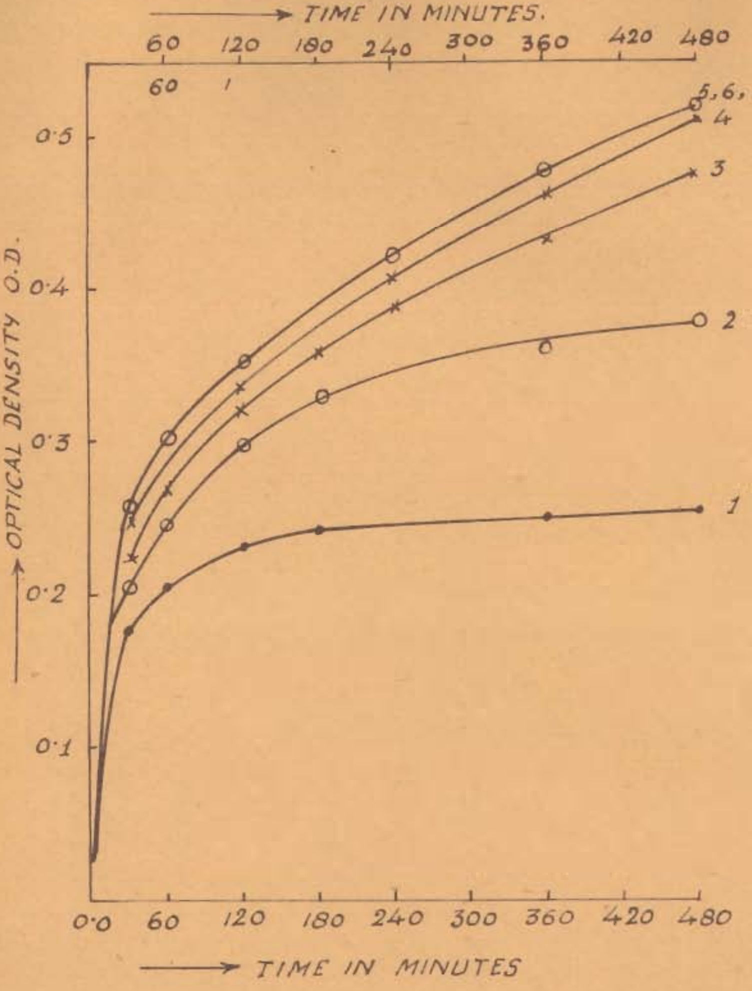
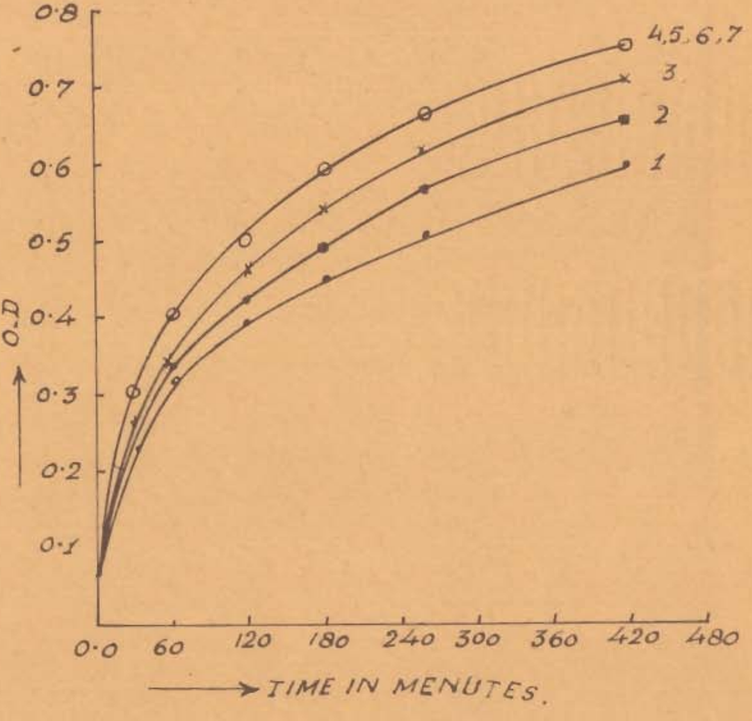


FIG. 11 (b)

EFFECT OF HEXACYANOFERRATE (II) CONCENTRATION.



8-hydroxyquinoline 5-sulphonic acid was kept constants. Results are tabulated below:

TABLE No.13

Effect of concentration of 8-hydroxyquinoline 5-sulphonic acid on reaction velocity (concentration of hexacyanoferrate (II) constant).

Time in minutes	Optical density values						
	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5	Mixture 6	Mixture 7
0.0	0.05	0.05	0.05	0.05	0.05	0.05	0.05
30.0	0.08	0.225	0.24	0.25	0.255	0.255	0.255
60.0	0.205	0.26	0.28	0.295	0.30	0.305	0.305
120.0	0.235	0.29	0.32	0.335	0.34	0.35	0.35
240.0	0.24	0.33	0.39	0.41	0.42	0.42	0.47
360.0	0.24	0.36	0.43	0.465	0.47	0.475	0.475
480.0	0.24	0.38	0.48	0.52	0.52	0.52	0.52
Curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)

Fig.11(a)

TABLE No.14

Effect of concentration of hexacyanoferrate (II) on reaction velocity (concentration of 8-hydroxyquinoline 5-sulphonic acid fixed).

Time in minutes	Optical density values						
	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5	Mixture 6	Mixture 7
0.0	0.07	0.07	0.07	0.06	0.06	0.06	0.06
30.0	0.23	0.25	0.26	0.29	0.29	0.29	0.29
60.0	0.315	0.33	0.345	0.40	0.41	0.41	0.41
120.0	0.39	0.41	0.46	0.48	0.48	0.48	0.48
180.0	0.45	0.49	0.54	0.60	0.60	0.61	0.61
270.0	0.50	0.57	0.62	0.67	0.67	0.67	0.67
420.0	0.60	0.65	0.70	0.74	0.75	0.75	0.75
Curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)

Fig.11(b)

Effect of foreign electrolytes:

The effect of foreign electrolytes on the reaction velocity was studied by measuring optical densities at different intervals at pH 4.0 at 30 ± 0.1°C for the following solutions.

Set I

Solution No.1 to 4 contained 4.0 ml of 10^{-2}M hexacyanoferrate (II), 4.0 ml of 10^{-2}M 8-hydroxyquinoline 5-sulphonic acid, 2.0 ml of 10^{-4}M mercuric chloride. 2.0 ml of the ~~following~~ electrolytes ~~of~~ (concentration 1.0M) potassium chloride, potassium nitrate and potassium cyanide and the total volume was made to 25.0 ml in each case by buffer of pH 4.0 Results are tabulated below:

TABLE No.15

Effect of potassium chloride, potassium nitrate, potassium cyanide on the reaction velocity:

Time in minutes	Optical density values			
	Mixture 1	Mixture 2	Mixture 3	Mixture 4
0.0	0.08	0.08	0.08	0.08
30.0	0.29	0.22	0.13	0.08
60.0	0.36	0.30	0.24	0.08
120.0	0.42	0.38	0.30	0.08
180.0	0.47	0.43	0.37	0.08
300.0	0.54	0.47	0.43	0.08
420.0	0.57	0.50	0.46	0.08
24 hours	0.63	0.58	0.50	0.08
Curve	(1)	(2)	(3)	(4)

Fig.12

Influence of Temperature:

The effect of temperature was studied by measuring the optical density values at temperatures 30, 40, 45, 60 and 70°C at different intervals at wave length 575. for the mixtures containing 4.0 ml of 10^{-2}M hexacyanoferrate (II), 4.0 ml of 8-hydroxyquinoline 5-sulphonic acid, 2.0 ml of

10^{-4}M mercuric chloride. Total volume was made to 20.0 ml by adding requisite quantity of buffer of pH 4.0. Results are tabulated below:

TABLE No.16

Influence of temperature on reaction velocity:

Time in minutes	Optical density values				
	40°C	45°C	60°C	70°C	30°C
0.0	0.145	0.170	0.205	0.225	0.07
15.0	-	0.395	0.732	1.06	0.10
30.0	0.34	0.462	0.70	1.10	0.26
60.0	0.41	0.54	0.95	1.24	0.29
120.0	0.43	0.62	1.20	-	-
180.0	0.49	-	1.30	1.49	0.34
240.0	0.54	0.81	-	-	0.42
300.0	0.57	-	1.42	-	0.45
360.0	0.60	1.12	1.50	1.62	0.47
420.0	-	-	-	-	-
480.0	-	1.18	-	-	-
540.0	-	-	-	-	-
Curve	(2)	(3)	(4)	(5)	(1)

Fig.13

TABLE No.17

O.D. after 30 minutes at different temperatures:

Temp. ^{o}C	O.D. after 30 minutes	log O.D	1/Temperature (absolute)
30.0	0.26	-58.5×10^{-2}	3.30×10^{-3}
40.0	0.34	-46.8×10^{-2}	3.19×10^{-3}
45.0	0.46	-33.7×10^{-2}	3.14×10^{-3}
60.0	0.70	-15.5×10^{-2}	3.07×10^{-3}
70.0	1.10	$+4.1\times10^{-2}$	2.91×10^{-3}

Fig. 14

RESULTS AND DISCUSSION:

Absorption of hexacyanoferrate (II) 8-hydroxyquinoline 5-sulphonic acid and that of the complex:

Maximum absorption for $1.0x10^{-4}$M, $4.0x10^{-4}$M solutions of hexacyanoferrate (II) and $0.5x10^{-4}$M $0.25x10^{-4}$M 8-hydroxyquinoline 5-sulphonic was obtained at 220 mμ and 242 mμ respectively Fig.1. Maximum absorption for the olive green complex obtained by mixing $1.0x10^{-2}$M and $0.2x10^{-2}$M solutions of the reactants in the ratio of hexacyanoferrate (II) to 8-hydroxyquinoline 5-sulphonic acid as 3:1, 2:1, 4:3, 3:2, 1:1, 3:4, 2:3, 1:2 and 1:3 in absence of buffer and at pH 4.0 (optimum pH for the reaction) respectively in presence of $0.5x10^{-4}$M mercuric chloride took place at 425mμ in the ratio 1:1. But a small peak was also realized at 575 mμ in all the test tubes. (Fig.1 curve 1-6) curves for the mixture of the reactants in the ratios, 3:4 1:2, and 1:3 are not shown in figure). Optical density values at various wave lengths in unbuffered and buffered solutions respectively are shown in table 2 and 3. Absorption of 8-hydroxyquinolines 5-sulphonic acid and hexacyanoferrate (II) was negligible at 575 mμ.

Composition of the complex:

The plots of O.D. Vs the ratio 8-hydroxyquinoline 5-sulphonic acid/hexacyanoferrate (II) + 8-hydroxyquinoline 5-sulphonic acid at wave length

575 mμ and the plots of difference of optical density values of reactants and product Vs the mole fraction mentioned above at 425 mμ indicated the formation of 1:1 complex (Fig.2 curve 1,2 and 3,4 at wave lengths 425 mμ and 575 mμ respectively).

The results of molar ratio method (Fig.3 curves 1,3 and 2,4 confirmed the formation of 1:1 complex.

The above results were further confirmed from the plots according to the slope ratio method (Fig.4, curves 1,3 and 2,4 at wave lengths 425 mμ and 575 mμ respectively). Evidence for the formation respectively of 1:1 complex was again forthcoming.

Variations in pH

It is evident from (Fig.5 curves 1,2 and 3) that pH of hexacyanoferrate (II) increased with time and became constant after 24 hours. The variations in pH with time are in the sequence Hg^{++} > Cr^{+++} > Be^{++}. No variations in pH of 8-hydroxyquinoline 5-sulphonic were realized. The pH of the mixtures of the reactants showed greater variation with time. The order was again the same as mentioned above.

The effect of varying concentration of hexacyanoferrate (II) or 8-hydroxyquinoline 5-sulphonic acid (0.05x10^{-2} to 0.3x10^{-2}M) on the mixtures containing fixed amount of 8-hydroxyquinoline 5-sulphoric acid or hexacyanoferrate (II) and mercuric chloride ($0.5x10^{-4}$M) was followed with a increase in pH in both the cases. The effect was more pronounced with 8-hydroxyquinoline 5-sulphoric acid (Fig.6(a);(b)).

Effect of pH:

Absorption data revealed that the effect of pH was maximum at pH 4.0 (Fig.7). In the alkaline range the reaction altogether stopped Moreover it was observed that the O.D. values at the optimum pH were much higher for the catalysed reactions than the uncatalysed one (absence of Hg^{++}, Cr^{+++} or Be^{++}) (Fig.10 curves 1,2).

Experiments carried out at pH 4.0 with varying concentration of catalysing ions (Hg^{++}) showed that the optical density increased with increase in concentration (Fig.8). The relative effect of Hg^{++}, Cr^{+++} and Be^{++} on the reaction velocity is shown in (Fig.9).

From the observations mentioned above it may be concluded that both pH and the concentration of catalysing ions influence the interaction of hexacyanoferrate (II) and 8-hydroxyquinoline 5-sulphonic acid.

From the curves Fig.11 (a), (b) obtained by plotting O.D. values measured at different intervals for mixtures containing $0.15x10^{-2}$M hexacyanoferrate (II) and increasing amounts of 8-hydroxyquinoline

5-sulphonic acid from 0.04×10^{-2}M to 0.28×10^{-2}M and for mixtures prepared in the reverse order (containing 0.04×10^{-4}M mercuric chloride) it is evident that the reaction is dependent on the concentration of both the reactants.

Effect of electrolytes:

Curves obtained by plotting optical density values against time in presence of various electrolytes viz., potassium chloride, potassium nitrate and potassium cyanide (each 0.08M) on the mixtures containing 0.16×10^{-2}M mercuric chloride it is observed that the reaction velocity is appreciably reduced in presance of potassium chloride and potassium nitrate. Negative salt effect was observed. In presence of potassium cyanide the reaction is completely stopped. From the latter it was concluded that cyanide ions were liberated during the course of reaction. (Fig.12)

Influence of Temperature:

Velocity was found to be dependent on temperature (Fig.13). The plot of log of optical density measured at 30th minute (log $O.D._{30}$) against 1/T resulted in a straight line (Fig.14) whose slope corresponded to an energy of activation = 15.75 K. calories/mole.

On the basis of above mentioned facts, the reaction may be assumed to take the following course. Let Q represents the molecule of 8-hydroxyquinoline 5-sulphonic acid and Hg^{++} as catalyst.

$$\text{I. } Hg^{++} + Fe(CN)_6^{----} \underset{H_2O}{\rightleftharpoons} Fe(CN)_5^{---} + Hg\ (CN)^+$$

$$\text{II. } Fe(CN)_6H_2O^{3-}+Q + \rightleftharpoons Fe(CN)_5^{---}\ Q + H_2O$$

$$\text{III. } Hg(CN)^+\ Fe(CN)_6^{4-} \rightleftharpoons Hg(CN)_2 + Fe\ (CN)_5^{3-}$$

$$\text{IV. } Hg(CN)_2 + 2H_2O \rightleftharpoons Hg^{++} + 2HCN + 2OH^-$$

Amongst reaction (I) is slow and depends upon the concentration of Hg^{++} (Cr^{+++} and Be^{++}) ions. While (II) is a fast reaction representing the formation of the olive green complex ($K_3Fe(CN)_5Q$) and is dependent on the concentration of 8-hydroxyquinoline 5-sulphonic acid (I II) represents the catalytic decomposition of hexacyanoferrate (II) by $Hg(CN)^+$ and is dependent on the concentration of hexacyanoferrate (II). The stoichiometric reaction (II) and catalytic reaction (III) proceed simultaneously.

Reaction (IV) takes place due to hydrolysis of potassium cyanide. Since potassium hydroxide is the product of hydrolysis pH would increase with time and would be dependent on the concentration of hexacyanoferrate (II). The reaction should stop in alkaline medium. This is what has actually been observed.

Besides the mechanism given above product of the reaction between Hg^{++} and $Fe(CN)_6^{3-}$ inweak acidic medium is probably the intermediate according to the scheme.

$$Hg^{++} + Fe(CN)_6^{4-} \rightleftharpoons (Fe(CN)_5\,H_2O)^{3-} + Hg\,(CN)^{+}$$

$$Hg(CN)^{+} + H^{+} \rightleftharpoons Hg^{++} + HCN$$

and hence catalytic action should be negligibly small in basic medium. This ~~is~~ has also been observed. In acidic solutions of hexacyanoferrate (II) the following equilibrium is possible.

$$H^{+} + Fe(CN)_6^{3-} \rightleftharpoons (H\,Fe(CN)_6) \text{ and}$$

$$H^{+} + (H\,Fe(CN)_6^{3-}) \rightleftharpoons (H_2\,Fe(CN)_6^{2-})$$

Moreover it is well known that the smaller the number of proton in complex ions, the easier is the loss of cyanide ions. Consequently in higher acid solutions of hexacyanoferrate (II) the reaction velocity should decrease. The two effect of H^{+} suppression of the dissociation of $H_4\,Fe(CN)_6$ and regeneration of the catalyst, are in opposition and this must lead to optimum pH (3.5-4.0) which is actually has been observed.

Similar type of mechanism can also be proposed, with Cr^{+++} and Be^{++} as catalyst. The proposed mechanis quite parallel with the mechanism given by S. Aspeyer (loc. cit) for the interaction of nitrosobenzene with hexacyanoferrate (II) catalysed by Hg^{++} ions.

CHAPTER III (Part II)

Polarographic studies on 8-hydroxy quinoline 5-sulphonate pentacyanoferrate (II) complex:

In the existing literature large number of references are available on the behaviour of quinolines (2-6) (quinoline, B-napthoquinoline and quinoline ethoxide) hydroxyquinolines (2-hydroxy quinoline, 8-hydroxyquinoline) and quinoline carboxylic acids (12-14) (quinoldinic acid, quinoline 8-carboxylic acid etc. at d.m.e; but its compounds with simple or complex inorganic ions have not so far been studied. The reduction of 8-hydroxyquinoline 5-sulphonic acid pentacyanoferrate (II) complex at d.m.e. was, therefore investigated on the similar lines as in the case of nitrosobenzene pentacyanoferrate (II) complex (1). Studies on 8-hydroxy quinoline 5-sulphonic acid were also carried out on the parallel grounds to compare reduction with that of the complex.

EXPERIMENTAL

Apparatus:

Heyrovsky LP 55A polarograph operated manually in conjunction with Pye sclamp galvanometer in external circuit was used. A dropping mercury electrode having drop time 4.32 sec. and weight of one drop = 0.0035 gms. at applied potential of 0.0V (in 0.5M KCl and phthalate buffer of pH-4) at the height of mercury column 49.5 cm. from the tip of the capillary, was used. The polarographic cell and the reference electrode (S.C.E.) were kept immersed in thermostatic water bath maintained at 25 ± 0.1°C. Purified hydrogen was used for deaeration. Beckmann pH-meter Model H-2 was used for measuring the pH of the solutions.

Reagents:

All the reagents used were of A.R. quality. Double distilled water was used for preparing the solutinns. Solution of 8-hydroxy quinoline 5-sulphonic acid was prepared by dissolving weighed quantity of the reagent in hot water and the crystals from cold were dissolved in potassium hydroxide at pH 7.0. Weighed quantity of hexacyanoferrate (II) was dissolved in water and its strength determined potentiometrically against potassium permanganate. Mercuric chloride solution was prepared by dissolving weighed quantity in water.

To study the effect of pH on the reduction steps, two sets of solutions were prepared. Set I consisted of 27 solutions each containing 1.0 c.c., 0.02M hexacyanoferrate (II), 1.0 c.c., 0.2M 8-hydroxy quinoline 5-sulphonic acid, 2.0 c.c. of 10^{-3}M mercuric chloride, 1.0 c.c. of 1.0M potassium chloride and 20.0 c.c. of the different buffers ranging from pH 1.0-12.0, to make the total volume to 25.0 c.c. Set II was exactly of similar type but without hexacyanoferrat (II), containing 21.0 c.c. buffers ranging from pH 1-12 in total 25.0 c.c. of the volume.

TABLE No.1

Current voltage data of mixtures containing 8.0×10^{-4}M each of the hexacyanoferrate (II) and 8-hydroxyquinoline 5-sulphonic acid, 8.0×10^{-6}M mercuric chloride 0.04M potassium chloride at different pH values.

Potential (-ve)volts	Sodium acetate and hydrochloric acid					
	Current A					
Senstivity	1/10	1/10	1/10	1/10	1/5	1/10
pH	1	2	3	4	5	
0.00	0.95	-	-	0.35	-0.05	-
0.05	-	-	-	0.50	+0.40	-
0.10	1.20	-	-	0.80	+0.80	-
0.15	-	-	-	-	1.15	-
0.20	1.30	-	-	1.15	1.70	-
0.30	1.40	-	-	1.25	2.00	-
0.40	-	-	-	1.30	2.15	-
0.50	1.50	-	-	1.30	2.25	-
0.60	-	-	1.50	-	-	1.20
0.70	-	1.10	1.55	-	-	1.20
0.80	1.70	1.15	1.60	1.50	-	1.30
0.90	1.95	1.30	1.70	1.60	-	1.40
0.95	2.60	1.70	2.00	1.70	-	1.45
1.00	3.85	2.65	3.05	2.05	-	1.55
1.05	4.80	3.55	3.40	2.80	-	1.75
1.10	5.55	4.10	3.75	3.20	-	2.00
1.15	5.80	4.30	4.10	3.45	-	3.20
1.20	5.90	4.55	4.35	3.60	-	3.40
1.25	6.85	4.80	4.55	3.80	-	-
1.30	9.15	5.10	4.70	4.00	-	3.60
1.35	-	5.90	4.95	4.20	-	-
1.40	Out of scale	7.50	10.40	4.45	-	4.00
1.45	-	-	5.95	4.75	-	-
1.50	-	-	8.85	4.95	-	4.20
1.55	-	-	-	6.00	-	-
1.60	-	-	-	9.00	-	5.00
Curve	(1)	(2)	(3)	(4)	5(B)	5(A)

Fig.1

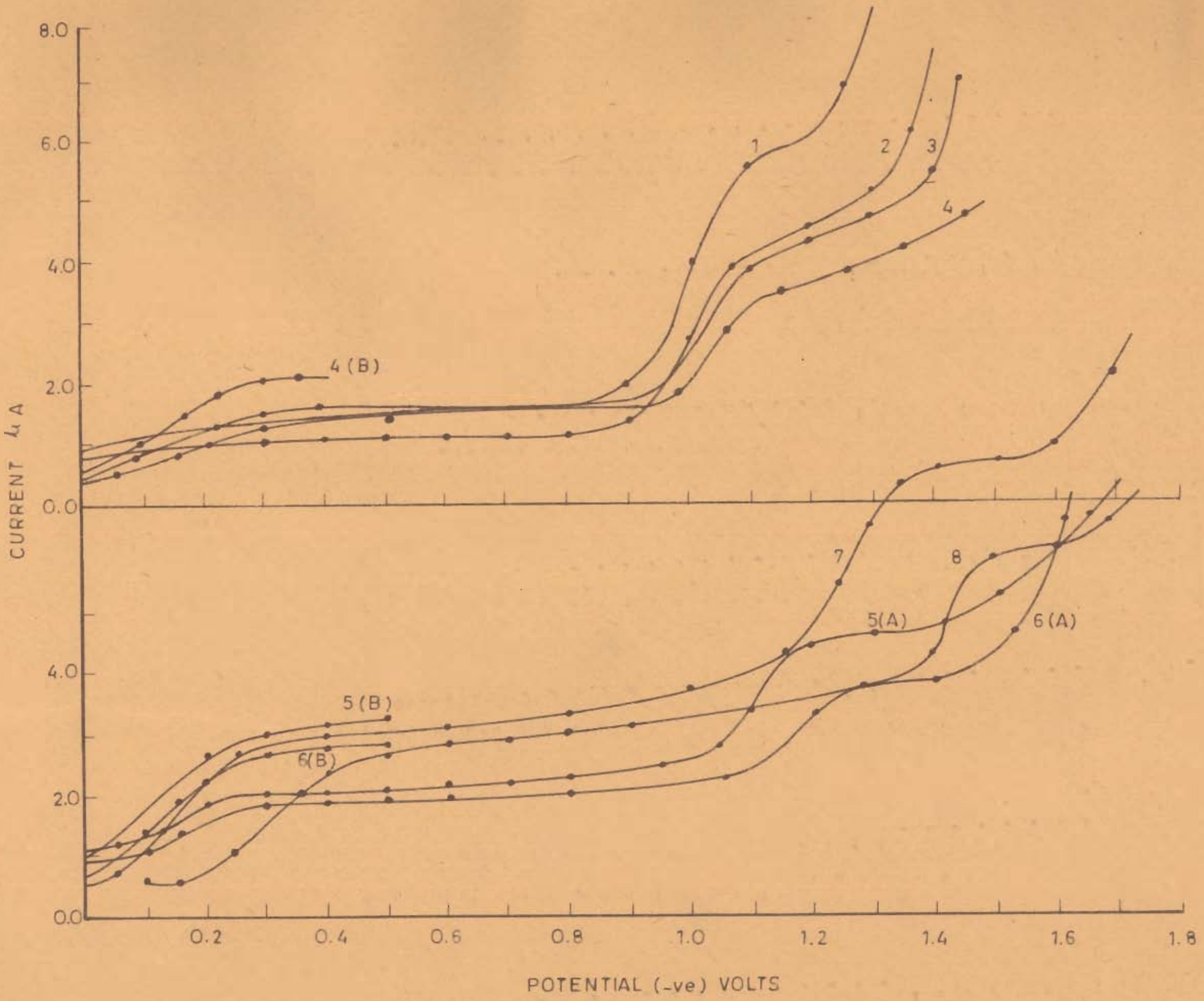

8.0
6.0
4.0
2.0
0.0
4.0
2.0
0.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3
4
4 (B)
7
8
5(A)
6 (A)
5 (B)
6(B)

FIGURE 1

TABLE No.2

Potential (-ve) volts	Dipotassium hydrogen posphate and sodium hydroxide			
pH	6.0		7.0	8.0
Senstivity	1/5	1/10	1/5	1/5
	Current A			
0.00	-0.35	-	-0.45	-0.45
0.05	-0.05	-	-0.25	-0.45
0.10	+0.40	-	+0.10	-0.15
0.15	+0.90	-	+0.70	+0.20
0.20	+1.20	-	+1.05	+0.60
0.25	+1.60	-	1.65	+1.00
0.30	+1.60	-	1.85	+1.40
0.40	+1.75	-	2.00	1.65
0.50	+1.85	-	-	1.70
0.60	-	0.95	1.60	1.85
0.70	-	1.00	-	1.95
0.80	-	1.05	2.40	2.10
0.90	-	1.10	-	2.25
1.00	-	1.20	2.85	2.45
1.05	-	1.30	2.95	-
1.10	-	1.35	3.00	2.60
1.15	-	1.75	3.15	-
1.20	-	2.40	3.60	2.80
1.25	-	2.70	4.50	2.90
1.30	-	2.75	5.40	3.40
1.35	-	2.85	5.00	4.50
1.40	-	2.90	6.30	4.90
1.45	-	3.05	6.40	5.00
1.50	-	3.25	6.45	5.10
1.55	-	3.75	-	-
1.60	-	4.85	6.70	5.50
1.65	-	6.45	-	-
1.70	-	9.10	8.00	-
1.75	-	-	-	-
1.80	-	-	-	-
1.85	-	-	-	8.30
1.90	-	-	-	8.40
1.95	-	-	-	8.65
2.00	-	-	-	8.95
Curve	6(B)	6(A)	(7)	(8)

Fig.1

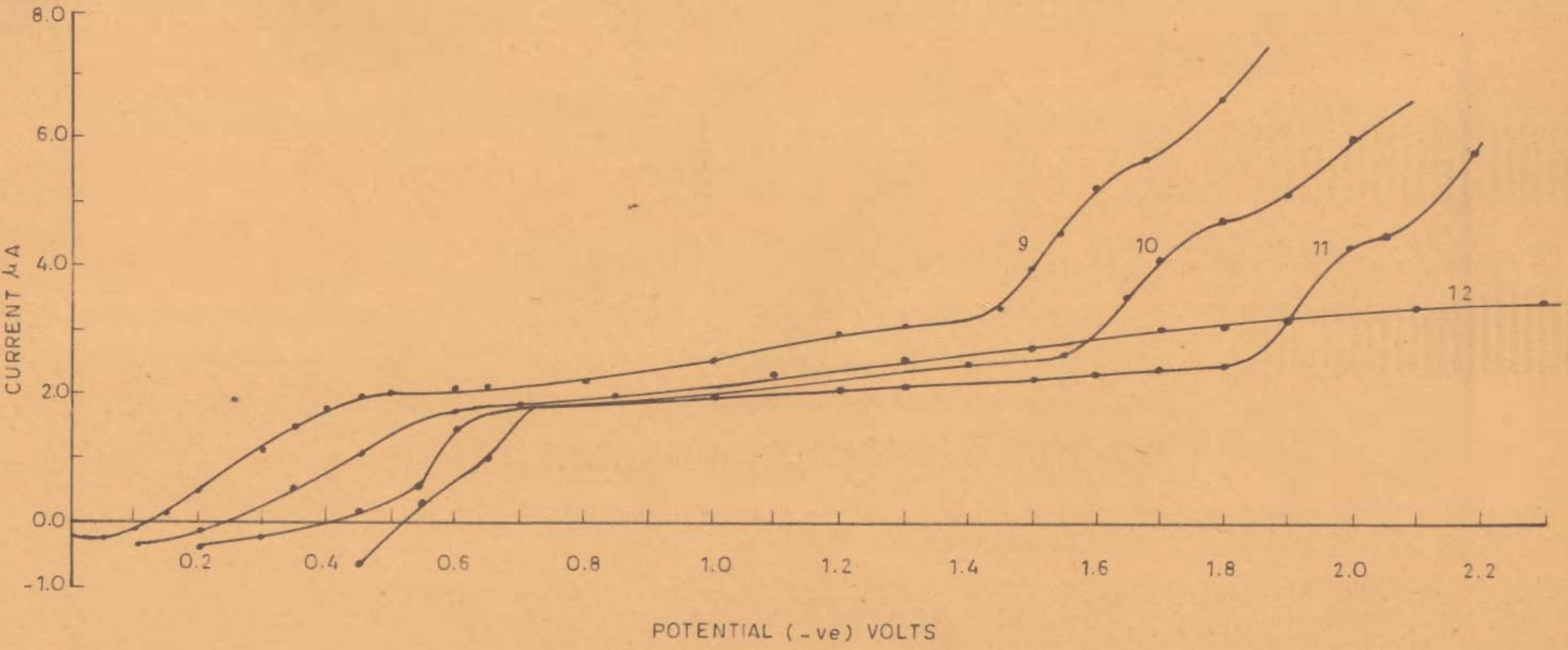

8.0
6.0
4.0
2.0
0.0
-1.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
POTENTIAL (-ve) VOLTS
9
10
11
12

FIGURE 1

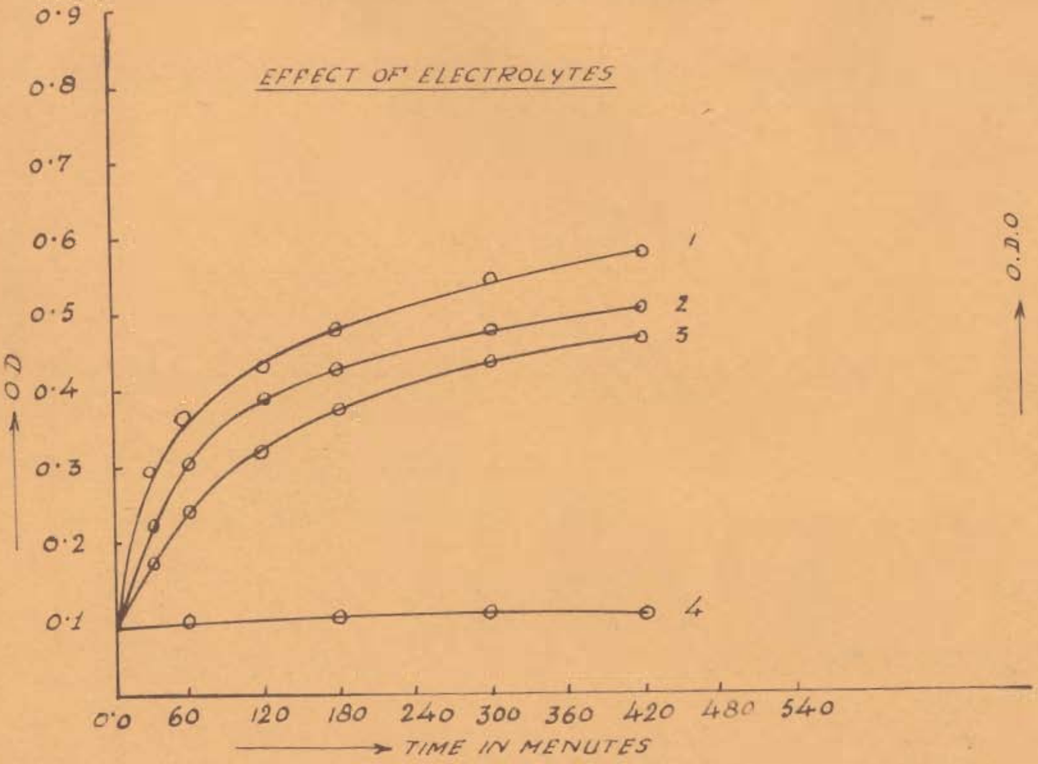
TABLE No.3

Sensitivity 1/5

Potential (-ve) volts	Borax buffer Current A pH 9.0	 10.0	 11.0	 12.0
0.00	-0.30	-0.40	-0.35	-
0.05	-0.30	-0.35	-0.25	-0.70
0.10	-9.10	-0.20	-0.15	-0.20
0.15	+0.10	-0.00	-0.00	+0.30
0.20	+0.50	+0.24	+0.10	+0.70
0.25	+0.75	+0.40	+0.20	+0.90
0.30	+1.10	+0.65	+0.35	+1.65
0.35	1.50	+1.00	+0.45	1.70
0.40	1.75	1.30	1.50	1.95
0.45	1.95	1.55	1.55	-
0.50	1.95	1.65	1.55	-
0.60	2.05	1.70	1.65	2.25
0.80	2.30	1.95	1.85	2.40
1.00	2.50	2.25	2.00	2.60
1.10	2.75	-	2.25	-
1.20	2.95	2.35	-	2.65
1.30	3.05	-	2.30	-
1.40	3.15	2.50	-	3.01
1.45	3.30	2.60	2.35	-
1.50	3.90	2.85	-	-
1.55	4.50	3.50	-	-
1.60	5.20	4.05	2.45	3.10
1.65	5.50	4.45	2.65	-
1.70	5.80	4.70	3.15	-
1.75	6.15	5.10	3.80	-
1.80	6.60	-	4.25	3.30
1.85	7.20	-	4.50	3.70
1.90	7.70	6.05	4.70	4.25
1.95	7.95	-	5.85	6.00
2.00	8.10	6.50	-	-
Curve	(9)	(10)	(11)	(12)

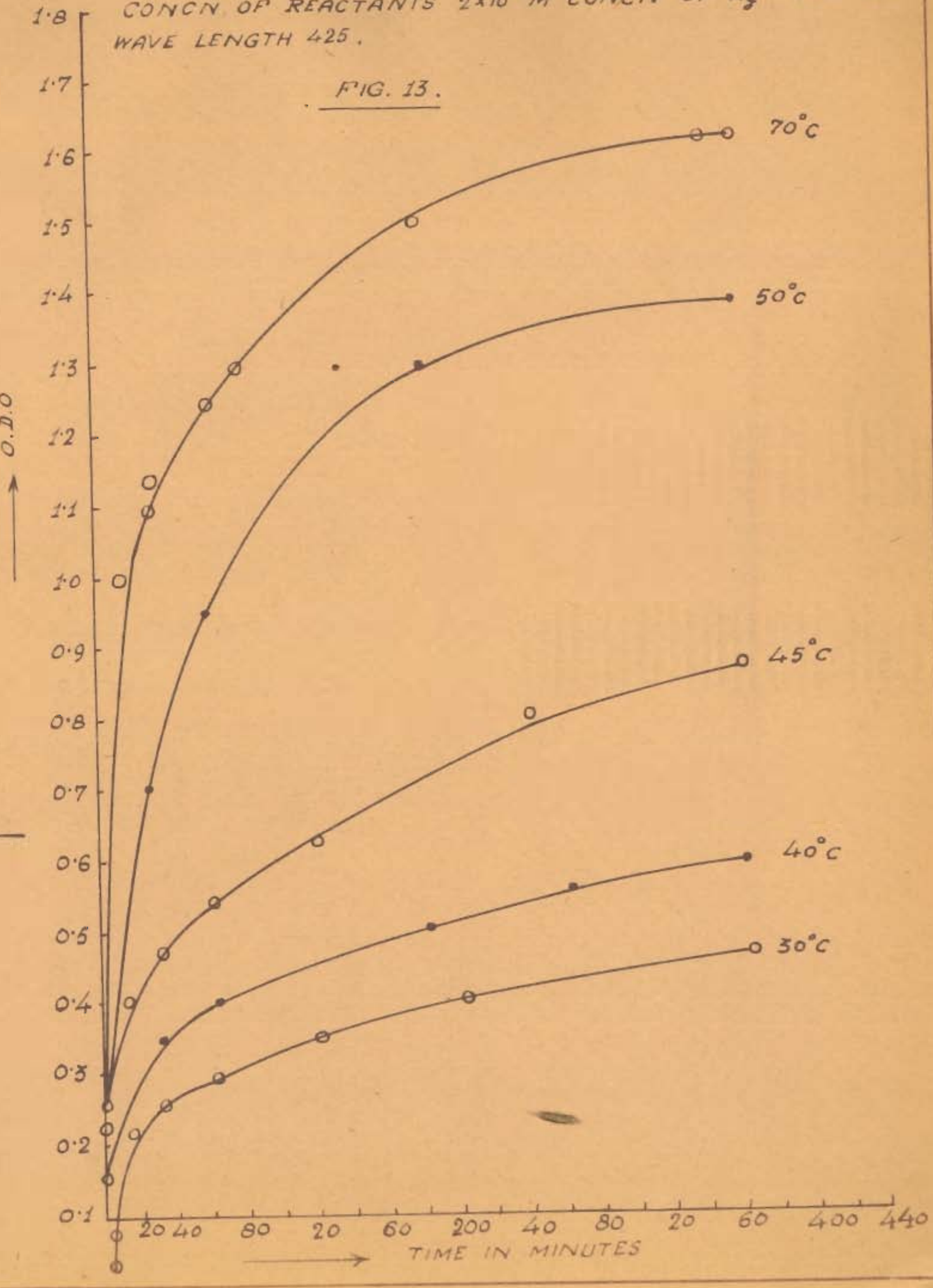
Fig.1

FIG. 12.



DEPENDENCE OF THE VELOCITY OF REACTION INDARK ON TEMP. IN PRESENCE OF Hg^{++} AT pH-4 CONCN. OF REACTANTS $2\times10^{-2}M$ CONCN OF Hg^{++} $1\times10^{-4}M$ WAVE LENGTH 425.

FIG. 13.



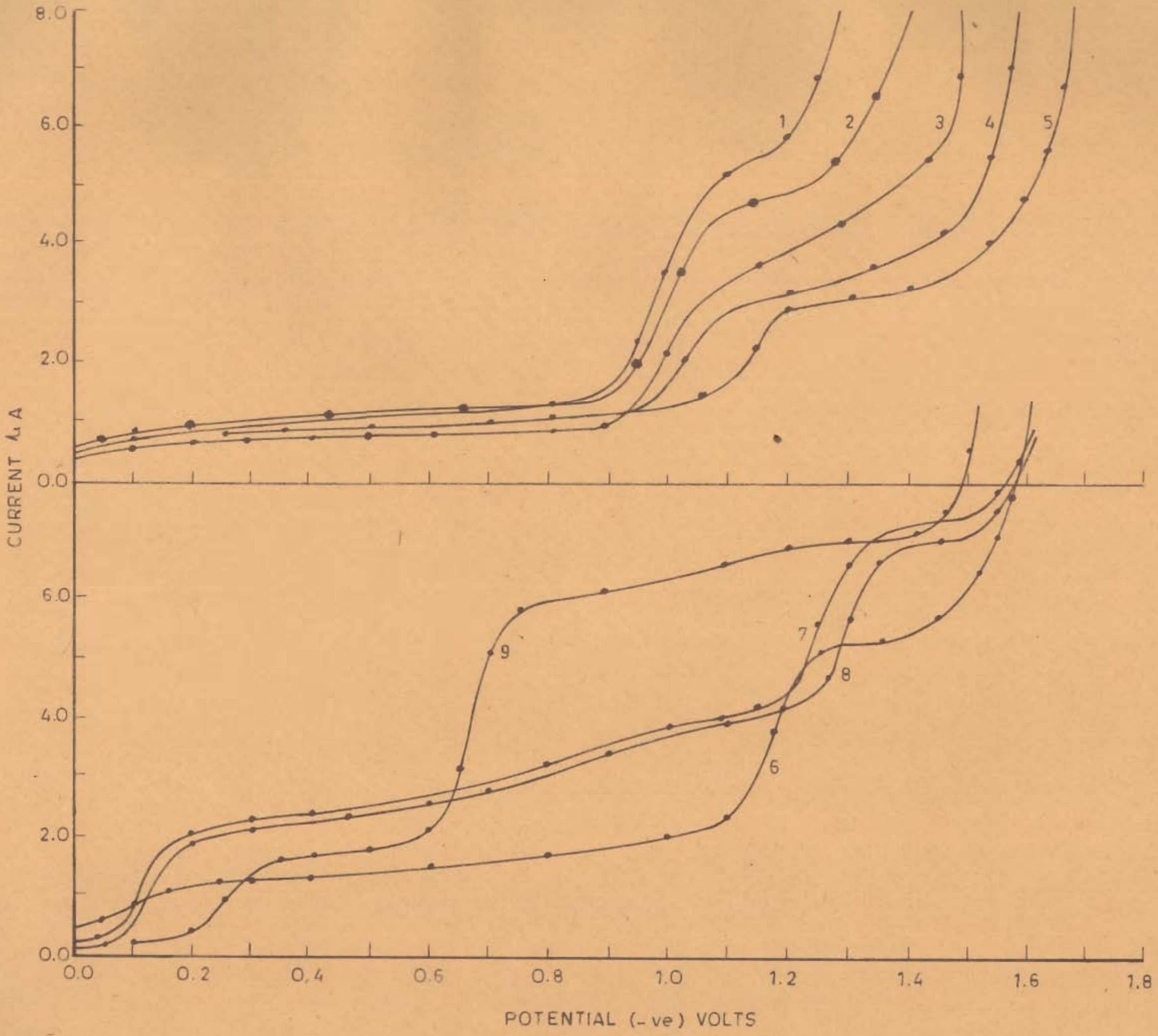

8.0
6.0
4.0
2.0
0.0
CURRENT μA
6.0
4.0
2.0
0.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3
4
5
6
7
8
9

FIGURE 2

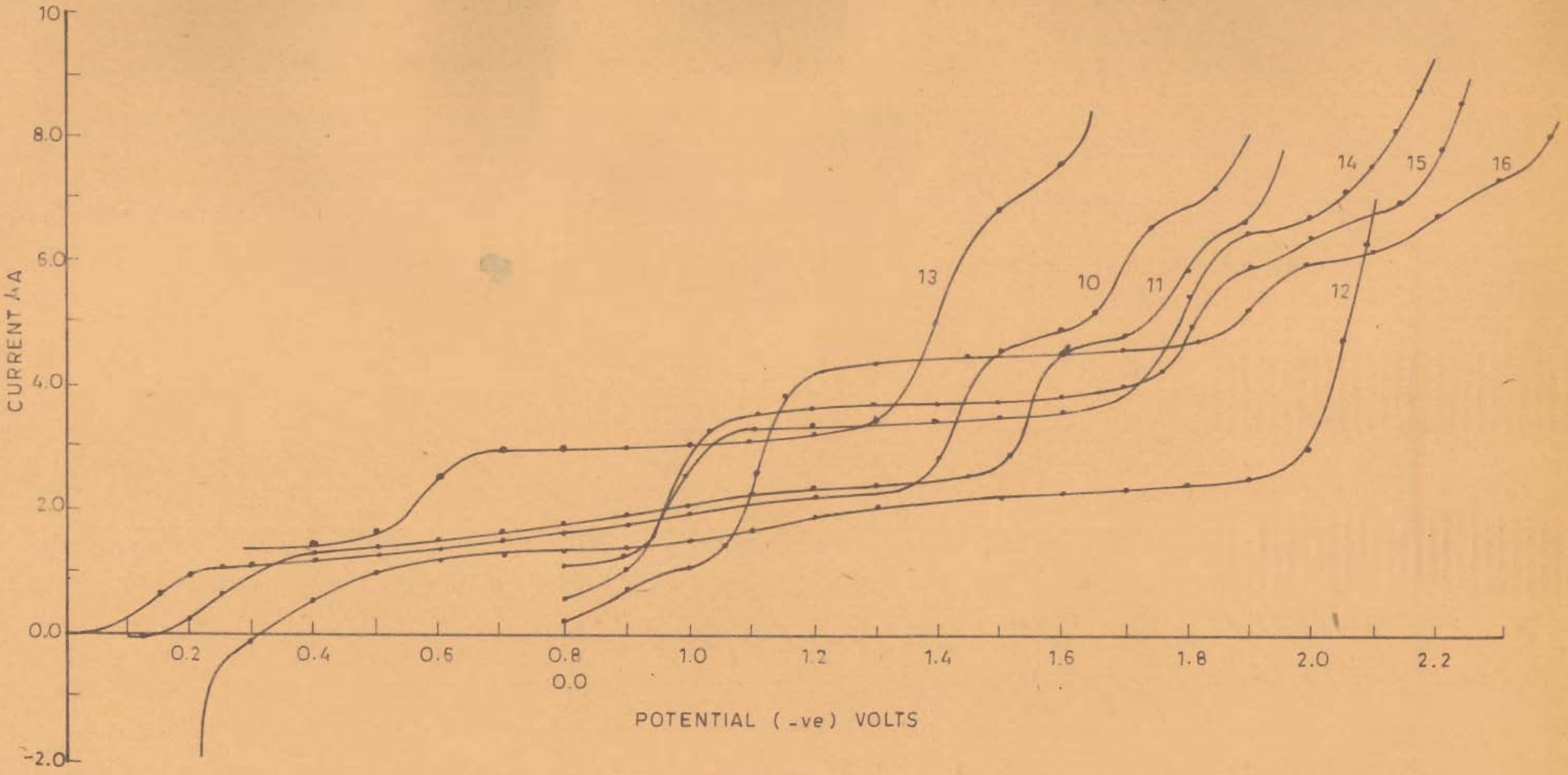

10
8.0
6.0
4.0
2.0
0.0
-2.0
CURRENT μA
0.2
0.4
0.6
0.8
0.0
1.0
1.2
1.4
1.6
1.8
2.0
2.2
POTENTIAL (-ve) VOLTS
13
10
11
12
14
15
16

FIGURE 2

TABLE No.4

Sensitivity 1/10

Potential (-ve) volts	pH			
	KCl and HCl		K_2HPO_4 and HCl	
	Current A			
	1.0	2.0	3.0	4.0
0.00	1.40	1.05	0.50	0.20
0.05	1.50	1.15	0.75	0.45
0.10	1.60	1.25	1.60	0.75
0.15	1.95	2.70	2.00	0.80
0.20	2.60	2.80	2.95	0.80
0.25	0.95	3.30	3.40	1.10
0.30	2.95	3.35	3.50	2.25
0.40	3.05	3.40	3.50	4.20
0.50	3.05	-	-	4.25
0.60	3.10	3.50	3.65	4.40
0.70	3.15	-	-	-
0.80	3.25	3.65	3.80	4.50
0.90	3.45	3.90	3.95	-
0.95	4.00	4.45	4.10	-
1.00	5.15	5.50	5.00	4.65
1.05	6.20	6.15	5.65	4.85
1.10	6.85	6.55	5.90	5.25
1.15	7.20	6.60	-	5.75
1.20	7.55	6.90	6.45	6.00
1.25	8.45	7.30	-	6.10
1.30	10.00	7.60	6.80	6.20
1.35	-	-	7.00	-
1.40	-	10.15	7.65	6.80
1.45	-	-	8.50	-
1.50	-	-	-	7.35
1.60	-	-	-	8.80
Curve	(13)	(14)	(15)	(16)

Fig.2

TABLE No.5

Potential (-ve)volts	Na_2HPO_4 and citric acid			
	Current A			
pH	5.0	6.0	7.0	8.0
Senstivity				
0.00	-0.05	-0.15	-0.25	-0.30
0.05	+0.20	0.00	--0.05	-0.05
0.10	+0.60	0.35	+0.25	+0.35
0.15	+1.20	0.85	+0.80	+1.05
0.20	2.35	1.05	+2.05	+2.05
0.25	3.35	-	+4.75	+4.70
0.30	3.65	2.90	6.75	+7.55
0,40	3.85	4.00	7.40	+9.00
0.50	3.90	4.10	7.55	+9.40
0.60	3.95	4.10	7.60	= -
0.70	-	-	-	-
0.80	4.05	4.20	7.90	9.45
1.00	4.45	4.35	8.00	9.55
1.10	4.85	4.45	-	9.75
1.15	5.45	4.75	-	-
1.20	5.20	5.30	8.25	10.00
1.30	6.90	5.75	8.80	10.05
1.35	-	-	9.35	-
1.40	7.10	5.85	9.80	10.05
1.50	-	6.15	10.05	-
1.60	-	7.30	-	-
Curve	(1)	(2)	(3)	(4)

Fig.3

TABLE No.6

Senstivity 1/10

Senstivity 1/5

Potential (-ve) Volts	pH			
	NH_4Cl and NH_4OH		Na_2HPO_4 and $NaOH$	
	9.0	10.0	11.0	12.0
0.04	-0.35	-	-	-
0.05	-0.25	-	-0.1	-
0.08	-	-0.50	-	-0.5
0.10	+0.35	-0.10	+0.1	-0.25
0.15	+0.53	+0.40	+0.4	+0.125
0.20	+0.80	+0.70	0.70	+0.50
0.25	1.45	1.10	1.075	+0.90
0.30	2.90	1.85	2.00	+1.65
0.35	3.90	3.45	3.10	+2.85
0.40	4.05	3.90	3.85	+3.45
0.60	4.10	4.55	4.00	+3.95
0.80	4.175	4.30	4.15	4.10
1.00	4.25	4.50	4.25	4.10
1.20	4.35	4.45	4.30	4.10
1.30	4.45	-	-	-
1.35	5.00	-	-	-
1.40	5.55	4.60	4.35	4.10
1.45	6.15	5.15	-	-
1.50	6.40	5.50	5.45	-
1.55	6.70	5.95	-	-
1.60	6.90	6.30	4.60	4.10
1.70	7.10	-	4.75	4.10
1.80	-	-	-	4.20
1.90	-	-	-	4.70
Curve	(5)	(6)	(7)	(8)

Fig.3

TABLE No.7

Senstivity 1/10

Potential (-ve) Volts	pH		
	K_2 HPO$_4$ and citric acid buffer		
	Current A		
	2.0	3.0	4.0
0.00	0.65	0.50	0.50
0.05	1.65	1.00	0.90
0.10	1.85	1.55	1.50
0.15	2.25	2.30	2.40
0.20	3.30	2.90	3.10
0.25	3.95	3.10	3.35
0.30	4.30	3.20	3.40
0.35	4.40	-	-
0.40	4.40	3.30	3.65
0.60	4.75	3.30	3.65
0.80	5.20	3.50	3.75
0.90	5.40	3.65	3.85
0.95	5.50	3.95	3.95
1.00	6.15	4.60	4.30
1.05	6.90	5.45	5.05
1.10	7.65	5.70	5.25
1.15	7.80	6.10	5.40
1.20	8.05	6.25	5.60
1.25	8.55	6.50	5.80
1.30	9.00	6.75	6.00
1.35	-	6.90	6.15
1.40	-	7.60	6.45
1.45	-	-	6.90
Curve	(1)	(2)	(3)

Fig.4

TABLE No.8

Current voltage data of the mixture containing 8.0x10^{-4} M 8-hydroxy quinoline 5-sulphonic acid, 0.04M potassium chloride and 8.0x10^{-5}M , Mircuric chloride at various pH Values.

Sensitivity 1/10

Potential (-ve)volts	pH				
	Sodium acetate and hydrochloric acid				
	Current A				
	1	2	3	4	5
0.00	0.55	0.55	0.45	0.45	0.40
0.05	0.65	0.70	0.55	0.50	0.55
0.10	0.80	0.80	0.60	0.55	0.65
0.15	0.90	0.90	0.65	0.75	0.70
0.20	0.90	-	0.65	0.75	0.80
0.30	1.00	-	0.75	0.80	0.80
0.40	-	1.10	-	-	-
0.50	1.10	-	0.77	-	-
0.60	-	1.20	-	0.90	0.95
0.70	-	-	-	-	-
0.80	1.30	1.35	0.90	1.00	1.10
0.90	1.55	1.50	1.00	1.10	-
0.95	2.30	2.00	1.35	-	-
1.00	3.65	2.95	2.15	1.65	1.30
1.05	4.55	3.95	2.90	2.40	1.40
1.10	5.20	4.55	3.35	2.85	2.10
1.15	5.45	4.75	3.65	3.05	2.75
1.20	5.80	4.90	3.85	3.20	2.95
1.25	6.70	5.20	4.15	3.50	3.00
1.30	8.20	5.05	4.30	3.80	3.15
1.35	11.15	6.50	5.50	-	3.30
1.40	-	8.50	5.10	4.05	3.55
1.45	-	11.75	5.40	4.25	3.70
1.50	-	-	7.90	4.50	3.80
1.55	-	-	12.45	5.45	4.00
1.60	-	-	-	8.90	4.65
1.65	-	-	-	-	5.65
1.70	-	-	-	-	7.25
Curve	(1)	(2)	(3)	(4)	(5)

Fig.2

TABLE No.9

Senstivity 1/5

Potential (-ve) Volts	pH		
	Dipotassium hydrogen phosphate and sodium hydroxide.		
	Current A		
	6.0	7.0	8.0
0.00	0.45	0.15	0.10
0.05	0.60	0.30	0.15
0.10	0.90	0.10	0.60
0.15	1.10	1.75	1.45
0.20	1.15	2.05	1.85
0.25	1.25	2.20	2.00
0.30	1.25	2.35	2.10
0.35	1.30	-	-
0.40	1.35	2.40	2.25
0.50	-	-	-
0.60	1.55	2.70	2.55
0.70	-	-	2.80
0.80	1.75	2.75	3.05
0.90	-	-	3.45
1.00	2.00	3.90	3.65
1.10	2.25	4.10	3.80
1.15	3.00	4.30	-
1.20	4.35	4.40	4.00
125	5.10	5.60	4.30
1.30	5.30	6.70	5.65
1.35	5.40	7.00	6.55
1.40	5.45	7.15	7.35
1.45	5.75	7.25	7.40
1.50	6.30	7.40	7.05
1.55	7.00	-	7.75
1.60	9.65	9.20	-
1.70	-	10.50	-
Curve	(6)	(7)	(8)

Fig.2

TABLE No.10

Senstivity 1/5

Potential (-ve) Volts	pH			
	Borax Buffer			
	Current A			
	9	10	11	12
0.00	0.15	0.05	-0.05	-
0.05	0.25	0.10	+0.15	-0.45
0.10	0.30	0.25	+0.25	-0.15
0.15	0.95	0.60	0.65	+0.20
0.20	1.40	0.90	0.95	+0.70
0.25	1.60	1.05	1.15	-
0.30	1.70	1.10	1.25	1.00
0.40	1.75	1.20	1.35	1.15
0.50	2.05	1.30	-	-
0.55	3.20	1.35	-	-
0.60	5.10	1.40	1.55	1.30
0.65	5.90	1.40	-	-
0.70	6.00	1.50	-	-
0.80	6.15	1.65	1.65	1.50
0.90	-	1.85	-	1.55
1.00	6.60	1.95	2.20	1.65
1.10	6.90	2.20	-	-
1.20	7.00	2.20	2.35	2.20
1.30	7.05	2.25	-	-
1.35	7.30	2.35	-	-
1.40	8.05	2.85	2.75	2.25
1.45	9.45	4.10	2.85	-
1.50	9.60	4.55	4.05	2.25
1.55	9.75	-	4.70	-
1.60	10.25	4.90	4.80	2.35
1.65	-	5.15	-	-
1.70	-	6.15	5.90	2.50
1.75	-	6.50	5.90	-
180	-	6.85	-	3.00
1.85	-	7.20	-	4.80
Curve	(9)	(10)	(11)	(12)

Fig.2

TABLE No.11

Senstivity 1/10

Potential (-ve)volts	pH			
	KCl and HCl		K_2HPO_4 and HCl	
	1.0	2.0	3.0	4.0
0.00	2.75	2.90	2.95	2.25
0.05	2.95	3.00	3.25	2.85
0.10	3.10	3.10	3.50	3.00
0.15	3.20	3.15	3.65	2.95
0.20	3.25	3.25	3.75	3.10
0.25	3.25	3.25	-	-
0.30	3.25	3.35	3.80	3.05
0.40	3.35	3.35	3.90	3.30
0.60	3.45	3.45	4.05	3.35
0.80	3.60	3.60	4.30	3.55
0.90	3.85	3.95	4.55	-
1.00	5.75	5.60	5.90	3.85
1.05	6.90	6.35	6.70	4.20
1.10	7.65	6.70	7.05	4.85
1.15	8.20	7.00	7.30	5.20
1.20	8.35	7.55	7.65	5.40
125	8.85	7.80	-	-
1.30	10.40	8.55	8.30	5.60
1.40	-	-	-	5.90
1.50	-	-	-	6.25
Curve	(9)	(10)	(11)	(12)

Fig.3

TABLE No.12

Senstivity 1/10

Potential volts	pH Na_2HPO_4 and citric acid 5.0	 6.0	 7.0	 8.0
0.00	2.75	2.10	1.95	1.75
0.05	2.90	2.25	2.00	1.90
0.10	3.10	2.40	2.15	2.00
0.15	3.25	2.60	2.35	2.30
0.20	3.40	2.70	2.50	2.50
0.30	3.55	2.85	2.60	2.60
0.40	3.60	2.95	2.70	2.60
0.60	3.70	3.10	2.85	2.80
0.80	3.95	3.30	3.05	2.95
1.00	4.20	3.50	3.25	3.30
1.05	4.35	3.50	3.30	-
1.10	4.90	3.60	3.30	3.25
1.15	5.60	3.95	-	-
1.20	5.95	4.60	3.30	3.30
1.30	6.20	4.95	4.05	3.60
1.40	6.40	4.90	4.60	4.35
1.50	6.70	5.35	4.60	4.65
1.60	8.10	6.35	5.20	5.30
1.70	-	6.55	6.90	5.80
Curve	(13)	(14)	(4)	(5)
	Fig.3		Fig.4	

TABLE No.13

Senstivity 1/10

Potential (-ve) Volts	pH			
	NH_4Cl and NH_4OH		Na_2HPO_4 and $NaOH$	
	9.0	10.0	11.0	12.0
0.00	-0.40	-	0.35	-0.25
0.05	+1.25	1.45	0.45	-0.45
0.10	1.55	2.90	0.45	+0.05
0.15	1.80	3.10	0.45	0.15
0.20	1.90	3.30	0.20	0.35
0.30	2.05	3.40	0.50	0.45
0.40	2.10	3.40	0.70	0.55
0.60	2.20	3.60	1.40	0.65
0.80	2.50	3.85	1.55	0.80
1.00	2.75	3.95	1.75	0.95
1.20	2.80	4.10	1.80	1.10
1.30	3.10	4.10	1.80	-
1.35	4.20	4.55	-	-
1.40	5.00	5.45	2.10	1.15
1.45	5.80	6.00	2.60	-
1.50	6.25	6.75	2.80	-
1.55	6.30	7.00	2.80	-
1.60	6.30	7.00	3.00	1.20
1.70	6.30	-	3.40	-
1.80	6.70	-	3.70	1.20
1.85	-	-	3.90	1.70
1.90	-	-	4.20	2.25
1.95	-	-	4.90	3.60
2.00	-	-	-	6.75
Curve	(6)	(7)	(8)	(9)

Fig.4

TABLE No.14

Senstivity 1/10

Potential (-ve) volts	pH		
	K_2HPO_4 and citric acid buffer		
	Current A		
	2.0	3.0	4.0
0.00	2.65	2.75	2.60
0.05	2.75	2.80	2.75
0.10	2.85	2.90	2.85
0.15	0.90	2.95	2.95
0.20	2.95	3.05	3.05
0.25	2.95	-	3.20
0.30	2.95	3.10	3.20
0.40	2.95	3.10	3.25
0.60	3.00	3.15	3.30
0.80	3.15	3.25	3.45
0.90	3.20	3.35	3.60
1.00	3.85	4.20	4.10
1.05	4.95	4.90	4.95
1.10	5.75	5.40	5.15
1.15	6.10	5.75	5.30
1.20	6.45	6.00	5.55
1.25	7.05	6.35	5.80
1.30	7.45	6.75	6.10
1.35	-	7.10	6.30
1.40	-	8.0	6.60
1.45	-	-	6.90
150	-	-	7.55
Curve	(10)	(11)	(12).

Fig.4

In order to study the effect of the concentration of the reactants on the reduction waves, the following three sets of solutions were prepared.

Set I

Five solutions containing increasing amounts of 1.0, 2.0, 3.0, 4.0 and 5.0 c.c. of 0.02M, 8-hydroxy quinoline 5-sulphonic acid, 1.0, 2.0, 3.0, 4.0 and 5.0 c.c. of 0.02M hexacyanoferrate (II) 1.0 c.c. 1M potassium chloride and 2.0 c.c. 10^{-3}M mercuric chloride and 27.0 c.c. buffer of pH 8.0 in total 40.0 c.c. of the volume.

Set II

Contained 5 solutions containing increasing amounts 1.0, 2.0, 3.0, 4.0 and 5.0 c.c. of 0.02M 8-hydroxy quinoline 5-sulphonic acid, 1.0 c.c. 1M potassium chloride, 2.0 c.c. of 10^{-3}M mercuric chloride, 27.0 c.c. of buffer. Total volume was made again 40.0 c.c. at pH 7.0.

Set III

12 solutions 1 to 6 containing fixed 3.0 c.c. of 0.02M hexacyanoferrate (II), 1.0 c.c. of 1.0M potassium chloride, 2.0 c.c. of 10^{-3}M mercuric chloride, 28 c.c. of buffer of pH 7.0 and increasing amounts, 1.0, 2.0, 3.0, 4.0 ~~xx~~ 5.0 and 6.0 c.c. of 8-hydroxy quinoline 5-sulphonic acid in total 40.0 c.c. volume. Solutions 7 to 12 contained fixed amount of 8-hydroxy quinoline 5-sulphonic acid and varying amounts of

hexacyanoferrate (II).

Exactly similar type of sets were prepared in potassium hydrogen phosphate and sodium hydroxide buffer of pH 7.0.

TABLE No.15

Current voltage data of the solutions containing increasing amounts (5.0, 10.0, 15.0,&20.0 and 25.0x10^{-4}M) of each of the reactants, 0.025M potassium chloride, 5.0x10^{-5}M mercuric chloride at pH 8.0 in dipotassium hydrogen phosphate and sodium hydroxide buffer.

Senstivity = 1/10

Potential (-ve) volts	Current A					
	Solution Nos.					Buffer only
	1	2	3	4	5	
0.00	-0.1	-0.15	-0.20	-0.20	-0.25	+0.15
0.05	-0.5	-0.1	-0.10	-0.15	-0.10	+0.40
0.10	+0.15	+0.05	+0.05	+0.05	+0.0	+0.50
0.15	+0.40	+0.30	+0.25	+0.35	0.35	+0.60
0.20	+0.80	+0.70	+0.65	+0.70	0.70	+0.60
0.25	+1.65	+1.55	+1.40	+1.45	1.45	-
0.30	+2.14	2.20	+2.10	+2.25	2.30	-
0.35	+2.45	2.40	+2.30	+2.55	2.50	-
0.40	+2.50	2.45	2.40	+2.55	2.60	0.75
0.60	2.60	2.50	2.50	+2.65	2.75	0.85
0.80	2.65	2.65	2.70	+2.85	2.85	1.00
1.00	2.80	2.75	2.85	+2.95	3.00	1.20
1.10	3.10	3.00	3.20	+3.40	3.85	-
1.15	-	3.55	3.95	4.55	5.00	-
1.20	3.30	3.80	4.70	5.40	6.05	1.35
1.25	3.30	3.95	4.85	5.90	6.70	-
1.30	3.35	4.20	5.00	6.00	6.90	-
1.35	3.40	4.45	5.15	6.20	7.20	-
1.40	3.55	4.65	5.85	6.40	7.35	-
1.45	3.70	4.80	-	6.65	7.50	1.35
1.50	3.80	4.85	6.00	7.00	-	1.35
1.55	3.90	5.20	-	-	-	-
1.60	4.15	5.50	-	-	-	1.60
1.65	4.55	-	-	-	-	-
1.70	4.75	-	-	-	-	2.00
1.80	5.40	-	-	-	-	-
1.85	6.05	-	-	-	-	3.10
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig.5

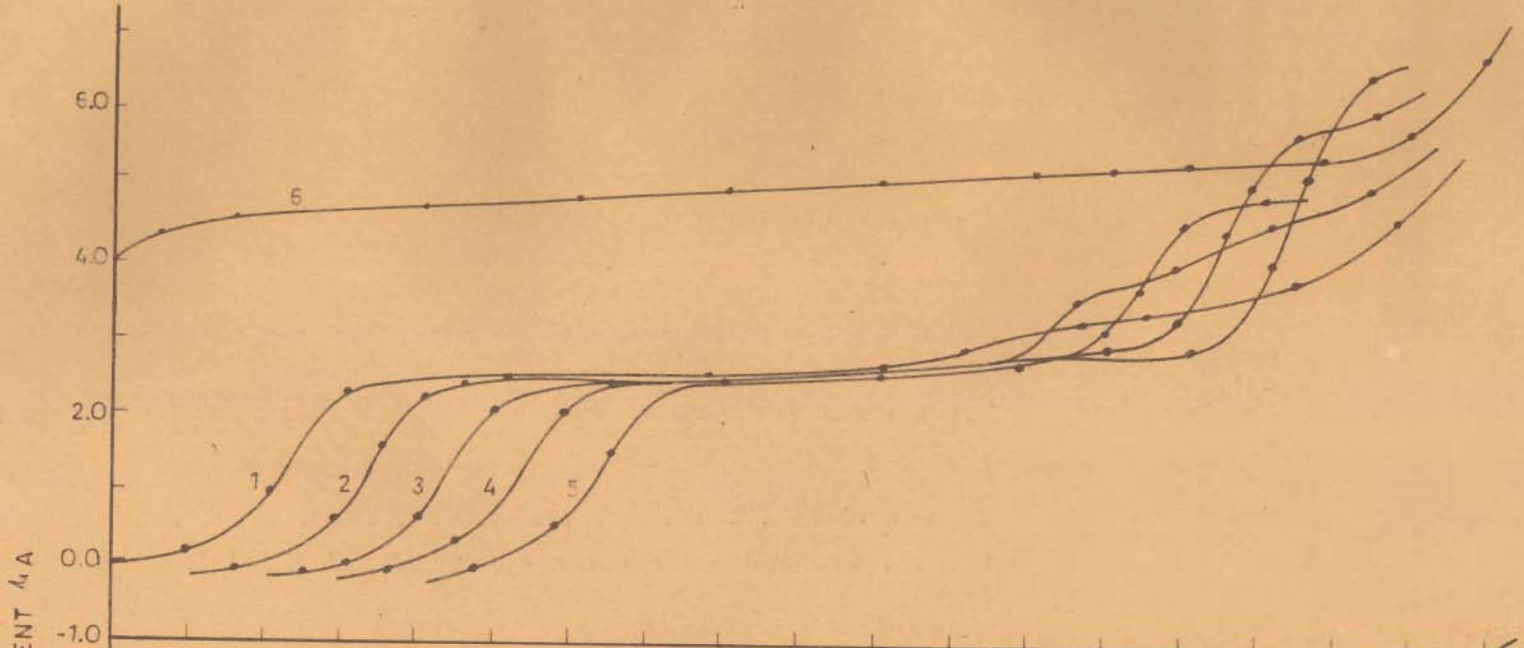


FIGURE 5

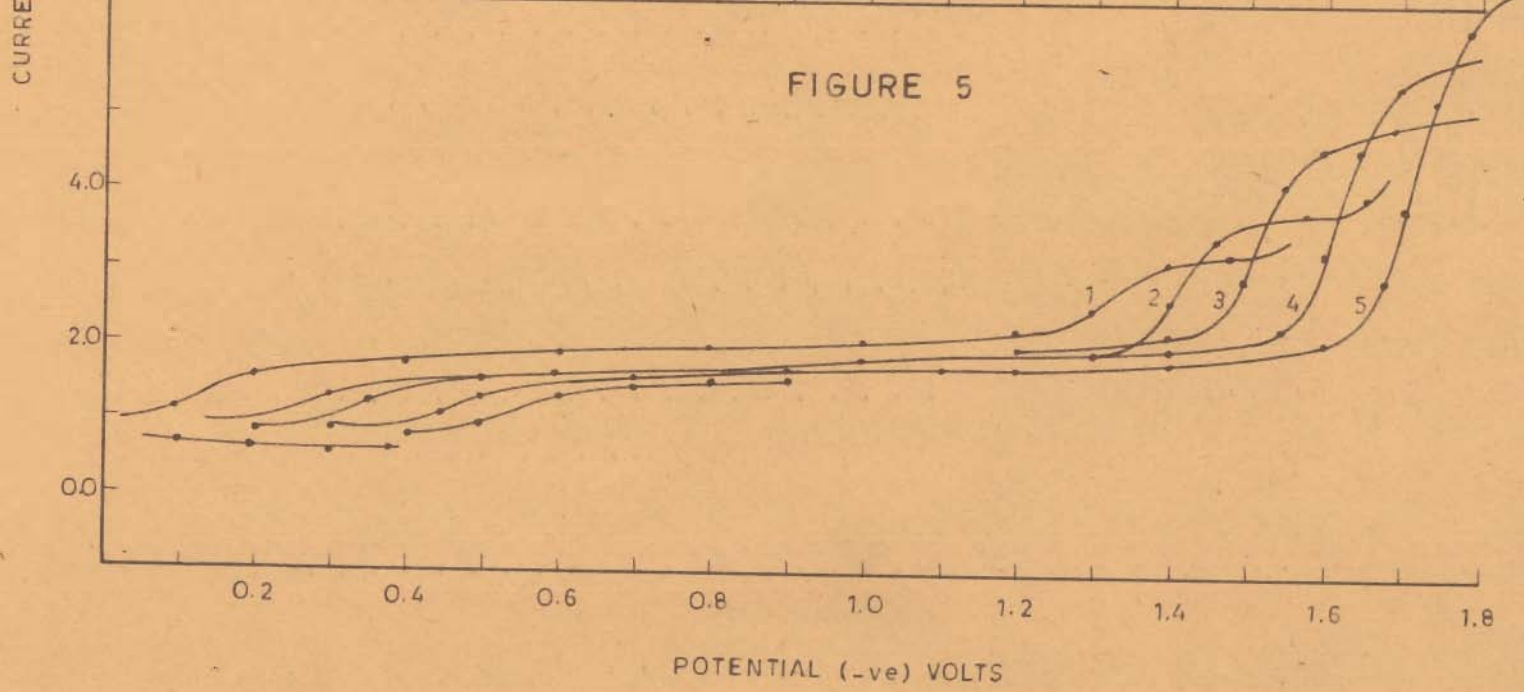


FIGURE 6

TABLE No.16

Current voltage data of the solutions containing increasing amounts (5.0, 10.0, 15.0, 20.0 and 25.0×10^{-4}M) of 8-hydroxy quinoline 5-sulphonic acid 0.025M potassium chloride and 5.0×10^{-5}M mercuric chloride at pH 8.0 in dipotassium hydrogen phosphate and sodium hydroxide buffer.

Senstivity 1/10

Potential (-ve)volts	Current A				
	Solution Nos.				
	1	2	3	4	5
0.0	0.90	0.90	0.90	0.85	0.90
0.05	1.00	0.90	0.90	0.90	0.90
0.10	1.1	1.00	1.00	0.90	0.90
0.15	1.40	1.35	1.25	1.10	1.15
0.20	1.55	1.50	1.45	1.40	1.40
0.40	1.75	1.50	1.45	1.55	1.45
0.60	1.85	1.60	1.55	1.55	1.60
0.80	1.95	1.70	1.65	1.70	1.75
1.00	2.10	1.85	1.85	1.95	1.95
1.20	2.20	1.95	2.15	2.05	2.05
1.25	2.25	2.00	2.25	2.25	2.35
1.30	2.60	2.65	3.25	3,35	2.80
1.35	3.10	3.40	4.35	4.70	5.30
1.40	3.25	3.65	4.65	5.54	6.30
1.45	-	3.85	4.85	5.75	6.70
1.50	-	3.85	4.95	5.85	6.80
1.55	-	-	-	6.25	7.00
Curve	(1)	(2)	(3)	(4)	(5)

Fig.6

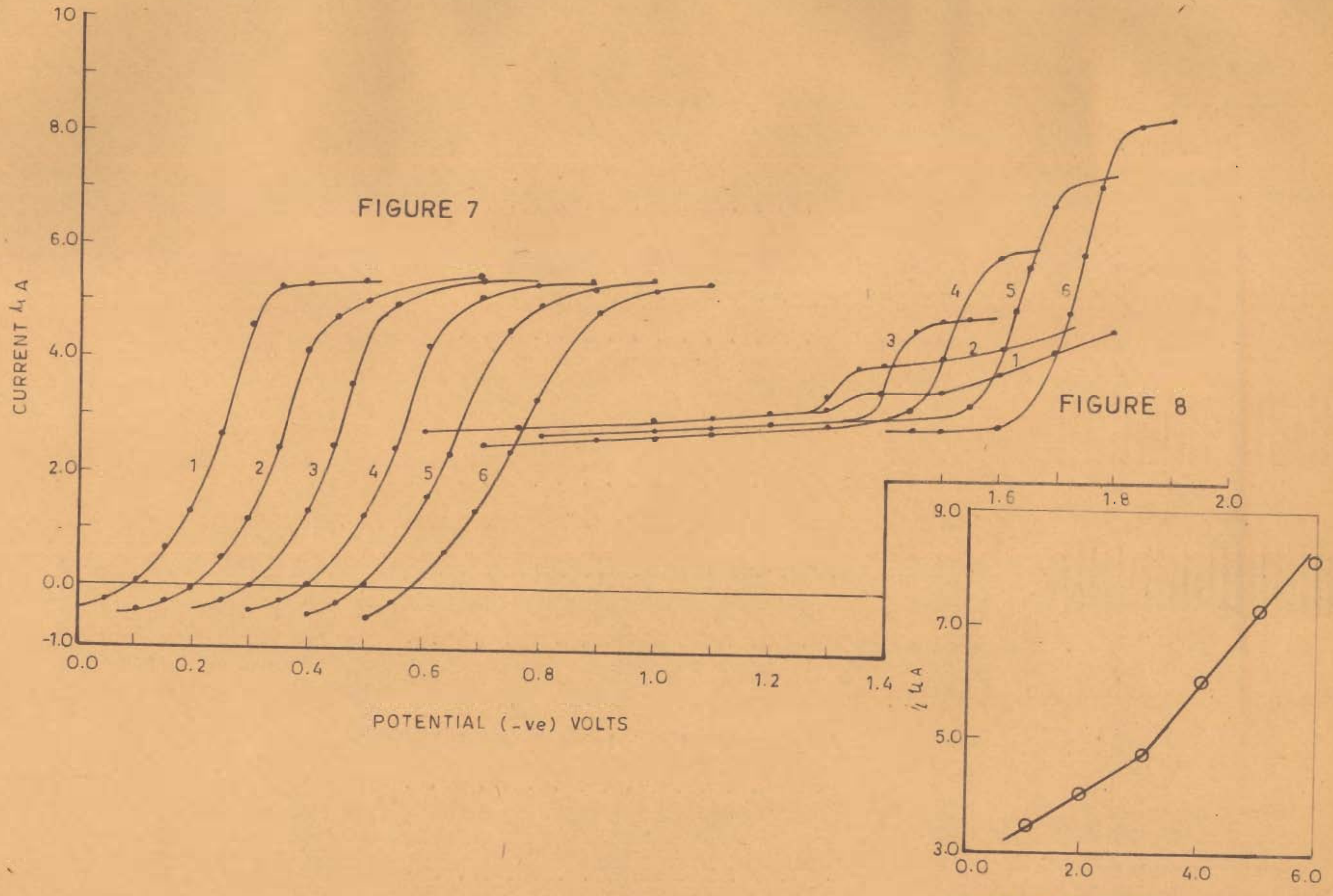


FIGURE 7

FIGURE 8

VOLUME OF 8-HYDROXY QUINOLINE 5-SULPHONIC ACID ml

LIMITING CURRENT (i) HAS BEEN MEASURED AT 1.4 V. FOR EACH CURVE (FIG. 8)

FIGURE 9

TABLE No.17

Current voltage data of the solutions containing 15.0x10^{-5}M hexacyanoferrate (II); increasing amounts (5.0, 10.0, 15.0, 20.0, 25.0, 30.0x10^{-4}M) of 8-hydroxyquinoline 5-sulphonic acid, 0.025M potassium chloride and 5.0x10^{-5}M mercuric chloride at pH 8.0 in dipotassium hydrogen phosphate and sodium hydroxide buffer:

Senstivity 1/5

Potential (-ve) volts	Current A					
	Solution Nos.					
	1	2	3	4	5	6
0.0	-0.45	-0.45	-0.45	-0.45	-0.45	-0.45
0.05	-0.25	-0.25	-0.25	-0.25	-0.25	-0.25
0.10	+0.10	-0.05	-0.05	0.00	0.00	+0.10
0.15	+0.70	+0.50	+0.50	+0.50	+0.50	+0.60
0.20	+1.30	+1.15	+1.15	+1.25	+1.25	+1.30
0.25	+2.65	+2.40	+2.45	+2.55	+2.45	+2.50
0.30	+4.60	+4.15	+4.15	+4.40	+4.25	+4.30
0.35	-	+4.70	+4.90	+5.00	+4.85	+4.85
0.40	+5.25	+5.00	+5.15	+5.15	+4.95	+5.10
0.50	+5.35	+5.30	+5.30	+5.25	+5.30	+5.25
0.60	+5.45	+5.35	+5.40	+5.35	5.40	5.40
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig.7

Senstivity 1/10

0.60	2.75	2.75	2.50	2.70	2.75	-
0.80	2.80	2.80	2.65	2.80	2.95	-
1.00	2.95	2.95	2.80	3.00	3.00	-
1.10	3.05	2.10	2.90	3.00	3.10	2.90
1.20	3.10	3.15	3.00	3.10	3.25	2.95
1.30	3.20	3.40	3.70	4.10	4.30	4.30
1.35	3.50	3.95	4.60	5.30	6.70	6.00
1.40	3.50	4.00	4.80	6.00	7.20	8.10
1.50	3.60	4.10	4.90	6.10	7.25	8.30
1.60	3.90	4.30	5.10	6.15	7.50	8.40
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig.8

TABLE No.18

Current voltage data of the solutions containing 15.0x10^{-4}M 8-hydroxyquinoline 5-sulphonic acid increasing amounts (5.0, 10.0, 15.0, 20.0, 25.0 and 30.0x10^{-4}M) of hexacyanoferrate (II), 0.025M potassium chloride and 5.0x10^{-5}M mercuric chloride at pH 8.0 in dipotassium hydrogen phosphate and sodium hydroxide buffer.

Senstivity 1/5

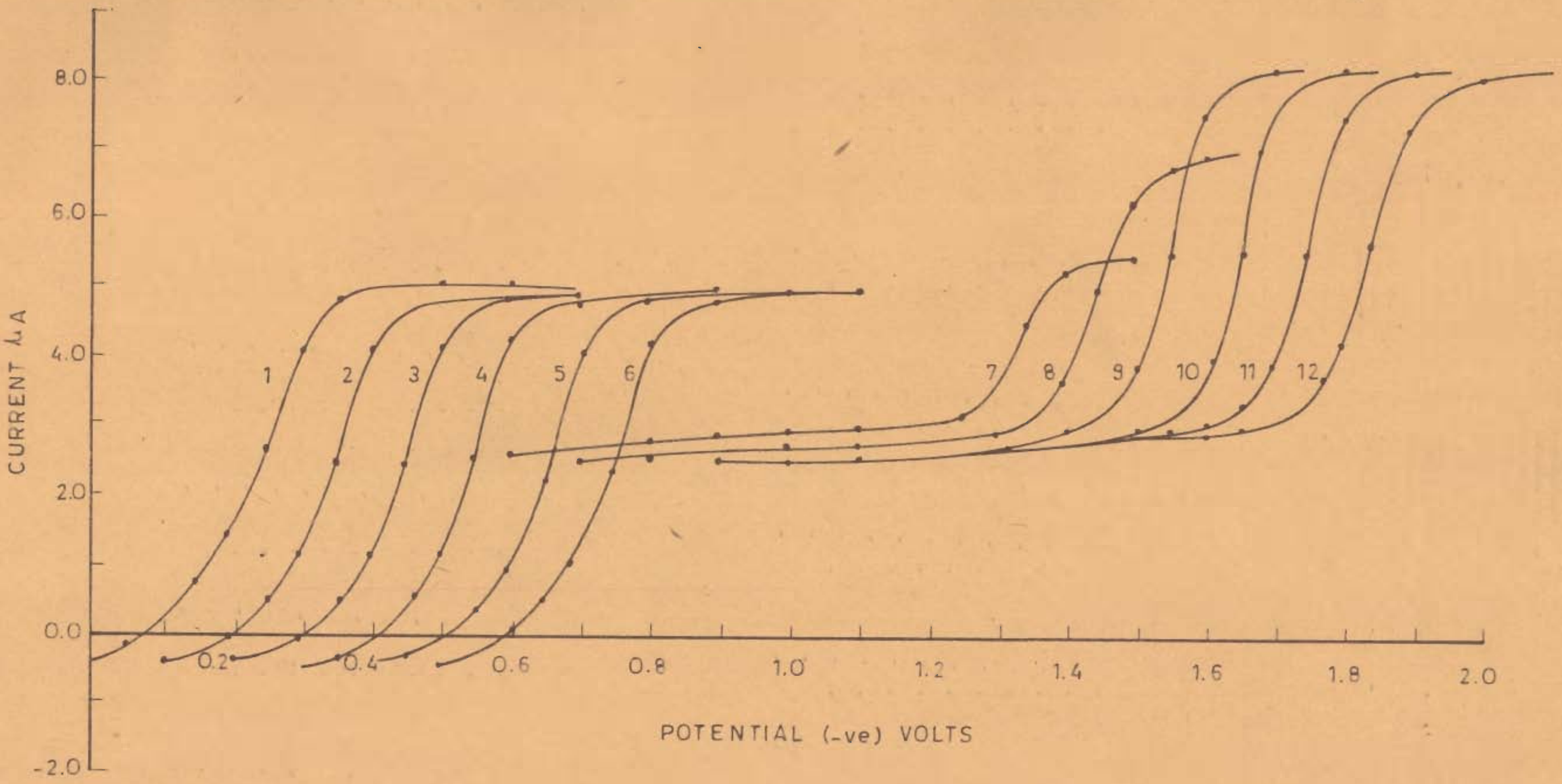
Potential (-ve) volts	Current A					
	Solution Nos.					
	1	2	3	4	5	6
0.00	-0.45	-0.45	-0.40	-0.45	-0.45	-0.45
0.05	-0.15	-0.25	-0.25	-0.25	-0.35	-0.35
0.10	+0.10	0.05	-0.10	-0.10	-0.10	-0.5
0.15	+0.70	+0.50	+0.50	+0.50	+0.35	+0.45
0.20	+1.35	+1.10	+1.15	+1.15	+0.90	+1.05
0.25	2.65	+2.40	+2.45	2.50	+2.30	+2.45
0.30	4.30	4.10	4.10	4.25	+4.00	+4.20
0.35	4.80	4.60	4.65	4.70	+4.75	+4.75
0.40	5.00	4.90	4.90	4.85	+4.85	+4.85
0.60	5.15	4.95	5.0	5.0	+5.00	+5.00
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig.10

Senstivity 1/10

0.60	2.60	2.50	2.40	2.40	2.40	2.40
0.80	2.75	2.65	2.50	2.50	2.50	2.50
1.00	2.95	2.80	2.60	2.60	2.60	2.60
1.20	3.05	2.90	2.95	2.95	2.95	2.95
1.25	3.10	-	-	-	-	-
1.30	3.60	3.60	3.80	3.80	3.80	3.80
1.35	4.60	5.00	5.50	5.50	5.50	5.50
1.40	5.15	6.30	7.50	7.50	7.50	7.50
1.45	5.40	6.70	8.00	8.00	8.00	8.00
1.50	5.40	6.90	8.10	8.10	8.10	8.10
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig.10



8.0
6.0
4.0
2.0
0.0
-2.0
CURRENT μA
1
2
3
4
5
6
7
8
9
10
11
12
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
POTENTIAL (-ve) VOLTS

FIGURE 10

Current voltage curves of the solutions containing increasing amounts (5.0, 10.0, 15.0x10^{-4}M) each of the reactants, 0.025M potassium chloride, 5.0x10^{-5}M mercuric chloride at pH 7.0 in dipotassium hydrogen phosphate and sodium hydroxide are shown in fig.11 (Curve 1, 2 and 3 senstivity of the polarograph 1/5).

Current voltage curves of the solutions containing increasing amounts (5.0, 10.0, 15.0x10^{-4}M) 8-hydroxy-quinoline 5-sulphonic acid under above mentioned conditions are shown in fig.12 (curve 1,2 and 3 at 1/5 sensitivity)

Current voltage curves of the solutions containing (1.0x10^{-4}M) each of the reactants, 5.0x10^{-5}M mercuric chloride and increasing amounts of potassium chloride (0.00, 0.005, 0.075 and 0.015M) at pH 8.0 are shown in Fig.13 (curve 1, 2, 3 and 4 were recorded at 1/5 senstivity)

Current voltage curves inpresence of increasing amounts of potassium nitrate (0.0, 0.025, 0.075 and 0.15M, curve 5-8) Sodium sulphate (0.0, 0.0125, 0.0375 0.075M, curve 9-12) and potassium chlorate (0.0, 0.175, 0.0375 and 0.075M, curve 13 to 16) at pH 8.0 are shown in Fig.13.

Current voltage curves of the solutions containing (8.0x10^{-4}M) each of the reactants, 8.0x10^{-5}M

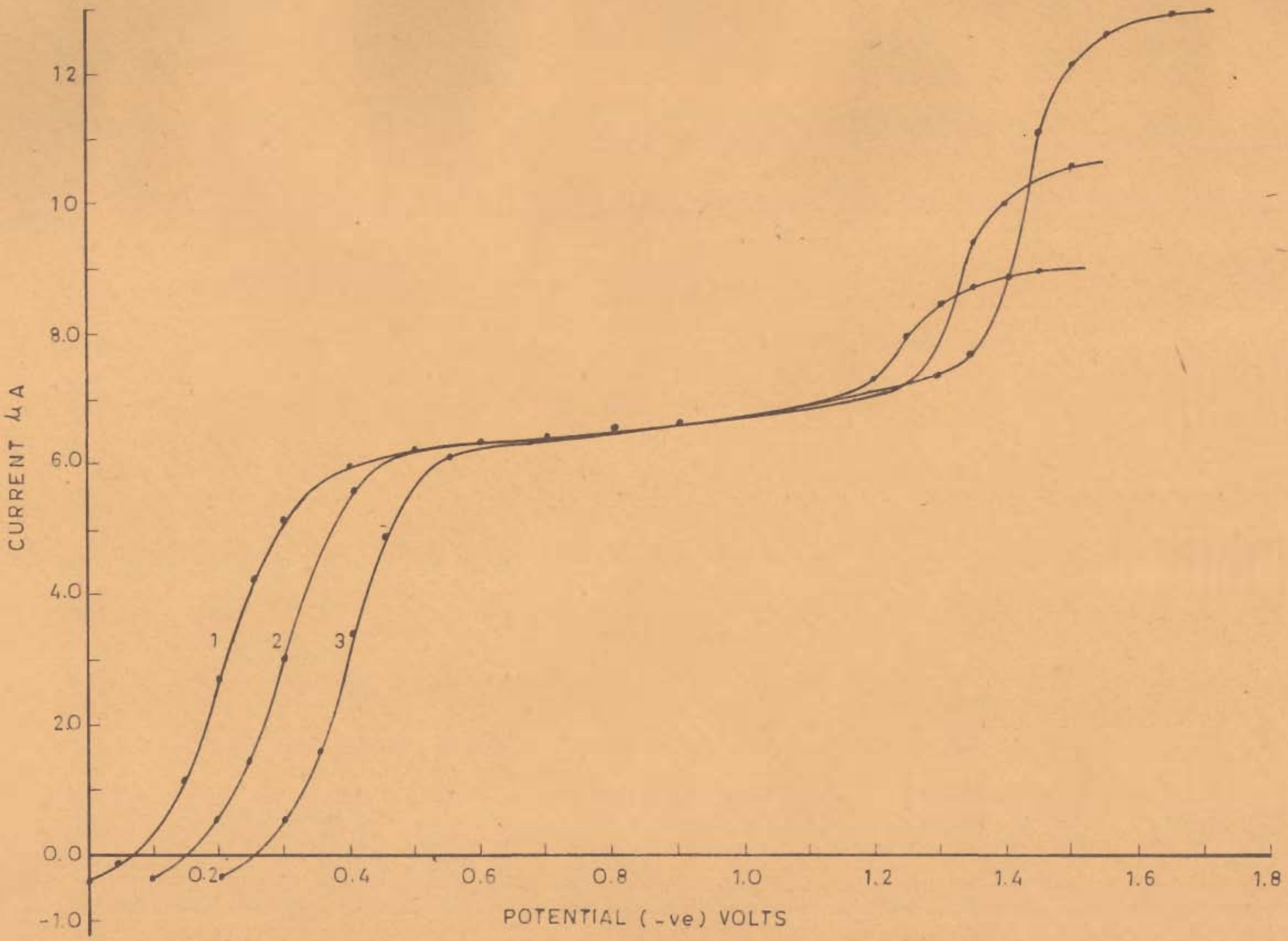
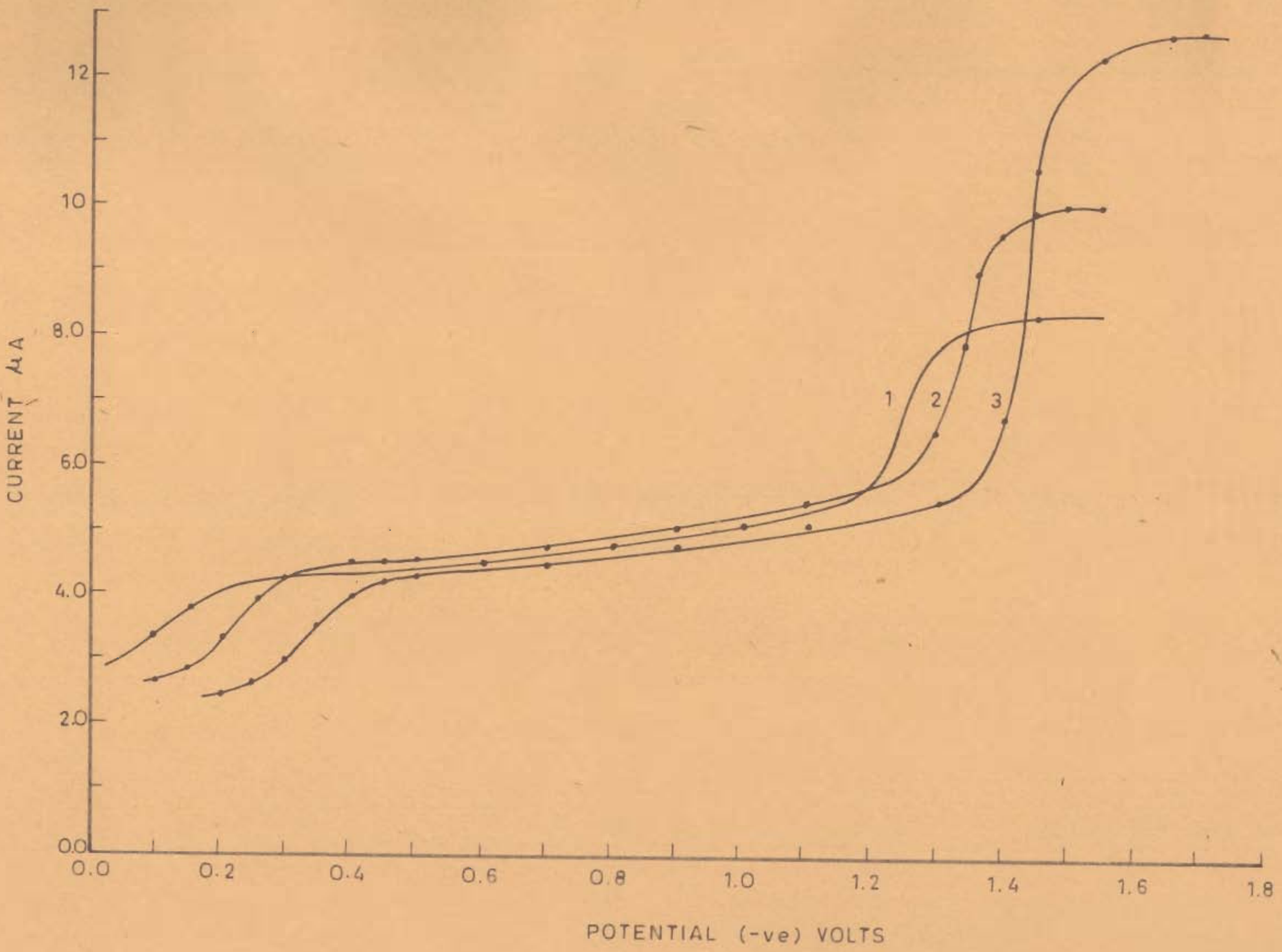

12
10
8.0
6.0
4.0
2.0
0.0
-1.0
CURRENT μA
1
2
3
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS

FIGURE 11



CURRENT μA
0.0
2.0
4.0
6.0
8.0
10
12
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 12

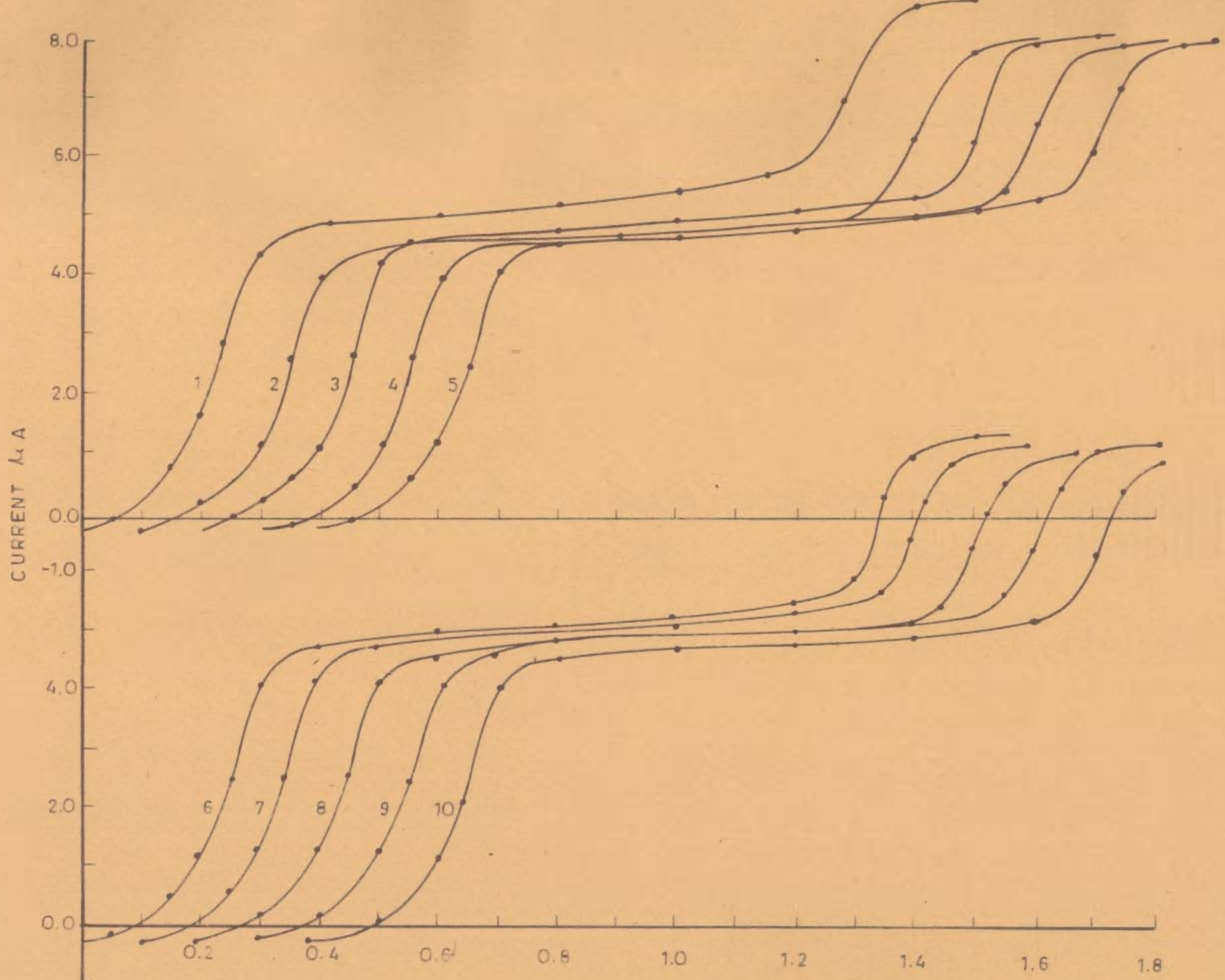

8.0
6.0
4.0
2.0
0.0
-1.0
4.0
2.0
0.0
CURRENT μA
1
2
3
4
5
6
7
8
9
10
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS

FIGURE 13

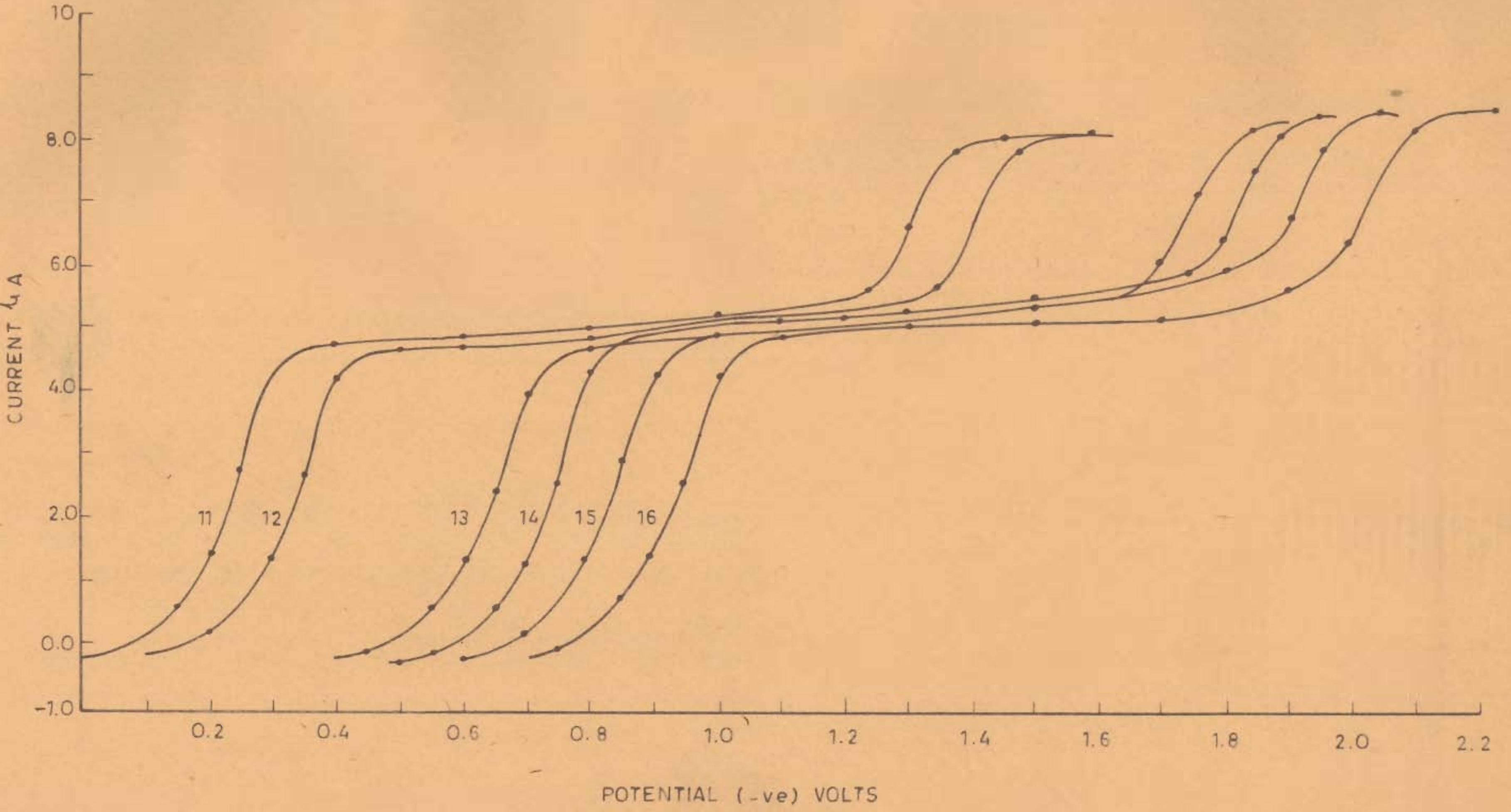

10
8.0
6.0
4.0
2.0
0.0
-1.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
POTENTIAL (-ve) VOLTS
11
12
13
14
15
16

FIGURE 13

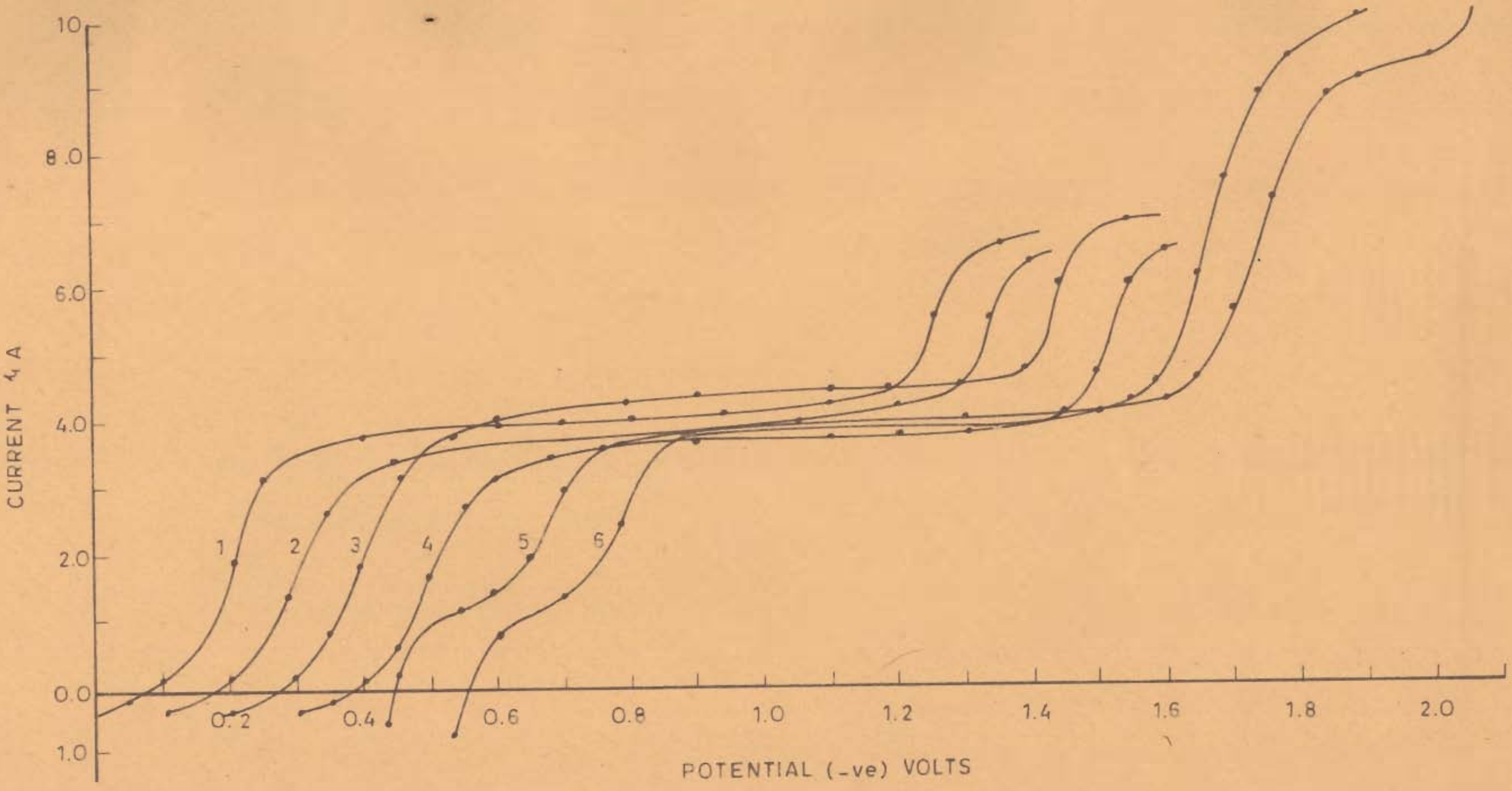

10
8.0
6.0
4.0
2.0
0.0
1.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
POTENTIAL (-ve) VOLTS
1
2
3
4
5
6

FIGURE 14

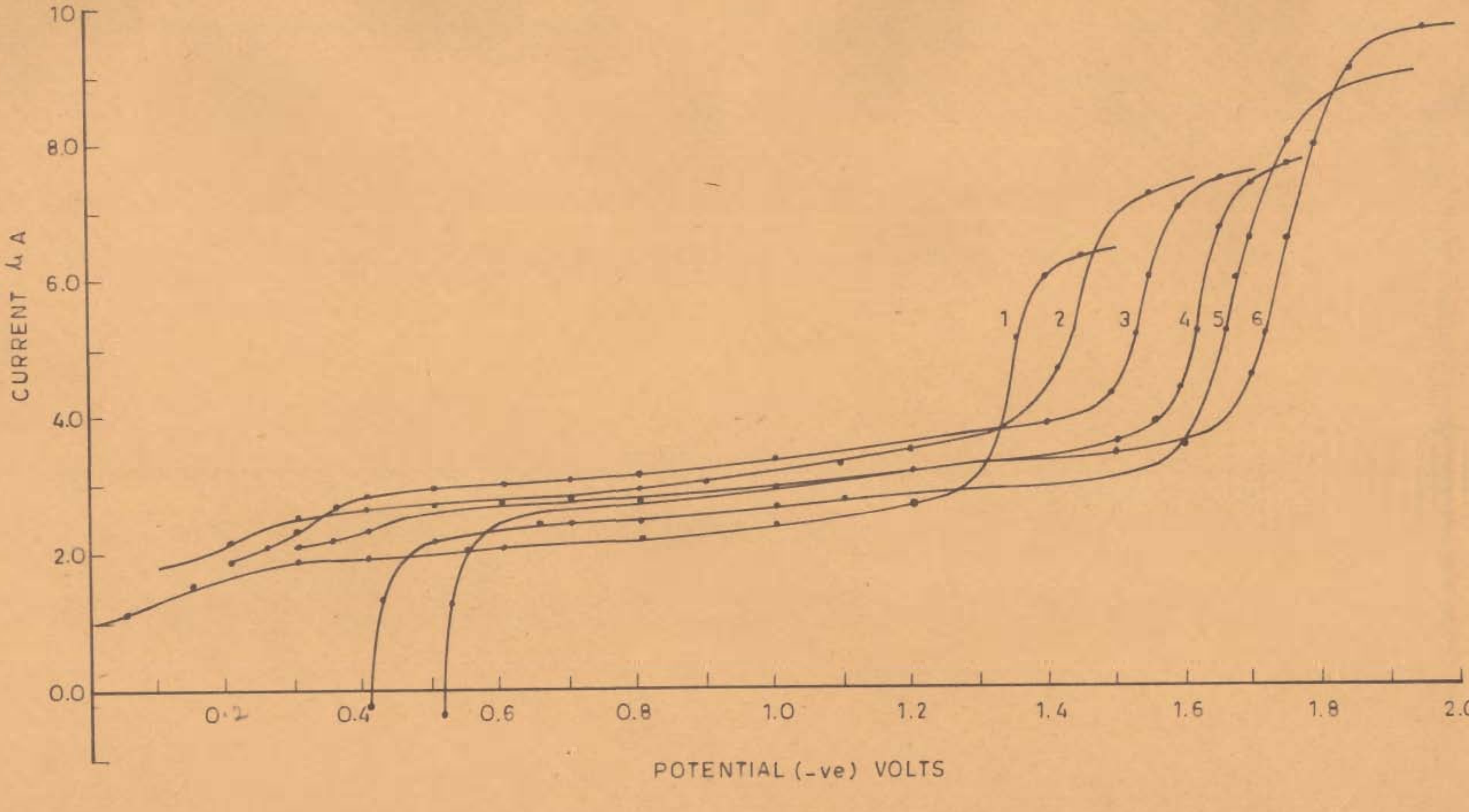

10
8.0
6.0
4.0
2.0
0.0
CURRENT µA
0·2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
POTENTIAL (-ve) VOLTS
1
2
3
4
5
6

FIGURE 15

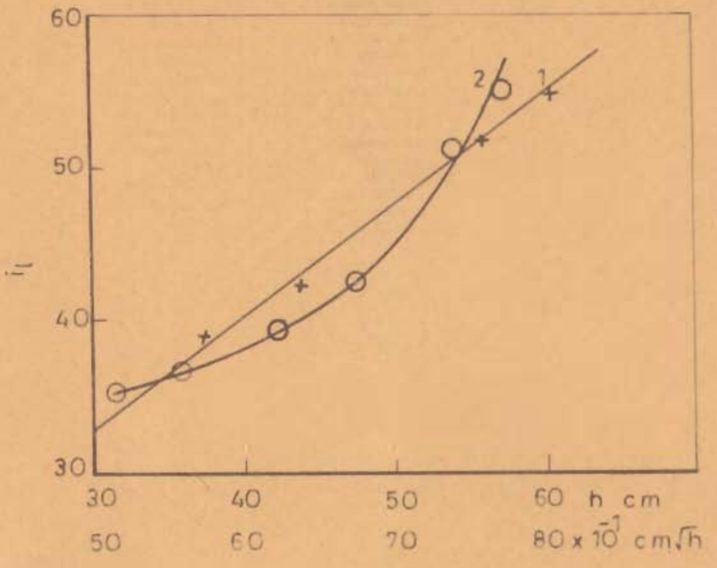
mercuric chloride and solution No.1 with-out electrolyte, 2 to 4 with (0.24M) lethium chloride, sodium chloride (each at pH 7.0) 5,6 with (0.24M), calcium chloride, barium chloride (each at pH 9.0) are shown in Fig.14 (curves 1,2,3,4,5 and 6 are recorded at 1/5 senstivity).

Current voltage curves of the above mentioned solutions (1 to 4 at pH 8.0 in K_2HPO_4 and NaOH Buffer; 5,6 at pH 10.0 in NH_4OH and NH_4Cl buffer) are shown in Fig.15 (curves 1,2,3,4,5 and 6 were recorded at 1/5 senstivity).

The effect of electrolytes at pH 8.0 on the reduction steps of hydroxy quinoline 5-sulphonate pentacyanoferrate (II) was studied by preparing 16 solutions. Each contained 2.0 c.c. of 0.02M 8-hydorxy quinoline 5-sulphonic acid, 2.0 c.c., 0.2M hexacyanoferrate (II), 28.0 c.c. buffer of pH8.0, solutions No.1 to 4,5 to 8,9 to 12 and 13 to 16 contained 0.0, 1.0, 3.0 and 6.0 c.c. of 1.0M potassium chloride, 1.0M potassium nitrate, 0.5M potassium sulphate and 0.5M potassium chlorate respectively in total 40 c.c. volume. (Fig.13).

The effect of alkali metals and alkali earth metals on the reduction steps of pentacyanoferrate (II) complex with 8-hydroxy quinoline 5-sulphonic acid was studied by preparing 12 solutions 1 to 6 contained 1.0 c.c. of 0.02M 8-hydroxy quinoline 5-sulphonic acid; 1.0 c.c. of 0.02M hexacyanoferrate (II), 1.0 c.c. of 10^{-3}M mercuric chloride. In solution No.1 3.00 c.c. water were added and in solutions 2 to 6 3.0 c.c. of electrolytes (lithium chloride, sodium chloride, potassium chloride, calcium chloride and barium chloride, potassium chlorid, each 2.0M) were added. Total volume of solution No.1 to 4 was made up to 25.0 ml by adding dipotassium hydrogen phosphate sodium hydroxide buffer of pH 7.0 and that of 5 and 6 was also made to 25.0 ml by ammonium chloride and ammonium hydroxide buffer of pH 9.0 (since with barium chloride and calcium chloride phosphate buffer gave precipitate). Solution No.7 to 10 and 11 to 12 were prepared as solutions 1 to 4 and 5 to 6 at pH 8.0 and 10.0 in the buffers mentioned above. The buffers were added in different sets of solutions after several hours of mixing the reactants. (Fig.14,15).

The nature of the electrode process was studied by the methods as recommended by Zuman (15) at pH 8.0 (in dipotassium hydrogen phosphate and sodium hydroxide buffer) for (I) and (II) steps of 8-hydroxy quinoline 5- sulphonic acid and its complex with hexacyanoferrate (II) (The electrode process of step (III) was studied at pH 9.0 in borax buffer).

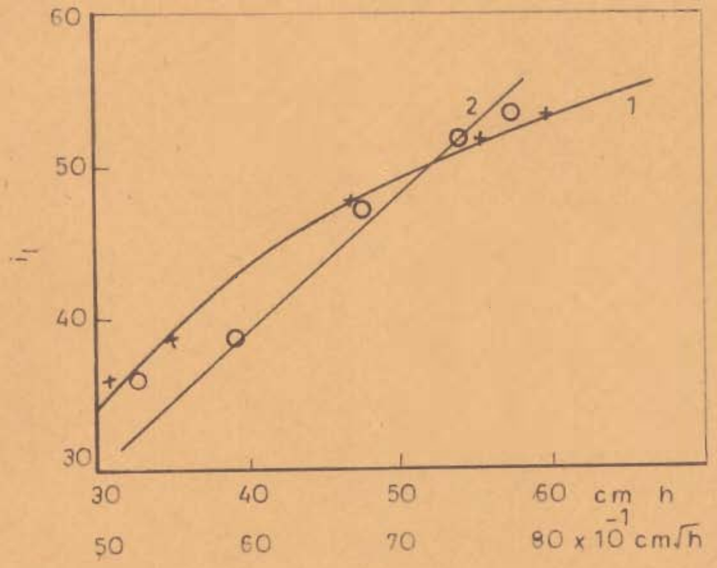


CURVE

1 _ PLOT OF h VS i_l x

2 _ PLOT OF $\sqrt{h}$ VS i_l ... ... O

FIGURE 16



CURVE

1 _ PLOT OF h VS i_l x

2 _ PLOT OF $\sqrt{h}$ VS i_l ... ... O

FIGURE 17

TABLE No.19

Limiting values the current at different heights for (I), (II) waves of the solution containing 10.0×10^{-4}M 8-hydroxyquinoline 5-sulphonic acid 5.0×10^{-5}M mercuric chloride and 0.025M potassium chloride at pH 8.0 in dipotassium hydrogen phosphate and sodium hydroxide buffer:

Height of mercury column h_{corr} in cm.	$\sqrt{h}$	Drop time in sec.		Limiting current (il) Senstivity 1/5	Senstivity 1/5	logi		logt	
		at-0.40V for II wave	AT-1.45V for I wave	at -0.40V for II wave	at -1.45V for (I) wave	For II wave	For (I) wave	For (I) wave	For (II) wave
31.0	5.25	7.85	4.85	3.5	3.60	-0.0868	0.1303	0.8949	0.6868
38.8	6.22	6.12	4.06	3.9	4.2	-0.0868	0.1139	0.7868	0.6085
45.7	6.76	5.10	3.38	4.2	4.70	-0.0868	0.0969	0.7076	0.5289
55.5	7.45	4.55	2.80	5.1	5.15	-0.0868	0.0414	0.6580	0.4427
60.0	7.74	4.0	2.51	5.5	5.30	-0.0706	0.0414	0.6021	0.3997

Fig.16 Fig.17

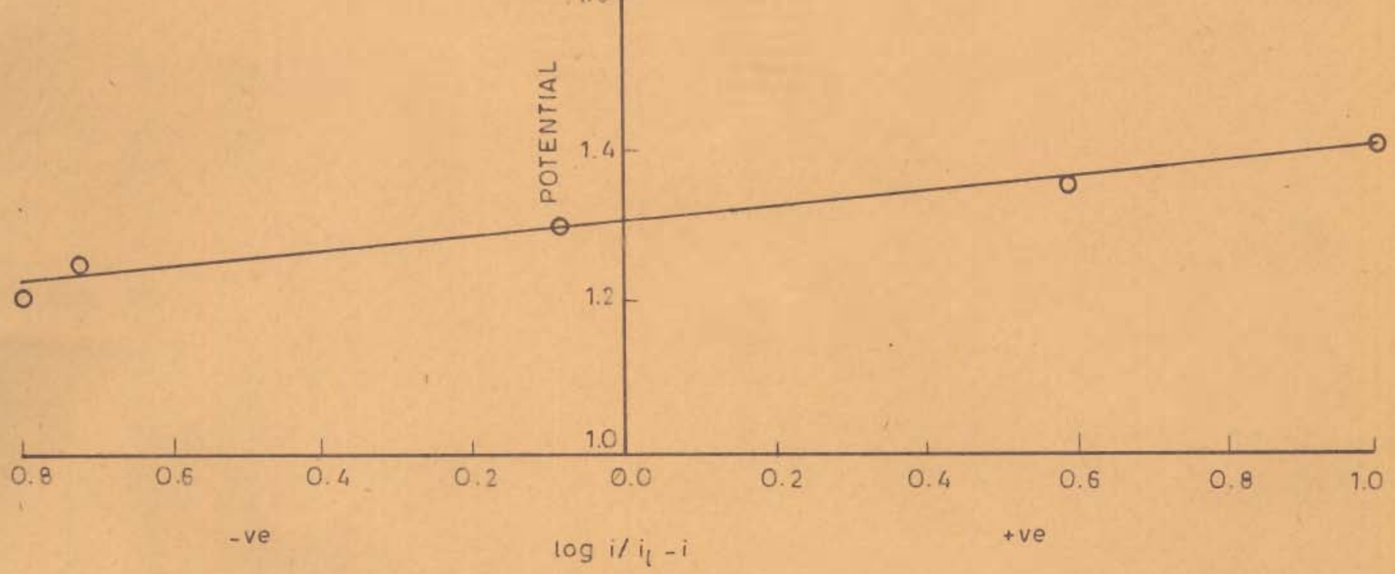
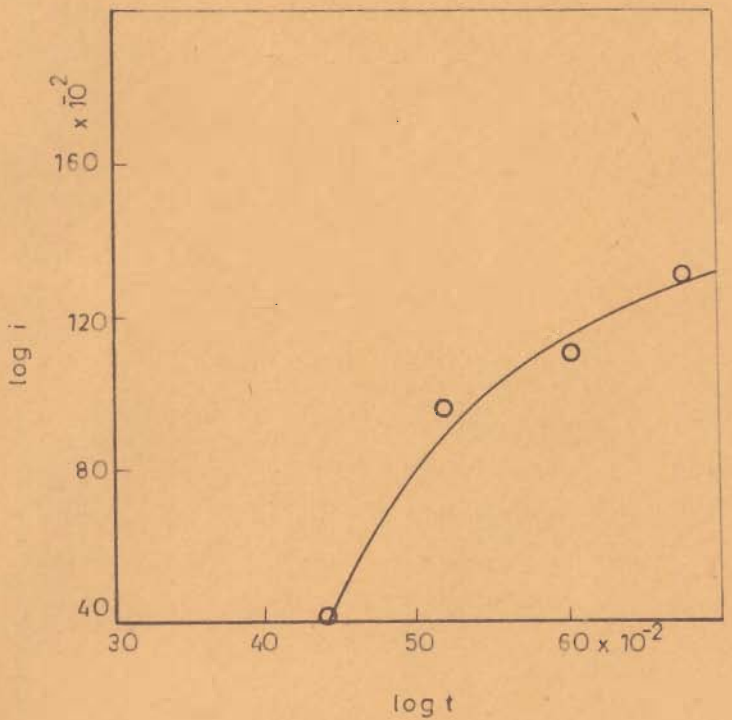


FIGURE 18



PLOT log i VS log t

FIGURE 19

TABLE No.20

Logarithmic analysis of the current voltage data for (I) wave of the solution (mentioned above in Table No.19).

Potential (-ve) volts	Current corrected for residual current senstivity 1/10	log $\frac{i}{i_1 - i}$
1.00	-	-
1.10	0.20	-1.0000
1.15	0.25	-0.8921
1.20	0.30	-0.8017
1.25	0.35	-0.7231
1.30	1.00	
1.35	1.75	-0.0792
1.40	2.00	+0.5898
1.45	2.20	+1.0000

Fig.18

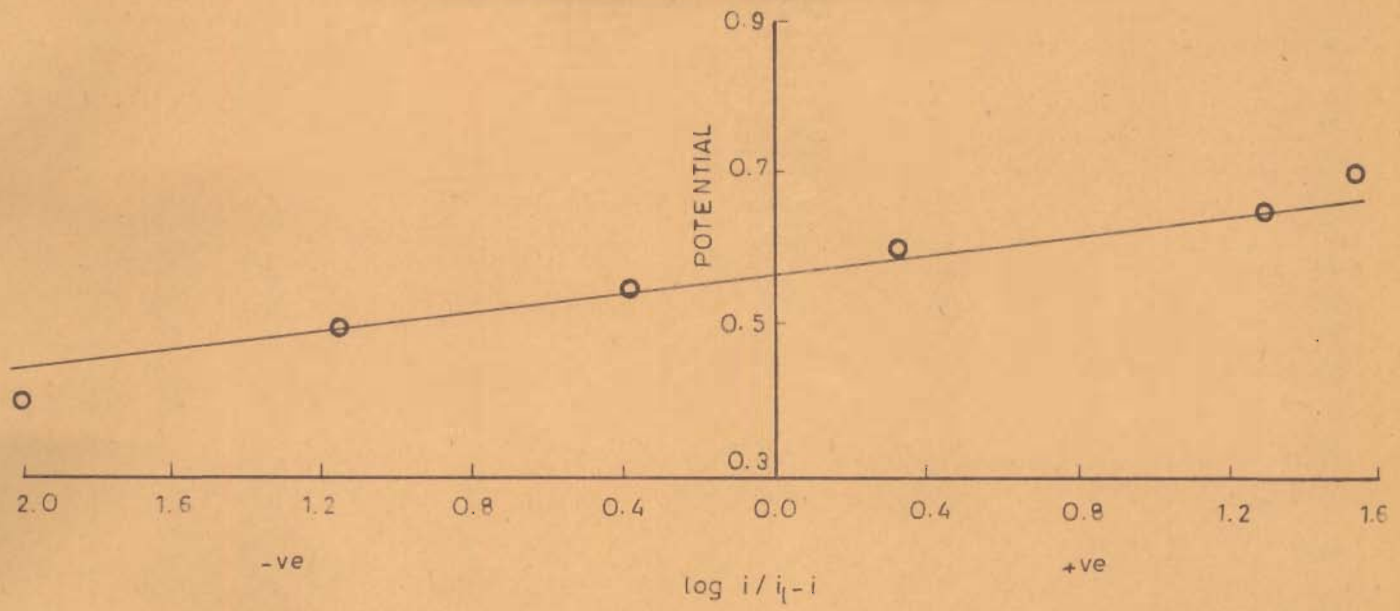
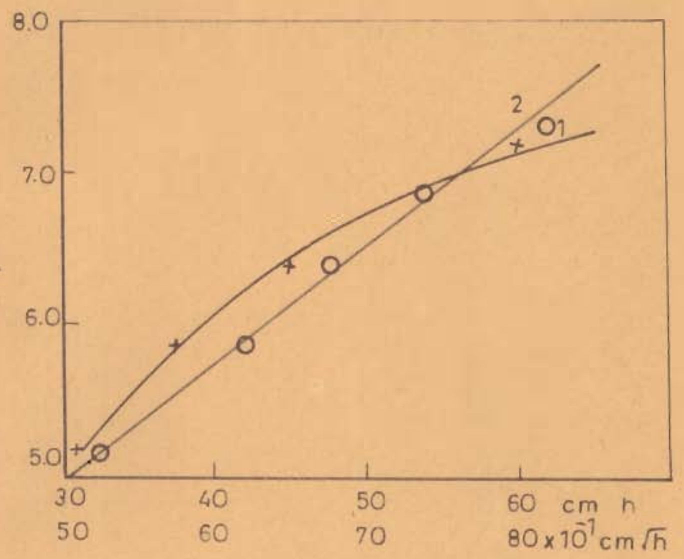


FIGURE 20



CURVE

1 _ PLOT OF h VS i_l x

2 _ PLOT OF $\sqrt{h}$ VS i_l ... ... O

FIGURE 21

TABLE No.21

Limiting values of the current at different heights for (III) wave of 8-hydroxyquinoline 5-sulphonic acid (concentration etc as mentioned in Table No.19) at pH 9.0 in borax buffer:

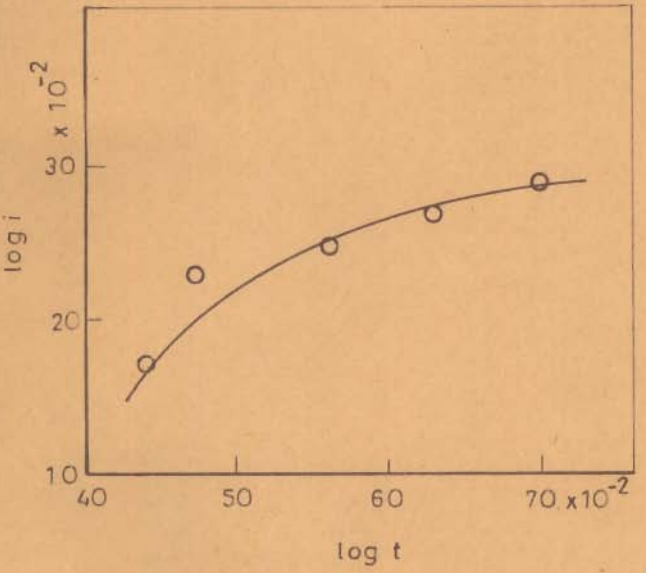
Height of mercury column	$\sqrt{h}$	Droptime in sec.	Limiting current (i_1)	logi	logt
h_{corr} in cm.		at-0.70V	at -0.70V	-	-
31.0	5.25	5.15	5.15	0.2900	0.7118
38.8	6.22	4.36	5.85	0.2788	0.6365
45.7	6.76	3.68	6.40	0.2553	0.5658
55.5	7.45	3.10	6.90	0.2304	0.4771
60.0	7.74	2.81	7.20	0.1761	0.4487

TABLE No.22

Logarithmic analysis of the current voltage data of (III) wave of 8-hydroxyquinoline 5-sulphonic acid (Concentration etc. as mentioned in Table No.19):

Potential volts (-ve)	current corrected for residual current μA	$\log \frac{i}{i_1 - i}$
0.30	-	-
0.40	0.05	-2.0086
0.50	0.35	-1.1371
0.55	1.50	-0.3862
0.60	3.40	+0.2643
0.65	5.90	+0.2923
0.70	5.00	+1.5229
0.80	5.15	-

Fig.20



PLOT OF log i VS log t

FIGURE 22

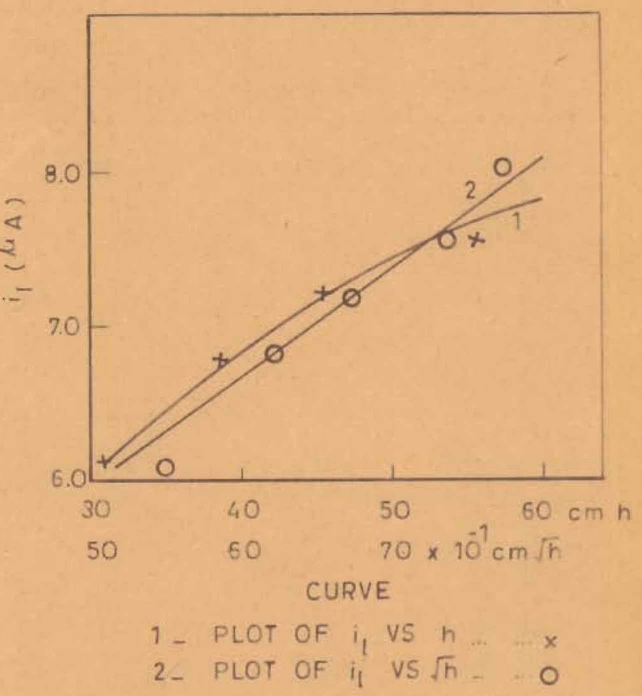
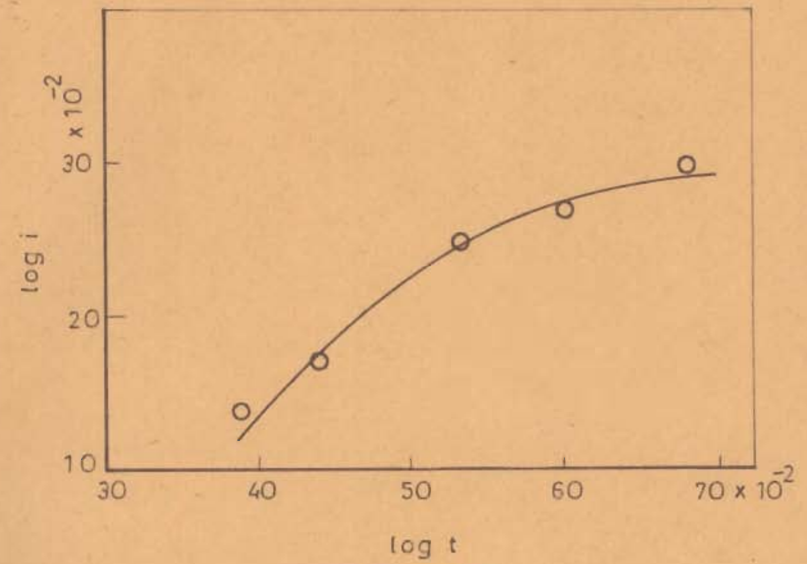


FIGURE 23



PLOT OF log i VS log t

FIGURE 24

TABLE No.23

Limiting values of the current at different heights for (I), (II) waves of the solution containing 10.0×10^{-4}M each of the reactants, 5.0×10^{-5}M mercuric chloride and 0.25M potassium chloride at pH 8.0 in dipotassium hydrogen phosphate and sodium hydroxide buffer:

Height of mercury column $h_{corr.}$ cm.	$\sqrt{h}$	Droptime in sec.		Limiting current i_l		logi		logt	
		at -0.45V for II wave	at-1.45V for I wave	at-0.45V for II wave	at -1.45V for I wave	For II waves	For I wave	For II wave	For I wave
31.0	5.52	7.90	4.87	-	6.10	-	0.3010	0.8976	0.6864
38.8	6.22	6.20	4.07	4.0	6.85	0.0792	0.2788	0.7924	0.6096
45.7	6.76	5.23	3.40	4.15	7.20	0.0607	0.2553	0.7165	0.5313
55.5	7.45	4.66	2.81	4.45	7.55	0.0607	0.1761	0.6675	0.4481
60.0	7.74	4.03	2.51	4.7	8.10	0.0792	0.1461	0.6053	0.3997
				Fig.26	Fig.23				Fig.24

TABLE No.24

Logarithmic analysis of the current voltage data for (I) wave of the solution under the conditions mentioned in table No.23:

Potential (-ve) volts	Current corrected for residual current μA	$\log \frac{i}{i_l - i}$
1.15	0.10	-1.3820
1.20	0.20	-1.0607
1.25	0.30	-0.8653
1.30	0.80	-0.3273
1.35	1.90	+0.5006
1.40	2.30	+1.0607
1.45	2.40	+1.3820
1.50	2.50	-

Fig.25

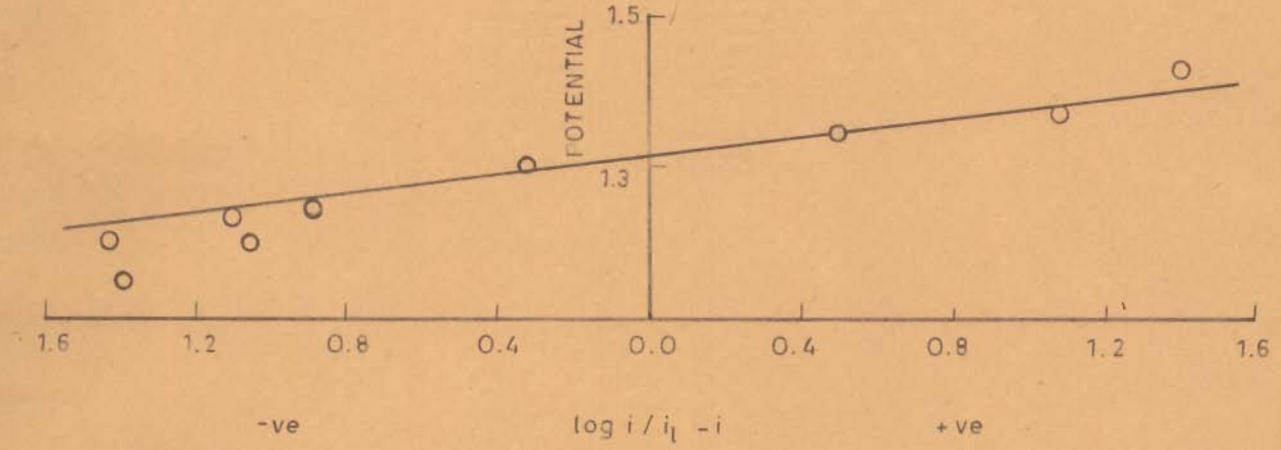


FIGURE 25

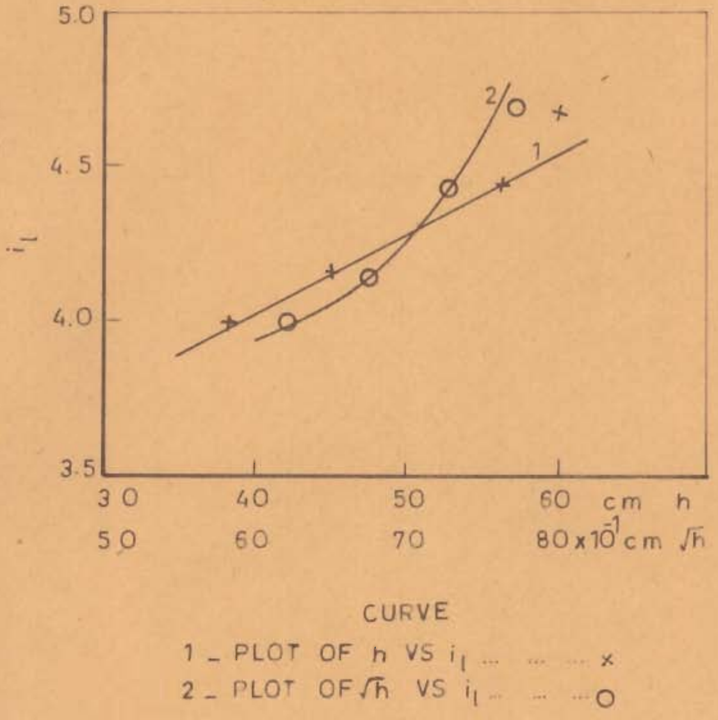


FIGURE 26

TABLE No.25

Reduction steps of 8-hydroxy quinoline 5-sulphonic acid and its complex with hexacyanoferrate (II)

Buffer	pH	Reduction steps of 8-hydroxy quinoline 5-sulphonic acid	Fig. No	Curve No.	Reduction steps of complex	Fig. No.	Curve No.
Sodium acetate and Hydrochloric acid	1.0-5.0	I	2	1-5	I,II	1	1-5
Potassium chloride and hydrochloric acid	1.0-2.0	I	3	7-8	I,II	2	13,14
Dipotassium hydrogen Phosphate and hydrochloric acid.	3.0-4.0	I	3	9,10	I,II	4	15,16
Dipotassium hydrogen phosphate and citric acid.	2.0-4.0	I	4	10,12	I,II	4	1-3
Disodium hydrogen phosphate & citric acid	5.0-6.0	I	3	11,12	I,II	3	1,2
-do-	7.0-8.0	I,II	4	4,5	I,II	3	3,4
Dipotassium hydrogen phosphate and citric acid	6.0	I	2	6	I,II	1	6
-do-	7.0-8.0	I,II	2	7.8	I,II	1	7,8
Borax	9.0-11.0	I,II,III	2	9-11	I,II	1	9-11
Ammonium chloride and Ammonium hydroxide	9.0-10.0	I	4	6,7	I,II	3	5,6
Disodium hydrogen phosphate and sodium hydroxide	11.0	I,II	4	8	I,II	3	7
-do-	12.0	-	-	-	I,II	3	8

TABLE No.26

Dependence of $E_{\frac{1}{2}}$ and i_d values on pH

pH Composition	1	2	3	4	5	6	7	8	9	10	11
	Sodium acetate and hydrochloric acid					Dipotassium hydrogen phosphate and sodium Hydroxide			Borax buffer		
Senstivity	1/10	1/10	1/10	1/10	1/10	1/10	1/5	1/5	1/5	1/5	1/5
8-hydroxy quinoline 5-sulphonate penta cyanoferrate (II).											
$(E_{\frac{1}{2}})_I$ Volt Vs. S.C.E.,-ve	0.992	1.01	1.03	1.055	1.10	1.17	1.25	1.32	1.44	1.55	1.65
$(i_d)_I$ A	3.8	2.3	1.6	1.45	1.25	1.2	2.4	1.95	1.9	1.9	1.6
Senstivity	-	-	-	1/5	1/5	1/5	1/5	1/5	1/5	1/5	1/3
$(E_{\frac{1}{2}})_{II}$	-	-	-	0.15	0.16	0.16	0.17	0.21	0.25	0.30	0.31
$(i_d)_{II}$	-	-	-	0.77	1.4	1.4	1.45	1.5	1.9	1.4	2.2
Senstivity	1/10	1/10	1/10	1/10	1/10	1/5	1/5	1/5	1/5	1/5	1/5
8-hydroxy quinoline 5-sulphonic acid											
$(E_{\frac{1}{2}})_I$	0.98	0.995	1.01	1.025	1.15	1.19	1.25	1.31	1.5	1.69	1.71
$(i_d)_I$	3.1	2.7	2.1	1.55	1.4	2.9	2.4	2.2	2.0	1.3	1.2
$(E_{\frac{1}{2}})_{II}$	-	-	-	-	-	-	0.105	0.11	0.15	0.15	0.15
$(i_d)_{II}$	-	-	-	-	-	-	1.1	1.1	1.1	1.0	1.0
$(E_{\frac{1}{2}})_{III}$	-	-	-	-	-	-	-	-	0.57	1.43	1.44
$(i_d)_{III}$	-	-	-	-	-	-	-	-	3.8	2.0	1.8

TABLE No.27

Dependence of $E_{\frac{1}{2}}$ and i_d values on pH

pH	1	2	3	4	3	4	5	6	7	8	9	10	11	12
Composition	Potassium chloride and hydrochloric acid		Dipotassium hydrogen phosphate & hydrochloric acid		Dipotassium hydrogen phosphate and citric acid		Disodium hydrogen Phosphate and citric acid				Ammonium chloride and ammonium hydroxide		Disodium hydrogen phosphate and sodium hydroxide	
Senstivity	1/10	1/10	1/10	1/10	1/10	1/10	1/10	1/10	1/5	1/5	1/10	1/10	1/10	1/10
Olive green complex														
$(E_{\frac{1}{2}})_I$ Volt Vs S.C.E.(-ve)	1.0	0.99	1.01	1.11	1.02	1.02	1.12	1.20	1.32	1.35	1.39	1.48	-	-
$(i_d)_I$ A	3.1	2.8	1.55	1.5	2.3	2.25	1.4	1.1	1.35	1.1	2.2	1.4	-	-
$(E_{\frac{1}{2}})_{II}$	0.18	0.17	0.18	0.31	0.12	0.12	0.235	0.245	0.245	0.24	0.29	0.30	0.33	0.33
$(i_d)_{II}$	1.2	2.0	2.3	3.0	2.3	2.3	3.0	3.15	6.7	8.4	3.0	3.0	2.8	2.8
Senstivity	1/10	1/10	1/10	1/10	1/10	1/10	1/10	1/10	1/10	1/10	1/10	1/10	1/10	1/10
8-hydroxy quinoline 5-sulphonic acid.														
$(E_{\frac{1}{2}})_I$	1.0	0.98	1.0	1.08	1.05	1.13	1.12	1.19	1.29	1.35	1.38	1.43	1.53	-
$(i_d)_I$	4.1	3.0	2.4	1.55	2.3	2.2	1.4	1.2	1.2	1.1	3.35	2.8	0.7	-
$(E_{\frac{1}{2}})_{II}$	-	-	-	-	-	-	-	-	0.135	0.14	-	-	0.43	-
$(i_d)_{II}$	-	-	-	-	-	-	-	-	0.55	0.6	-	-	0.70	-

TABLE No.28

Effect of anions(chloride, nitrate, sulphate and chlorate) on $E_{\frac{1}{2}}$ and i_d values of complex at pH 8.0.

Electrolyte	Without electrolyte.	KCl			KNO_3			K_2SO_4			$KClO_3$		
Concentration (M)	-	0.025	0.085	1.5	0.025	0.085	1.5	0.012	0.0425	0.075	0.012	0.0425	0.075
$(E_{\frac{1}{2}})_I$ Volt Vs S.C.E. -ve	1.285	1.30	1.31	1.31	1.30	1.31	1.31	1.31	1.31	1.31	1.32	1.32	1.32
$(i_d)_I$ A	2.65	2.75	2.7	2.7	2.5	2.5	2.5	2.5	2.5	2.5	2.75	2.75	2.75
$(E_{\frac{1}{2}})_{II}$ Volt Vs S.C.E. -ve	0.23	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
$(i_d)_{II}$ A	4.55	4.15	4.10	4.10	4.45	4.4	4.4	4.4	4.3	4.3	4.4	4.4	4.5

TABLE No.29

Effect of alkali and alkaline earth metals on $E_{\frac{1}{2}}$ and i_d values. Concentration of these cations = 0.24M

pH	Dipotassium hydrogen phosphate and sodium hydroxide pH-7				Ammonium chloride and ammonium hydroxide pH-9		
	No cation	Li^+	Na^+	K^+	No cation	Ca^{++}	Ba^{++}
Olive green complex							
$(E_{\frac{1}{2}})_I$ Volt (-ve)	-1.25	1.24	1.23	1.22	-1.39	-1.28	-1.265
$(i_d)_I$ A	1.9	1.8	1.7	1.7	4.4	4.0	4.0
$(E_{\frac{1}{2}})_{II}$ Volt	-0.21	-0.20	-0.20	-0.20	-0.295	-0.275	-0.275
$(i_d)_{II}$ A	3.3	3.2	3.2	3.2	3.0	2.5	2.5

$(i_d)_I$ $(i_d)_{II}$

$(E_{\frac{1}{2}})_I$; $(E_{\frac{1}{2}})_{II}$, $(E_{\frac{1}{2}})_{III}$, $(i_d)_I$, $(i_d)_{II}$ and $(i_d)_{III}$ correspond to I, II and III steps respectively.

RESULTS

On 8-hydroxy quinoline 5-sulphonic Acid:

From the current voltage curves it was found that the compound was reducible at d.m.e. over wide pH range (1.0 to 11.0). During the reduction besides main step (I) other subsidiary reduction steps depending upon the composition and pH of the buffer were also realized. The existense of various steps is summarised in Table No.1.

The values of $E_{\frac{1}{2}}$ and i_d for these steps were found to be highly dependent on pH. In the pH range 1.0 to 6.0 one wave (reduction step I) was obtained with all the buffers used (Fig.2 curve 1 to 6). The dependence of $E_{\frac{1}{2}}$ with pH was found to be in accordance with the expression $E_{\frac{1}{2}} = -(0.965 + 0.015\ pH)$ in the pH range 1.0 to 4.0. Moreover, the wave height was found to decrease with increase in pH.

From pH 6.0 appearance of the other waves besides the main reduction step (I) took place. Then in pH range 7.0 to 11.0 another wave designed as (II) was realized. The $E_{\frac{1}{2}}$ and i_d values for this reduction step was almost independent of pH and the nature of the supporting electrolyte. This could be attributed to the adsorption of free base on the surface of mercury drops (16). The nature of this wave was further confirmed by seeing the influence of mercury height at pH 8.0 (Fig.16). The existance of this wave could also be quessed from the fact that current voltage curve had a peculiar shape even when recorded below pH 6.0.

Besides the above mentioned behaviour about the reduction of 8-hydroxy quinoline 5-sulphonic acid at d.m.e. there were few other interesting facts worth mentioning:

(1) Wave (I) was more defined at pH 7.0 to 8.0 and therefore, could be easily characterised. The step height was found to increase with increase in the concentration of 8-hydroxy quinoline 5-sulphonic acid (Fig.6 table 16 at pH 8.0); (Fig.12 at pH 7.0) and it was completely diffusion controlled two electron transfer process as verified by the effect of mercury pressure (Fig.17) logarithmic analysis (Fig.18) and plot of logi against logt (Fig.19).

(2) Wave (II) was not realized in the pH range 9.0 to 10.0 in ammonium chloride and ammonium hydroxide buffer.

(3) A new wave well defined (designed as step III) was realized in the pH range 9.0 to 11.0 only in the case of borax buffer. The $E_{\frac{1}{2}}$ and i_d values for which were also found to be dependent on pH (Fig.2 curve 9,10,11). The step at pH 9.0 was also found to be diffusion controlled; a two electron transfer process, tested by logarithmic analysis (Fig.20) mercury pressure (Fig.21) and by the plot of logi Vs logt (Fig.22).

(4) No reduction step was obtained at pH 12 although as would be seen later, this step was

possible in the case of the 8-hydroxy quinoline 5-sulphonate pentacyanoferrate (II) complex.

The $E_{\frac{1}{2}}$ and i_d values for various steps are summarised in tables 26 and 27. These results are quite comparable with the studies carried out by Peach (3) , Tachiand Kabai (2), Stock (8), Stone and Furman (9) on quinoline and its derivatives.

On the reduction of 8-hydroxy quinoline 5-sulphonate pentacyanoferrate (II):

The behaviour of this complex at d.m.e. is quite different from that of 8-hydroxy quinoline 5-sulphonic acid. The comparative statement for the existance of different steps for this complex and 8-hydroxy quinoline 5-sulphonic acid under similar condition of pH etc. are summarised in table I and the comparative statement of $E_{\frac{1}{2}}$ and i_d values in table (2A and 2B).

This complex gave the main step (I) over the wide pH range 1 to 12 in all the buffers used. The $E_{\frac{1}{2}}$ and i_d values here were also highly dependent on pH, composition of the buffer etc. The dependenee of $E_{\frac{1}{2}}$ was in accordance with the expression $E_{\frac{1}{2}} = -(0.972 + 0.02 \text{ pH})$ in sodium acetate hydrochloric acid buffer, pH range, 1.0 to 4.0. Similar expressions $E_{\frac{1}{2}} = -(0.92 + 0.1 \text{ pH})$; $E_{\frac{1}{2}} = -(1.33 + 0.11 \text{ pH})$ were found to hold good in disodium hydrogen phosphate and citric acid buffer, pH 5.0 to 7.0, borax buffer pH 9.0 to 11.0 respectively.

Step (I) in pH range 7.0 to 9.0 was well defined, the step height was dependent on the concentration of the complex (Fig.5 table No.15 at pH 8.0 and Fig.11 at pH 7.0). The electrode process was diffusion controlled with 2 electron transfer as tested by logarithmic analysis (Fig.25) and by the effect of mercury pressure (Fig.23) and by the plot of logi Vs logt (Fig.24).

Unlike 8-hydroxy quinoline 5-sulphonic acid step (II) was realized over the entire pH range 1.0 to 12.0. The $E_{\frac{1}{2}}$ and i_d values for this step were independent of pH. This was characterised as adsorption wave probably due to the adsorption of ions in acidic range and adsorption of free base in the alkaline range on the surface of mercury drops (17). The effect of mercury pressure gave evidence for adsorption wave (Fig.26 Table No.23).

Other interesting points worth noting were:

(1) Step (II) could not be realized in sodium acetate and hydrochloric acid buffer, pH 1.0 to 3.0 for this complex.

(2) Step (III) which was realized in the case of 8-hydroxy quinoline 5-sulphonic acid could not be realized in the case of this complex.

(3) Step (II) which was not realized incase of 8-hydroxy quinoline 5-sulphonic acid in ammonium hydroxide buffer pH 9.0 to 10.0 was realized in the case of complex.

The waves obtained with mixtures containing fixed amounts of hexacyanoferrate (II) and varyigg amounts of 8-hydroxy quinoline 5-sulphonic acid and vice versa at pH 7.0 and 8.0 have i_d values which increased with increasing concentrations either of the reactants (potassium hexacyanoferrate (II) or 8-hydroxy quinoline 5-sulphonic acid), but the values became constant at a combining ratio 1:1 (Fig.8,10 Table 17,18 at pH 8.0). Although the values increased above the combining ratio 1:1 when hexacyanoferrate (II) was kept constant but a sharp break was realized at 1:1 ratio (Fig.9). This increase was due to the reduction of excess of the 8-hydroxy quinoline 5-sulphonic acid, for which the $E_{\frac{1}{2}}$ is very near to the complex.

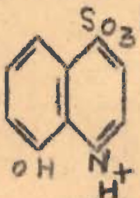
The waves obtained with the mixtures containing the increasing amounts of electrolytes, were followed with a half wave potential change to more negative potential with a small decrease in i_d for step (I). Above 0.75M concentration of potassium chloride and potassium nitrate both $E_{\frac{1}{2}}$ and i_d values became constant. A little effect on i_d was observed with potassium sulphate and potassium chlorate, A constant but more negative $E_{\frac{1}{2}}$ values (as compared with the $E_{\frac{1}{2}}$ values in the absence of potassium chlorate and potassium sulphate) were obtained even on increasing the concentrations (Fig.13, table 28).

The waves obtained with mixtures of (0.24M) alkali metals at pH 7.0, 8.0 and alkaline earth metals at pH 9.0, 10.0 (alkaline earth metals got precipitated at pH 7.0), were followed with a change in $E_{\frac{1}{2}}$ and i_d values and a shift in $E_{\frac{1}{2}}$ to more positive side, in the sequence potassium sodium lithium and calcium barium has been observed. Results at pH 7.0, 9.0 are summarised in (Table No.29 Fig.14) and at pH values 8.0, 9.0 are shown in Fig.15.

DISCUSSION

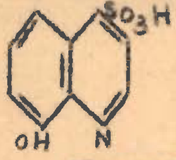
8-hydroxyquinoline 5-sulphonic acid:

The study of ultra violet absorption spectrum of quinaldinic acid and cinconic acid and other quinoline derivatives indicated the presence of hydrogen positive (H^+) on the nitrogen atom upto pH 4.0. These results were confirmed from the polarography of 8-hydroxy quinoline (stock) (14) and on this basis the 2 electron transfer reduction step (I) for the formation of dihydro-derivative of 8-hydroxy quinoline 5-sulphonic acid in acidic solutions may be attributed to the equation.



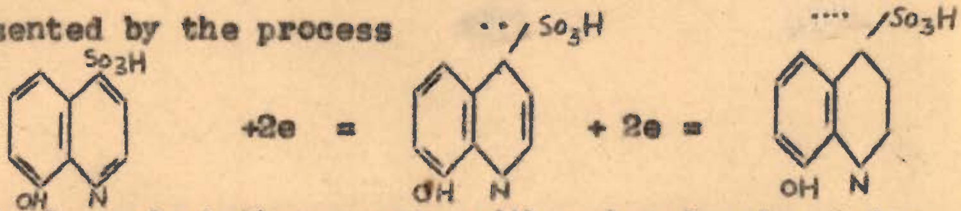
$+H^+ \quad + 2e =$ Dihydroderivative

In neutral region the existance of step (I) can be attributed with the equation



$+2H^+ \quad + 2e =$ Dihydroderivative.

The step wise reduction in two waves pH 9.0 to 11.0 (borax buffer step (III) and (I)) may be represented by the process



The final product then reacts with water to give tetra, hydroderivative. This type of mechanism is quite comparable with the reduction of cinconic acid at d.m.e. as proposed by Casimir and Lyons (16).

8-hydroxy quinoline 5-sulphonate pentacyanoferrate (II) complex:

The mechanism of reduction process of the complex in acidic range with two electron transfer wave may be given by the equation

8-hydroxy quinoline 5-sulphonate
pentacyanoferrate (II) $+H^+$ + 2e = Dihydroderivative.

and in neutral range by the equation

8-hydroxy quinoline 5-sulphonate pentacyanoferrate (II)
+ 2e + $2H^+$ = Dihydroderivative.

The expression in alkaline range may be given by the equation

8-hydroxy quinoline 5-sulphonate pentacyanoferrate (II)
+ 2e = Dihydroderivative obtained by the interaction of water with the electrode product.

CHAPTER IV

Redox Amperometric titrations with hexacyanoferrate (III).

(Part I)

Amperometric Titrations of Co(II)with hexacyanoferrate (III) in glycine and amm. citrate media. The reduction of the resulting complexes at a.m.e.

Dickens and Messen (1); Tomicek Freiberger (2); for the first time, reported the estimation of Co(II) with hexacyanoferrate (III) in ammonical medium. The red product formed by this reaction was represented by the formula $Co^{III}(NH_3)_5CyFe(Cy)_5$. This reaction was also utilised for the potentiometric determination of Co(II) by a number of workers (4-8) with metal salt as the titrant. Reverse titrations, with Co(II) in the cell, could not, however, be performed with out the use of complexing agents like ethylenediamine, triethylenetetramine, tetraethylene pentamine, glycine, mixture of alamine or phenyl alamine, glutamic acid (9-13) due to air oxidation of Co(II) to Co(III) in ammonical medium. More recently poppe and Den Boef (14) had reported the results of photometric titrations between the two reagents in the presence of various cations, employing ammonia and glycine as complexing agents.

The palarographic aspect of the above reaction, has however, not been studied so far although many references on the polarography of other oxidation product of Co(II) are available in the literature. For example Watters and Kolthoff (15) had reported the estimation of Co(II) from the reduction steps of trivalent hexamino complex obtained by the oxidation of divalent hexamino complex using sodium per borate as oxidant in absence of Cu(II), Cr(III) and Mn(II). Souchay and Faucherre (16) had used the steps given by the reduction of cobaltic ions to determine cobalt in steel. Willis and Co-workers (17) had reported the one step reduction of hexamino cobaltous and two steps reduction of hexamino cobaltic complex for analytical use. Kolthoff and Watters (18) had also determined Co(II) by employing the step given by the reduction of trioxalato cobaltic ions to dioxalato cobaltous state. They used hydroxylamine hydrochloride to decompose the oxalate complexes of metals like Mn(II), Ce(III), Ce(IV) and Cr(III) which interfered in the reduction steps.

Recently Maki and Coworkers (19-20) had carried out polarographic studies of tetra-cyanomono (ethylene diamine) cobalt (III); ethylenediamine tetra acetato cobalt (III); cobalt (II) and bis (dipyridyl) Co(III) complexes.

Section A of the present part of the chapter deals with the amperometric estimation of Co(II) against hexacyanoferrate (III) in ammonium citrate and glycine media at pH 9.8 and 8.0 respectively (reaction takes place in pH range 7.0 to 11.0). The determination has been carried out in presence of Cr(III), Ce(III), V(v), Cu(II), Ni(II) and Mn(II) the most common metals which generally interfere in polarographic determination of Co(II).

In section B the results of the polarographic reduction of resulting Co(III) binuclear, Co(II) ammonia, Co(III) ammonia and glycine complexes are described. Interference of the above mentioned metals on the reduction steps of the resulting complexes has also been discussed to test the suitability of the polarographic method for the estimation of Co(II).

Section C gives a critical account of the reduction of the Co(III) and Co(II) glycine complexes in the buffers of (pH range 8.0 to 11.0) different compositions in various supporting electrolytes.

Apparatus:

Heyrovsky LP-55A Polarograph operated manually in conjunction with Pye sclamp Galvanometer in external circuit was used. A dropping mercury electrode having m = 0.0035 gm/sec; t = 4.31 sec per drop of mercury in closed circuit at applied potential of 0.0 v.Vs. C.E. was used. Mercury column height 49.5 cm. The Hshped Polarographic cell and the reference electrode were kept immersed in a water thermostatic bath maintained at 25 ± 0.1^{o}C. Purified nitrogen was used for the deaeration of the solutions.

Beckmann pH-meter model H_2 was used to measure pH.

Reagents:

All the reagent used were of A.R. quality section (A).

Ammonium citrate:

50.0 gms of citric acid was dissolved in double distilled water, added 150.0 ml of 14N ammonia solution (pH was adjusted to 9.8)and diluted to one litre.

Hexacyanoferrate (III) solution:

Recrystallised potassium hexacyanoferrate (III) was dissolved in required amount of double distilled water. Its strength was determined iodometrically and kept in amber coloured bottle.

Cobalt Chloride Solution:

This was prepared in double distilled water, its strength was determined by weighing as cobalt mercuric-thiocyanate.

Potassium chloride:

1.0M potassium chloride was prepared by dissolving weighed quantity in double distilled water.

Solutions of Metal ions:

Solutions of different metal ions were prepared in double distilled water and their strengths determined by the respective standard methods. Solutions of required concentration were obtained by diluting the stock solution.

Section (B) Glycine:

For obtaining 2.8M solution 21.0 gms of the reagent was disolved in water. pH was adjusted to 8.0 by adding potassium hydroxide and the total volume was made to 100 ml.

Hexacyanoferrate (III):

As in section A

Cobalt chloride:

As in section A

Potassium chloride 1.0M.

Section (C):

Glycine buffers:

Separately in each of the four conical flasks 30 gms of glycine was dissolved, pH was adjusted to 8.0, 9.0, 10.0 and 11.0 respectively by adding potassium hydroxide and total volume in each case was made to one litre. Similarly the buffers of pH 8.0, 9.0, 10.0, and 11.0 were prepared, by dissolving 40.0 and 50.0 gms of glycine. Thus 12 buffered solutions of different compositions were prepared. The first four contained 0.40M. The second four 0.514M and the last four 0.666M glycine, respectively. In these three sets (each of four solutions), the pH values were 8.0,9.0, 10.0 and 11.0 respectively.

Electrolytes:

Solutions were prepared in double distilled water. Solutions:

1.0M sodium fluoride.

1.0M Potassium nitrate.

1.5M Potassium chlorate

0.5M Sodium sulphate, and

2.0M calcium chloride were prepared.

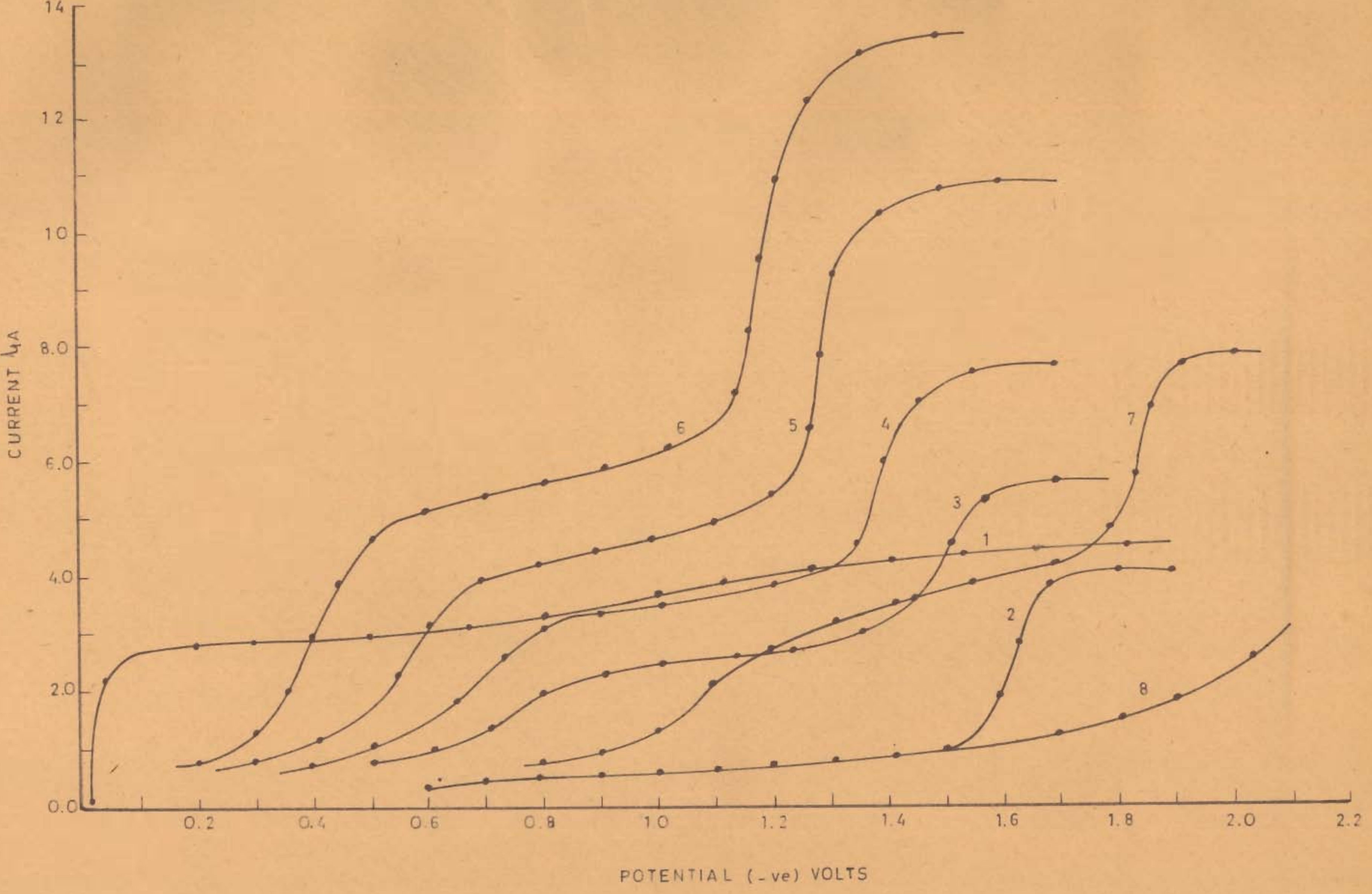

14
12
10
8.0
6.0
4.0
2.0
0.0
CURRENT µA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
POTENTIAL (-ve) VOLTS
6
5
4
7
3
1
2
8

FIGURE 1A

EXPERIMENTAL

Section A:

Amperometric Titrations:

To carry out amperometric titrations in the medium of ammonium citrate four solutions were prepared: Solution (1) contained 1.0 ml of 10^{-2}M hexacyanoferrate (III), 1.0 ml of 1.0M potassium chloride and 18.0 ml of ammonium citrate buffer of pH 9.8 solution (ii) 1.0 ml of 10^{-2}M cobalt chloride, 1.0 ml of 1.0M potassium chloride and 17.0 ml of ammonium citrate buffer of pH 9.8 solution (iii) 17.0 ml of ammonium citrate buffer, 1.0 ml of 1.0M potassium chloride and 3.0 ml of water. Polarogms were recorded from -0.1 to -1.6 V. at constant senstivity. It is evident from Fig.1 that the limiting value of the current for solution No.1 lies in the potential region of -0.2 to -0.3 for solution No.2 in the potential region of -1.50 to -1.6 V. Two reduction steps were obtained for solution No.3 with limiting value of current in the potential region of -0.55 to -0.65 V. for the first step and in the potential region of -1.4 to -1.5 for second step. Therefore, the potentials having the values -0.3 and -1.5 V. were selected for the amperometric titrations (Fig.1A curve 1,2,8).

Similar types of solutions were prepared in glycine medium instead of ammonium citrate glycine buffer of pH 8.0 was used. Polarograms were recorded from -0.1 to -1.6 V. Potentials selected for amperometric titrations were -0.55 and -1.5 V for both the direct and the reverse titrations. The results are shown in (Fig.2A curve 1,2,7).

Procedure:

To carry out amperometric titrations in ammonium citrate medium 1.0 ml of 10^{-2}M to 10^{-5}M solutions of Co(II) in direct titrations and 1.0 c.c. 10^{-2}M to 10^{-5}M hexacyanoferrate (III) in reverse titrations were placed in the titration cell. To each solution was added 1.0 ml of 1.0M of potassium chloride and the total volume was made to 20.0 ml by adding requisite amount of buffer of pH 9.8. Titrants (hexacyanoferrate (III) in direct titrations and cobalt chloride in back titrations) were added in fractions from microburette. Solution in the cell was stirred with nitrogen after each addition and current was noticed when attained constancy. Concentrations of the titrant were adjusted in such a way so that not more than 2.0 c.c. of it was required for complete titration. The end points were detected from the intersections of the two straight lines obtained by plotting current against the volume of the titrant added in (Fig.3,4).

Titrations in presence of metal ions:

These were carried out at -0.3V.To 1.0 ml of 10^{-2}M cobalt chloride in direct titrations or hexacyanoferrate (III) in reverse titrations was added 1.0 ml of potassium chloride and required folds of concentration of metal ion present in not more than 2.0 ml. Total volume was made to 20.0 ml buffer of pH 9.8. Titrant hexacyanoferrate (III) in direct titrations and Co(II) in reverse titrations were added in fractions in the usual way (Fig.5).

Titrations in similar fashion were also carried in the medium of glycine. (Fig.6).

In order to see the superority of the resulting binuclear complex, formed with Co(II) and hexacyanoferrate (III), over the other Co(II) and Co(III) complexes under similar conditions with the stand point of the polarographic determination of Co(II) from their reduction steps, and to differentiate the binuclear complex with Co(II) ammonia and Co(III) complexes, the polarograms in three sets of, solutions were recorded.

Set I comprised of 8 solutions each containing 15.0 ml ammonium citrate, 1.0 ml of 1.0M potassium chloride and increasing amounts 0.5, 1.0, 1.5 and 2.0 ml of each of 10^{-2}M cobalt chloride and hexacyanoferrate (III). Total volume was made to 20.0 ml by adding requisite amount of water (Fig.1, curve 3,4,5,6). Solutions 5-8 were prepared as 1-4 but the concentration of each of cobalt chloride and hexacyanoferrate (III) was 10^{-3}M. (Fig.8 curve 1,2,3,4).

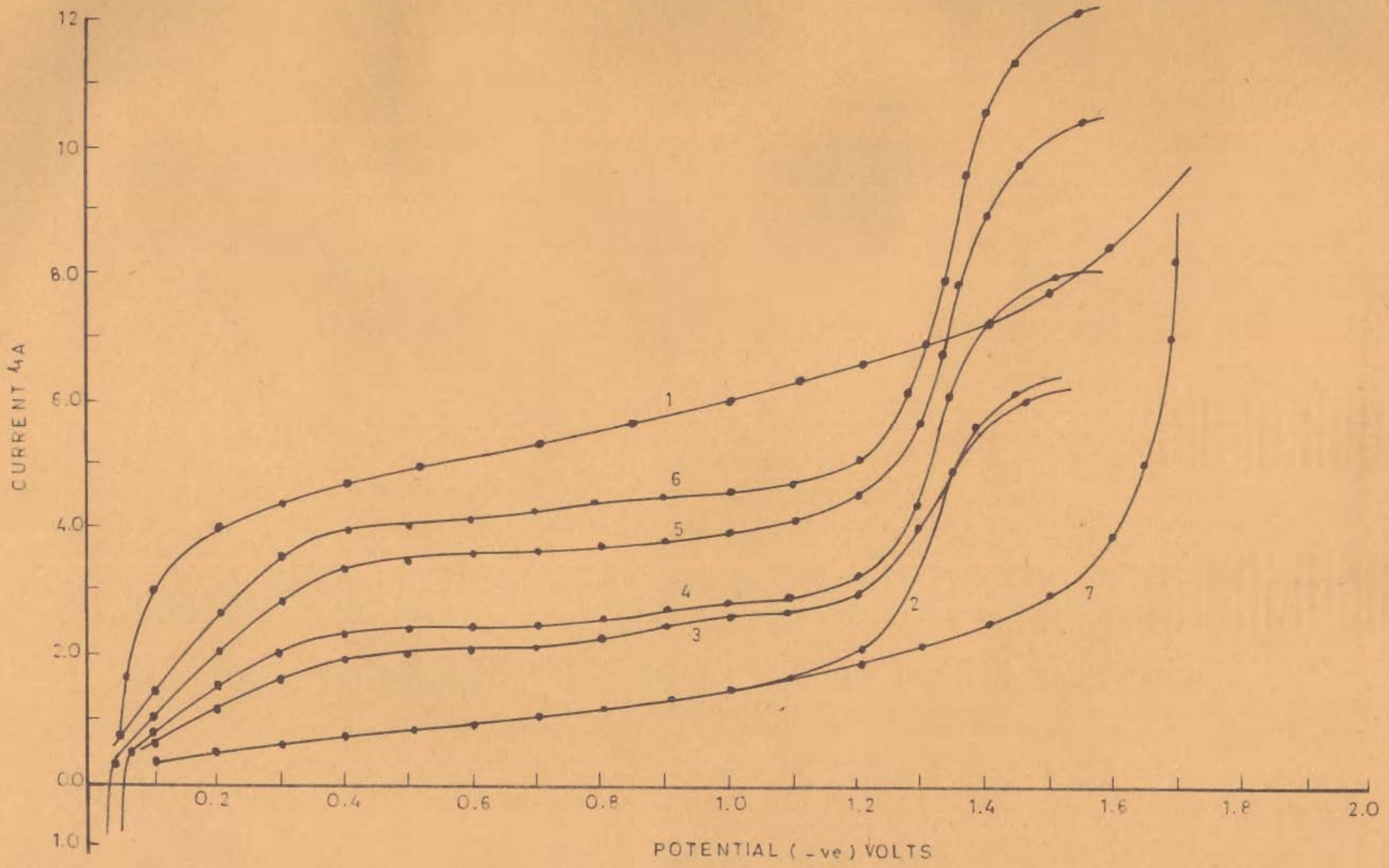

12
10
8.0
6.0
4.0
2.0
0.0
1.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
POTENTIAL (-ve) VOLTS
1
6
5
4
3
2
7

FIGURE 2A

Set No.2 included three solutions No.1 contained 5.0 ml of 10^{-2}M cobalt. Chloride 5.0 ml of 1.0M potassium chloride, 90.0 ml of ammonium citrate. Solution No.2 contained same contents as in solution No.1 but to this oxygen was passed (since the slow oxidation of hexa-amino cobaltous complex to cobaltic hexaamino complex takes place 9) for 24 hours. The loss of volume due to evaporation of ammonia was made up by 14N ammonia keeping the pH -8.9. Solution No.3 contained 5.0 c.c. 10^{-2}M cobalt chloride, 5.0 c.c. 10^{-2}M hexacyanoferrate (III) 5.0 c.c. 1.0M potassium chloride and 85.0 ml of ammonium citrate (Fig.1A, curve 2,7,4).

Set No.3 included 6 solutions, in each were present, 18.0 ml of ammonium citrate 1.0 ml of 1.0M potassium chloride, 1.0 c.c. of 10^{-3}M cobalt chloride and 1.0 c.c. 10^{-3}M hexacyanoferrate (III). Then 1.0 ml of Cu(II), Ni(II), Ce(III), Cr(III), Mn(II) and V(V) each of 10^{-3}M were added in solution No.1 to 6 respectively (Fig.1B curve 1-6).

Similar types of polarograms of the solutions in three sets were recorded in the medium of glycine except the type of solution No.2 in second set above (since no oxidation of Co(II) glycine complex to Co(III) glycine complex takes place by atomospheric oxygen). (Fig.2A curve 3,4,5,6; Fig.9 curve 1,2,3,4 for set I and Fig.2B curve 1-6 for Set III).

Section C

Effect of composition of buffers and pH on the reduction of Co(II) glycine complex, resulting Co(III) complex in solutions has been studied by recording the polarograms (at 1/5 senstivity of polarograph) in several sets of solutions. Each set included three solutions No.1 in each set contained 1.0 ml of 10^{-2}M hexacyanoferrate (III), 1.0 ml of 10^{-2}M cobalt chloride and 1.0 ml of electrolytes (sodium fluoride, potassium nitrate, potassium chlorate, sodium sulphate and calcium chloride of concentrations mentioned already) with required amount of buffer to makes the total volume 15.0 ml.

No.2 contained 1.0 ml of 10^{-2}M cobalt chloride in 15.0 ml of total volume with 1.0 ml of required electrolyte and buffer.

No.3 in each set contained only buffer and electrolyte in total 15.0 ml of volume. When the polarograms in calcium chloride as supporting electrolyte were recorded 0.2 ml of 0.04 percent of nonionic soap (No-nidate p-40) as maximum suppessor was used (Table No11 Fig.10-29).

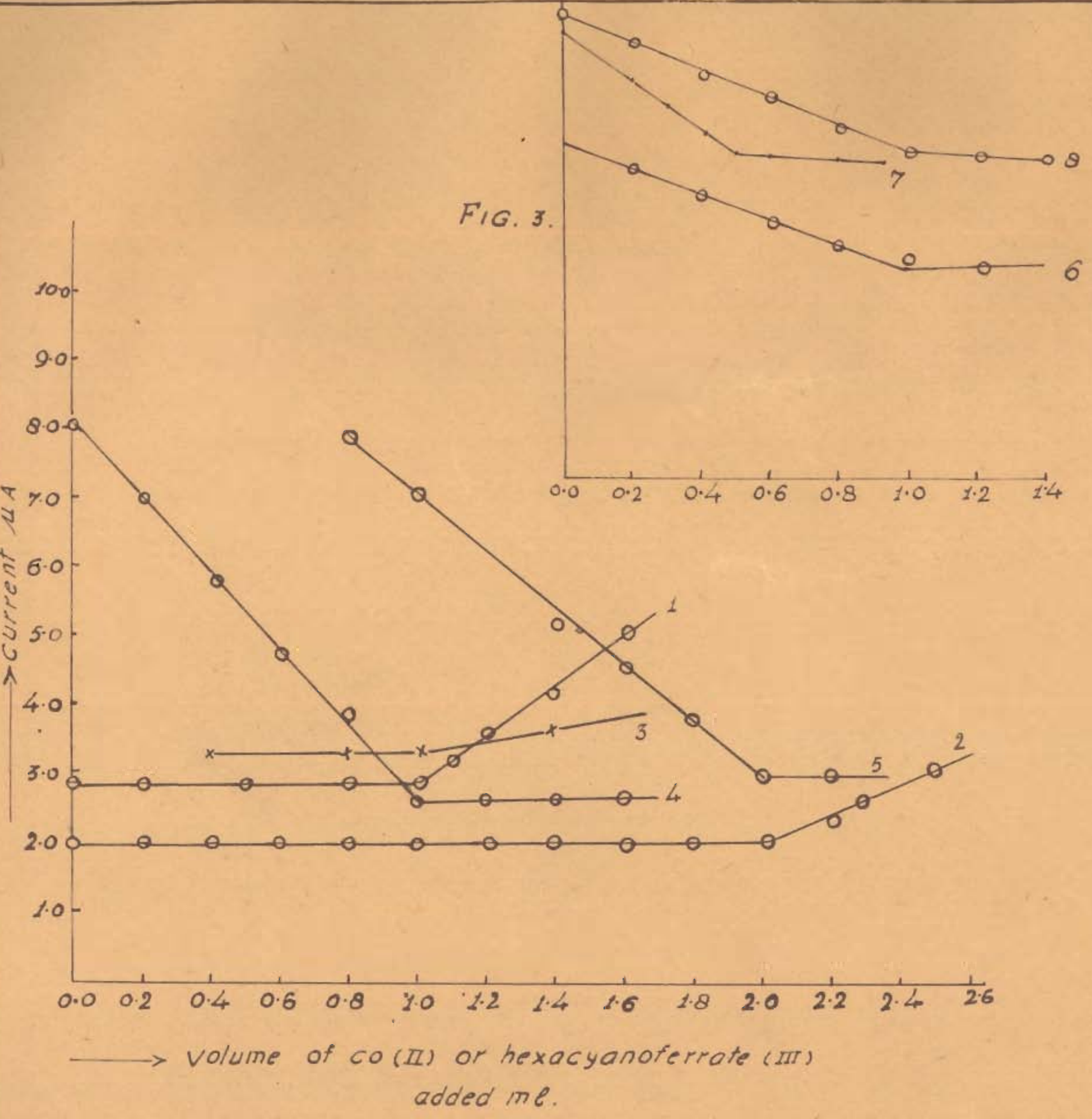
TABLE No.1

Representation of figures and curves of the reduction of glycine complexes of Co(II) and Co(III) at different pH values in different supporting electrolytes (Senstivity for each curve = 1/5) (Concentration of Co(II), hexacyanoferrate (III) = 0.05 x 10^{-2}M in respective solutions).

Concentration of glycine	8.0 pH			9.0 pH			10.0 pH			11.0 pH		
	0.32M	0.40M	0.53M	0.32M	0.40M	0.53M	0.32M	0.40M	0.53M	0.32M	0.40M	0.53M
0.666 M Sodium Fluoride												
Fig.No.	10	10	10	11	11	11	12	12	12	13	13	13
Curve No.	1-3	4-6	7-9	1-3	4-6	7-9	1-3	4-6	7-9	1-3	4-6	7-9
0.066 M P.A. Nitrate												
Fig.No.	-	-	14	-	-	15	-	-	16	-	-	17
Curve	-	-	1-3	-	-	1-3	-	-	1-3	-	-	1-3
0.066 M potassium chlorate. Fig.No., curve No.	- -	- -	18 1-3	- -	- -	19 1-3	- -	- -	20 1-3	- -	- -	21 1-3
0.033M Sod. Sulphate												
Fig.No.	-	-	22	-	-	23	-	-	24	-	-	25
Curve No.	-	-	1-2	-	-	1-2	-	-	1-2	-	-	1-2
0.133M Cal.Chloride												
Fig.No.	-	-	26	-	-	27	-	-	28	-	-	29
Curve No.	-	-	1-3	-	-	1-3	-	-	1-3	-	-	1-3

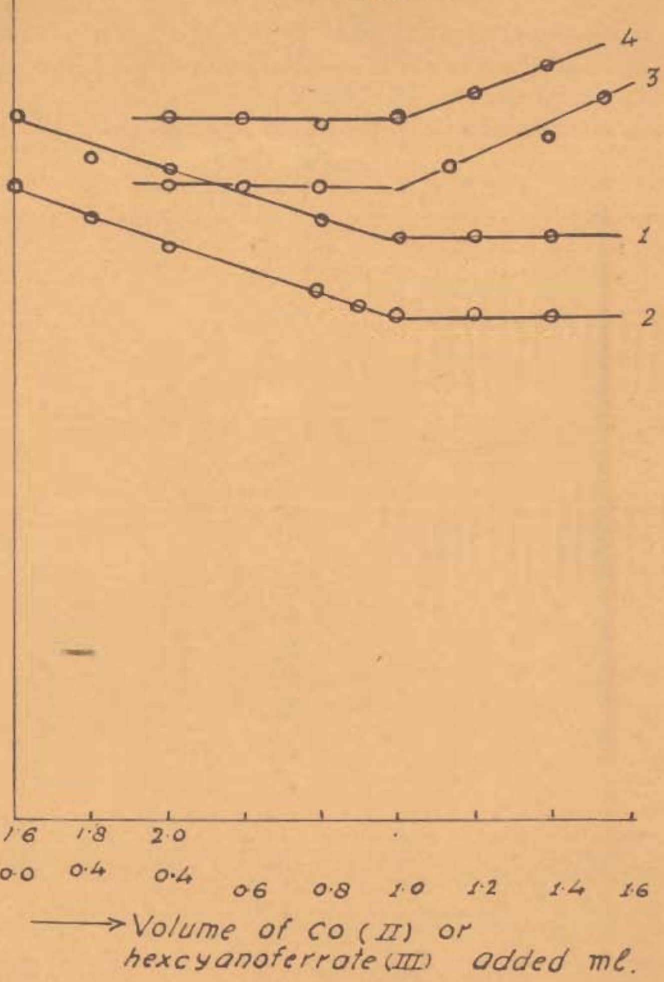
(For Figures see captions)

FIG. 3.



8
7
6
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
→ Current μA
1
2
3
4
5
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
2·6
→ volume of Co (II) or hexacyanoferrate (III) added ml.

FIG. 4.



4
3
1
2
1·6
1·8
2·0
0·0
0·4
0·4
0·6
0·8
1·0
1·2
1·4
1·6
→ Volume of Co (II) or hexcyanoferrate (III) added ml.

In order to study the relationship between limiting current and the concentration of the complex the polarograms (at 1/10 senstivity) of the solutions containing increasing amounts of 10^{-2}M solutions of hexacyanoferrate (III) and Co(II) as 0.5, 1.0, 1.5, 2.0 ml with 1.0 ml of calcium chloride (since both the steps were wëll defined in presence of calcium chloride) in 20.0 ml of volume at pH 8.0 in 0.53M glycine (Fig.30).

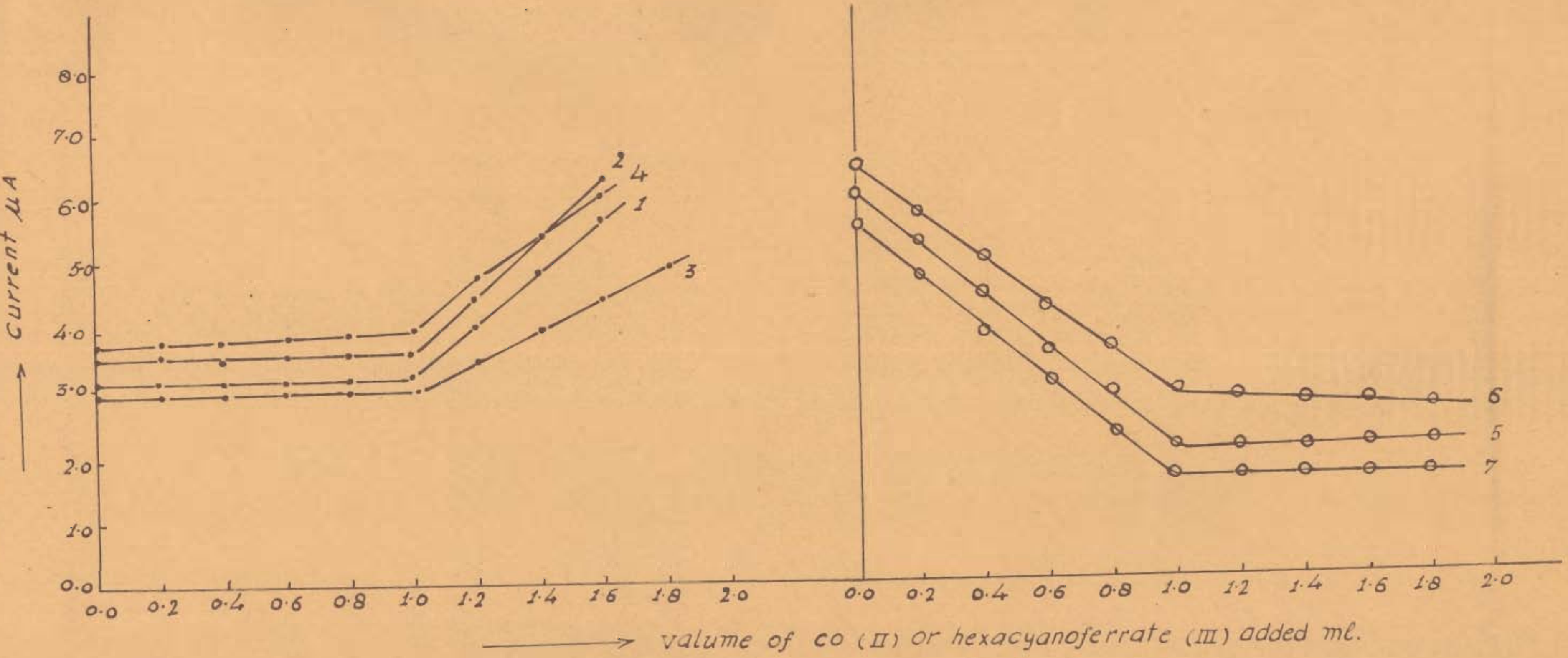
Results and Discussions:

Section A:

Medium of ammonium citrate:

In absence of (interfering metal ions). Under given conditions at applied potential of -0.3V. Co(II) was determined up to the concentration of 0.5×10^{-4}M in direct titrarions (Co(II) in cell) and upto the concentration of 0.5×10^{-5}M in back titrations (hexacyanoferrate (III) in cell) with error less than ± 0.5 percent. Applied potential of -1.5 V. in direct and reversed titrations Co(II) concentration of the order of 10^{-3}M could not be determined (error greater than ± 1.0 percent) But the concentration of the order of 10^{-5}M was determined with error less than ± 1.0 percent. This may be due to the fact that the complex which was formed during the reaction also gave its own contribution to the current at this potential as its reduction is very

FIG. 5



Current μA
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2
4
1
3
6
5
7
valume of CO (II) or hexacyanoferrate (III) added ml.

near to the reduction of Co(II) ammonia complex. Contribution to the current due to this complex during its formation appreciably effected ~~a~~end point in the higher concentration range but was negligible in the lower concentration range and therefore, and point was almost uneffected. Typical L-shaped curves are shown in Fig.4. Results are summarised below:

TABLE No.2

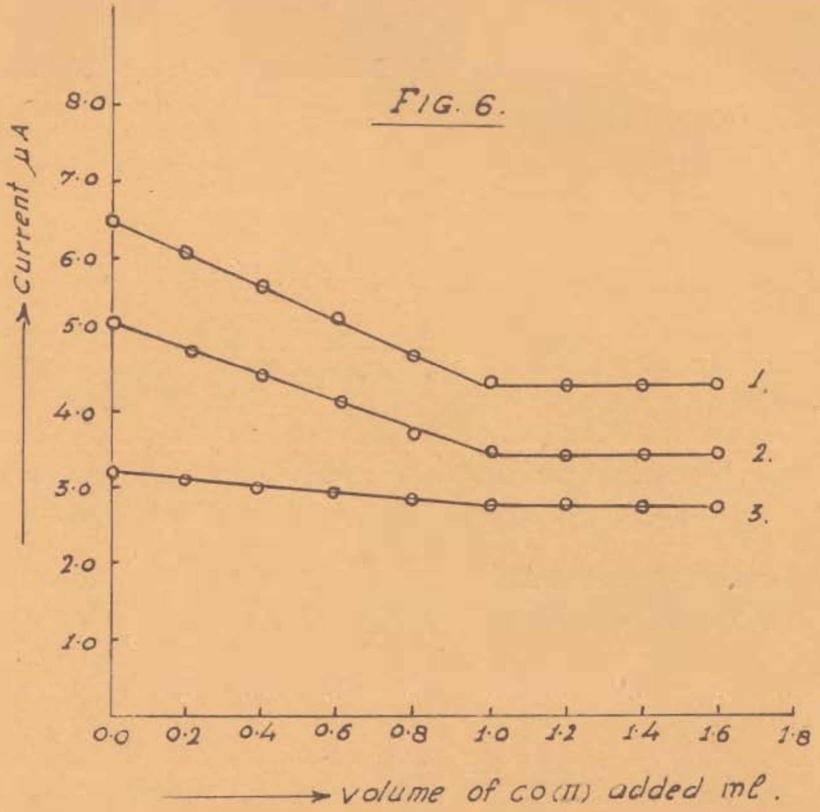
Results of amperometric titrations in absence of metal ions at pH 9.8.

Mgs.of Co(II) per litre	Co(II) found mgs. direct titrations at-0.3V	Co(II) found mgs. direct titrations at-1.55V	Mgs. of Co(II) per litre	Co(II) found mgs. Reverse titrations at -0.3V	Co(II) found mgs. Reverse titrations at -1.55V
29.465	29.435	-		-	-
58.93	58.93	-		-	-
2.946	2.917	-		-	-
			29.465	29.465	-
			58.930	58.930	-
			5.8930	5.834	-
			2.9465	2.917	-
			0.29465	0.2891	-
2.9465	-	2.975	-	-	-
0.29465	-	0.30	-	-	-
			2.9465	-	2.9465
			0.29465	-	0.2891

Presence of interferring metals:

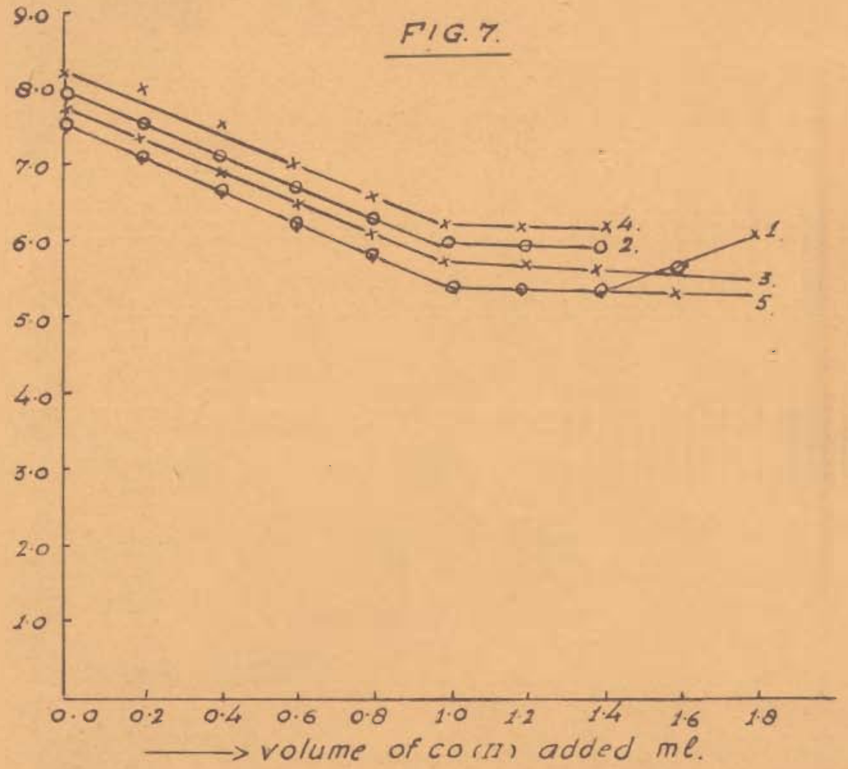
The interference of different metal ions was studied at an applied potential of -0.3V. In direct titrations, Co(II) was determined in presence of 10 fold of Cu(II) and in back titrations in presence of 5 fold of Cu(II). No interference was observed even when Ni(II) was present upto 100 fold for both direct and reverse titrations. Cr(III) when present in equal concentration did not interfere in direct titrations. In reverse titrations, appreciable oxidation of Cr(III) to chromate took place in presence of hexacyanoferrate (III) in this medium. Therefore reverse amperometric titration could not be carried out successfully, Ce(III) interfered in determination of Co(II) to an appreciable extent in direct and reverse titrations even when present to 1/10fold of Co(II) concentration. Probably due to the oxidation of Ce(III) to Ce(IV) by hexacyanoferrate (III) in ammonical medium. V(V) did not interfere when present upto 10 times of Co(II) in direct or reverse titrations. Fe(III) interfered due to the precipitation of hydroxide Fig.5, Table 3).

FIG. 6.



current µA
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
1.
2.
3.
volume of co(II) added ml.

FIG. 7.



9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
4.
2.
1
3.
5
volume of co(II) added ml.

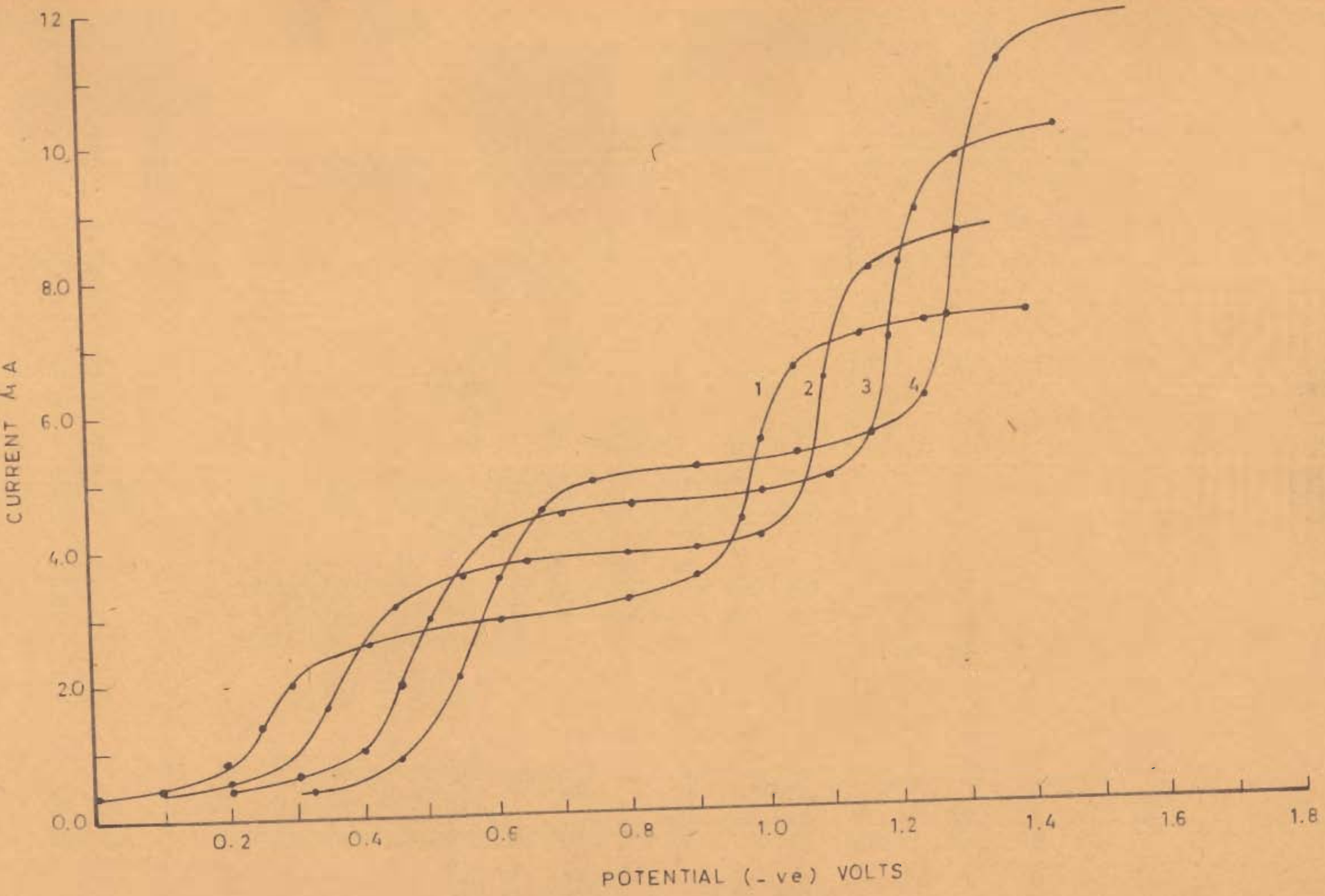

12
10
8.0
6.0
4.0
2.0
0.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3
4

FIGURE 8

TABLE No.3

Results of amperometric titrations in presence of metal ions at pH 9.8.

Mgs. of Co(II) per litre	Foreign metals added	Mgs. of foreign metal added	Mgs. of Co(II) found at -0.3V	
			Direct titration	Reverse titrations
29.465	Cu(II)	31.70	29.465	-
29.465	Ni(II)	2935.50	29.465	-
29.465	Cr(III)	25.60	29.465	-
29.465	V(V)	204.70	30.03	-
29.465	Cu(II)	158.50	-	28.914
29.465	Ni(II)	2935.50	-	29.465
29.465	V(V)	204.31	-	29.755

Gycine as complexing agent:(Absence of interfering metals):-

Back titrations could be carried out successfully at applied potential of -0.55 V. Direct titrations were not successful (error greater than ± 1.0 per cent). It was found possible to detect Co(II) upto the concentration of 0.5×10^{-5}M (Fig.6) Results are tabulated below:

TABLE No.4

Results of amperometric titrations in absence of metal ions at pH 8.0.

Mgs. of Co(II) per litre	Mgs. of Co(II) found at -0.55V. Reverse titrations
29.645	29.645
2.9645	2.9645
0.29645	0.2907

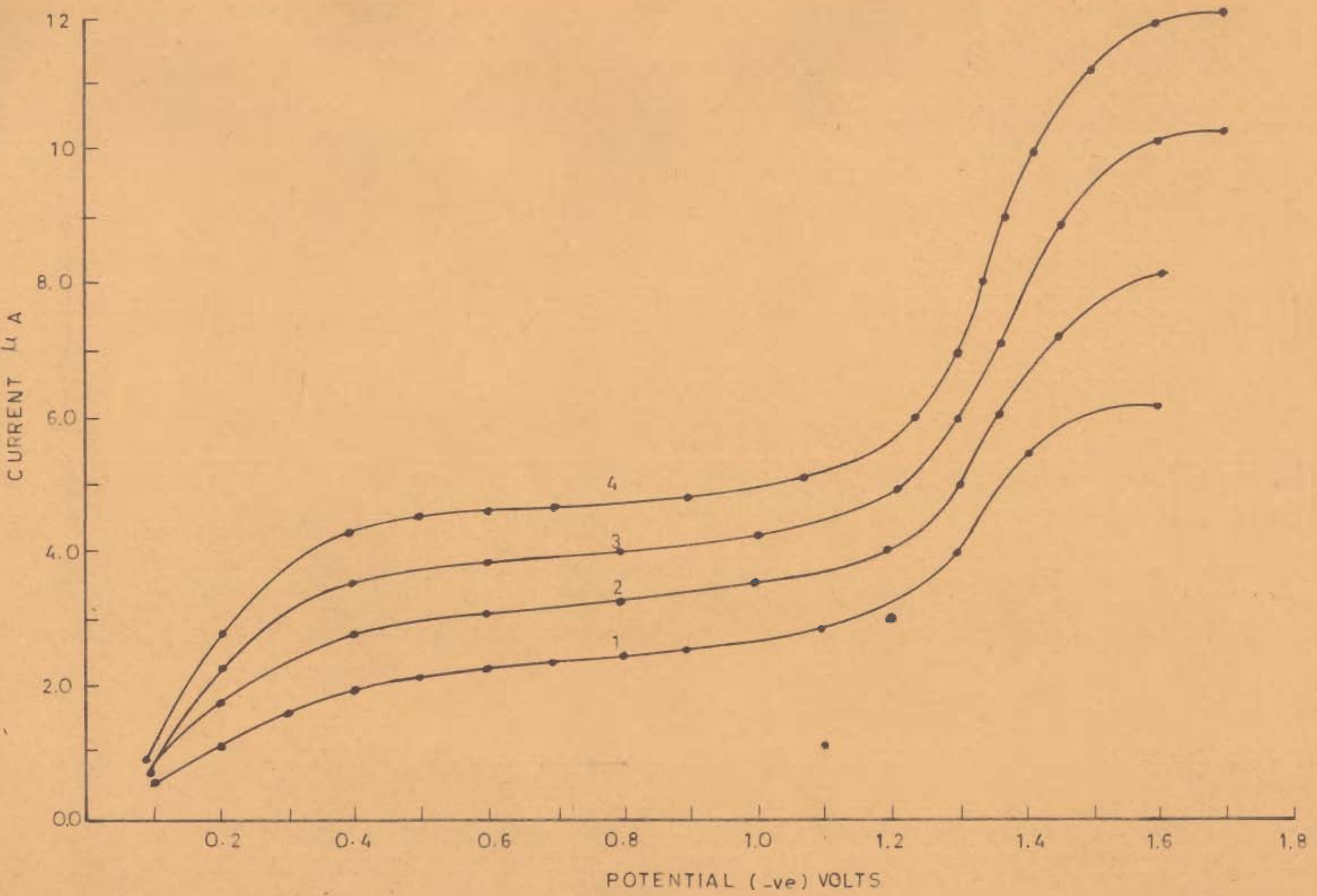

12
10
8.0
6.0
4.0
2.0
0.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
4
3
2
1

FIGURE 9

Presence of interfering metals:

Manganese (II) did not interfere when the use of citrate was avoided. Vanadium (V) interfered when present in small amounts. Fe(III) upto 10 fold did not interfere in this medium. Ni(II) did not interfere upto 100 fold of concentration. However, Cu(II) interfered when present even in traces. Ce(III) did not interfere when present in equal parts. Titrations in presence of 10 fold of Cr(III) in terms of concentration could be carried out without any interference. Results are tabulated below:

TABLE No.5

Results of amperometric titrations in presence of metal ions at pH 9.8.

Mgs. of Co(II) per litre	Foreign metals added	Mgs. of Foreign metals added	Mgs. of Co(II) found at -0.55 V.
			Reverse titrations
29.465	Mn(II)	274.00	29.17
29.465	Fe(III)	279.25	29.465
29.465	Ni(II)	2935.50	29.755
29.465	Ce(III)	70.06	30.03
29.465	Cr(III)	256.00	30.03

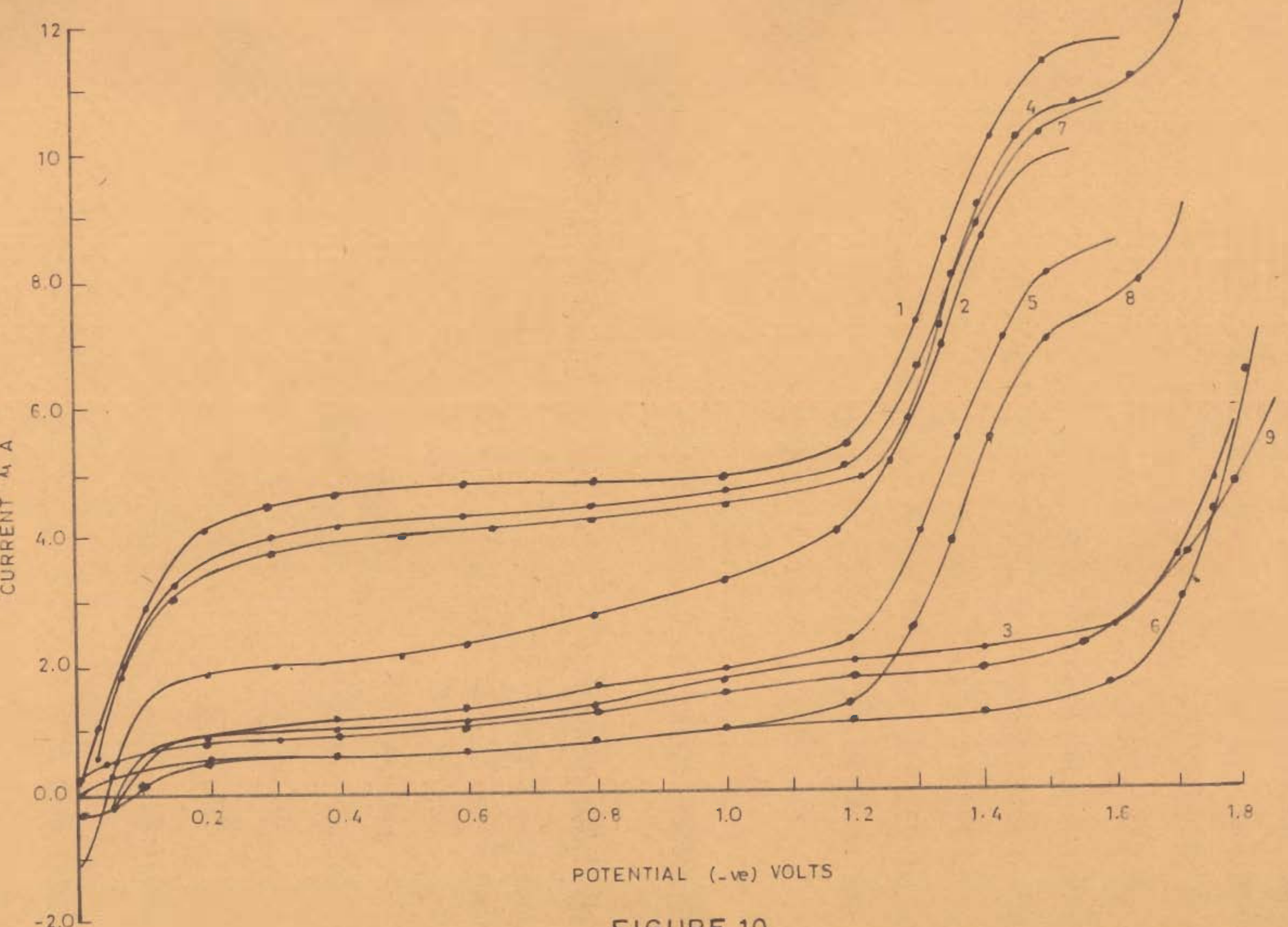

12
10
8.0
6.0
4.0
2.0
0.0
-2.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3
4
5
6
7
8
9

FIGURE 10

TABLE No.6

Logarithmic analysis of current voltage data for the second step of the solution containing 0.05×10^{-2}M cobalt chloride, 0.05M potassium chloride at pH 9.8. (Oxygen was passed for 12 hours)

(Reading from curve 7 Fig.1A)

Potential volts (-ve)	Current corrected for residual current	$\log \frac{i}{i_1 - i}$
1.15	0.10	-1.591
1.20	0.85	-0.4680
1.23	1.70	-0.1613
1.25	2.75	-0.3424
1.30	3.70	+1.0911
1.35	3.90	+1.5911
1.40	4.00	-

Fig.31

TABLE No.7

Limiting values of the current at different heights of mercury column for the second wave of the solution containing 0.5×10^{-3}M each of the reactants (binuclear complex) 0.05M pot. chloride at pH 9.8.

Height of mercury column hcorrected h(cm)	$\sqrt{h}$	Limiting current (i_1) at (1.4V)
36.2	1.5587	7.15
43.65	1.6400	7.65
52.60	1.7210	8.10
58.64	1.7682	8.25
66.50	1.8225	8.35

Fig.32

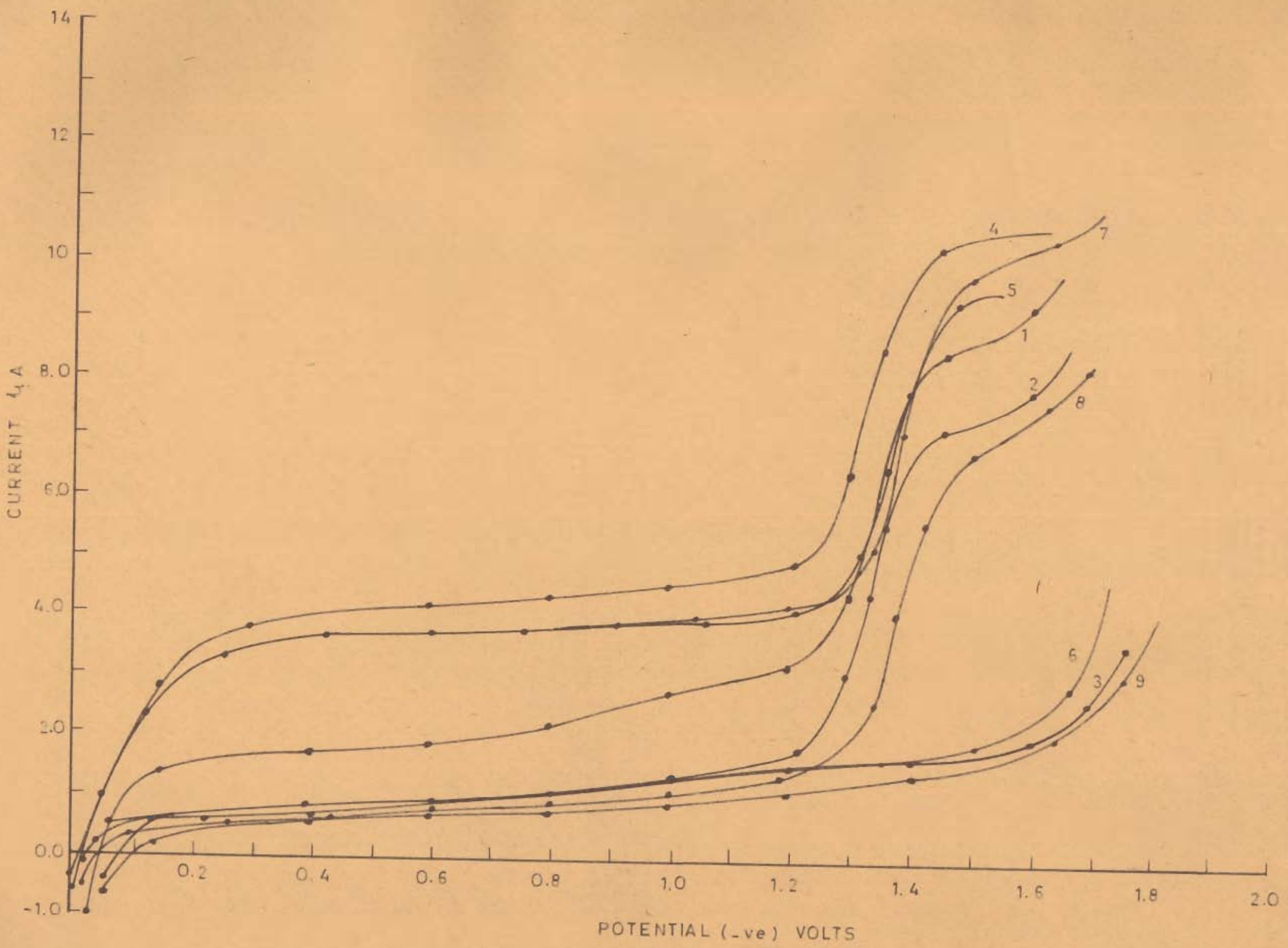

14
12
10
8.0
6.0
4.0
2.0
0.0
-1.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
POTENTIAL (-ve) VOLTS
4
7
5
1
2
8
6
3
9

FIGURE 11

TABLE No.8(A)

$E_{\frac{1}{2}}$ values of Co(II) and Co(III) complexes in amm. citrate:

Complex	$(E_{\frac{1}{2}})_I$	$(E_{\frac{1}{2}})_{II}$	No. of electransferred	
			Ist wave	2nd wave
Co(III) Binuclear Complex	-0455V	-1.195V	One	Two
Co(III) ammonia complex	-0.47V	-1.235V	One	Two
Co(II) ammonia complex	-1.230	-	-	One

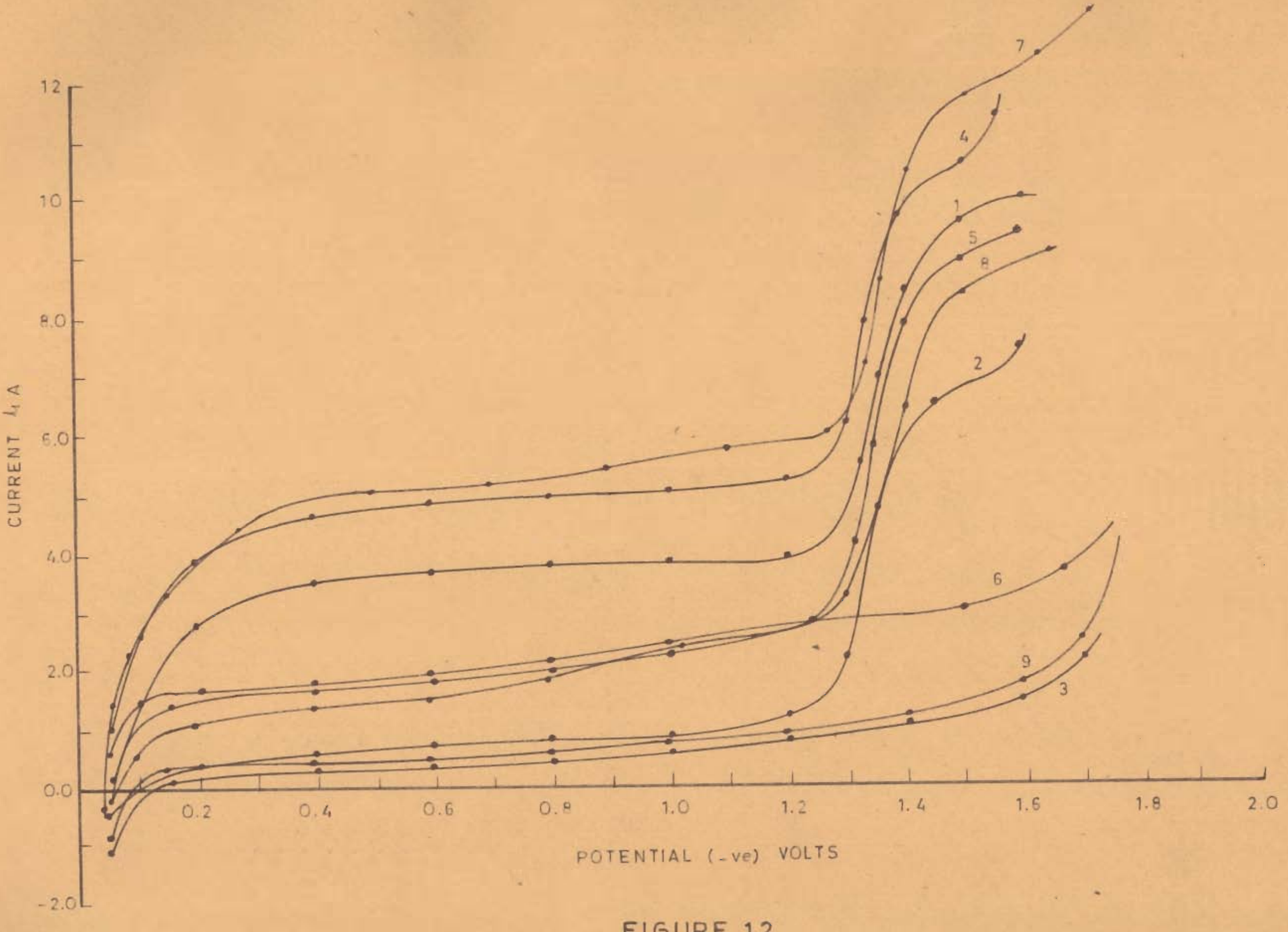
$(E_{\frac{1}{2}})_I$ and $(E_{\frac{1}{2}})_{II}$ represent the half wave potentials for Ist and 2nd step respectively.

TABLE No.8

Logarithmic analysis of the solution as mentioned in Table No.7 (Readings from curve 4 Fig.1A):

Potential (-ve) volts	Current corrected for residual current μA	$\log \frac{i}{i_1-i}$
1.10	0.1	-1.5441
1.15	0.5	-0.7924
1.17	1.2	-0.3010
1.20	2.0	+0.0969
1.22	2.9	+0.6173
1.25	3.1	+0.7924
1.30	3.4	+1.2304
1.35	3.55	+1.8524
1.40	3.6	-

Fig.33



12
10
8.0
6.0
4.0
2.0
0.0
-2.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
POTENTIAL (-ve) VOLTS
7
4
1
5
8
2
6
9
3

FIGURE 12

TABLE No.9

Logarithmic analysis of the current voltage readings for the second wave of the solution containing 0.05x10^{-2}M each of the reactants, 0.05M potassium chloride in glycine at pH 8.0 (data from curve 4 Fig.2A):

Potential (-ve) volts	Current corrected for residual current	log $\frac{i}{i_1-i}$
1.15	0.10	-1.5375
1.20	0.30	-1.0348
1.25	0.70	-0.3019
1.30	1.20	-0.6087
1.35	2.15	-0.3019
1.40	2.90	+0.1963
1.45	3.30	+1.6495
1.50	3.55	-

Fig.34

TABLE No.10

Limiting values of current at different heights for the solution (as mentioned in Table No.9)

Height of mercury column h_{cm}	$\sqrt{h}$	Limiting current at -1.5V.
36.20	1.5587	5.50
43.65	1.6400	6.00
52.60	1.7210	6.35
58.64	1.7682	6.50
66.50	1.8225	6.60

Fig.35

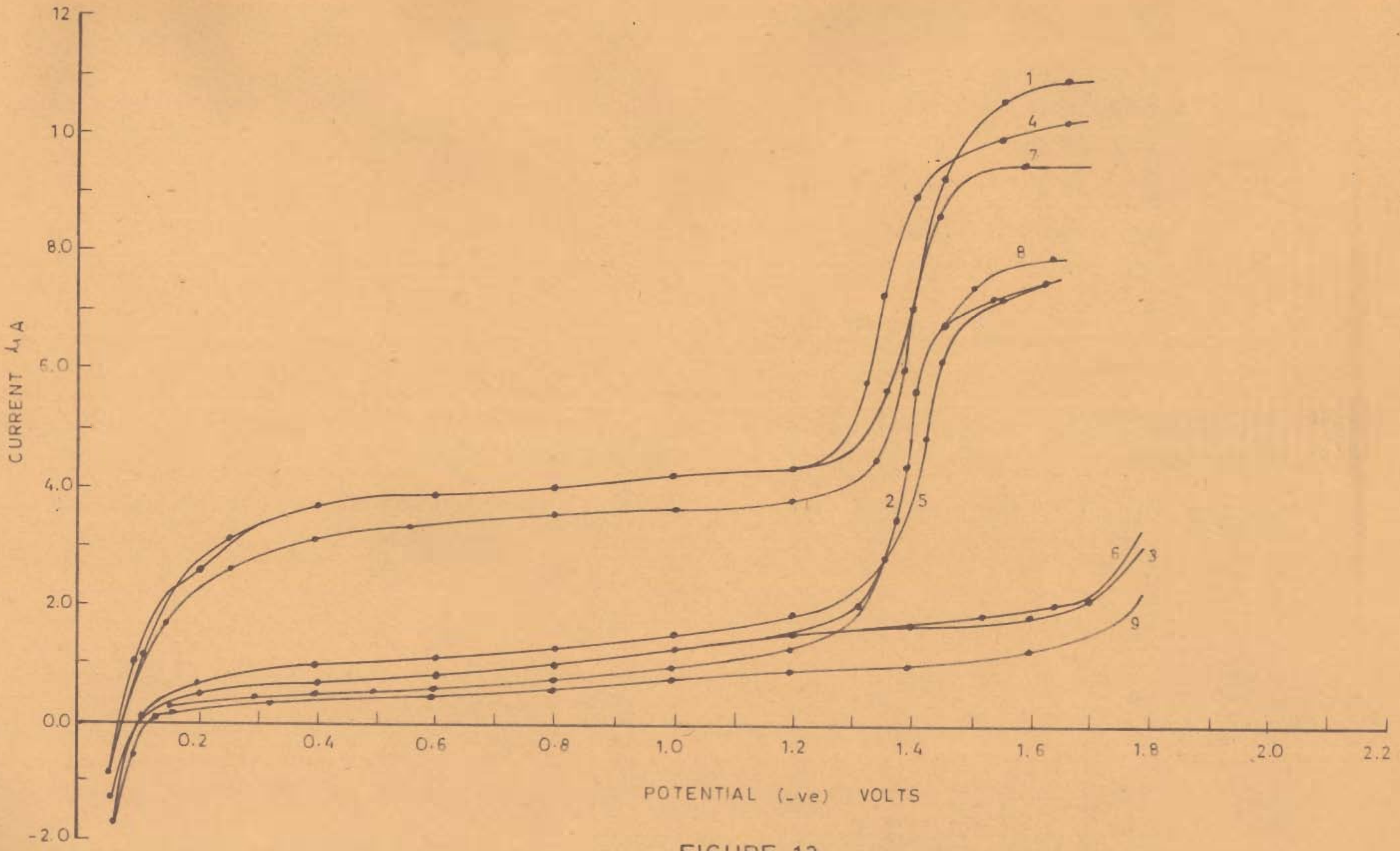

12
10
8.0
6.0
4.0
2.0
0.0
-2.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
POTENTIAL (-ve) VOLTS
1
4
7
8
2
5
6
3
9

FIGURE 13

TABLE No.11

Logarithmic analysis of the current voltage data for the second wave of solution solution containing 0.05×10^{-2} M each of Co(II) and hexacyanoferrate (III), 0.066 M sodium fluoride, and 0.53M glycine at pH 11.0 (data from curve 7 Fig.13).

Potential (-ve) volts	Current corrected for residual current	$\log \frac{i}{i_1 - i}$
1.1	0.25	-1.3767
1.20	0.35	-1.2156
1.25	0.50	-1.0492
1.30	0.70	-0.8973
1.35	1.00	-0.7076
1.38	1.95	-0.6403
1.40	3.30	+0.0713
1.45	5.15	+0.7341
1.50	5.90	+1.4764
1.55	6.05	+2.0928
1.60	6.10	-

Fig.36

TABLE No.12

Limiting value of current at different heights for the solution mention in table No.11

Height of mercury column h(cm)	$\sqrt{h}$ cm	Limiting value of current at -1.6V.
36.20	1.5587	8.50
43.65	1.6400	9.25
52.60	1.7210	9.75
58.64	1.7682	10.05
66.50	1.8225	10.20

Fig.37

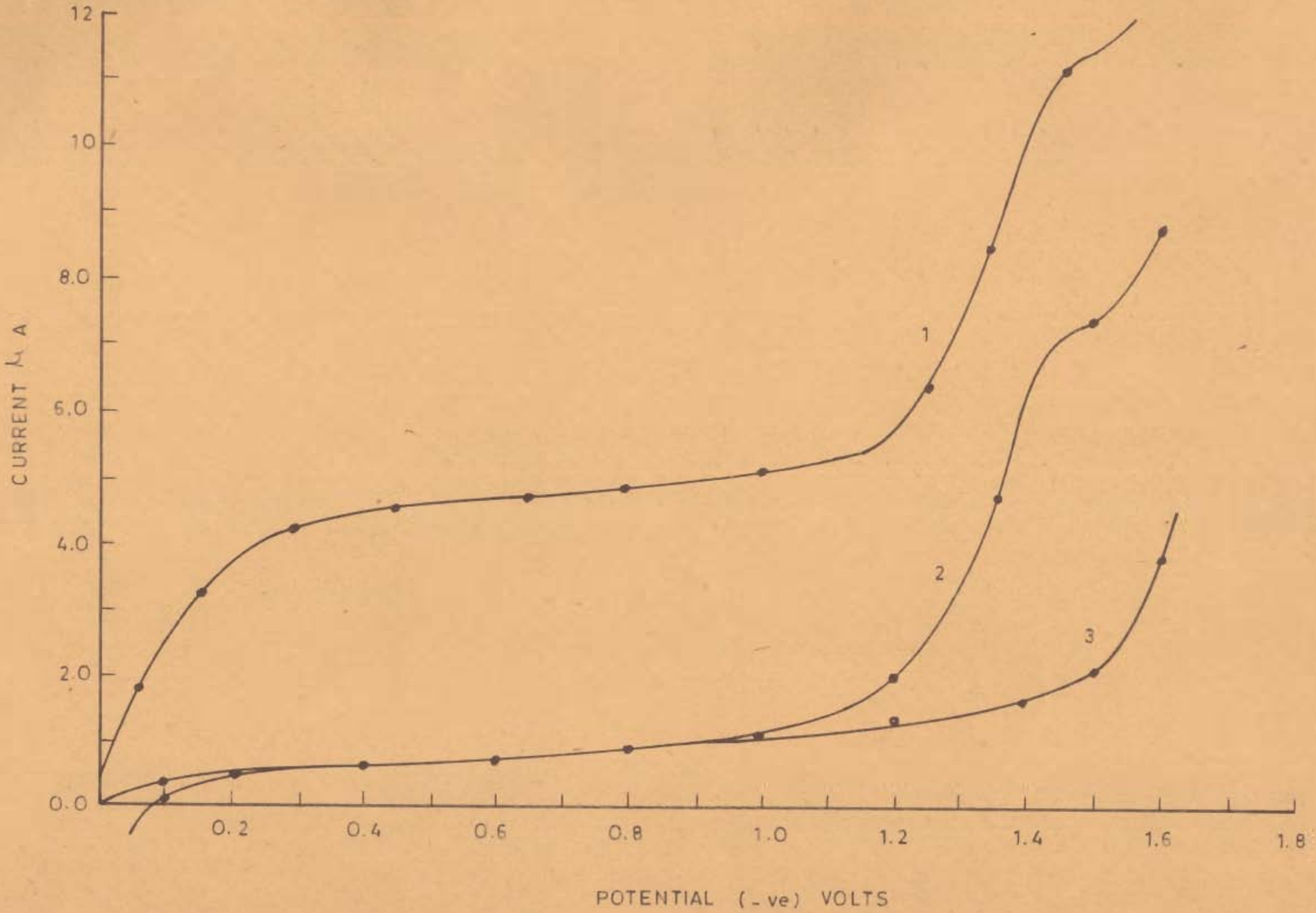

12
10
8.0
6.0
4.0
2.0
0.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 14

TABLE No.13

Logarithmic analysis of the current voltage data of the solution containing 0.05×10^{-2}M Co(II), 0.066M sodium fluoride and 0.53M glycine at pH 11.0 (data from curve 8 Fig.13).

Potential (-ve) volts	Current (i) currected for residual current	$\log \frac{i}{I_1 - i}$
1.10	0.1	-1.8239
1.20	0.2	-1.5218
1.25	0.3	-1.3278
1.30	0.7	-0.9438
1.35	1.55	-0.5340
1.38	2.8	-0.2603
1.40	4.6	+0.2826
1.45	5.7	+0.6952
1.50	6.3	+1.1007
1.55	6.7	+1.6500
1.60	6.85	-

Fig.38

TABLE No.14

Limiting values of current at different height of mercury column for the solution as mention in table 13

Height of mercury column h_{corr}	$\sqrt{h}$	Limiting current at (-1.60V).
cm	cm	
36.20	1.5587	7.15
43.65	1.6400	7.60
52.60	1.7210	7.95
58.64	1.7682	8.20
66.50	1.8225	8.25

Fig.39

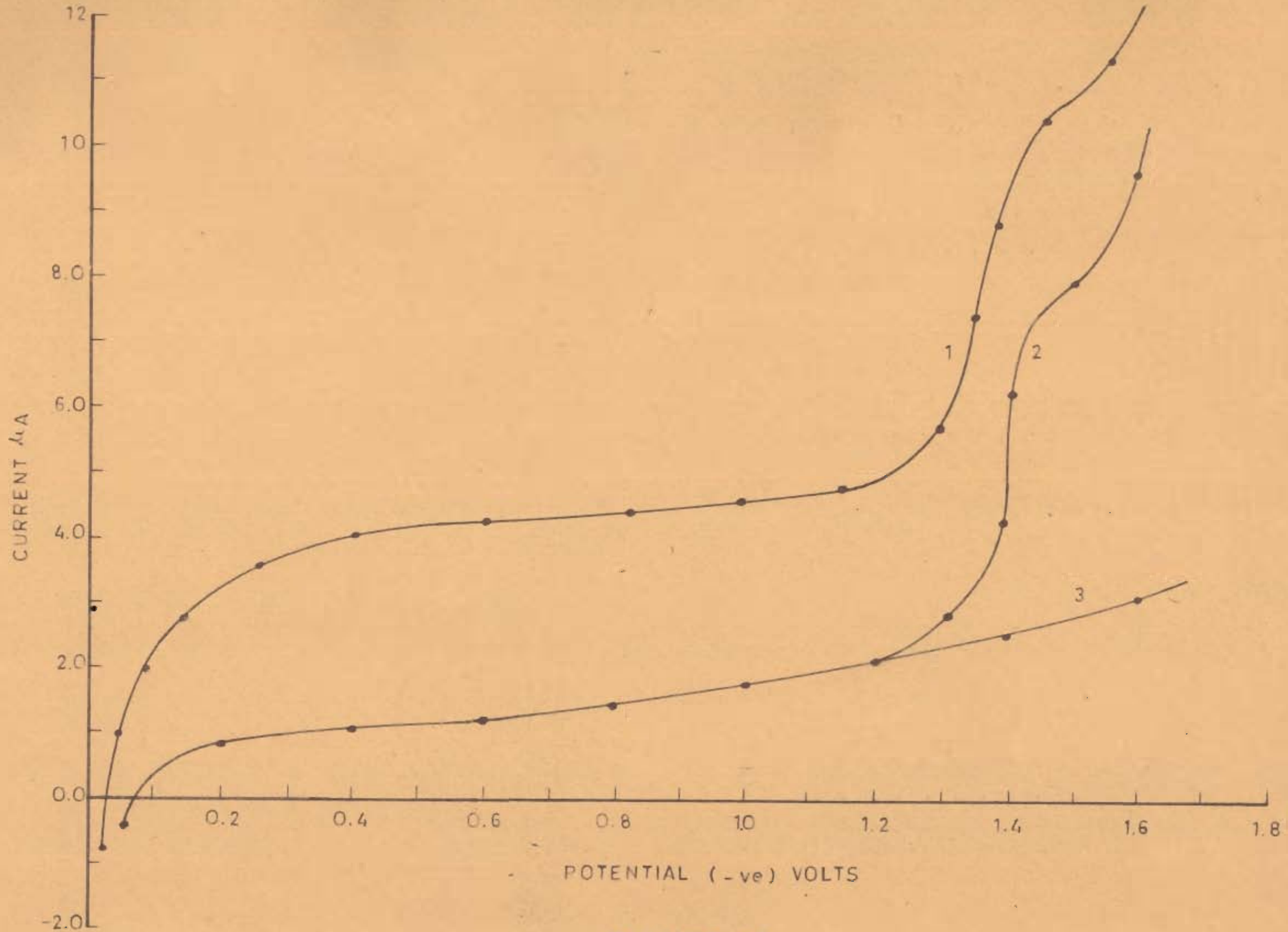

12
10
8.0
6.0
4.0
2.0
0.0
-2.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 15

TABLE No.15

Effect of pH and concentration of electrolytes on half wave potential of resulted Co(III) and Co(II) glycine complexes.

Concentration of glycine	0.32M				0.40M				0.53M			
pH	8.0	9.0	10.0	11.0	8.0	9.0	10.0	11.0	8.0	9.0	10.0	11.0
Co(III)glycine complex Half wave potential $=E_{\frac{1}{2}}$ (-ve.V.)												
Sodium fluoride 0.066M												
$(E_{\frac{1}{2}})_I$	0.08	-	-	-	0.08	-	-	-	0.08	-	-	-
$(E_{\frac{1}{2}})_{II}$	1.365	1.365	1.365	1.42	1.36	1.36	1.36	1.41	1.35	1.38	1.385	1.4
Potassium Nitrate 0.066M $(E_{\frac{1}{2}})_{II}$	-	-	-	-	-	-	-	-	1.34	1.36	1.40	1.42
Potassium chlorate 0.066M $(E_{\frac{1}{2}})_{II}$	-	-	-	-	-	-	-	-	1.36	1.37	1.38	1.40
Sodium Sulphate 0.033M$(E_{\frac{1}{2}})_{II}$	-	-	-	-	-	-	-	-	1.335	1.35	1.395	1.41
Calcium Chloride 0.133M$(E_{\frac{1}{2}})_{II}$	-	-	-	-	-	-	-	-	-	0.25	0.26	0.27
$(E_{\frac{1}{2}})_{II}$	-	-	-	-	-	-	-	-	1.31	1.36	1.39	1.40
Co(II) glycine complex half wave potential$=E_{\frac{1}{2}}$(-ve)volts												
Sodium Fluoride 0.066M$(E_{\frac{1}{2}})$	1.34	1.34	1.34	1.42	1.36	1.36	1.36	1.39	1.345	1.36	1.37	1.40
Potassium nitrate -do-	-	-	-	-	-	-	-	-	1.34	1.39	1.40	1.40
Potassium chlorate0.033M-do-	-	-	-	-	-	-	-	-	1.35	1.39	1.365	1.38
Sodium sulphate 0.033M -do-	-	-	-	-	-	-	-	-	1.335	1.345	1.365	1.38
Calcium chloride 0.133M-do-	-	-	-	-	-	-	-	-	1.31	1.36	1.39	1.40

$(E_{\frac{1}{2}})_I$ and $(E_{\frac{1}{2}})_{II}$ represent the half wave potentials for Ist and second steps of the Co(III) glycine complex respectively, and $(E_{\frac{1}{2}})$ represents the half wave potential of Co(II) glycine complex.

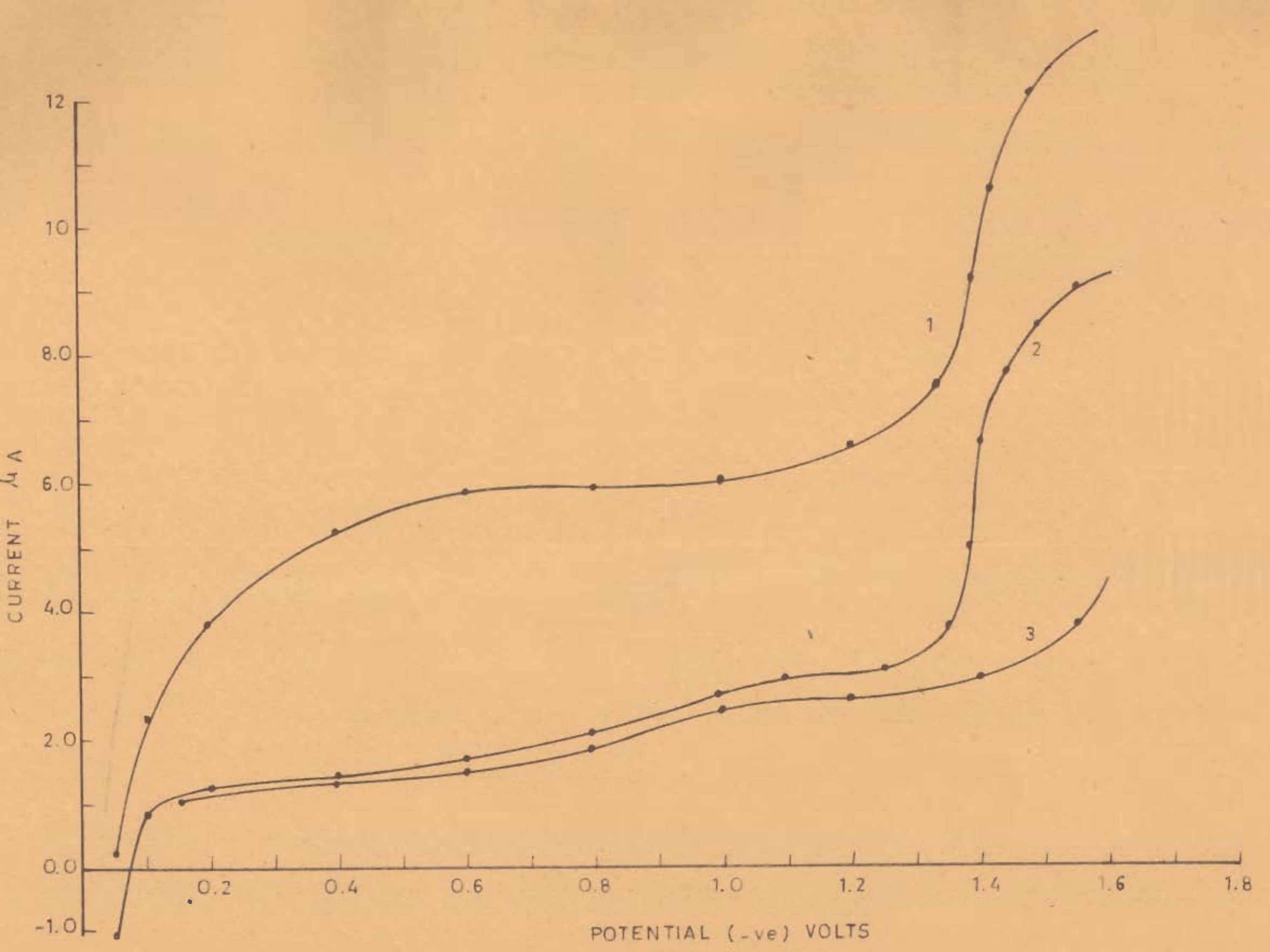

12
10
8.0
6.0
4.0
2.0
0.0
-1.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 16

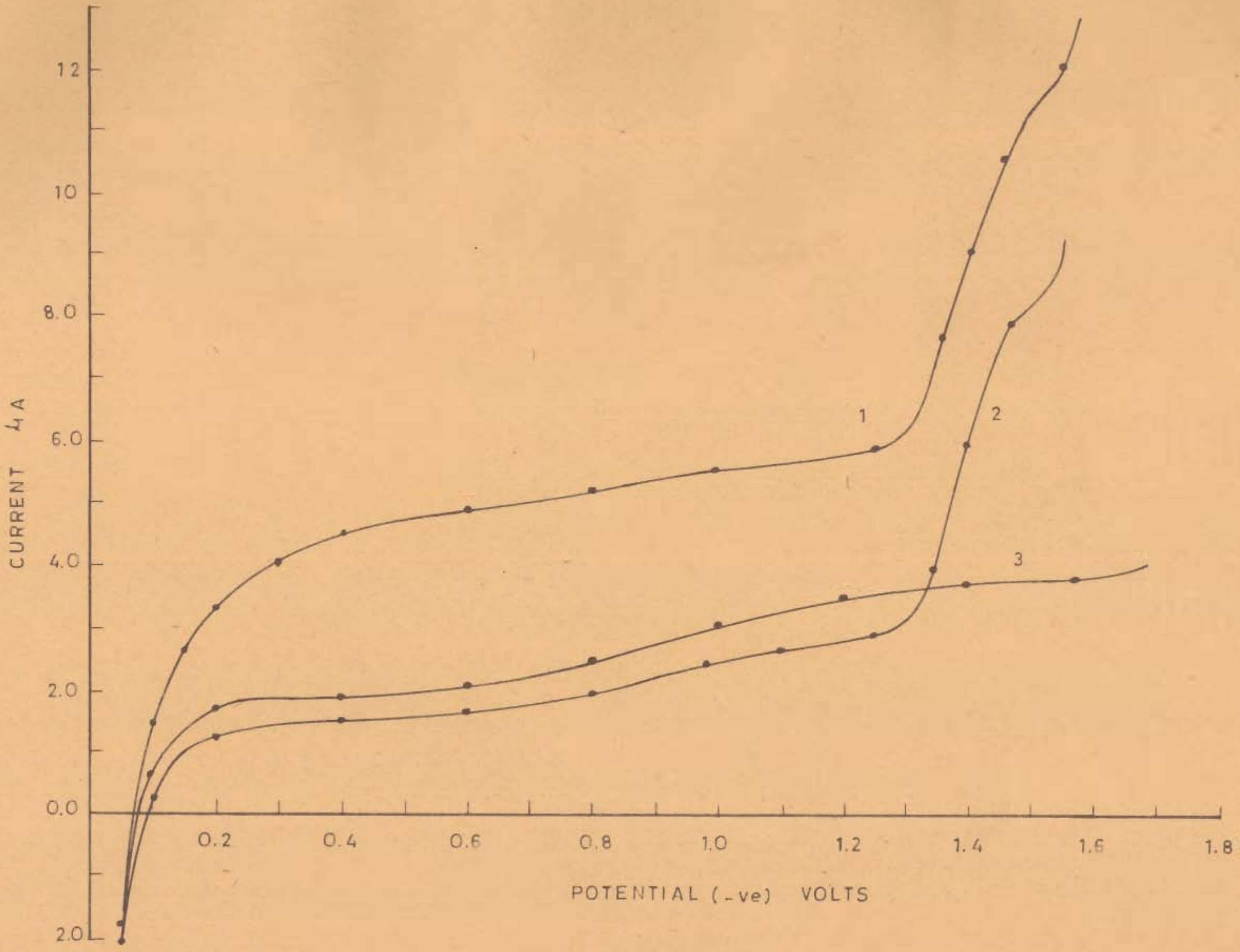

12
10
8.0
6.0
4.0
2.0
0.0
2.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 17

CAPTIONS

Fig.1 A:

Curves 1,2,3,4,5,6,7 and 8 represent the polarograms of the solutions in ammonium citrate buffer pH 9.8 containing:

1. 0.05x10^{-2}M hexacyanoferrate (III); 0.05M potassium chloride.
2. 0.05x10^{-2}M Cobalt (II); 0.05M potassium chloride.
3. 0.025x10^{-2}M hexacyanoferrate (III); 0.025x10^{-2}M Cobalt (II) and 0.05M potassium chloride.
4. 0.05x10^{-2}M hexacyanoferrate (III); 0.05x10^{-2}M Cobalt (II) and 0.05M potassium chloride.
5. 0.075x10^{-2}M hexacyanoferrate (III); 0.075x10^{-2}M Cobalt (II) and 0.05M potassium chloride.
6. 0.10x10^{-2}M hexacyanoferrate (III); 0.10x10^{-2}M Cobalt (II) and 0.05M potassium chloride.
7. 0.05x10^{-2}M hexacyanoferrate (III); 0.05x10^{-2}M Cobalt (II) and 0.05M potassium chloride (oxygen was passed for 12 hours).
8. 0.05M potassium chloride.

The curge No.1 starts from 0.0V and No.2 to 8 each starts from -0.2V. Each curve was recorded at 1/5 senstivity.

Fig.1 B:

Effect of metal ions on the reduction steps in amm. citrate buffer pH 9.8 curves 1,2,3,4,5 and 6 respectively represents the current voltage curves of the solutions containing:

1. 0.05x10^{-2}M hexacyanoferrate (III), 0.05x10^{-2}M
2. As in (1) and 0.05x10^{-2}M Cu (II).

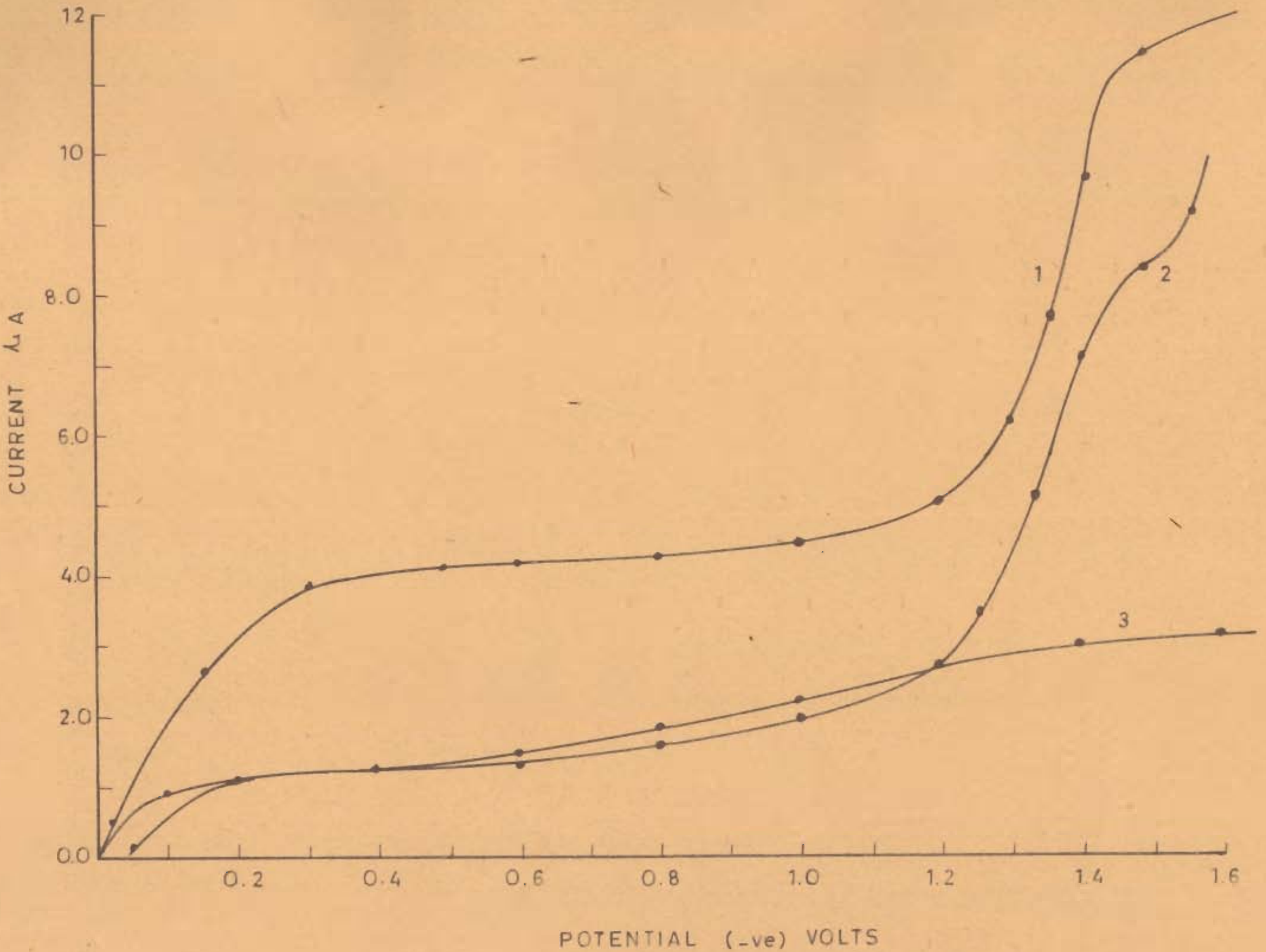

12
10
8.0
6.0
4.0
2.0
0.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 18

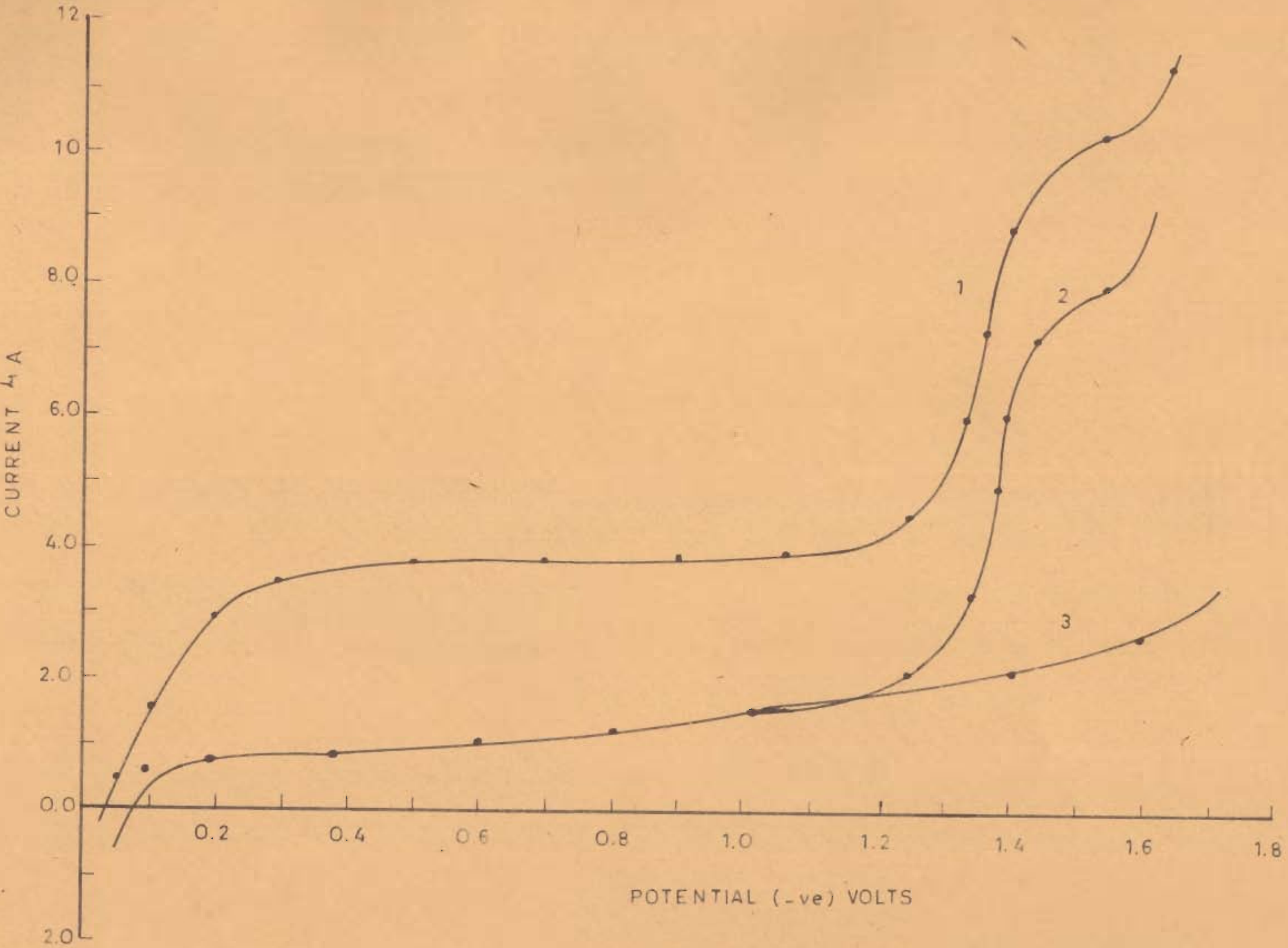

12
10
8.0
6.0
4.0
2.0
0.0
2.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 19

3. As in (1) and 0.05×10^{-2}M Cr (III).
4. As in (1) and 0.05×10^{-2}M Ce (III).
5. As in (1) and 0.05×10^{-2}M Ni (II).
6. As in (1) and 0.05×10^{-2}M V (V).

Curves 1,2,3,4,5 and 6 were pecorded at 1/5, 1/7, 1/5, 1/5, 1/5 and 1/10 senstivities (origion at -0.1V)

Fig.2A:

Curve 1,2,3,4, and 5 represent the polarograms of the solutions in glycine buffer pH 8.0 containing.

1. 0.5×10^{-3}M hexacyanoferrate (III); 0.05M potassium chloride.
2. 0.5×10^{-3} Cobalt (II) 0.05M potassium chloride.
3. 0.25×10^{-3}M hexacyanoferrate (III), 0.25×10^{-3}M Cobalt (II) and 0.05M potassium chloride.
4. 0.5×10^{-3}M hexacyanoferrate (III); 0.5×10^{-3}M Co(II) and 0.05M potassium chloride.
5. 1.0×10^{-3}M Co(II), 1.0×10^{-3}M hexacyanoferrate (III), 0.05M potassium chloride.
6. 1.0×10^{-3}M hexacyanoferrate (III), 1.0×10^{-3}M Co(II) and 0.05M potassium chloride.
7. 0.05M potassium chloride.

The origion of curves (1,3) and (2,4) are at (0.0) and (-0.1) V. respectively. Each curve was recorded at 1/5 senstivity.

Fig.2B:

Effect of metal ions on the reduction steps in glycine buffer pH 8.0 curves 1,2,3,4,5 and 6 represents the current voltage curves of the solutions containing reactants and metal ions as mentioned in (Fig.1B) Curve 7 contains 0.05×10^{-2}M Mn (II). Curves 1-5, 7 and 6 were

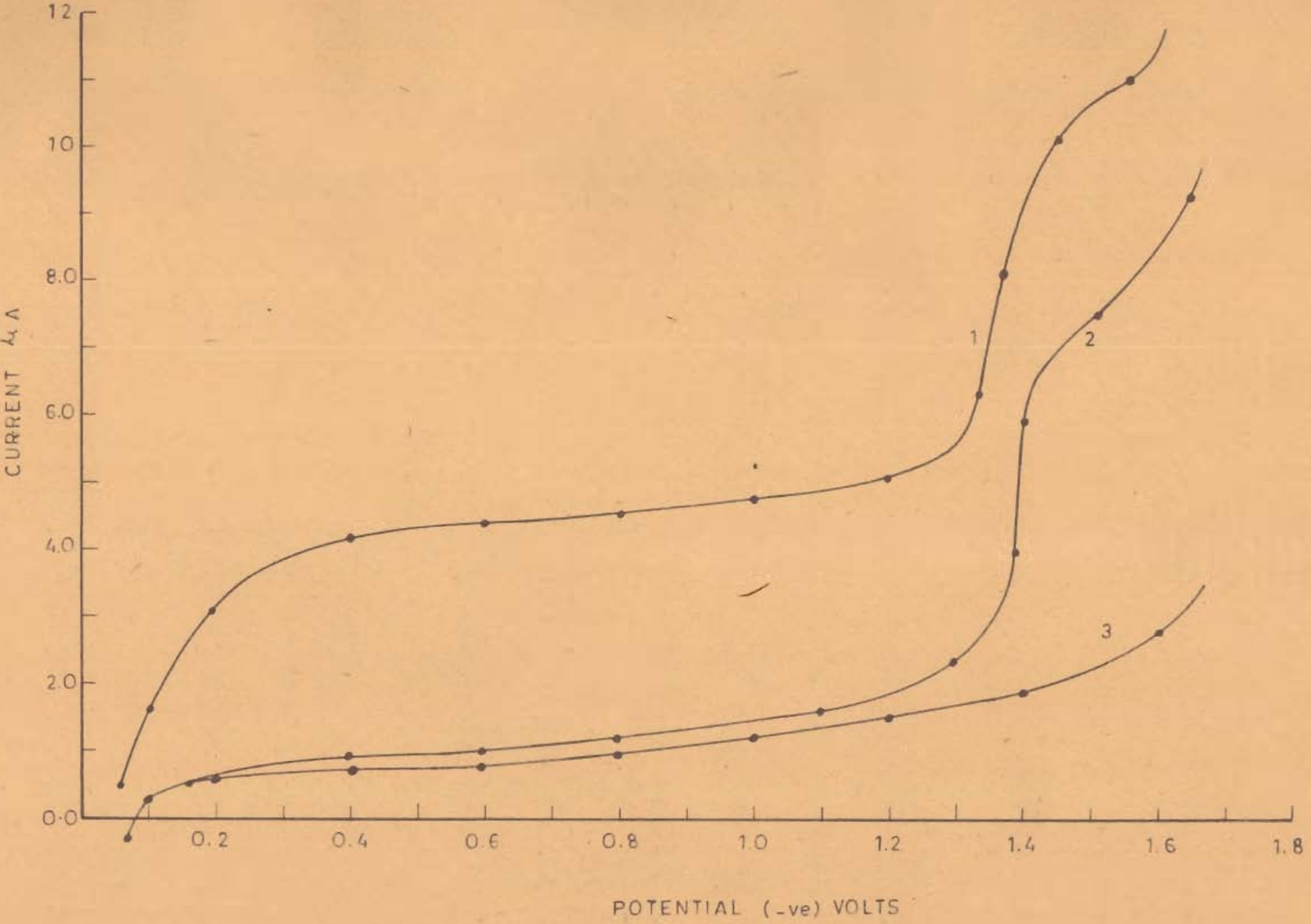
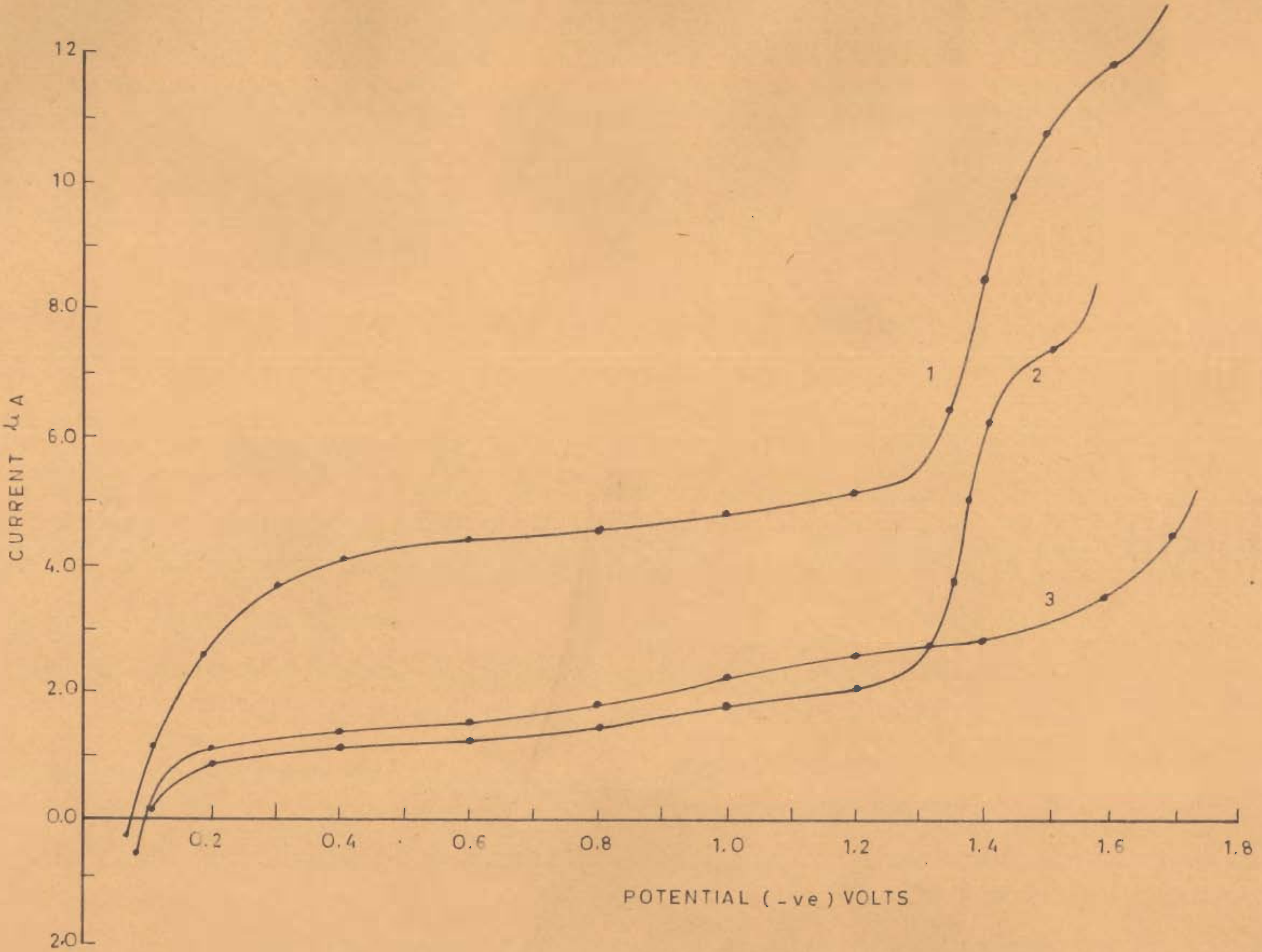

12
10
8.0
6.0
4.0
2.0
0·0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 20



12
10
8.0
6.0
4.0
2.0
0.0
2.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 21

recorded at 1/5 and 1/10 senstivities (origion at -0.1V).

Fig.3:

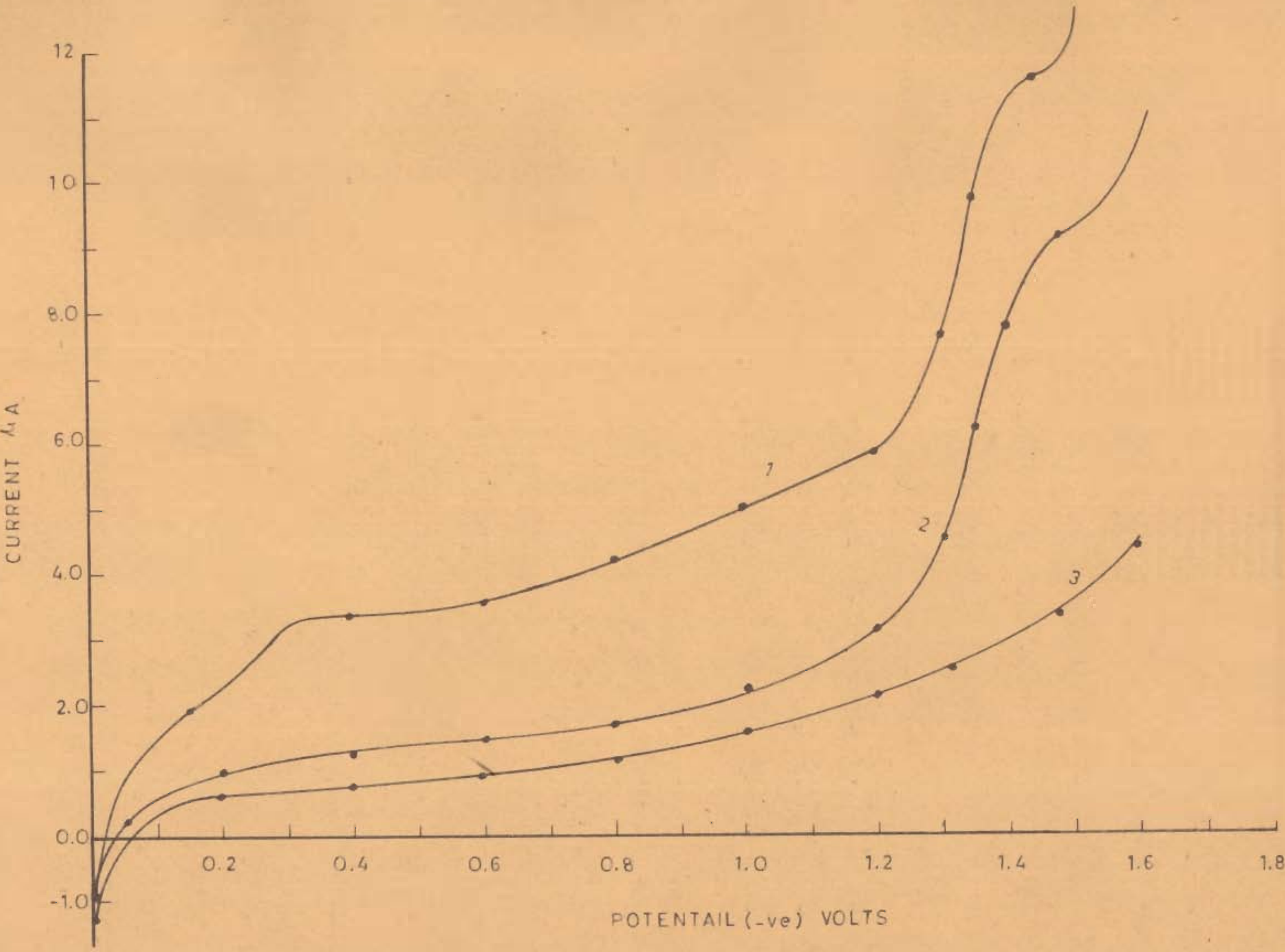
Amperometric titration curves at -0.3 V in ammonium citrate buffer pH 9.8. 1,2,3 direct titration curves Co(II) in cell (concentration of the reactants $0.5x10^{-3}$M, $1.0x10^{-3}$M and $0.5x10^{-4}$M respectively) Curves 4,5,6,7 and 8 reverse titration curves (hexacyanoferrate (III) in cell) concentration of hexacyanoferrate (III) $0.5x10^{-3}$M, $1.0x10^{-3}$M, $1.0x10^{-4}$M, $0.5x10^{-4}$M, $0.25x10^{-4}$M and $0.5x10^{-5}$M and that of Co(II) $0.5x10^{-3}$M, $1.0x10^{-3}$M $1.0x10^{-4}$M, $0.5x10^{-4}$M, $0.5x10^{-4}$M and $0.5x10^{-5}$M.

Fig.4:

Amperometric titration curves at -1.5V in ammonium citrate buffer pH 9.8 curve 1,2 direct titratior (Cobalt II in cell) Concentration of the reactants, ($0.5x10^{-4}$M), $0.5x10^{-5}$M). 3,4 reverse amperometric titration curves (concentration of reactants $0.5x10^{-4}$M, $0.5x10^{-5}$M).

Fig.5:

Amperometric titration curves at -0.3V in amm. citrate buffer pH 9.8. Curve 1,2,3,4 direct titrations in presence of $0.5x10^{-2}$M, $0.5x10^{-1}$M, $0.5x10^{-3}$M, $0.5x10^{-2}$M Cu(II), Ni(II), Cr(III), V(V), (Concentration of reactants $0.5x10^{-3}$M). Curve 5,6 and 7 reverse amperometric titrations in presence of $0.25x10^{-2}$M, $0.5x10^{-1}$M and $0.5x10^{-2}$M Cu(II), Ni(II) and V(V) respectively (concentration of reactants ($0.5x10^{-3}$M).



12
10
8.0
6.0
4.0
2.0
0.0
-1.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTAIL (-ve) VOLTS
1
2
3

FIGURE 22

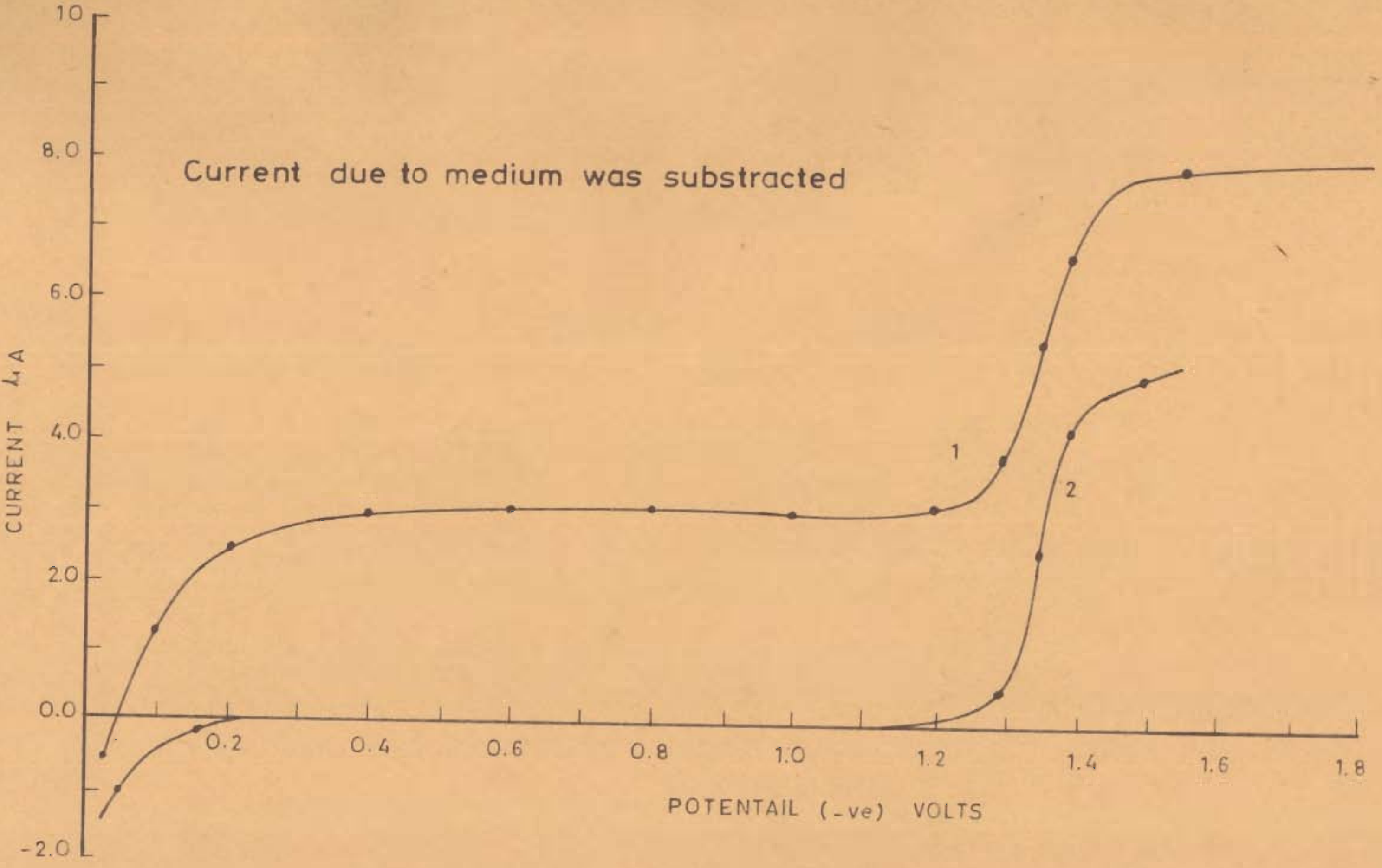

10
8.0
6.0
4.0
2.0
0.0
-2.0
CURRENT μA
Current due to medium was substracted
1
2
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTAIL (-ve) VOLTS

FIGURE 23

Fig.6:

Amperometric titration curves at -0.55V in glycine buffer of pH 8.0. 1,2,3 back amperometric titration curves (hexacyanoferrate (III) in cell) (concentration of the reactants 0.5x10^{-3}M, 0.5x10^{-4}M 0.5x10^{-5}M).

Fig.7:

Amperometric titration curves at -0.55V in glycine buffer of pH 8.0. 1,2,3,4 and 5 back titrations in presence of 0.5x10^{-2}M, 0.5x10^{-2}M, 0.5x10^{-1}M 0.5x10^{-3}M and 0.5x10^{-2}M; Mn (II), Fe(III), Ni(II), Ce(III) and Cr(III) (concentrations of the reactants (0.5x10^{-3}M).

Fig.8:

Curves 1,2,3,4 represent the polarograms of the solution containing reactants and electrolyte of the concentrations as given in Fig.1A for the curves 3,4,5,6 but the order of concentration of reactants was 10^{-3}M in-stead of 10^{-2}M. (each curve starts from -0.2V at 1/2 senstivity).

Fig.9:

Curves 1,2,3,4, represent the polarograms of the solutions containing reactants and electrolytes of the concentrations as given in Fig.2A for the curves 3,4,5,6 but the order of concentration was 10^{-4}M instead of 10^{-3}M (each curve starts from -0.1V at 1/2 senstivity).

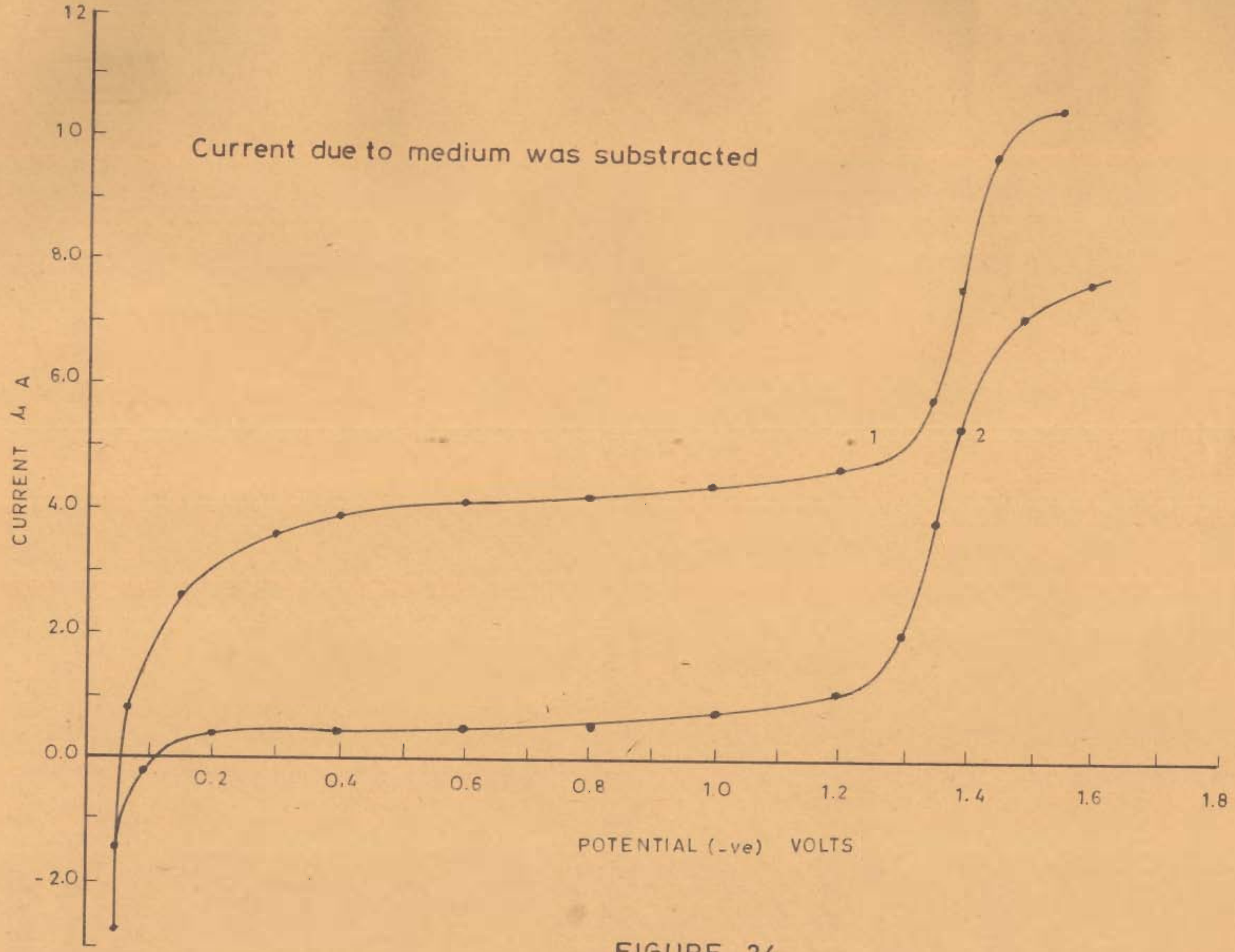

Current due to medium was substracted
CURRENT μ A
12
10
8.0
6.0
4.0
2.0
0.0
- 2.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2

FIGURE 24

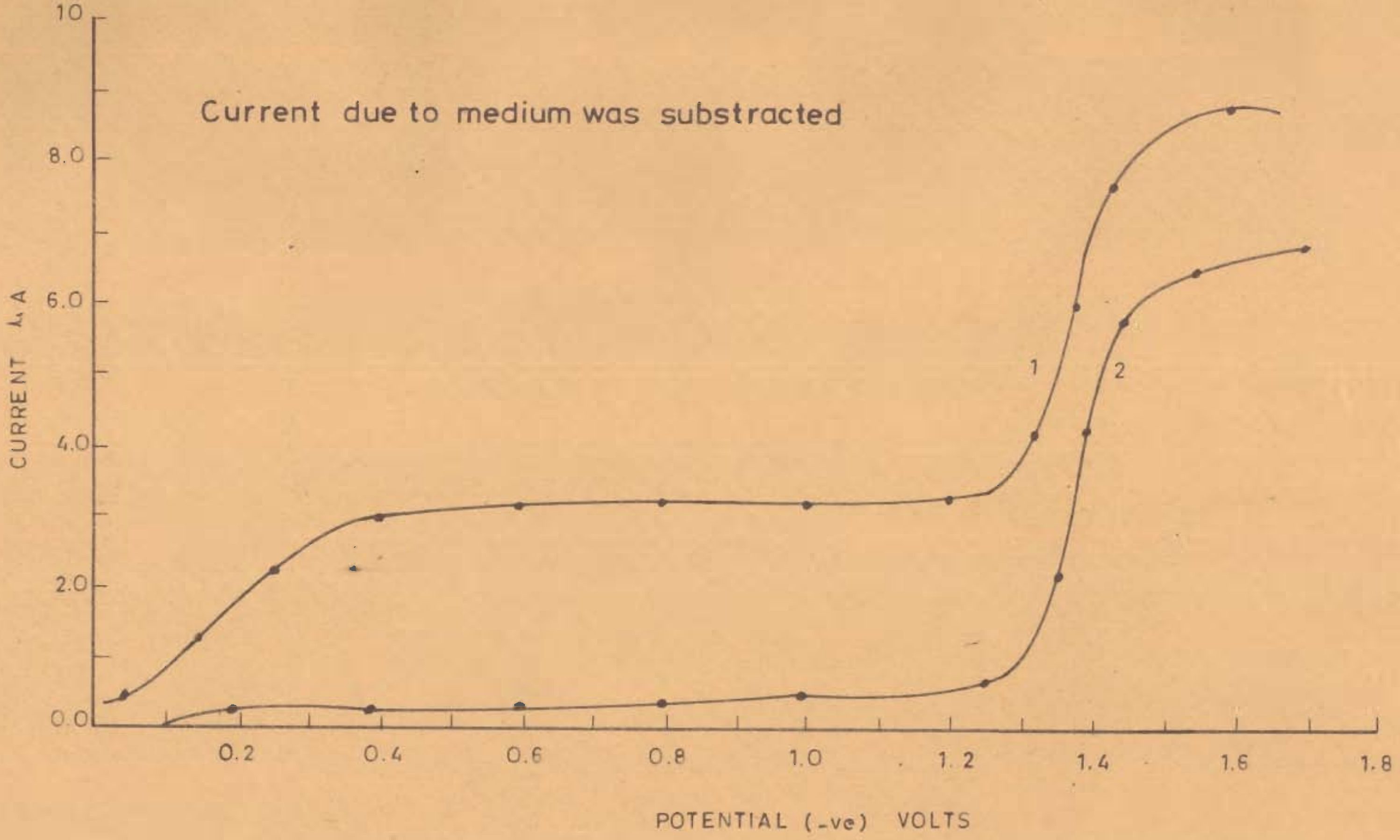

Current due to medium was substracted
10
8.0
6.0
4.0
2.0
0.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2

FIGURE 25

Fig.10-29:

(As given in Table1,15).

Fig.30:

Curves 1,2,3,4 represents the polarograms of the solutions containing (0.025, 0.05, 0.075, 0.10×10^{-2}M) each of Co(II) and hexacyanoferrate (III), 0.133M calcium chloride and 0.53M glycine at pH 8.0.

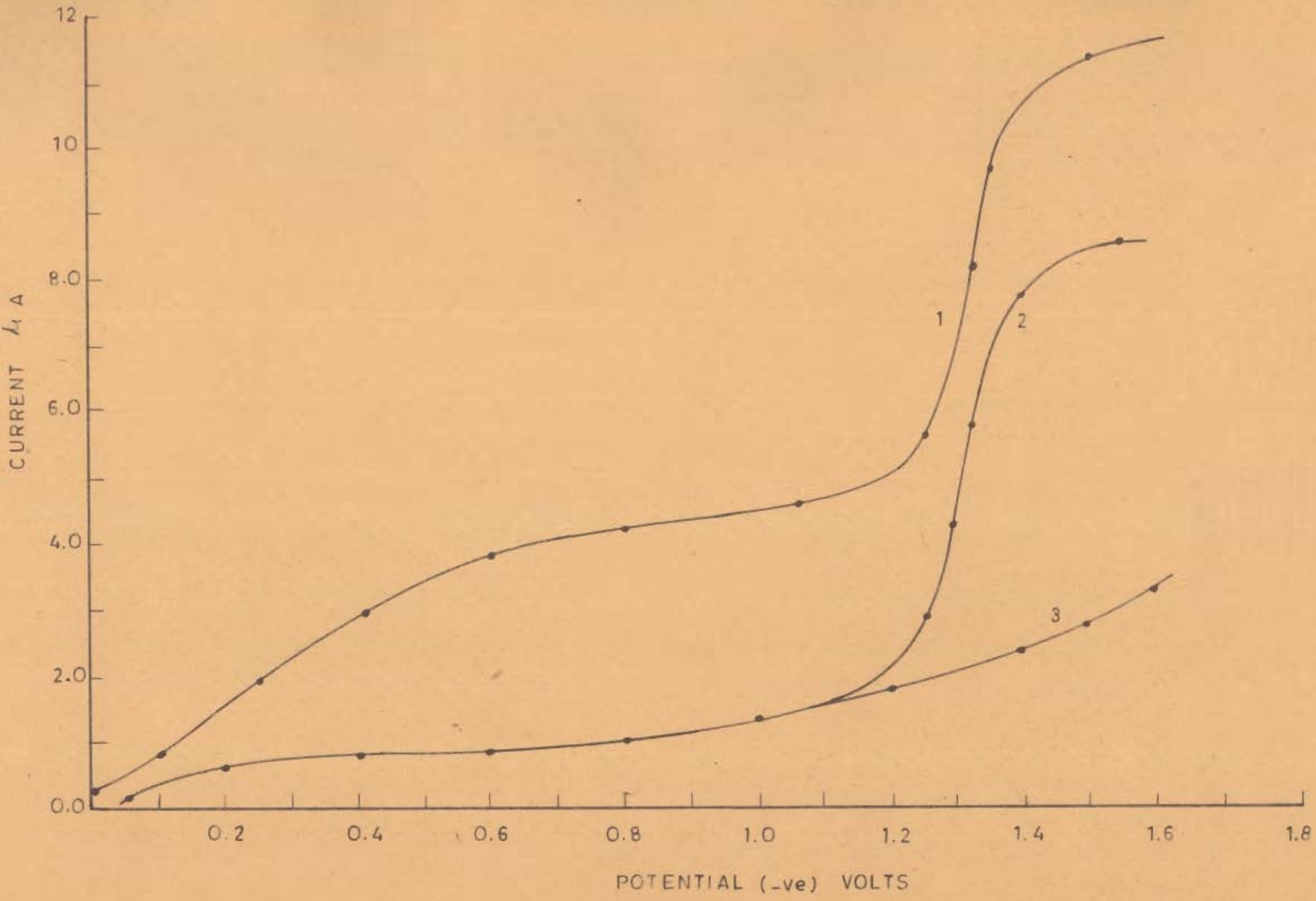

12
10
8.0
6.0
4.0
2.0
0.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 26

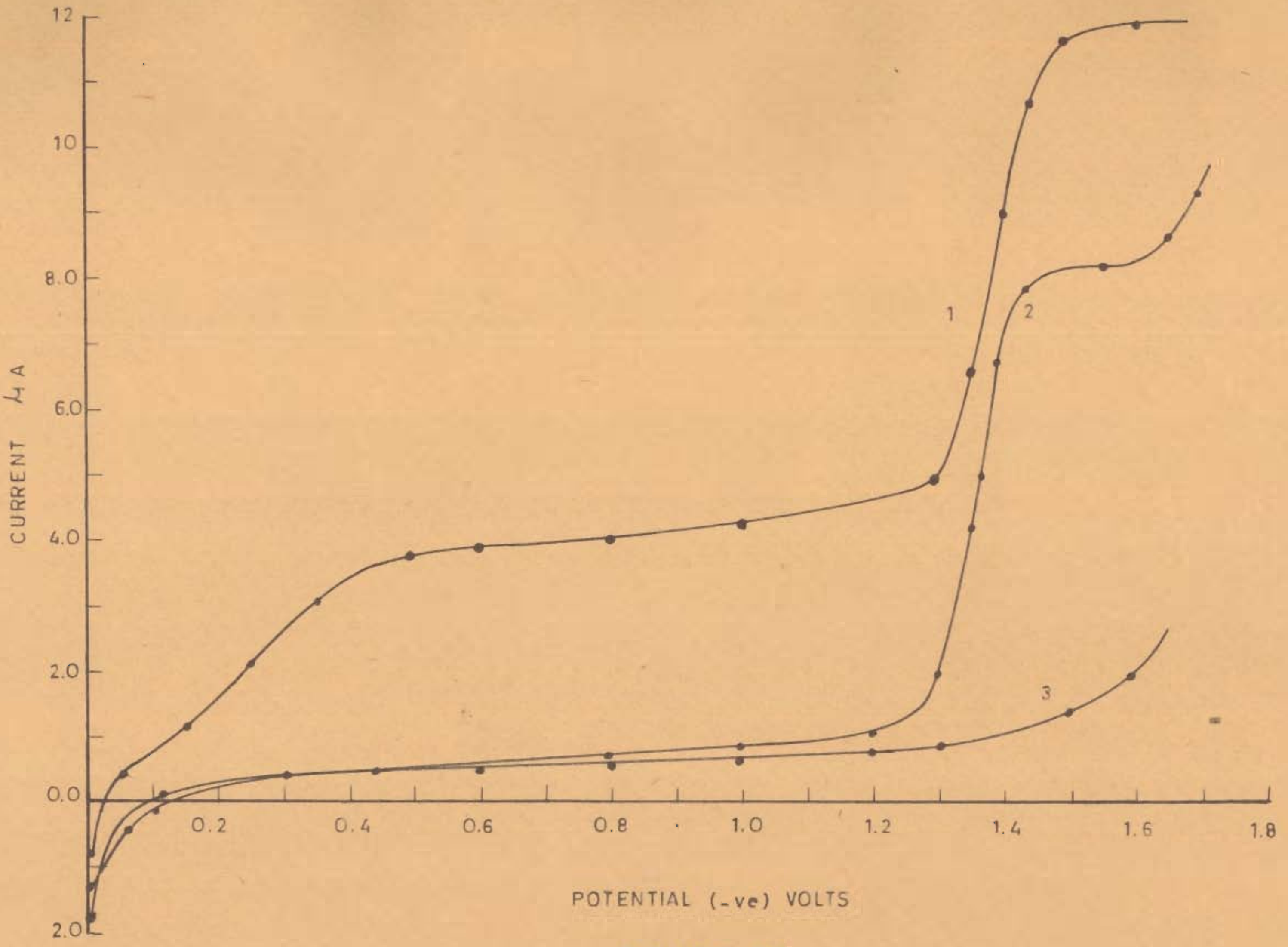

12
10
8.0
6.0
4.0
2.0
0.0
2.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 27

Section B(ammonium citrate medium):-

From the current voltage curves it was found that the resulting complex with the probable structure $Co^{III}(NH_3)_5$-N-C-$Fe^{II}(CN)_5$ got reduced in two steps correspond to the reduction of Co(III) complex to cobalt (II) complex and Co(II) complex to cobalt metal. But the behaviour of this complex was quite different from that of Co(III) ammonia complex. The electrode process for the reduction of Co(III) ammonia complex appeared to be irreversible as varified by logarthmic analysis, the points of logarthmic analysis corresponding to the upper half of the wave were far away from straight line (Fig.31 Table No.6). The same irreversible electrode process for the reduction of Co(III) ammonia complex has been also reported by Laitinen (22,23). But the electrode process for this binuclear complex appared diffusion controlled as verified by the effect of mercury pressure, and logarithmic analysis (Fig.32, 33, Table No.7,8). The half wave potential corresponded to the reduction of Co(II) ammonia, Co(III) ammonia and binuclear complexes are shown in (Table No.8A). The height of the first wave was just half the second eave. Limiting value of the current for both the reduction steps were linear function of concentration (studied in the concentration of the complex of the complex of the order of 10^{-3}M and 10^{-4}M) (Fig.1A,8). The second reduction step remained un-

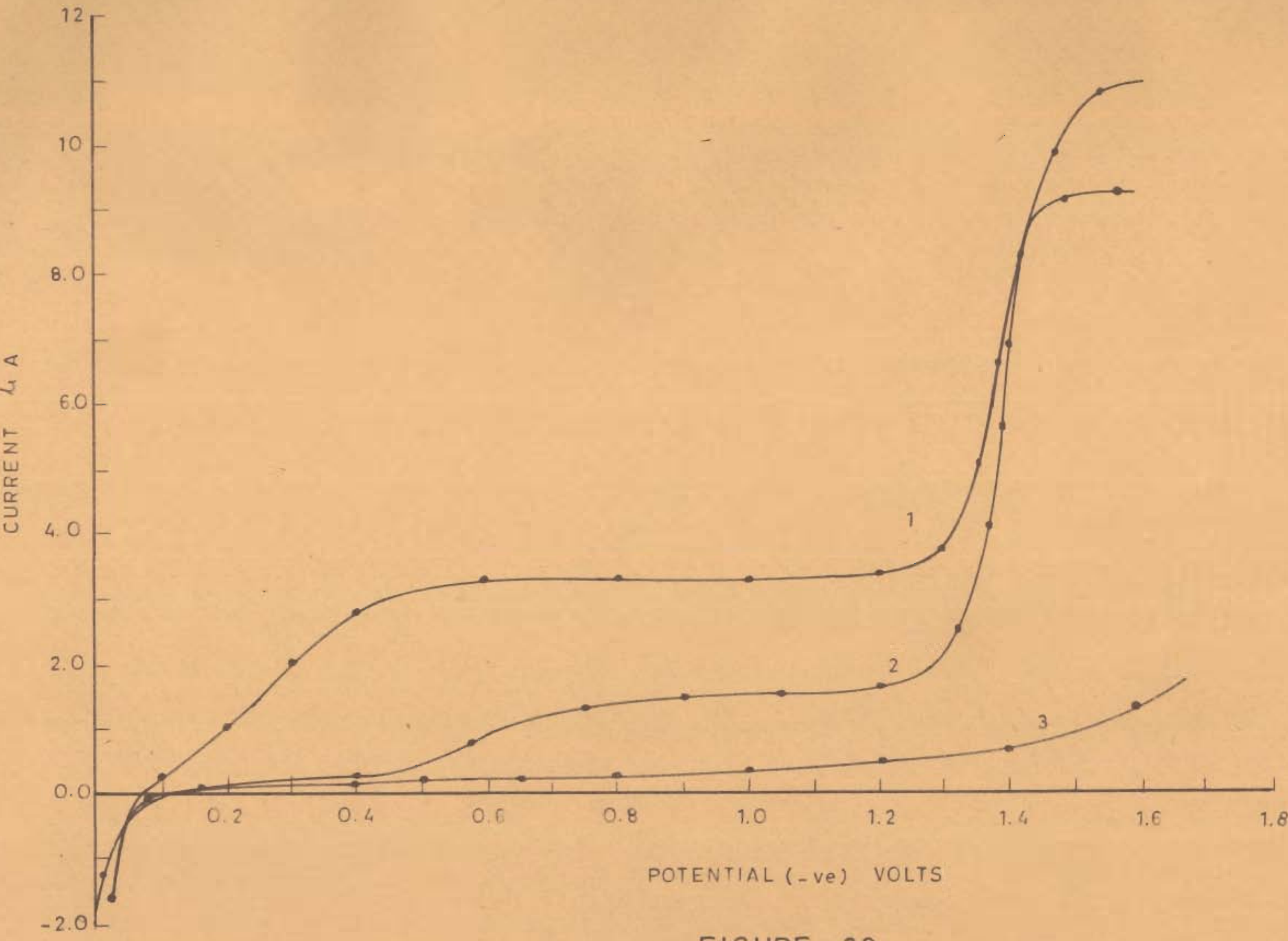

12
10
8.0
6.0
4.0
2.0
0.0
-2.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 28

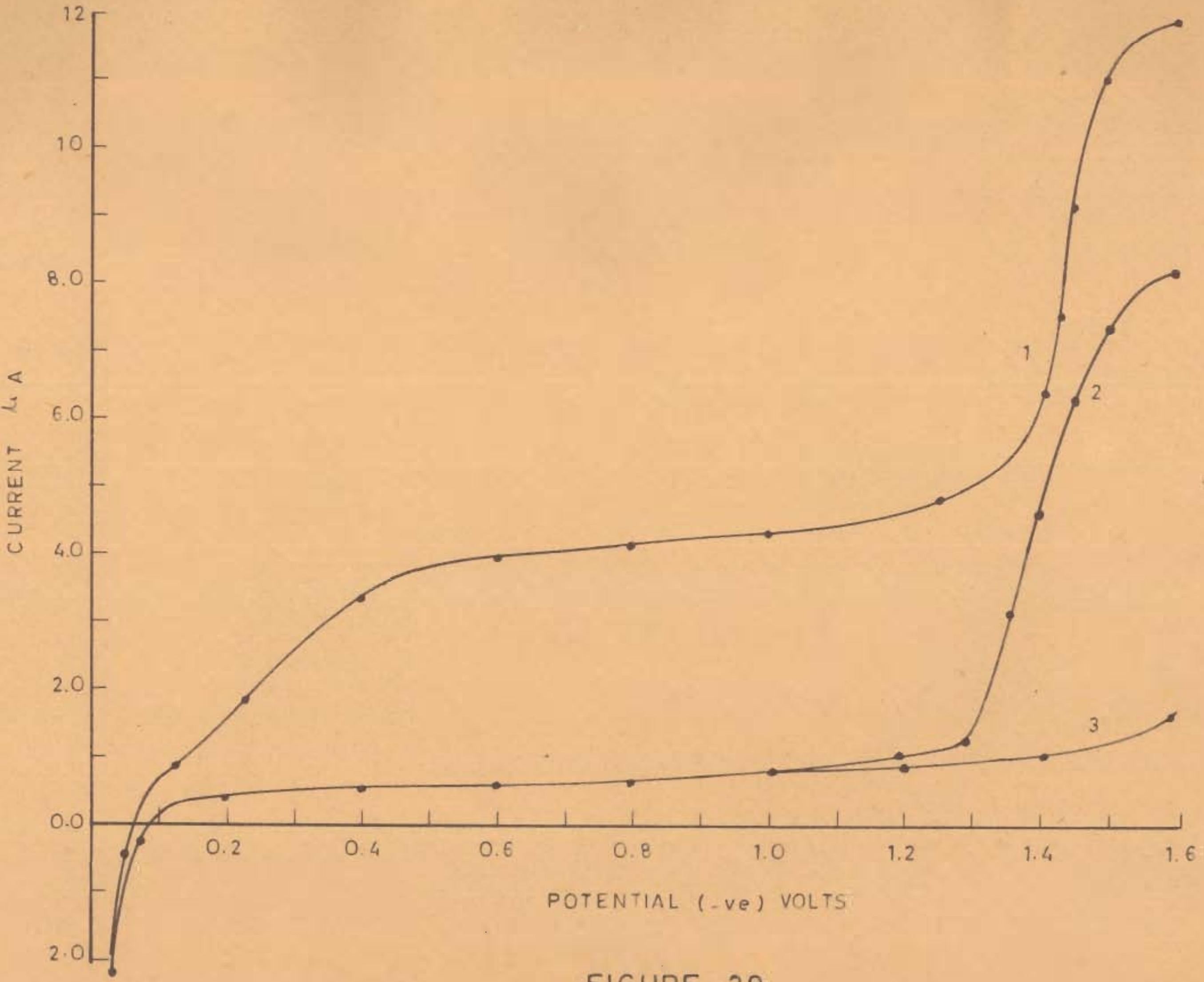

12
10
8.0
6.0
4.0
2.0
0.0
2·0
CURRENT μ A
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
POTENTIAL (-ve) VOLTS
1
2
3

FIGURE 29

effected in presence of equal concentration of Cu(II). Both the reduction steps remained uninfluenced by the presence of Co(III), Cr(III) but equal concentrations of Ni(II) and V(V) appreciably interfered. Mn(II) gave a preciptitate in ammonium citrate medium. This interference was avoided by employing the glycine medium. Polarograms are shown in (Fig.1B).

Glycine medium:

Probably some binuclear complex was also formed from the oxidation product of Co(II) and reduction product of hexacyanoferrate (III) under experimental conditions.

This complex was also found to reduce in two steps. The first wave though was not well defined but the limiting value of current was dependent on the concentration of complex (Fig.2A curve 2,3,4,5; Fig.9 curve 1,2,3,4). The second reduction step was well defined. Step height was dependent on concentration and electrode process appeared to be diffusion controlled as verified by the logarithmic analysis and mercury pressure (Fig.34,35 Table NO.9,10). The slope of the straight line (-0.062V) obtained from the plot of potential Vs log i_l/i_l-i suggested one electron transfer process for the second reduction step.

The second reduction step of the resulting

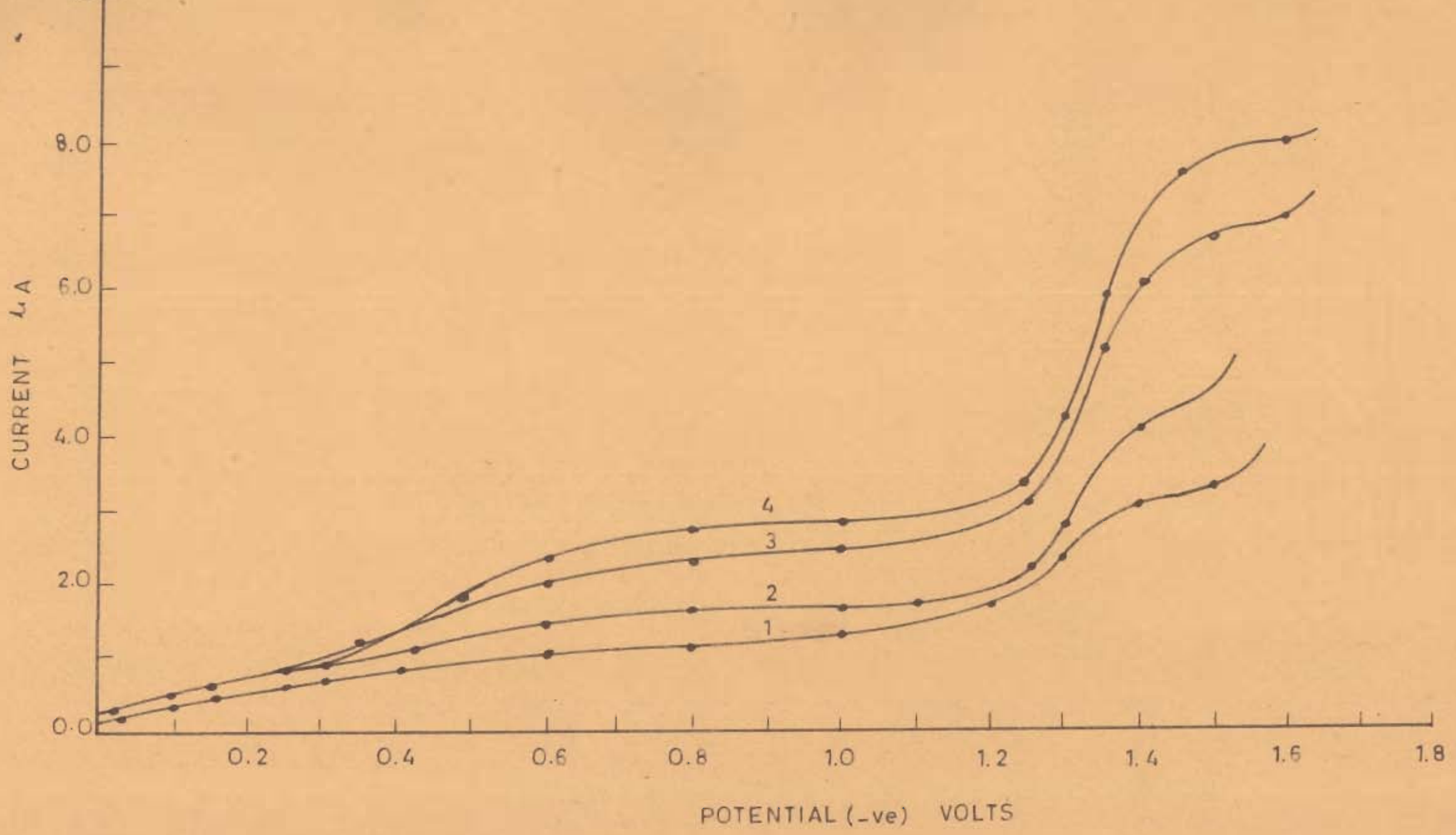

10
8.0
6.0
4.0
2.0
0.0
CURRENT μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
POTENTIAL (-ve) VOLTS
1
2
3
4

FIGURE 30

FIG. 31.

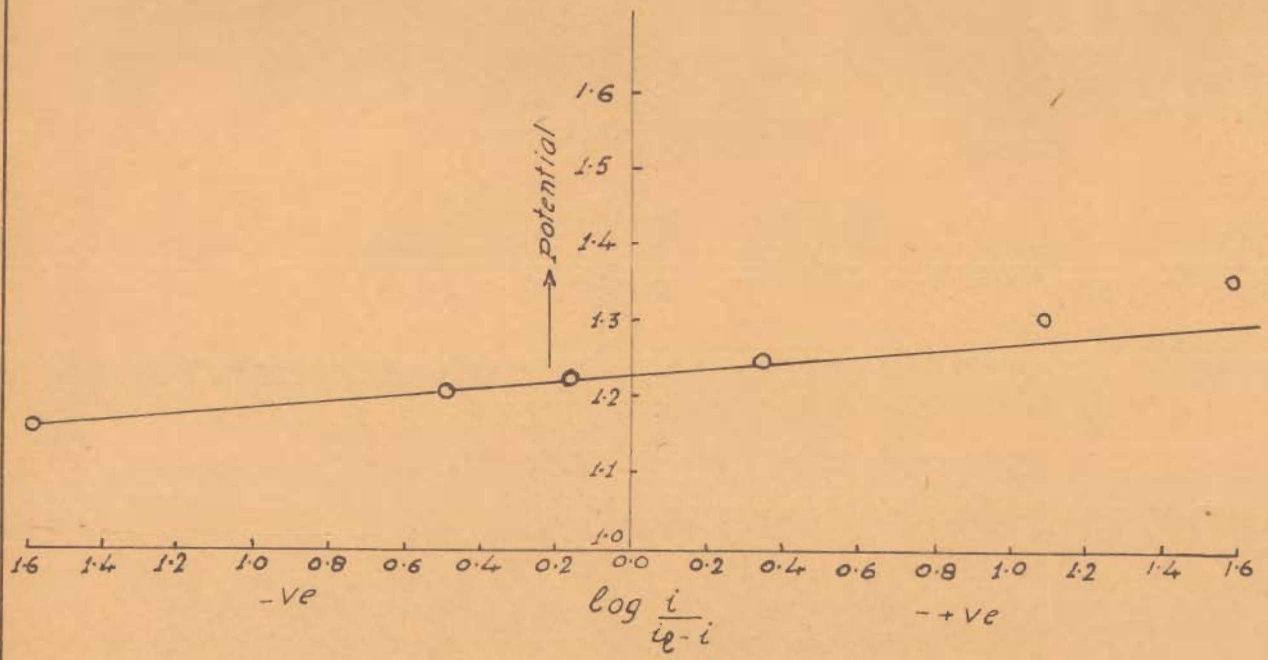
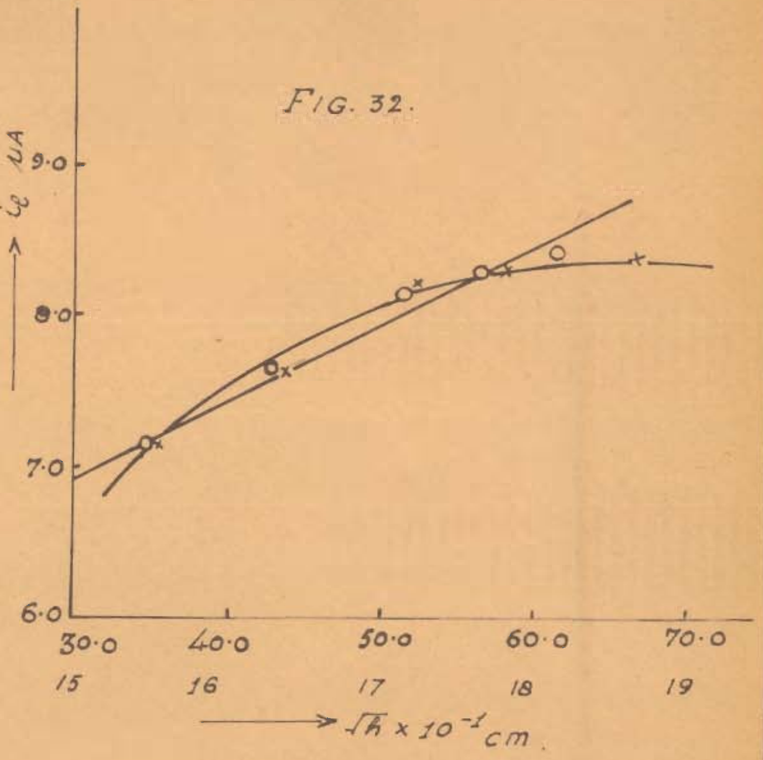


FIG. 32.



Curve. 1. Plot of i_l vs h ×

Curve. 2. Plot of i_l vs $\sqrt{h}$ ○

complex was found to be of analytical importance. Mn(II) did not intefere in this step a well defined step of which was obtained after the second reduction step. The polarograms are shown in (Fig.2B). Although Cu(II) itself in glycine medium gave two reduction steps but its presence did not interfere the second reduction step of the complex. Cr(III), Ce(III) also did not interfere in both the reduction steps of the complex when tested in presence of equal concentrations as that of Co(II). But V(V) and Ni(II) seriously interfered both the reduction steps.

Section(C):

From the current voltage curves it was realized that Co(III) glycine complex was reduced in two steps irreversibly in different electrolytes and buffers of different compositions ranging from pH 8.0 to 12.0. The first wave was not well defined almost in all the buffers and electrolytes used, but it was comparatively well defined in 0.066M sodium fluoride 0.33M glycine at pH 8.0 and in 0.133 calcium chloride; 0.53M glycine from pH 9.0 to 11.0. The half wave potential for the first step in almost all the buffers could not be exactly calculated as the foot of the wave was deviating from the normal behaviour.

The second reduction step was well defined in all the buffers and electrolytes, the electrode

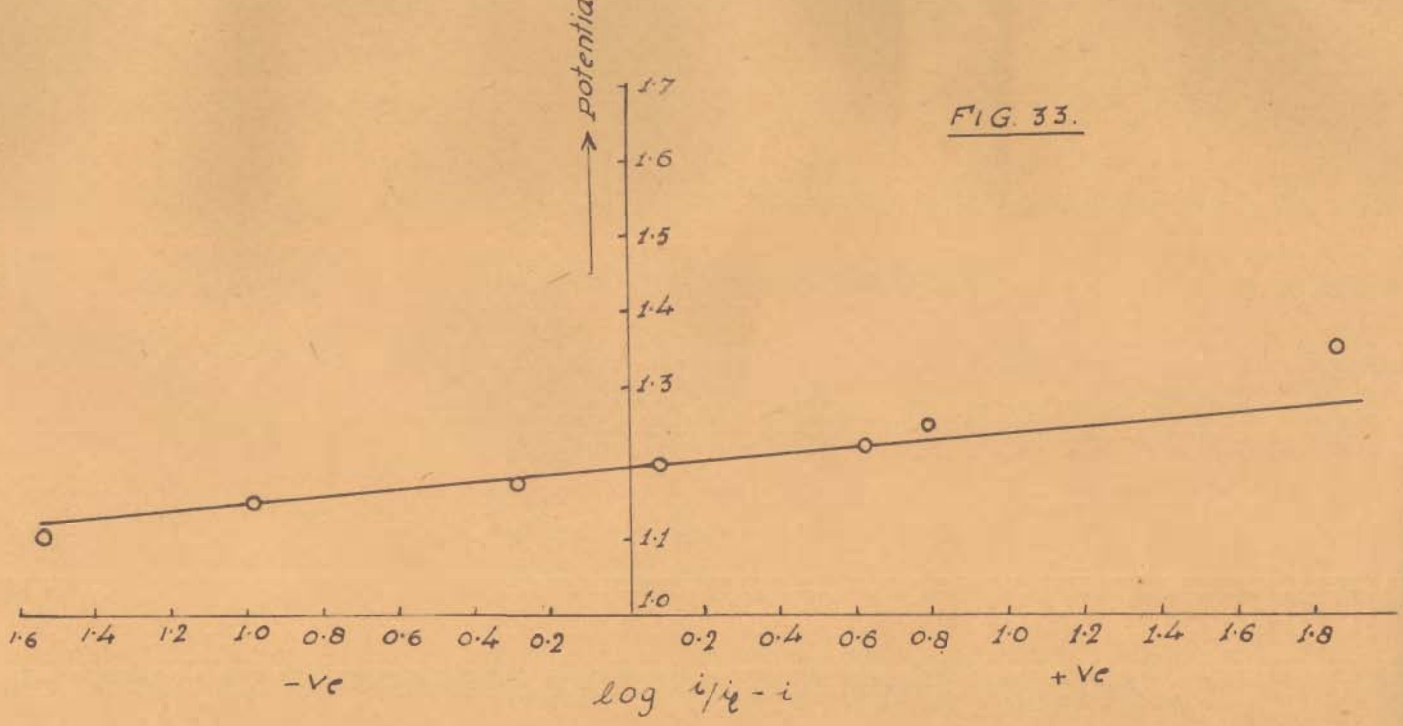

potential
1·7
1·6
1·5
1·4
1·3
1·1
1·0
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
-ve
+ve
log i/ie - i

FIG. 33.

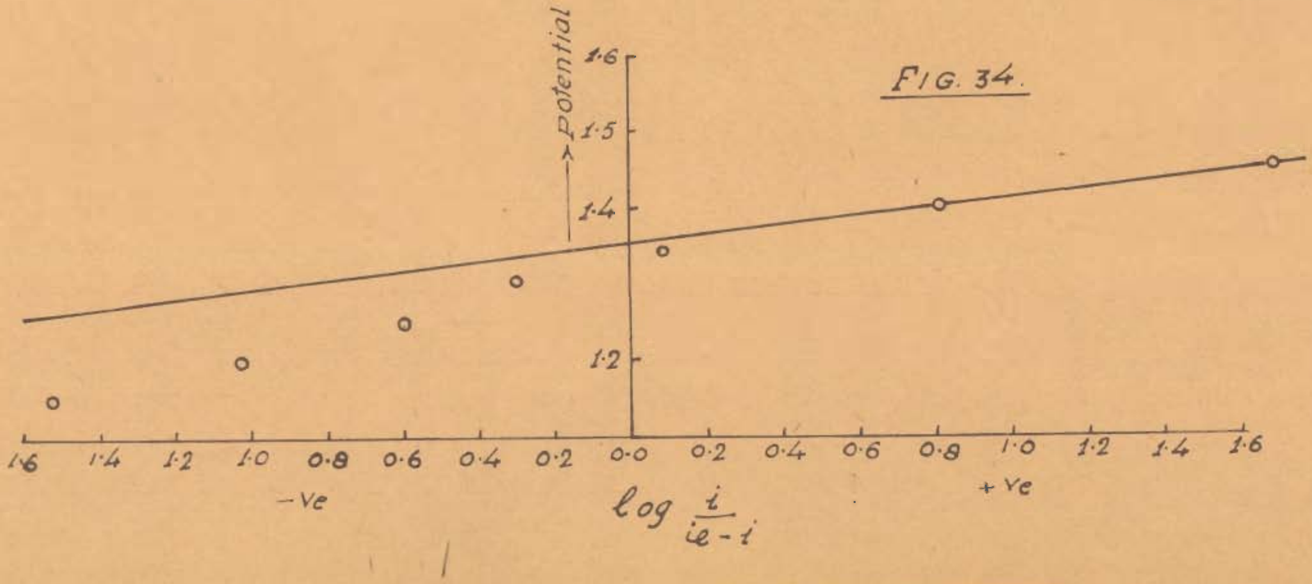
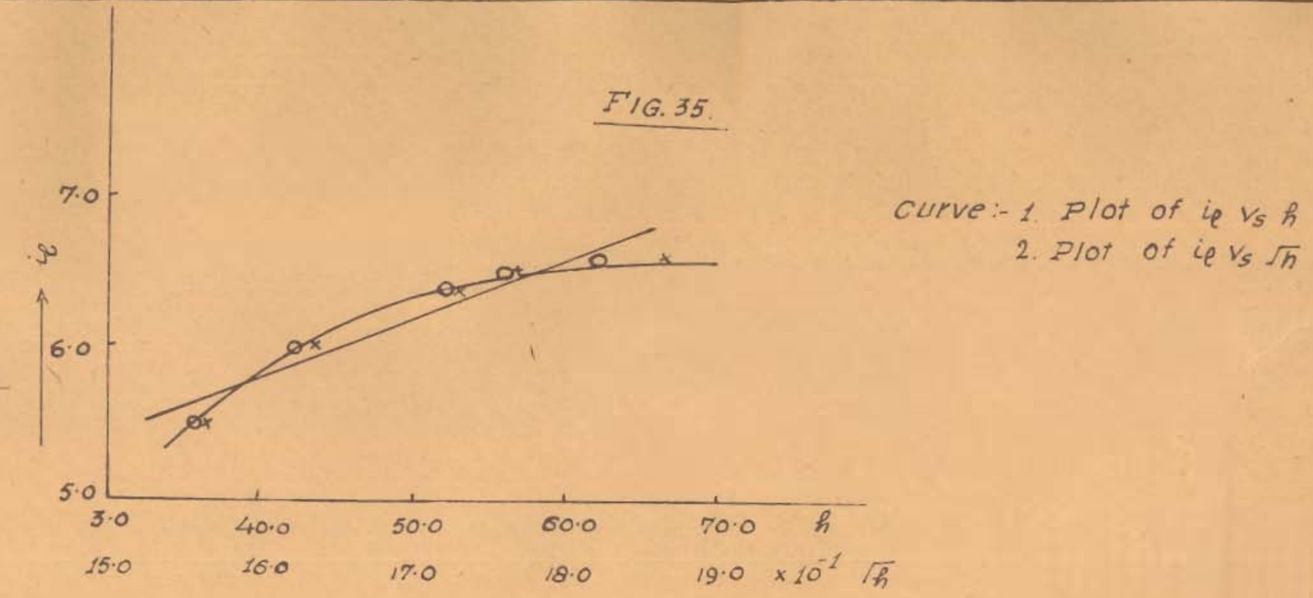

potential
1·6
1·5
1·4
1·2
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
-ve
+ve
log i/(ie - i)

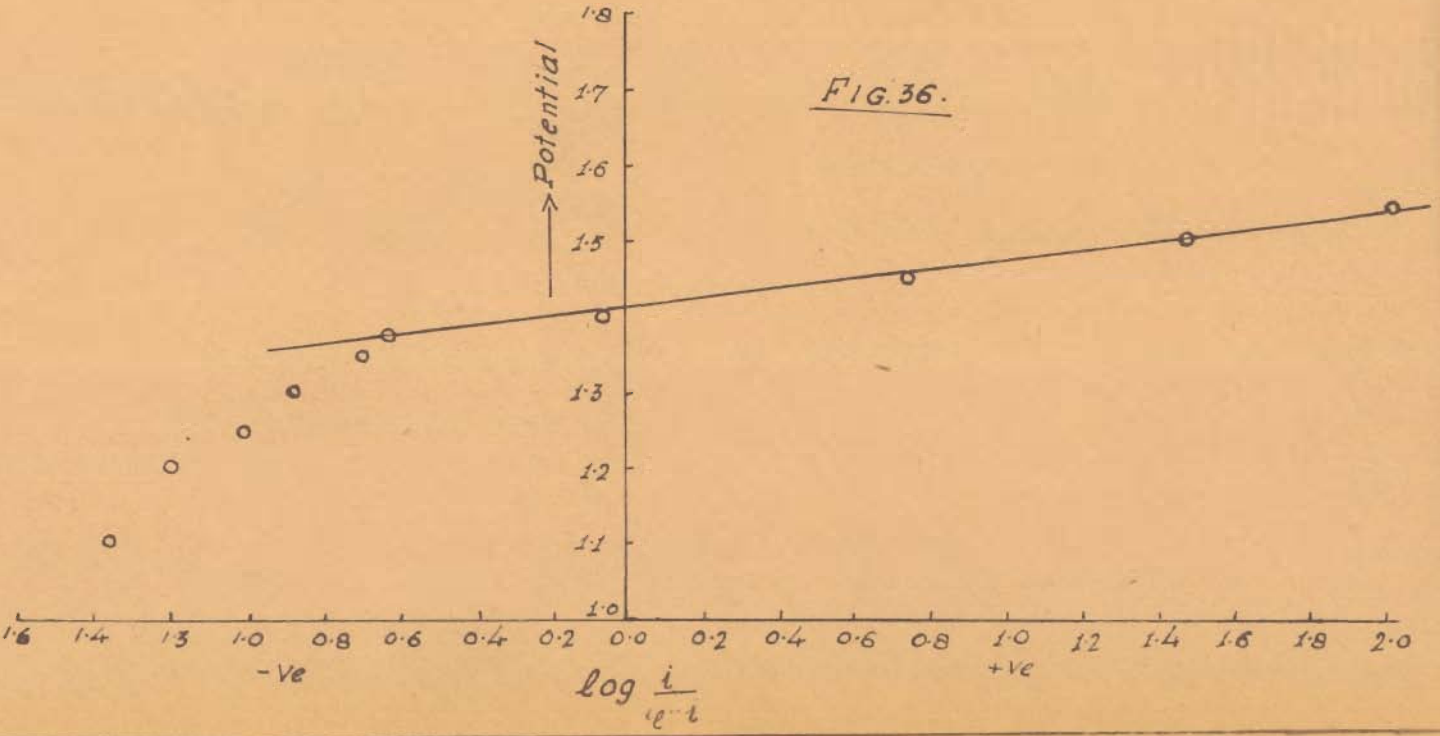
FIG. 34.

FIG. 35.



Curve:- 1. Plot of i_l vs h
2. Plot of i_l vs $\sqrt{h}$
i_l
7.0
6.0
5.0
3.0
40.0
50.0
60.0
70.0
h
15.0
16.0
17.0
18.0
19.0
$\times 10^{-1}$ $\sqrt{h}$

FIG. 36.



→ Potential
1.8
1.7
1.6
1.5
1.3
1.2
1.1
1.0
1.6
1.4
1.3
1.0
0.8
0.6
0.4
0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
-Ve
+Ve
$\log \frac{i}{i_l - i}$

process was completely diffusion controlled as verified by the effect of mercury pressure (Fig.37, Table No.12) Logarithmic analysis in 0.066M sodium fluoride at pH 11.0 (Fig.36, Table No.11) suggested a one electron transfer wave (slope = -0.66V). The limiting value of current was dependent on concentration studied in the concentration of the order of 10^{-3}M of the complex (Fig.30). The limiting current and half wave potential values were not much effected by pH. Generally at the same pH value in the given concentration of supporting electrolyte the increase in the concentration of glycine tended wave from more distorted to less distorted form, but increase in pH at difinite concentration of glycine and supporting electrolyte the waves were found to be more distorted. In 0.53M glycine in defferent supporting electrolytes on increasing pH from 8.0 to 12.0 the half wave potential values were shifted to more (-ve) side (Table No.15).

Co(II) glycine complex was found to reduce in single step due to the reduction of Co(II) to Co(I) complex. The step was well defined in all the buffers having different electrolytes at different pH values. Although the reduction was diffusion controlled as verified by the effect of mercury pressure (Fig.39 Table No.14) but appeared to be irreversible as few points for the plot of logarithmic analysis of lower

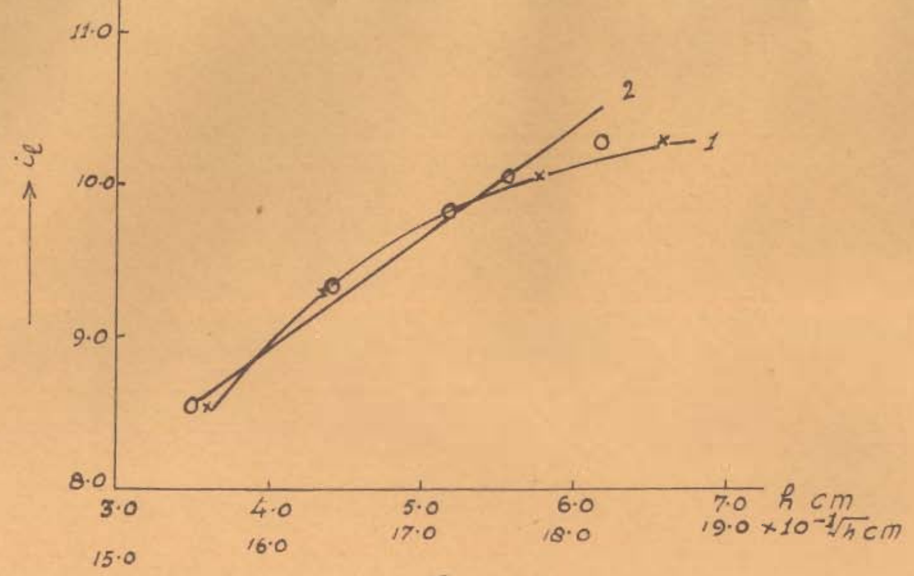


FIG. 37.

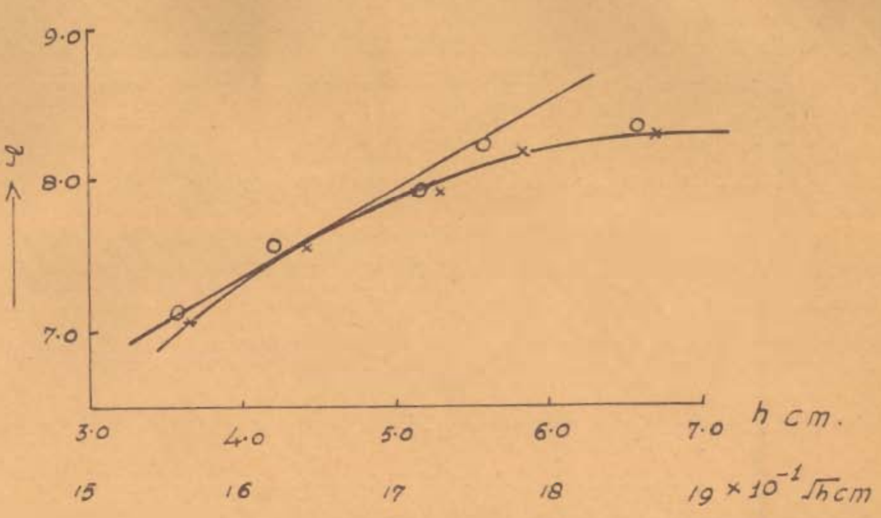


FIG. 39.

curve 1 plot of i_l vs h

Plot of i_l vs $\sqrt{h}$

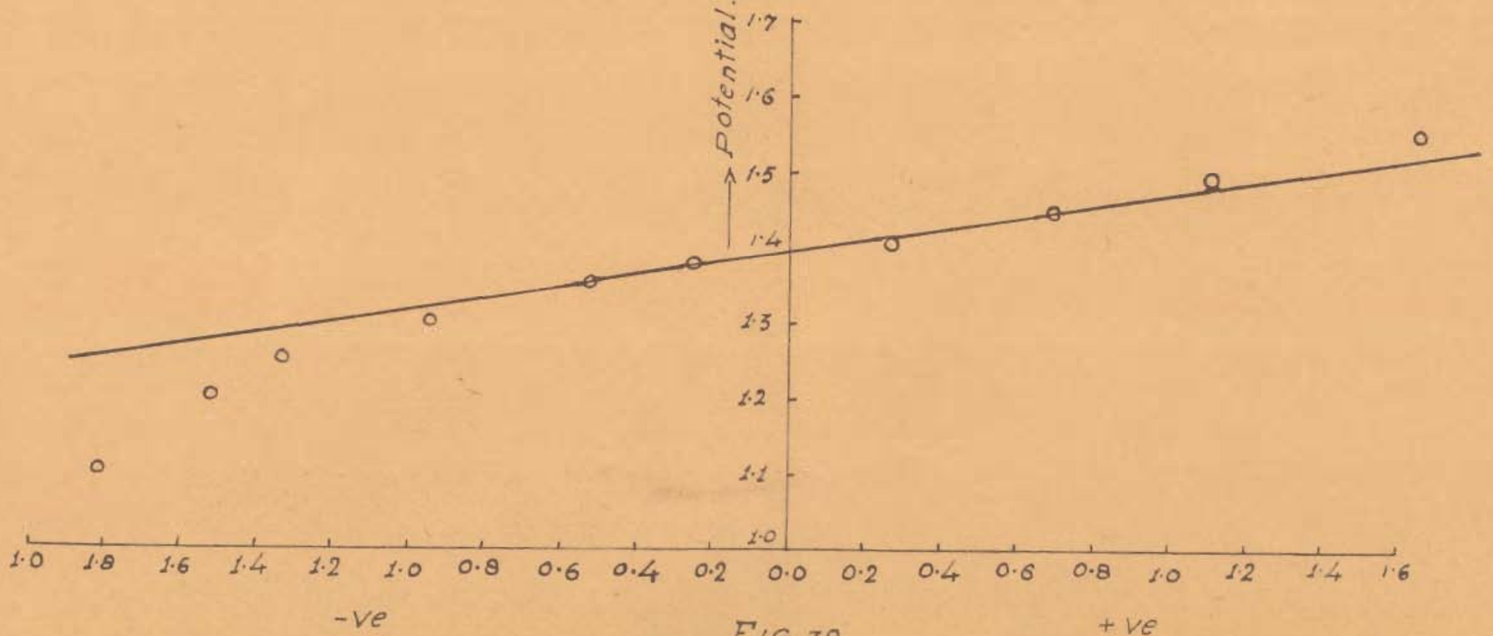


FIG. 38.

$\log \frac{i}{i_l - i}$

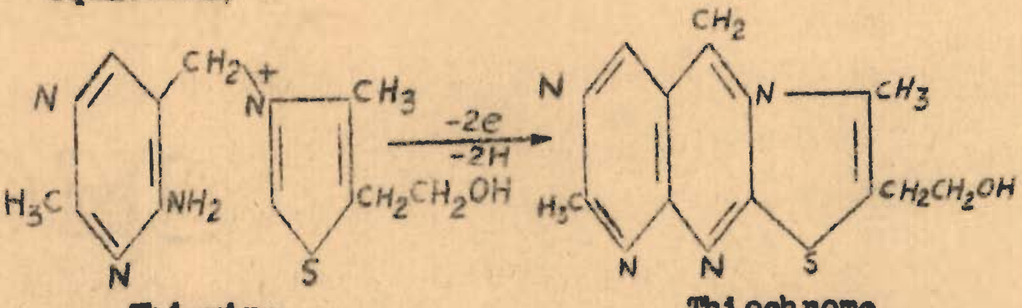
half of the wave were far away from the straight line (Fig.38 Table No.13). The nature of the wave appeared to be quite similar with the second wave of Co(III) complex. Under similar condition of pH and electrolytes concentration, the half wave potential values for this step was quite ressembling with that of second step of resulting Co(III) glycine complex in many cases.

The comparative statement for half wave potential values in different buffers and supporting electrolytes for Co(II) and Co(III) glycine complexes are shown in Table No.15 and polarograms in (Fig.10-29).

CHAPTER IV (Part II)

Amperometric titrations of Thiamine (Vitamin B_1) with hexacyanoferrate (III).

Thiamine is readily oxidised (1) under controlled conditions by alkaline hexacyano-ferrate (III). Thiachrome is formed according to following equations.



Thiamine   Thiochrome

$$2\ Fe(CN)_6^{---} + 2e = 2\ Fe(CN)_6^{----}$$

and mainly this is the basis for the quantitative determination of thiamine.

So far as the estimation of thiamine is concerned Horwitt (2) has developed, polarographic, chromatographic and colorimetric methods. Mickelson and Yamamoto (3) have reviewed analytical methods including, physicochemical enzymatic and microbiologic techniques developed by many investigators over the years.

Pletich (4) is reported to have developed an indirect polarographic method for the determination of this vitamin in pharmaceutical products. Vitamin B_1 gives red precipitate with complex anion Bi I_4 when dissolved in 10 percent Rochelle salt solution. An anodic step at d.m.e. due to iodide ion is recorded. The height of this step is found to be directly proportional to vitamin B_1 concentration.

Detailed investigations on the polarographic behaviour of this vitamine have been carried out by Tachi (5-13). The investigations based on catalytic waves have also been reported by a number of workers (14-17). For instance concentration greater than 1 mg litre can be determined in phosphate buffer of pH ranging from 6.6 to 7.3 from the studies on catalytic waves.

It is evident from the literature cited above that the polarographic methods so far used for the estimation of vitamin B_1 are either less accurate (based on catalytic waves) or more time consuming (based on indirect polarographic estimation). It was, therefore considered worth while to develope a simpler and direct method. Amperometric titrations of thiamine with hexacyanoferrate (III) were, therefore, tried for this purpose.

In the present section of the chapter results on the amperometric titrations of thiamine with alkaline hexacyanoferrate (III) have been reported. The accuracy of the method was chacked by determining its quantities in multivitamine tablets supplied by Glaxo and Sqquib laboratories Private Ltd. India. The method was also extended for the estimation of vitamin B_1 in Elexir Eupeptine supplied by Raptakos Brett. and Co. India.

Each multivitamine tablet supplied by Glaxo and sqquib laboratories contains 0.3 mg of thiamine and thiamine hydrochloride respectively together with several other vitamines and minerals. 10 ml of Eupeptin contain 0.3 mg of thiamine hydrochloride. these quantities have been estimated with a fairly good accuracy by amperometric titration.

EXPERIMENTAL

Apparatus:

Heyrovsky LP-55 A polarograph operated mannually in conjunction with a Pye Scalamp Galvanometer in external circuit was used. A dropping mercury electrode having droptime 4.32 secs, and weight of one drop = 0.0035 gm at applied potential of 0.0 volt in 0.5M potassium chloride and phthalate buffer of pH-4 at a height of mercury column 49.5 cm. was used. The H-shaped polarographic cell and reference electrode were kept immersed in thermostatic bath maintained at 30 ± 0.1°C. Purified hydrogen was used for dearation.

Reagents:

All the reagents were of A.R. quality, solutions of lithium chloride, sodium hydroxide were prepared in double distilled water, Solutions of thiamine of required concentrations were prepared in double distilled water by dissolving weighed quantities. The solution of hexacyanoferrate (III) was also prepared by dissolving weighed quantities in water and strength was determined iodometrically by titrating against sodium thiosulphate.

Selection of Potential:

To select appropriate potential for amperometric titrations polarograms of the solutions containing:

(1) 1.0 ml 1.13×10^{-2}M thiamine, 2.0 ml 2.0M lithium chloride, 4.0 ml 0.5M sodium hydroxide and 8.0 ml water.

(2) 2.0 ml 1.13×10^{-2}M hexacyanoferrate (III) 1.0 ml 1.13×10^{-2}M thiamine, 2.0 ml lithium chloride 4.0 ml, 0.5M lithium chloride and 6.0 ml water.

(3) 2.0 ml 1.13×10^{-2}M hexacyanoferrate (III) 2.0 ml 2.0M lithium chloride, 4.0 ml 0.5M soludim-hydroxide and 2.0Ml water.

(4) 4.0 ml 0.5M sodium hydroxide 2.0 ml 2.0M lithium chloride + 9.0 ml water were recorded. Results are tabulated below:

FIG. 1

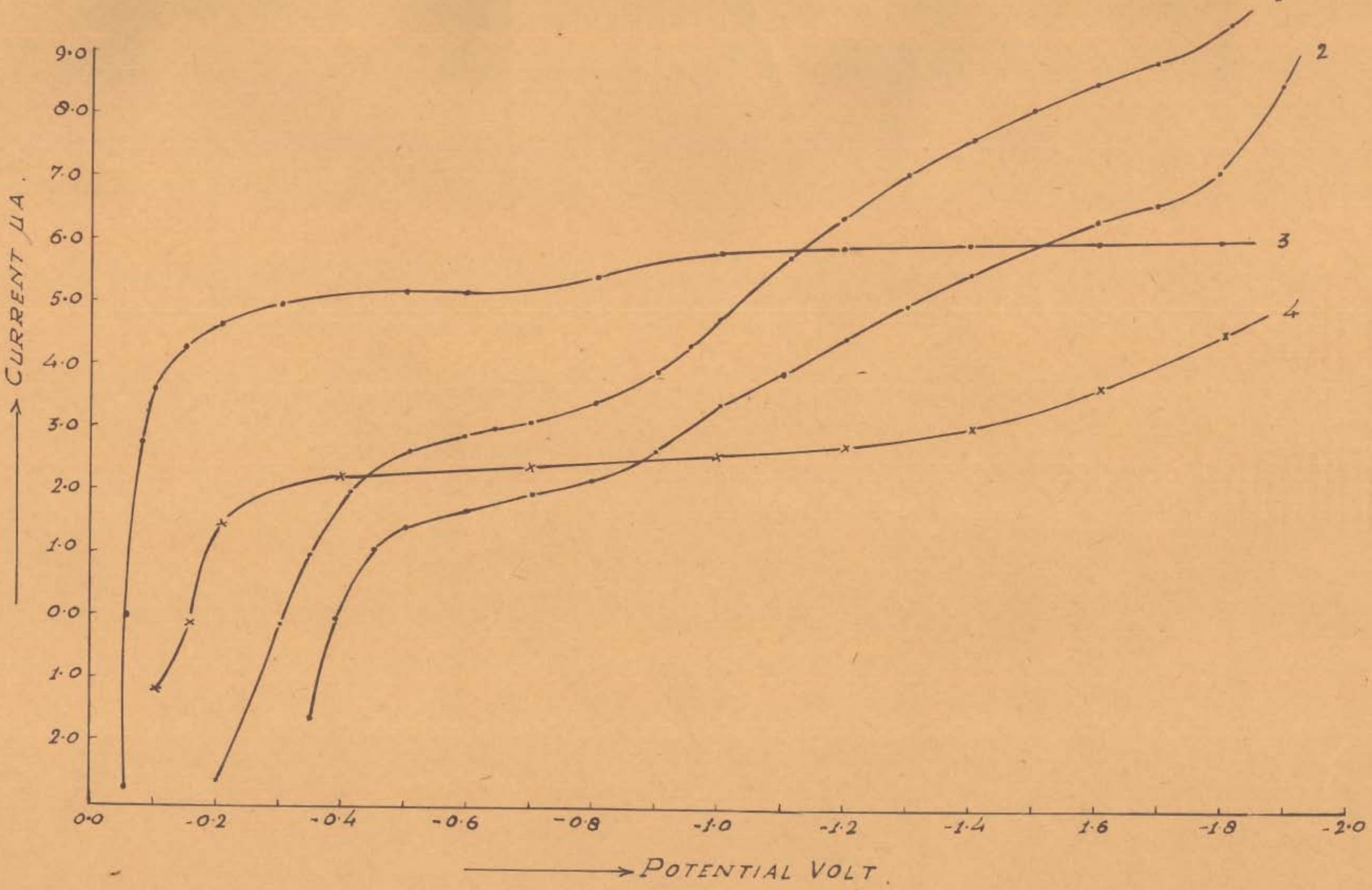

1
2
3
4
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0·0
1·0
2·0
CURRENT μA.
0·0
-0·2
-0·4
-0·6
-0·8
-1·0
-1·2
-1·4
1·6
-1·8
-2·0
POTENTIAL VOLT.

TABLE No.1

Voltage (-)	Solution			
	Current µA 1	Current µA 2	Current µA 3	Current µA 4
0.05	-	-	-2.75	-
0.06	-	-	0.00	-
0.08	-	-	2.75	-
0.10	-	-	3.55	-1.15
0.15	-	-	4.20	-0.10
0.20	-	-2.65	4.70	1.55
0.30	-	-0.15	4.95	-
0.35	-1.70	+0.95	-	2.00
0.40	-0.10	1.95	-	-
0.45	+1.10	-	-	-
0.50	1.40	-	-	-
0.60	1.65	2.55	5.15	-
0.70	1.90	3.10	-	2.30
0.80	2.25	3.40	5.40	-
0.90	2.65	3.85	-	-
1.00	3.35	4.70	5.75	2.60
1.10	3.95	5.80	-	-
1.20	4.45	6.35	5.85	2.80
1.30	5.00	7.10	-	-
1.40	5.40	7.70	6.00	3.10
1.50	5.75	8.15	-	-
1.60	6.40	8.60	6.15	3.70
1.70	6.65	8.95	-	-
1.80	7.15	-	6.15	4.50
1.90	8.60	-	-	5.00
Curve	(1)	(2)	(3)	(4)

Fig.1

Thiamine and mixture of thiamine and hexacyanoferrate (III) did not gave will defined polarograms but hexacyanoferrate (III) gave a diffusion current at zero applied potential with a limiting value of the current in the potential region from -0.25 V. to -0.4 Volts. The appropriate potential for reverse (hexacyanoferrate (III) in cell) and direct (thiamine in cell) amperometric titrations was chosen as -0.25V. from the plateau of hexacyanoferrate (III) polarogram. Results are tabulated below:

TABLE No.2

Potential applied -0.35 (Reverse titrations)
(2.0 ml of hexacyanoferrate (III) in cell)
Concentration of thiamine = 0.0113, 0.00113M and
0.000113N for titrations 1,2 and 3 respectively.

Volume of thiamine added	Concentration of hexacyanoferrate (III)		
	0.01M	0.001M	0.0001M
	Current µA	Current µA	Current µA
0.0 ml	-	-	-
0.2 ml	7.95	5.70	6.95
0.4 ml	5.00	5.00	6.20
0.6 ml	2.85	4.40	5.70
0.8 ml	0.80	3.80	5.25
0.9 ml	0.15	-	-
1.0 ml	0.50	3.50	4.95
1.2 ml	0.50	3.40	4.55
1.4 ml	0.50	3.30	4.20
1.6 ml	0.50	3.20	3.85
Curve	(1)	(2)	(3)

Fig.

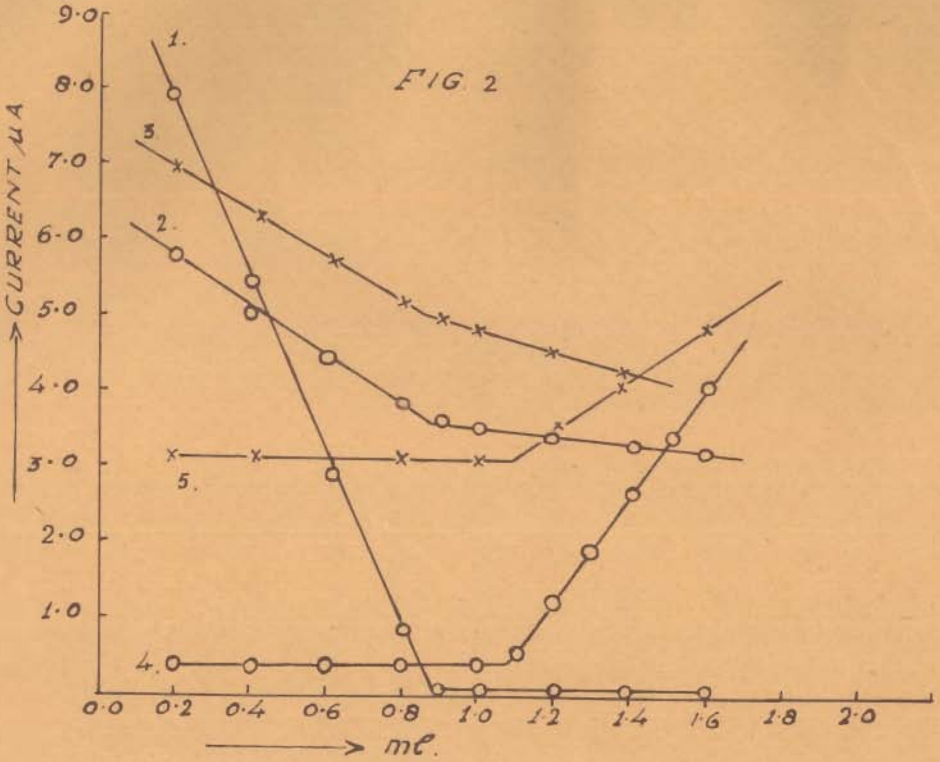
Amperometric Titrations:

Procedure:

Reverse titration:

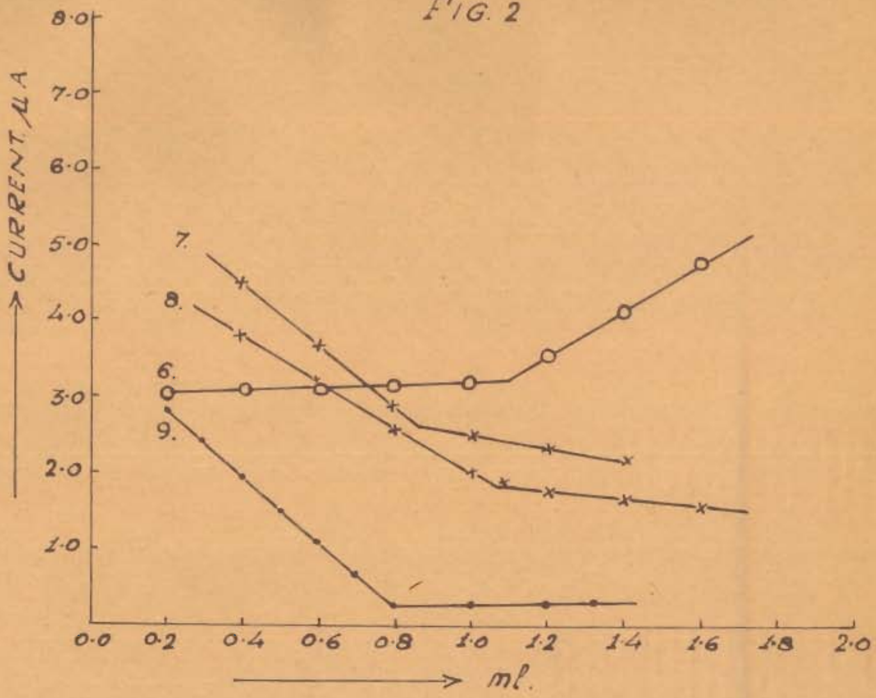
2.0 ml of hexacyanoferrate (III) concentration ranging between 0.01M to 0.0001M was placed in the polarographic cell, to this was added 5.0 ml of 0.5M sodium hydroxide and 1.0 ml of 2.0M

FIG. 2



volume of titrant, hexacyanoferrate (III) or thiamine added.

FIG. 2



volume of titrant, hexacyanoferrate (III) or thiamine added.

lithium chloride and total volume was made to 15.0 ml by water in each case. Oxygen was removed by passing purified hydrogen, and titrated with required concentration of thiamine added from microburette at 0.35 V. Vs. S.C.E. solution was stirred by hydrogen after each addition and reading was recorded after a lapse of approximately five minutes. The end points were detected from the intersections of two straight lines obtained by ~~by~~ plotting current against the volume of the titrant added. Readings are recorded below:

TABLE No.3

Potential applied -0.35V (Direct titrations) (2.0 ml of thiamine in cell) concentration of hexacyanoferrate (III) as mention in table for titration 1,2,3 respectively.

Volume of hexacyanoferrate (III) added	Concentration of thiamine		
	0.0113M	0.00133M	0.000133M
	Current μA	Current μA	Current μA
0.0 ml	0.35	3.1	3.05
0.2 ml	0.35	3.1	3.05
0.4 ml	0.35	3.1	3.05
0.6 ml	0.35	3.1	3.05
0.8 ml	0.35	3.1	3.10
0.9 ml	-	-	-
1.0 ml	0.40	3.1	3.20
1.1 ml	0.60	-	-
1.2 ml	1.30	3.6	3.70
1.3 ml	1,90	-	-
1.4 ml	-	4.2	4.10
1.5 ml	3.40	-	-
1.6 ml	-	4.9	4.80
Curve	(4)	(5)	(6)

Fig.(2)

Direct Titrations:

Similar to reverse titrations 0.5 ml of thiamine of the concentration ranging from (0.0113M to 0.000113M) was placed in the polarographic cell. Titrations were carried out exactly under similar conditions as in direct titrations. Hexacyanoferrate (III) was used as titrant. Results are tabulated below:

Estimation of thiamine in Multivitamin Tablets:

One tablet of multivitamin either Glaxo or Sqquib was crushed to powder and dissolved in water, undissolved residue was rejected by filteration. Filtrate was diluted to 100 ml. reverse titrations were carried out under the conditions mentioned above by taking 2.0 ml of 1.0×10^{-4}M hexacyanoferrate (III) in the cell. Readings are recorded below:

TABLE No.4

Estimation of thiamine in the tablet of multivitamine (Glaxo) Potential applied -0.35V.
Volume of 2.0 ml of hexacyanoferrate (III) in cell (1.13×10^{-4}M).

Volume of vitamin added	Senstivity 1/1 current µA
0.0 ml	5.75
0.2 ml	4.50
0.4 ml	3.65
0.6 ml	2.95
0.8 ml	2.60
0.9 ml	2.60
1.0 ml	2.40
1.2 ml	2.25
1.4 ml	1.95
1.6 ml	1.70
1.8 ml	1.45
Curve	(7)

Fig.2

Estimation of thiamine in Eupeptine:

15.0 ml of Eupeptine was dissolved in water. The filtrate was diluted to 100.0 ml. Amperometric titrations were carried out in the usual way by taking 2.0 ml of hexacyanoferrate (III) solution in the cell. Readings are recorded below.

Table No.5

Estimation of thiamine in the tablet of multivitamine (squibb), potential applied -0.35V.
Volume of hexacyanoferrate (III) in cell = 2.0 ml (1.13×10^{-4} M).

Volume of vitamine added	Senstivity 1/1 current μA
0.0 ml	5.8
0.2 ml	4.9
0.4 ml	3.8
0.6 ml	3.2
0.8 ml	2.5
1.0 ml	2.0
1.3 ml	2.1
1.5 ml	1.9
1.8 ml	1.65
2.0 ml	1.55

Curve (8)

Fig.2

TABLE No.6

Estimation of thiamine in Eupeptine Syrup
Potential applied -0.35V.
Volume of hexacyanoferrate (III) in cell = 2.0 ml
(1.13×10^{-4}M).

Volume of the syrup added	Senstivity 1/1 current μA
0.0 ml	6.55
0.2 ml	2.90
0.3 ml	2.45
0.4 ml	1.90
0.5 ml	1.55
0.6 ml	1.10
0.8 ml	0.30
1.0 ml	0.30
1.2 ml	0.30
1.4 ml	0.30

Curve (9)

Fig.2

RESULTS AND DISCUSSION:

From the amperometric titration curve it was found possible to determine 2.0 mg. of the thiamine in 15.0 ml of the solutions, in direct and reverse titrations with a fairly good accuracy. Good results were also obtained when thiamine was determined in Eupeptine. Results are summarised in Table No.7.

(Fig.2) curves (I.II) represent the typical amperometric titration curves with hexacyanoferrate (III) in the cell. In the dilute solutions of the reactants the nature of the curves (Fig.2) deviated slightly from the aspected behaviour. But however, from the point of interactions of the two branches of curves the concentration of the vitamin could still be determined with accuracy.

In the case of direct titrations (vitamin in the cell) typical curves were obtained at all concentrations of the vitamin (Fig. curves IV to VI). Sharp inflexion points were obtained even with very dilute solutions of the reactants.

TABLE No.7

Results of the Estimation of Variations contents of the ia amine.

Amount of Thiamine Present per 100 ml	Found from Ampenometric titrations
Reverse Titrations	
(1) 300 mgs	301 mgs.
(2) 30 mgs	29.88 mgs.
(3) 3 mgs	2.994 mgs.
Direct Titrations	
(4) 300 mgs	299.45 mgs.
(5) 30 mgs.	29.78 mgs.
(6) 3 mgs.	2.9 mgs.
Multivitamine Tablets	
(7) Glaxo 30.0 mgs	2.968 mgs.
(8) Sqquib 2.43 mgs	2.382 mgs.
Syrup	
(9) Eupeptine 3.296 mgs.	3.254 mgs.

CHAPTER V

Interaction of pyridine with hexacyanoferrate (II).

(Part I)

Spectrophotometric studies on the composition and stability of pyridine complex with hexacyanoferrate (II):

W.M. Cumming has reported a number of reaction products of organic bases (1) (aniline, O-toluidine, dimethylaniline, pyridine, bengidine and isoquinoline) and that of basic dye stuffs (bismark brown, auramine, chrysoidine y, mangenta malachite green, methyl violet, proflavine and acriflavine etc.) with hexacyanoferrate (II) and ferrate (III). Gadreau (2) reported several alkolids and Barbieri (3) prepared tetramine derivatives of hexacyanoferrate (II). The former worker also extended his studies for the estimation of several hydroferro and ferricyanides of methyldiphenylamine, tetraphenyl-diamonodiphenyl methane, hexamethylenetetraamine, dimethyl aminoazobenzene, monomethyl-p-amino phenol etc. All these workers employed either purely analytical methods for determining the composition of these products. No attention was, however, paid to determine composition and stability of these products in solutions with the help of physico-chemical methods.

Considering the limitations of gravimetric and volumetric methods adoptted by these workers, to study their composition, spectrophotometric studies on the stability and composition on the reaction product of pyridine with hexacyanoferrate (II) were carried out.

Preliminary experiments indicated that on mixing the dilute solutions of pyridine and hexacyanoferrate (II) no change in colour, was observed even on keeping the reaction mixture for several days. But when the pH of the reactants mixture was adjusted between 3.0 to 4.5 by hydrochloric acid a dark yellowish colour was developed within few hours. Therefore the nature of the complex was studied spectrophotometrically.

EXPERIMENTAL

Apparatus and solutions:

Baush and Lomb spectronic-20 was used for carrying out the optical density measurements. Beckman pH meter model H-2 was used for adjusting the pH of the solutions.

Stock solution of hexacyanoferrate (II) was prepared by dissolving weighed quantity in double distilled water and its strength was determined potentiometrically against potassium permanganate. Solutions of required concentrations were prepared by diluting the stock solution and adjusted them at required pH.

Pyridine was purified by the method recommended by Wahlin (4) and its solutions of required concentrations were prepared in double distilled water at required pH.

The following experiments were performed to study the nature of the complex.

Effect of pH:

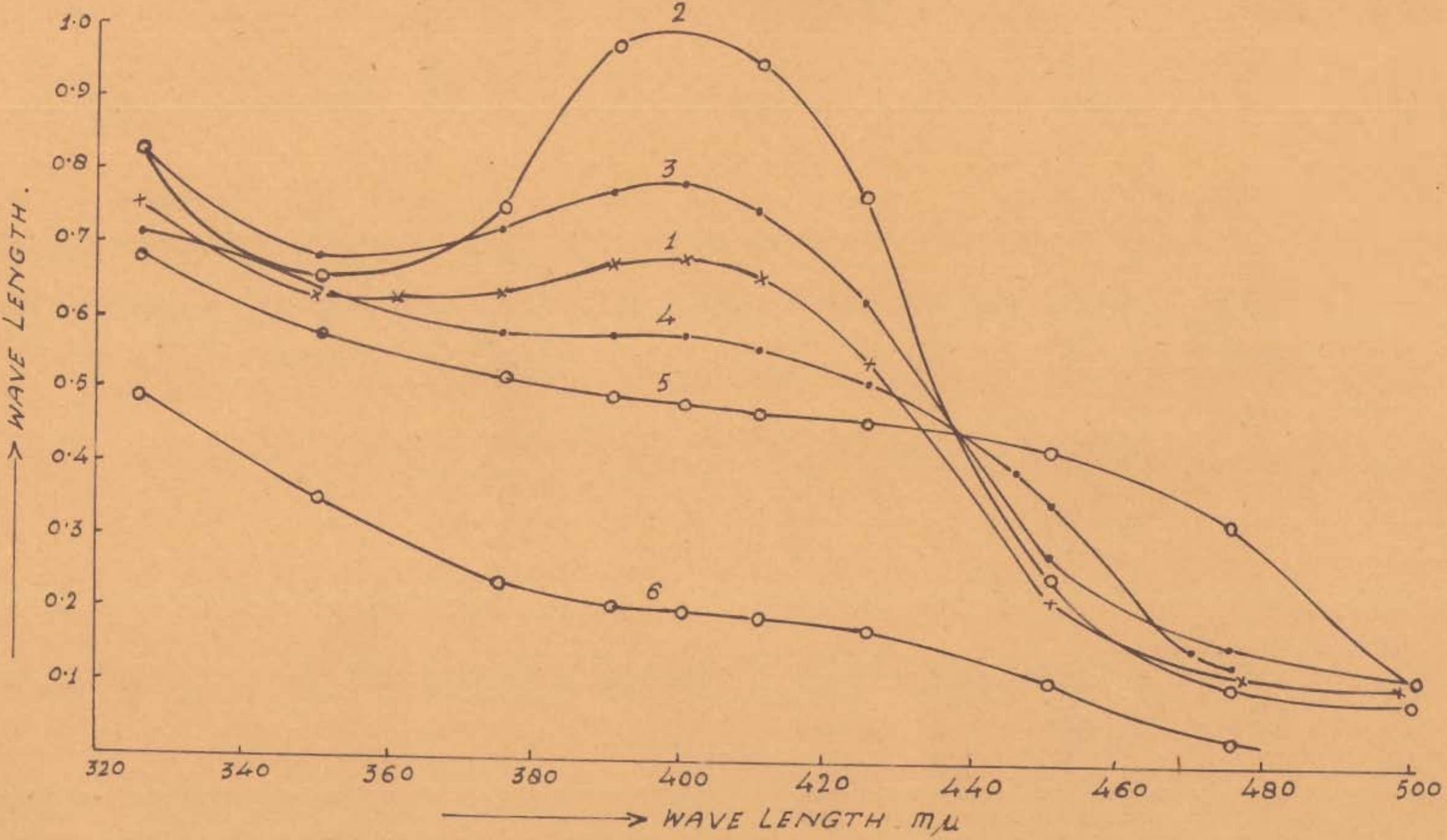
In order to select a suitable pH for studying the composition of the complex 4.0 ml 10^{-2}M hexacynoferrate (II) was mixed with 4.0 ml 10^{-2}M pyridine separately in six pyrex conical flasks. Total volume was made to 30.0 ml by adjusting pH to 3.0, 3.5, 4.0, 4.5, 5.0 and 6.0 respectively. Kept the mixtures for 24 hours and their optical density values were

FIG.1.

PLOT OF WAVE LENGTH Vs O.D.

concentration of hexacyanoferrate (II) and pyridine $(0.4 \times 10^{-2} M)$

curve	pH	curve	pH
1	0·3	4	4·5
2	3·5	5	5·0
3	4·0	6	6·0



measured in visible region. Maximum change in optical density values was observed at pH 3.5 at 400 m μ. Therefore this pH was used for carrying out further studies. Results are tabulated below:

TABLE No.1

Effect of pH on the absorbance of the mixtures of hexacyanoferrate (II) : pyridine (each 0.4×10^{-2} M) at different wave lengths:

Wave length m μ	Optical density					
	pH					
	3.0	3.5	4.0	4.5	5.0	6.0
325	0.75	0.83	0.83	0.72	0.68	0.49
350	0.63	0.65	0.68	0.64	0.57	0.35
375	0.64	0.75	0.72	0.59	0.52	0.23
390	0.68	0.97	0.77	0.58	0.49	0.21
400	0.68	0.98	0.78	0.57	0.48	0.20
410	0.66	0.95	0.75	0.52	0.47	0.19
425	0.55	0.77	0.63	0.35	0.46	0.17
450	0.22	0.25	0.28	0.14	0.43	0.10
475	0.12	0.10	0.15	-	0.33	0.03
500	0.10	0.09	0.11	-	0.11	-
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig.1

Composition of the complex:

In order to ascertain the possibility of more than one complex 0.01M solution of the reactants (pH of each was adjusted to 3.5 by hydrochloric acid) were mixed in the ratios of hexacyanoferrate (II) to pyridine as 1:0, 2:1, 1:1, 1:2 and 1:3 (VosBurgh and Cooper's method (5)), in each case total volume was made to 20.0 ml by water maintaining the pH to 3.5 with hydrochloric acid. The mixtures were kept for 48 hours. Each solution (except No.1 which contained 0.1x10^{-2}M hexacyanoferrate (II) and the O.D. of which continuously decreased beyond 375 mμ) gave an absorption maximum at 400 mμ and maximum value was observed in the mixture containing hexacyanoferrate (II) and pyridine in the ratio 1:2. Results are tabulated below:

TABLE No.2

Absorbance of various mixtures of pyridine and hexacyanoferrate (II) (each 0.1x10^{-2}M) at different wave lengths at pH 3.5.

Ratio of hexacyanoferrate (II) to pyridine	Optical density				
	1:0	2:1	1:1	1:2	1:3
Wavelength mμ					
325	0.25	0.55	0.72	0.62	0.54
350	0.18	0.40	0.61	0.45	0.38
375	0.11	0.42	0.54	0.49	0.44
390	0.10	0.48	0.58	0.54	0.50
400	0.09	0.49	0.58	0.60	0.52
410	0.08	0.48	0.56	0.58	0.51
425	0.07	0.30	0.46	0.47	0.32
450	0.04	0.12	0.20	0.18	0.09
475	0.02	0.04	0.11	0.05	-
500	0.01	0.03	0.08	0.04	-
Curve	(1)	(2)	(3)	(4)	(5)

Fig.2

FIG. 2.

PLOTS OF O.D. Vs WAVE LENGTH FOR VOSBURGH AND COOPER'S METHOD.

1, 2, 3, 4 and 5 represent the absorbance curve for the ratios of hexacyanoferrate (II) to pyridine as 1:0, 2:1, 1:1, 1:2 and 1:3.

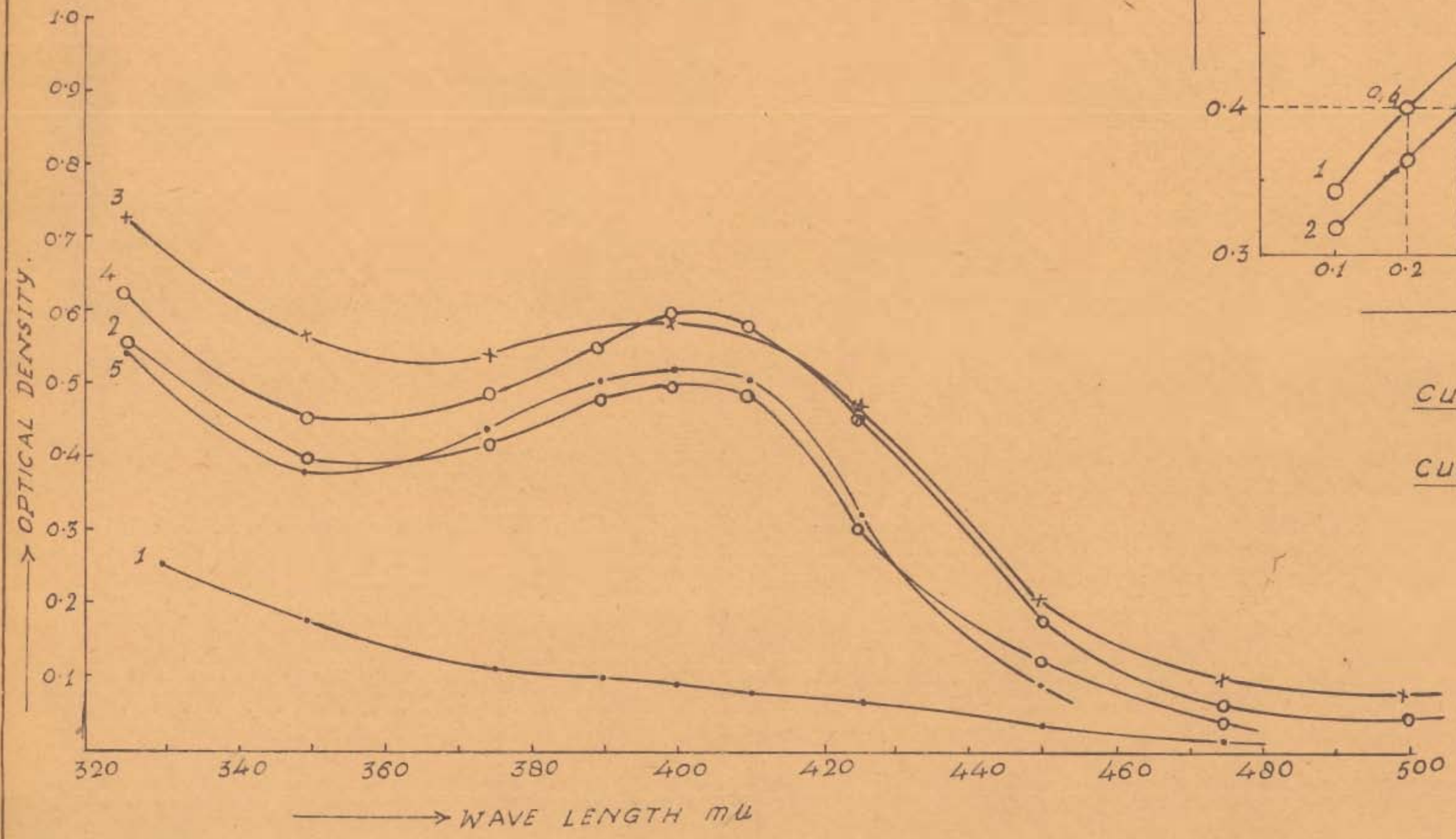
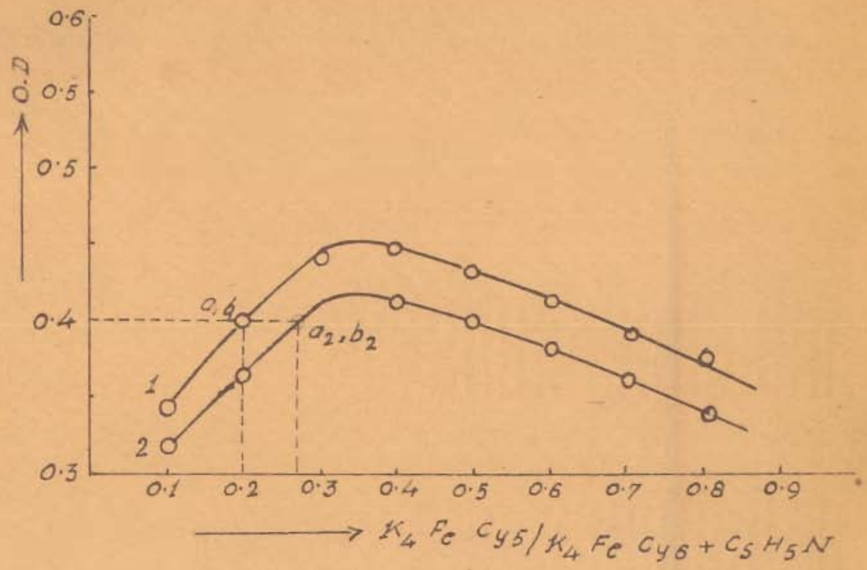


FIG. 3.

JOB'S METHOD OF CONTINUED VARIATION.



Curve 1. Total molarity = $0{\cdot}25 \times 10^{-2}$ M.

Curve 2. Total molarity = $0{\cdot}1666 \times 10^{-2}$ M.

The composition of the complex was studied by Job's method of continued variation. The absorption of the two sets of mixtures of the equimolecular solutions of two different concentrations (1.0×10^{-2}M and 0.666×10^{-2}M) of hexacyanoferrate (II) and pyridine in 20.0 ml of total volume maintained at pH 3.5 were measured at 400 mμ after keeping the mixtures for 48 hours. From Fig.3 it will be seen that complex species responsible for the maximum colour change has a hexacyanoferrate (II), pyridine ratio as 2:1. Results are tabulated below:

TABLE No.3

Job's method of continued variation. Concentration of the reactants (1st set) = 1.0×10^{-2}M. Concentration of the reactants (2nd set) = 0.666×10^{-2}M. Total volume = 20.0 ml.
Wave length 400 mμ pH = 3.5

Volume of hexacyanoferrate (II) ml	Volume of pyridine ml	Difference of optical density values between complex and hexacyanoferrate (II)	
		Set I	Set II
4.5	0.5	0.37	0.315
4.0	1.0	0.40	0.360
3.5	1.5	0.435	0.405
3.0	2.0	0.45	0.410
2.5	2.5	0.43	0.400
2.0	3.0	0.41	0.385
1.5	3.5	0.39	0.360
1.0	4.0	0.365	0.340
0.5	4.5	-	-
Curve		(1)	(2)

Fig.3

The composition of the complex was also confirmed by molar ratio method (7). For which solution in two sets with 1.0×10^{-2}M and 0.666×10^{-2}M reactants were prepared. In both the sets 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 ml of hexacyanoferrate (II) was mixed with 4.0 ml of pyridine and total volume was made to 20.0 ml by mainting the pH 3.5. Optical density values for both the sets of solutions were measured at 400 mμ. It will be seen from Fig.4 that the hexacyanoferrate (II) and pyridine combines in the ratio 2:1. Results are tabulated below:

TABLE No.4

Molar ratio method:

Concentration of the reactants (Set I) = 1.0×10^{-2}M
Concentration of the reactants (Set II) = 0.666×10^{-2}M
Volume of pyridine (fixed) = 4.0 ml
Total volume = 20.0 ml
Wave length 400 mμ pH = 3.5

Volume of hexacyano ferrate (II) ml	Optical density values	
	Set I	Set II
0.5	0.25	0.185
1.0	0.38	0.28
1.5	0.47	0.36
2.0	0.52	0.44
2.5	0.56	0.47
3.0	0.565	0.48
4.0	0.57	0.49
Curve	(1)	(2)

Fig.4

Formation constant:

Apparant formation constant of the complex has been determined following the method of Anderson et al (8) and Dey et al (9). Taking the case of general system.

$$mA + nB = A_m B_n$$

$$K = \frac{x}{(a-mx)(b-nx)} \qquad (1)$$

where x is the concentration of the complex and a, b are the initial concentrations of the reactants. For the formation of 1:2 complex, equation 1 can be written as:

$$K = \frac{x}{(a-x)\ (b-2x)^2} \qquad (2)$$

Taking the two concentrations a_1, a_2 and b_1 and b_2 having the same absorbance i.e. for the same value of x we can have from equation No.2.

$$K = \frac{x}{(a_1-x)(a_2-2x)^2} = \frac{x}{(b_2-x)(b_2-2x)^2} \qquad (3)$$

$$\text{or } 4\ x^2\ (a_1+b_1)-(a_2+b_2)\ + x\ b_2^2 - b_1^2\ x\ +$$

$$4\ (a_2\ b_2-a_1\ b_1)x+(a_1\ b_1^2 - a_2\ b_2^2\ ) = 0$$

$$X = \frac{\left[(b_2^2-b_1^2)+4(a_2\ b_2-a_1 b_1)\right] \pm \sqrt{\left[(b_2^2 - b_1^2)+4\ (a_2\ b_2-a_1\ b_1)\right]^2 - 16\ \left[(a_1+b_1)-(a_2+b_2)\ \ (a_1\ b_1^2 - a_2\ b_2^2)\right]}}{8\ \left[(a_1+b_1)-(a_2+b_2)\right]} \qquad (4)$$

Knowing the value of x from equation 4 the value of K, the apparent formation constant can be found out from equation 3.

For determining the value of the formation constant, the O.D. readings recorded during the Job's method were utilized. In this O.D. values were ploted against the ratio $K_4Fe(CN)_6/K_4Fe(CN)_6$ + Pyridine. Thus taking the two concentration of the reactants 1.0×10^{-2}M and 0.666×10^{-2}M, the fermation constant of the pyridine hexacyanoferrate (II) complex was calculated as:

Taking $a_1 = 0.05 \times 10^{-2}$M $a_2 = 0.045 \times 10^{-2}$M
$b_1 = 0.20 \times 10^{-2}$M $b_2 = 0.122 \times 10^{-2}$M

The value of x from equation (4) came out to be 30.6×10^{-2}M and K from equation (3) came out to be 2.686$^{\times 10^{2}}$ at pH 3.5 maintained with hydrochloric acid.

Beer's Lambert's Law:

The coloured system obeyed the Beer's lambert's at 400 m μ. Fig.(5) shows the results of experiments carried out with 0.02 to 0.12×10^{-2}M hexacyanoferrate (II) in 0.5×10^{-2}M concentration of pyridine. Results are tabulated below:

TABLE No.5

Beer's Law

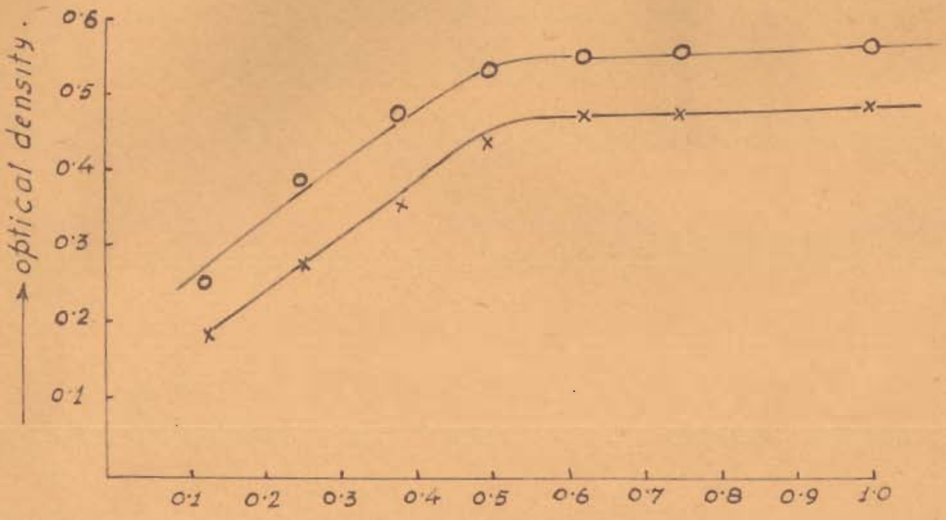
Concentration of the reactants = 1.0×10^{-2}M
Wave length 400 m μ pH = 3.5
Volume of pyridine (fixed) = 5.0 ml
Total volume = 10.0 ml

Volume of hexacyanoferrate (II) ml	Optical density ~~ml~~
0.2	0.16
0.4	0.32
0.6	0.45
0.8	0.58
1.0	0.70
1.2	0.85
Curve	(1)

Fig.5

CHAPTER V (Part II)

FIG. 4



MOLAR RATIO METHOD.

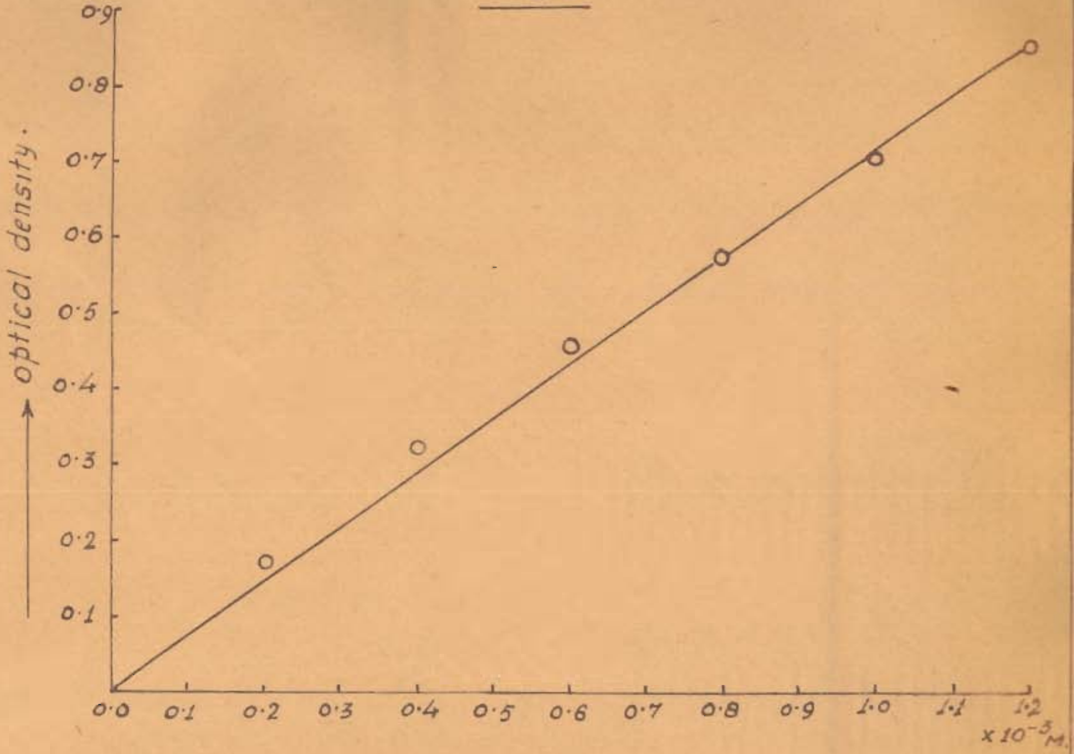
Moles $K_4 Fe\ Cy_6$/Moles C_6H_5N

Curve 1. concentration of reactants $0{\cdot}1 \times 10^{-2}$ M.

Curve 2. concentration of reactant $0{\cdot}666 \times 10^{-2}$ M.

Total volume 20·0 ml.

FIG. 5



Concentration of $K_4 Fe\ Cy_6$
validity of beer's law

Polarographic behaviour of bipyridine tetracyanoferrate (II) complex at dropping mercury electrode:

Existing literature provides several references on the polarographic behaviour of pyridine and its derivatives (1-10)(piconilic acid, nicotinic acid, isonicotionic acid, nicotinamide, methyl pyridinium hydroxide, trigonelline and homarine etc.).

Several mixed complex cyanides of pyridine and phenonthroline have been investigated by Shilt (11) and Hamer (12). These so far have not been studied polarographically. Therefore it was thought worth while to carry out studies in this direction, with a view to estimate bipyridine tetra~~hexa~~cyanoferrate (II) complex at dropping mercury electrode.

EXPERIMENTAL

Apparatus:

Heyrǒsky polarograph LP 55A operated mannually was used (details are given in Chapter III part II page) 153. The polarographic cell and the reference electrode (S.C.E.) were kept immersed in thermostatic bath maintained at 25 ± 0.1°C. Nitrogen was used for deaeration.

Beckman pH-meter Model H-2 was used for measurin the pH of the solutions.

Bipyridine tetracyanoferrate (II) trihydrate:

This was prepared by the method as recommended by Shilt (11). The solution of the dark violet crystalline product was prepared in double distilled water assuming the formula $K_2Fe(CN)_4\ (bipy)_2.3H_2O$.

Buffers and electrolytes:

Solutions of buffers and other electrolytes were prepared in double distilled water. Walpole (sodium acetate and hydrochloric acid each 0.2M); disodium hydrogen phosphate (0.1M) and citric acid (0.1M); dipotassium hydrogen phosphate (0.1M) and hydrochloric acid (0.1M); dipotassium hydrogen phosphat (0.1M) and sodium hydroxide (0.1M); Naegeli and Tyabji (borax 0.5 and sodium hydroxide 0.1M) buffers in pH range (2.0 to 5.0); (2.0 to 8.0); (3.0 to 4.0); (5.0 to 8.0) and (9.5 to 12.0) respectively were prepared by mixing requisite quantities.

To study the reduction of complex over a wide range of pH, several solutions were prepared. Each consisted of 3.0 ml 10^{-2}M complex and 17.0 ml of buffers of pH values ranging from 2.0 to 12.0.

Since catalytic waves were realised in sodium acetate and hydrochloric acid buffer pH range 2.0 to 5.0, the effect of complex concentration on the catatytic wave, only at pH 3.0 was studied. The following six solutions were prepared.

Increasing amounts of(0.0, 2.0, 4.0, 6.0, 8.0, 10.0 ml of 10^{-2}M) of the complex was added to 30.0 ml of buffer of pH 3.0, total volume was made to 40.0 ml by adding requisite quantity of water.

In pH range 6.0 to 8.0 both the catalytic and reduction waves were obtained. In order to study the effect of the complex concentration on these two waves, similar type of solutions as mentioned above were prepared in dipotassium hydrogen phosphate, sodium hydroxide buffer at pH 8.0. The effect of complex concentration on the reduction wave was also studied in disodium hydrogen phosphate and citric acid buffer at pH 8.0. Results are tabulated below:

TABLE No.1

Current potential readings of the mixtures containing 0.15×10^{-2}M bipyridine tetracyanoferrate (II) complex, sodium acetate and hydrochloric acid buffers of pH 2.0 to 5.0.

Potential (-ve) volts	pH			
	Current μA			
	2.0	3.0	4.0	5.0
1.0	0.15	-	-	-
1.1	0.20	-	-	-
1.2	0.25	0.25	-	-
1.25	0.30	0.30	-	-
1.30	0.70	0.35	0.30	-
1.35	1.50	0.60	-	-
1.40	2.90	0.70	0.45	0.40
1.45	4.55	2.30	1.00	0.50
1.50	5.50	4.00	2.00	0.80
1.53	5.80	5.00	-	-
1.55	6.10	-	4.00	1.80
1.58	6.40	5.60	-	-
1.60	6.60	5.80	5.00	3.30
1.63	6.65	-	-	4.30
1.65	7.00	6.20	5.60	5.30
1.68	-	6.30	-	-
1.70	8.50	6.80	5.80	5.35
1.75	-	8.30	6.40	5.40
1.80	-	-	7.20	6.20
1.85	-	-	-	7.20
Curve	(1)	(2)	(3)	(4)

Fig.1

TABLE No.2

Current potential data of the mixtures containing increasing amounts of complex at pH 3.0 in sodium acetate and hydrochloric acid buffer:

Potential (-ve) volts	Current μA					
	Concentration $x10^{-2}M$					
	0.1	0.2	0.3	0.4	0.5	Blank
1.2	0.2	0.2	0.2	0.2	0.2	0.2
1.3	0.2	0.2	0.2	0.2	0.2	0.2
1.35	0.65	0.5	0.6	0.7	0.7	-
1.40	1.3	1.1	1.4	1.5	1.5	0.3
1.45	2.3	2.3	3.0	2.8	3.0	-
1.50	4.0	4.0	4.5	4.5	4.9	0.5
1.55	5.0	5.45	5.9	5.7	6.9	-
1.60	5.85	6.2	6.6	6.7	6.0	0.7
1.63	6.0	6.3	7.0	7.1	7.1	-
1.65	6.3	6.6	7.3	7.3	7.4	-
1.70	7.35	7.5	7.8	7.7	7.8	1.2
1.80	-	-	-	-	-	5.4
Curve	(1)	(2)	(3)	(4)	(5)	(6)

Fig.2

TABLE No.3

Current potential data for the catalytic waves of the mixtures containing 0.15×10^{-2}M complex and disodium hydrogen phosphate and citric acid buffer pH 2.0 to 8.0

Potential (-ve) volts	Current µA						
	pH						
	2.0	3.0	4.0	5.0	6.0	7.0	8.0
1.0	0.3	0.3	0.3	0.3	0.3	0.3	-
1.1	0.3	0.3	0.3	0.3	0.3	0.3	-
1.2	0.4	0.4	0.35	0.35	0.35	0.35	-
1.3	0.6	0.45	0.45	0.45	0.45	0.45	-
1.35	2.0	0.7	0.50	0.45	0.45	0.45	-
1.40	5.2	2.0	0.55	0.60	0.50	0.50	-
1.45	6.2	5.0	2.00	1.00	0.50	-	-
1.47	6.5	5.5	4.00	2.50	0.60	-	-
1.50	6.7	6.0	4.40	4.00	0.90	-	0.6
1.55	7.5	6.5	6.00	4.50	3.00	1.00	0.65
1.60	-	7.5	6.50	5.90	4.50	2.50	1.20
1.62	-	-	-	-	5.30	3.50	-
1.65	-	-	7.40	6.50	5.60	4.60	3.00
1.67	-	-	-	-	-	5.20	4.00
1.70	-	-	-	7.10	6.00	5.30	4.80
1.75	-	-	-	-	6.80	5.80	5.00
1.80	-	-	-	-	-	6.70	5.80
1.85	-	-	-	-	-	-	6.7
Curve	(1)	(2)	(3)	(4)	(5)	(6)	(7)

Fig.3A

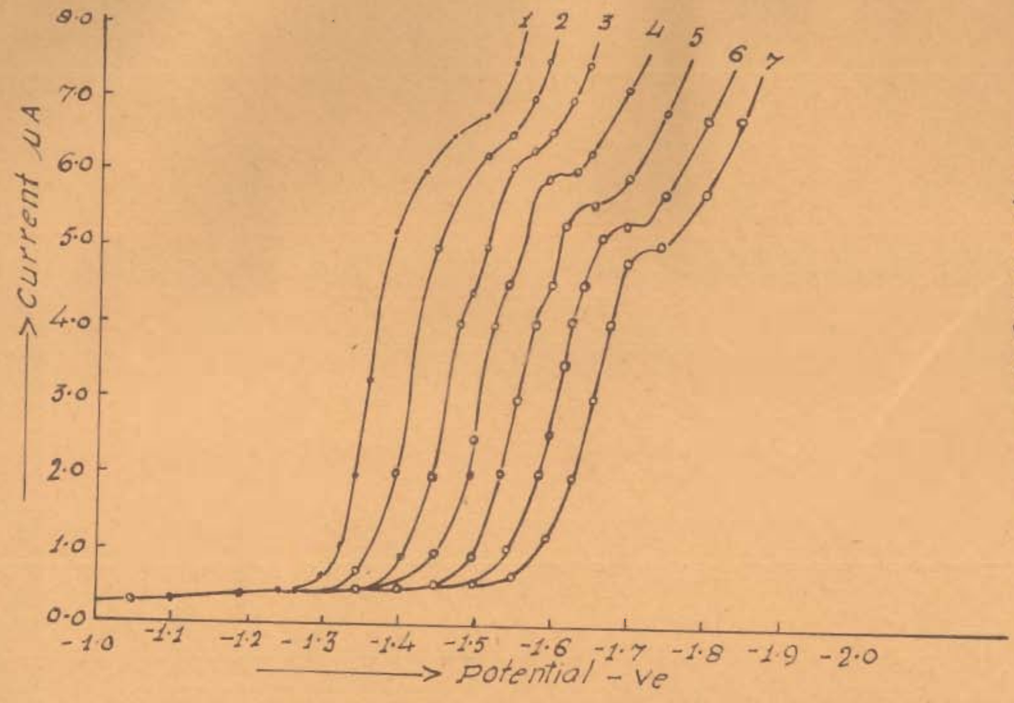


FIG. 3

Dependence of the height of the catatytic wave of the Complex ($0{\cdot}15 \times 10^{-2}M$) on pH (pH 2·0, 3·0, 4·0, 5·0, 6·0, 7·0 and 8·0 for curves 1,2,3,4,5,6 and 7 respectively) in disodium hydrophosphate and citric acid buffer.

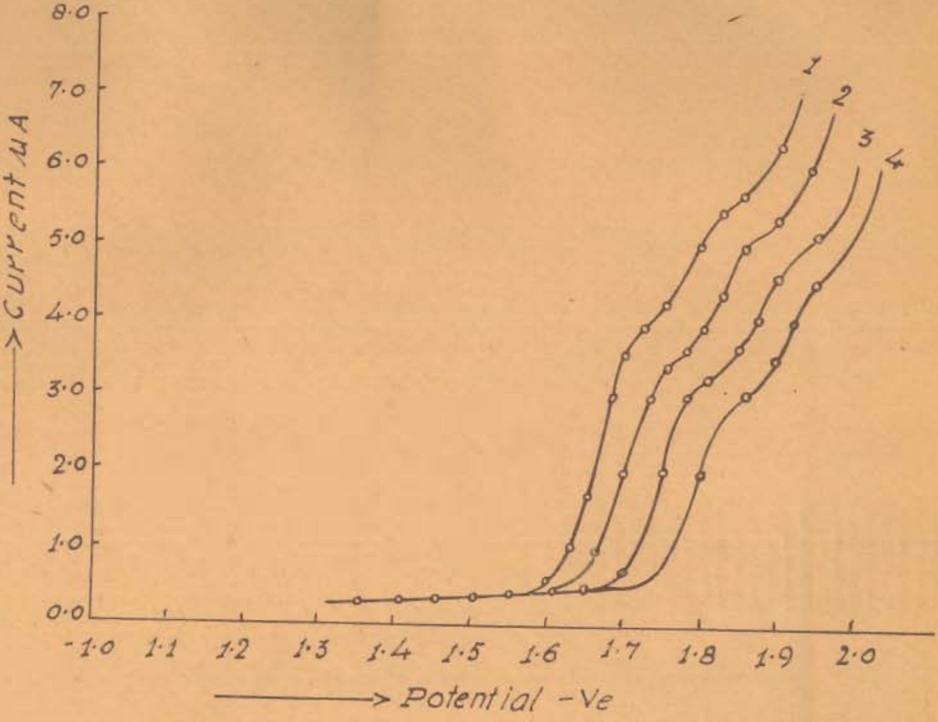


FIG. 6

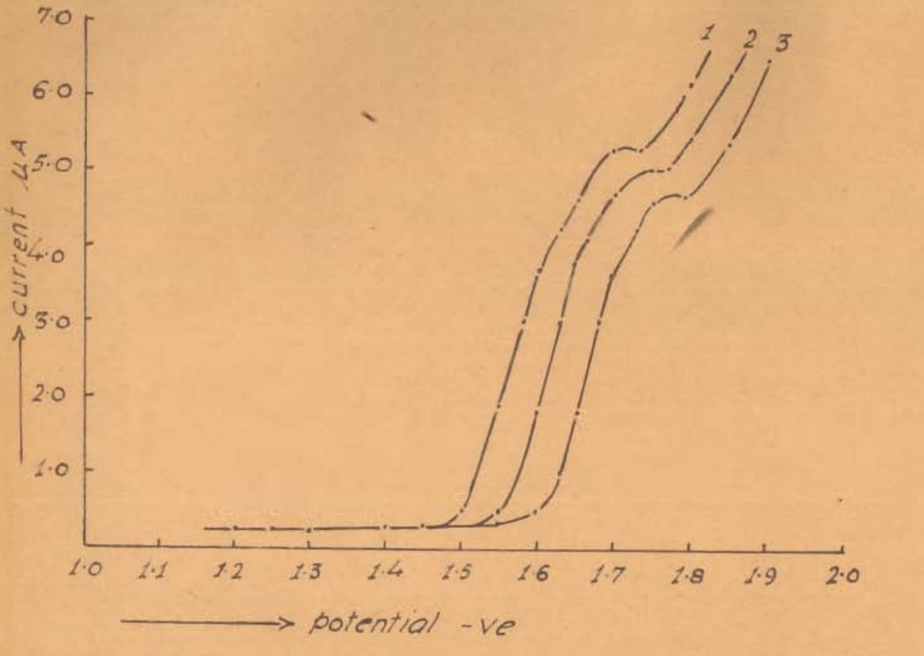
Dependence of kinetic current of the complex ($0{\cdot}15 \times 10^{-2}M$) on pH (pH 9·5, 10·0, 10·5 and 11·0 for curves 1, 2, 3 and 4 respectively) in borax and sodium hydroxide buffer.

TABLE No.4

Current potential data for catalytic waves of the mixtures containing 0.15×10^{-2}M complex and disodium hydrogen phosphate and sodium hydroxide buffer pH (6.0 to 8.0):

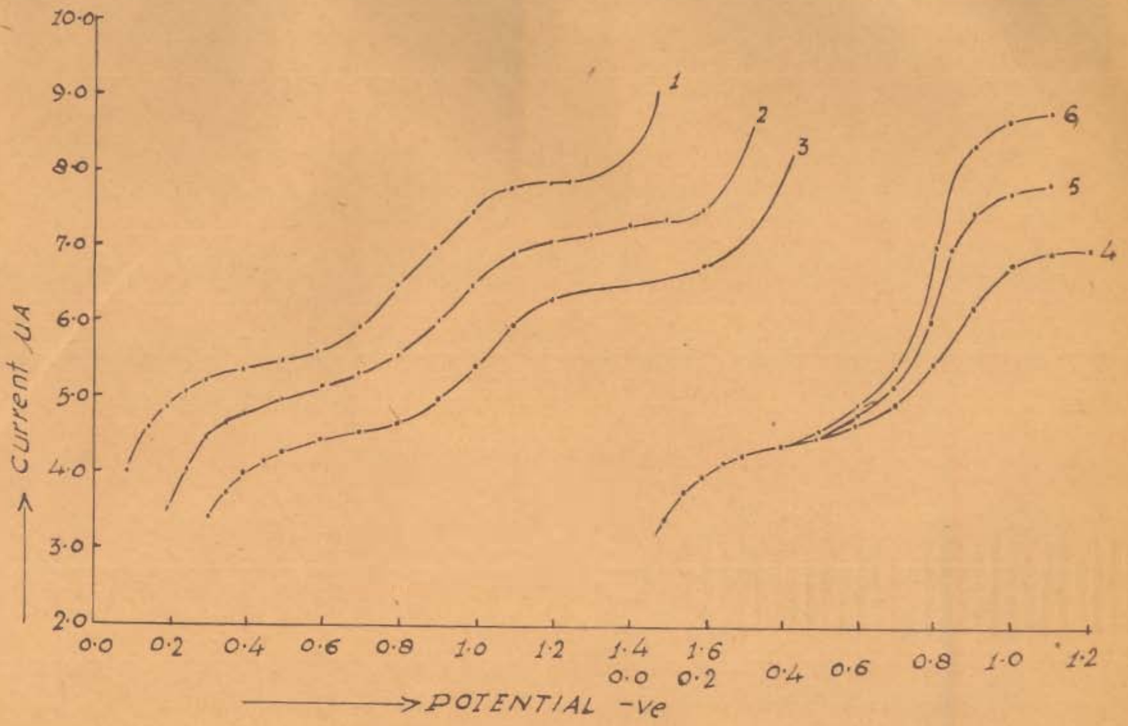
Potential (-ve) volts	Current μA		
	pH		
	1.0	2.0	3.0
1.2	0.25	0.25	-
1.3	0.25	0.25	-
1.4	0.30	0.30	-
1.45	0.30	0.30	-
1.50	0.50	0.35	-
1.55	1.90	0.50	-
1.58	3.00	-	-
1.60	3.70	1.80	-
1.63	4.20	-	0.5
1.65	4.60	3.70	1.0
1.67	-	4.10	1.8
1.70	5.30	4.70	-
1.73	5.30	-	3.60
1.75	5.60	5.00	4.30
1.77	-	5.00	4.60
1.80	6.10	5.40	4.70
1.85	-	6.30	5.40
1.90	-	-	6.50
Curve	(1)	(2)	(3)

Fig.3B



Dependence of the height of catalytic wave of the complex (0.15×10^{-2}M) on pH (pH 6.0, 7.0 and 8.0 for for curves 1, 2 and respectively) in dipotassium hydrogen phosphate and sodium hydroxide buffer.

FIG 3B



Curve 1,2,3 represent the reduction of the complex (0.15×10^{-2}M) IN disodium hydrogen phosphate and citric acid buffer of pH 6.0, 7.0 and 8.0 curve 4,5 and 6 represent The dependence of limiting current on concentration of complex (0.2, 0.3, 0.4 × 10^{-2}M). at pH 8.0.

FIG. 5

TABLE No.5

Current potential data for reduction waves of the mixtures containing 0.15×10^{-2} M complex and dipotassium hydrogen phosphate and sodium hydroxide buffer pH 6.0 to 8.0

Potential (-ve) volts	Current μA pH 6.0	Current μA pH 7.0	Current μA pH 8.0
0.0	1.80	1.45	1.40
0.02	2.10	1.65	1.65
0.05	2.85	2.15	2.40
0.10	3.95	2.95	3.15
0.15	4.50	3.35	3.60
0.20	4.85	3.55	4.05
0.30	5.20	3.75	4.55
0.40	5.25	3.95	4.85
0.50	5.45	4.10	4.90
0.60	5.50	4.20	5.15
0.70	5.95	4.40	5.35
0.80	6,35	4.80	5.75
0.85	6.70	-	5.95
0.90	6.95	5.20	6.25
1.00	7.45	5.50	6.80
1.10	7.75	5.80	7.10
1.20	7.95	5.85	7.20
1.30	8.00	5.95	7.25
1.35	8.05	-	-
1.40	8.25	6.40	7.40
Curve	(1)	(2)	(4)

Fig.4

Fig. 4.

Curve 1,2 represent the reduction wave of the complex (0.15×10^{-2}M) in dipotassium hydrogen phosphate and sodium hydroxide buffer at pH 6.0, 7.0

Curves

3,4,5,6 and 7 represent the dependence of limiting current on concentration of the complex (0.10, 0.15, 0.20, 0.30, 0.40 M) at pH 8.0 .

TABLE No.6

Current potential data for the reduction waves of the mixtures containing 0.15×10^{-2} M complex and disodium hydrogen phosphate and citric acid buffer pH (6.0 to 8.0).

Potential (-ve) volts	Current μA		
	pH		
	6.0	7.0	8.0
0.10	4.00	3.50	3.40
0.15	4.60	4.00	3.75
0.20	4.85	4.45	4.00
0.25	5.05	4.65	4.20
0.30	5.20	4.75	4.30
0.40	5.35	4.95	4.40
0.50	5.50	5.15	4.50
0.60	5.60	5.35	4.65
0.70	5.90	5.55	4.95
0.80	6.50	6.00	5.40
0.90	6.95	6.45	6.00
1.00	7.40	6.90	6.30
1.10	7.80	7.00	6.40
1.20	7.80	7.15	6.50
1.25	7.85	7.30	6.60
1.30	7.90	7.40	6.60
1.40	-	-	6.75
Curve	(1)	(2)	(3)

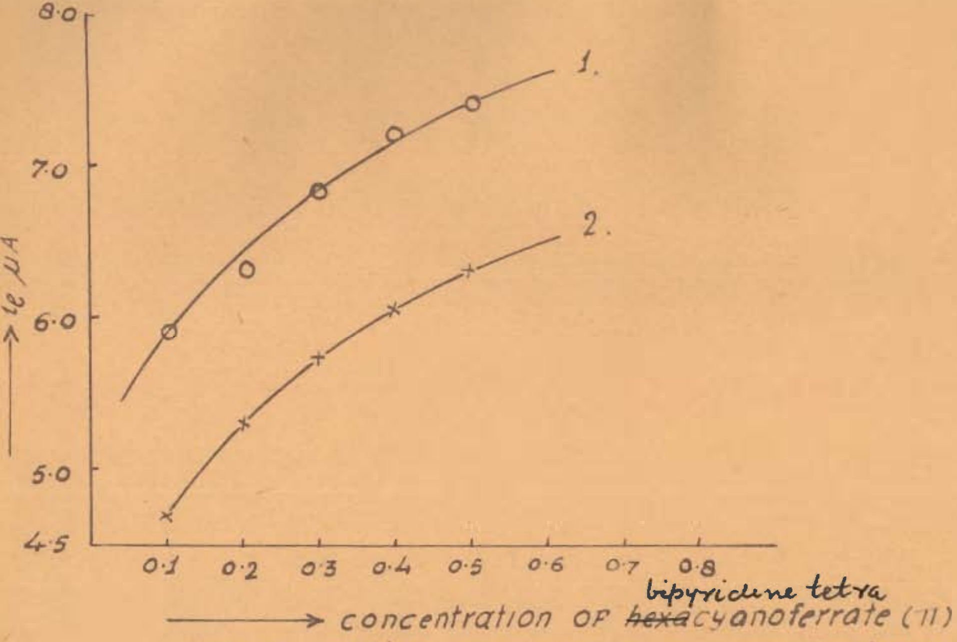
Fig.5

TABLE No.7

Current potential data for the reduction waves of the mixtures containing increasing amounts of the complex at pH 8.0 in dipotassium hydrogen phosphate and sodium hydroxide buffer:

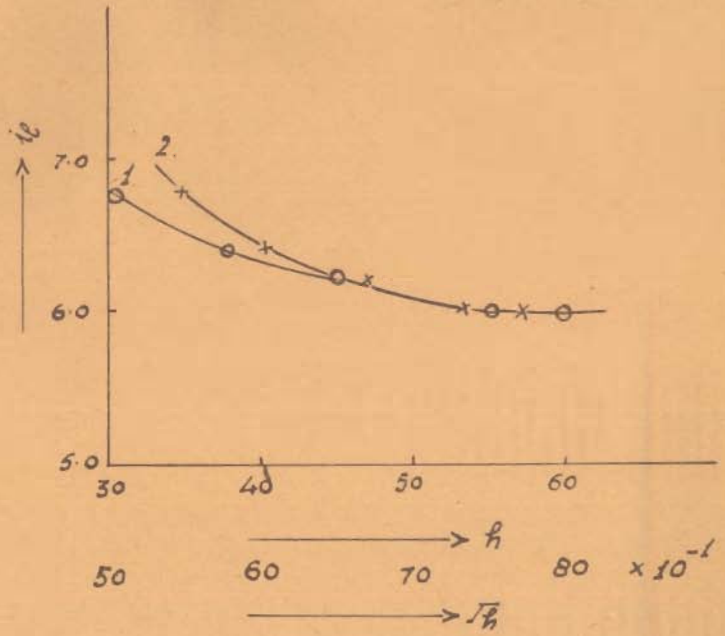
Potential (-ve) volts	Current µA			
	Concentration x10^{-2}M			
	0.1	0.2	0.3	0.4
0.00	1.40	-	-	-
0.05	2.40	-	-	-
0.10	3.15	-	-	-
0.15	3.60	-	-	-
0.20	4.00	-	-	-
0.30	4.50	-	-	-
0.40	4.80	4.80	-	-
0.50	4.90	4.90	-	-
0.60	4.95	5.00	5.00	5.00
0.70	5.05	5.20	5.25	5.30
0.80	5.20	5.50	5.60	5.70
0.90	5.60	6.30	6.50	8.10
1.00	6.00	7.80	8.60	9.60
1.10	6.30	8.10	9.10	10.00
1.20	6.40	8.20	9.40	10.40
1.30	6.45	8.25	9.60	10.60
1.40	6.60	8.40	9.80	10.80
1.50	7.00	9.00	-	-
Curve	(3)	(5)	(6)	(7)

Fig.4



Plot of limiting current (i_ℓ) vs concentration of the complex curve(1) pH at 3.0 (sodium acetate and hydrochlonic acid buffer) and curve 2 at pH 8.0 (disodium hydrogen phosphate and citric acid buffer)

FIG. 8.



Curve 1 Plot of h vs i_ℓ and curve 2 Plot of $\sqrt{h}$ vs i_ℓ at pH 3.0 in sodium acetate and hydrochloric acid buffer.

FIG. 7.

TABLE No.8

Current potential data for the reduction waves of the mixtures containing increasing amounts of the complex at pH 8.0 in disodium hydrogen phosphate and citric acid buffer:

Potential (-ve) volts	Current μA		
	Concentration x10^{-2}M		
	0.20	0.30	0.40
0.10	3.40	3.40	3.40
0.15	3.75	3.75	3.75
0.20	4.00	4.00	4.00
0.25	4.15	4.15	4.15
0.30	4.25	4.25	4.25
0.40	4.35	4.35	4.35
0.50	4.50	4.55	4.60
0.60	4.55	4.70	4.90
0.70	4.90	5.15	5.40
0.80	5.45	6.00	7.00
0.90	6.20	7.00	8.40
1.00	6.80	7.45	8.70
1.10	6.90	7.70	8.80
1.20	6.95	7.80	8.80
Curve	(4)	(5)	(6)

Fig.5

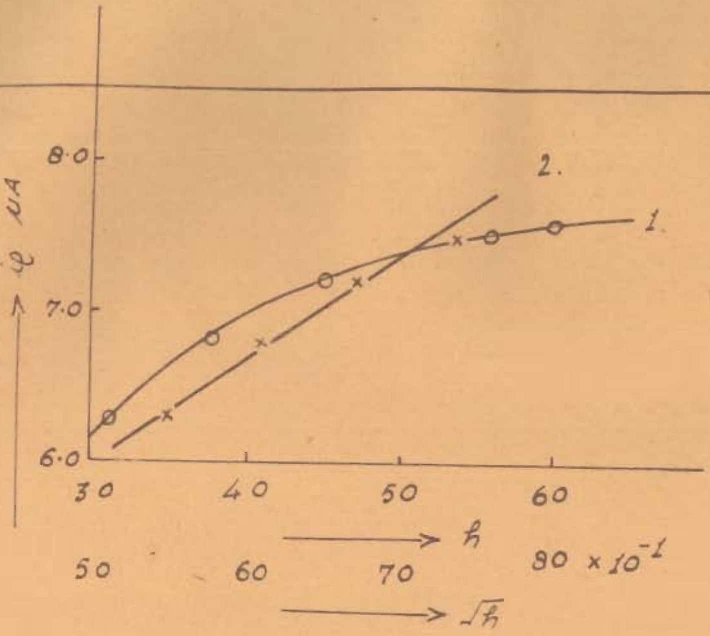


FIG. 9.

Curve 1. Plot of h vs i_e and Curve 2 Plot of $\sqrt{h}$ vs i_e at pH 8·0 for reduction wave (·potassium hydrogen phosphate and sodium hydroxide buffer)

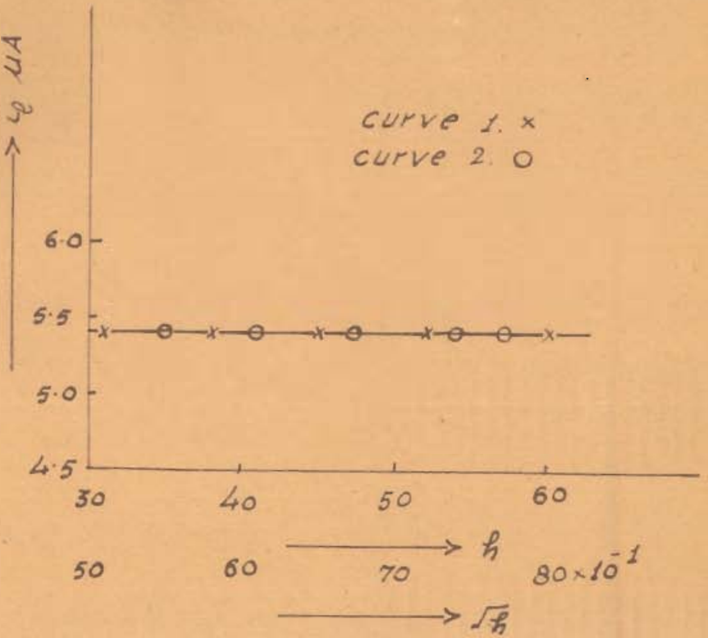


FIG. 10.

Curve 1. Plot of h vs i_e and

Curve 2. Plot of $\sqrt{h}$ vs i_e at

ph 10·0 for kinetic wave.

(borat and sodium hydroxide buffer)

TABLE No.9

Current potential data for the kinetic waves of the mixtures containing 0.15×10^{-2}M complex, borax and sodium hydroxide buffers pH (9.5 to 11.0):

Potential (-ve) volts	Current μa			
	pH			
	9.5	10.0	10.5	11.0
1.30	0.25	-	-	-
1.40	0.25	-	-	-
1.50	0.35	-	-	-
1.60	0.50	0.45	0.40	0.40
1.63	1.00	-	-	-
1.65	1.70	1.00	0.50	0.45
1.68	3.00	-	-	-
1.70	3.60	2.00	0.70	0.50
1.72	3.90	-	-	-
1.75	4.20	3.40	-	-
1.78	-	3.60	3.00	-
1.80	5.00	3.90	3.20	2.00
1.82	5.40	4.30	-	-
1.85	5.60	5.00	3.70	3.00
1.87	-	-	4.00	-
1.90	6.30	5.30	4.50	3.50
1.92	-	-	-	4.00
1.95	-	6.00	5.10	4.50
1.97	-	-	-	4.90
Curve	(1)	(2)	(3)	(4)

Fig.6

The nature of the electrode processes was ascertained by studying the effect of mercury pressure on the limiting current (i_l) of 0.15×10^{-2}M complex concentration at the required pH. Curves were plotted between h Vs i_l and $\sqrt{h}$ Vs i_l where $h = h_{exp.} - h_{back}$ and $h_{back} = 3.1/m^{1/3}t^{1/3}$.

Results and Discussion:

From current voltage curves it was concluded that the compound gave catalytic hydrogen and kinetic waves in pH range (2.0 to 9.0), and (9.5 to 11.0) respectively. In addition to these waves a reduction wave in pH range (6.0 to 8.0) was also realised.

In sodium acetate and hydrochloric acid buffer (pH range 2.0 to 5.0) catalytic hydrogen wave was obtained (Fig.1, Fig.7) the $E_{\frac{1}{2}}$ of which became more -ve with an increase in pH. The wave height was dependent on pH and concentration of the complex. It decreased on increasing the pH while it increased with increase in concentration (Fig.2). On plotting the step height at pH 3.0 against the concentration, a curve of the type of Langmuir isotherm (Fig.8 curve 1) was obtained.

In disodium hydrogen phosphate and citric acid buffer pH range(2.0 to 8.0) catalytic waves (Fig.3A) were obtained. Their $E_{\frac{1}{2}}$ values were also dependent on pH but the values were quite different as compared with those obtained in sodium acetate and hydrochloric acid in the pH range 2.0 to 5.0. The step height decreased on increasing the pH and increased on increasing the concentration. Plots of step height against concentration again gave a Langmuir adsorption isotherm type curve (Fig.8 curve 2).

In addition to this catalytic wave a reduction wave at much less -ve potential was realized in the pH range 6.0 to 8.0. The step height of which was dependent on concentration (Fig.5). The electrode process was diffusion controlled as verified by the effect of mercury pressure. The $E_{\frac{1}{2}}$ (-0.80 V.) of this wave was independent of pH (Fig.5).

In potassium hydrogen phosphate and sodium hydroxide buffer (pH range 6.0 to 8.0) in addition to the catalytic wave (Fig.3) a reduction wave(Fig4) ($E_{\frac{1}{2}}$ = -0.85 V.) was obtained (plot of i_l Vs h and $\sqrt{h}$ for reduction wave Fig.9). The effect of concentration pH and mercury pressure on these waves was the same as already described in the previous two cases but the $E_{\frac{1}{2}}$ values were quite different for catalytic waves obtained in different buffers of pH range 6.0 to 8.0.

In borax and sodium hydroxide buffer (pH 9.5 to 11.0) a kinetic character (Fig.6) of the current was indicated (since the limiting current was found to be independent of mercury pressure but was dependent on pH Fig.8,10). At pH 12.0 no waves were observed irrespective of the buffers used.

The studies on the ultra violet and visible spectra of such type of complexes (11-12) reveal the fact in acidic and neutral solutions these are protonise establishing an equilibrium with the free base according to the equation (taking this complex as example):

$$K_2Fe(CN)_4(bipy)_2 + 2H_2O \rightleftharpoons K_2Fe(CN)_4(bipy)_2(H^+)_2 + 2OH^- \quad ..(1$$

The existance of catalytic waves in acidic and neutral range can be represented by the equation:

$$K_2Fe(CN)_4(bipy)_2(H^+)_2 + 2e \rightleftharpoons K_2Fe(CN)_4(bipy)_2 + 2H$$

$$2H \longrightarrow H_2 \qquad ...(2)$$

and the kinetic nature of the wave in alkaline solutions can be explained due to the reprotonation of the complex at dropping mercury electrode envolved, may be represented by equation (1).

RESUME

The development of the co-ordination chemistry, especially that of cyanogen complexes was virtually started with prepration of Prussian blue. The German artist, Dieshbach (1704) was the first to obtain Prussian blue by heating animal refuse and sodium carbonate together in an iron pot, subsequent work led to the isolation of potassium ferrocyanide and preparation of a large number of iron blues of varying composition both soluble and insoluble. Later on a large number of cyanide complexes of most of the transitional metals as well as those of non-transitional metals were prepared. Further development in the form of substituted products with groups, like nitroso-nitro-, amino-, carbonyl, hydroxy etc. took place. Other mixed complex cyanides of organic bases, basic dyestuff's, alkolides were also prepared. Besides a number of methods, starting from the conventional ones of chemical analysis to those based on purely physical techniques were, employed to determine their composition, structure etc. and these had yielded results of far reaching importance. For example, the results of these investigations had revealed the facts that the majority of these metal complex cyanides were hexaco-ordinated (octahedrol) and that quite a few existed as a tetra co-ordinated (tetrahedral or square planar, e.g. copper, zinc, palladium, nickel, mercury, platinum, gold etc.) or in the form of tricyano (planar) or dicyano (linear) complexes. Other (dodeca hedral) complex cyanides (like those of Mo, W and Re) having the co-ordination number larger than six (eight with a tendency to extend the co-ordination number to ten) in mixed complex cyanides were discovered.

Investigations on metal ferrocyanogen complexes were not completely devoid of their applied aspect. The use of metal ferrocyanogen reaction for the estimation of metal ions, the utility of ferro-ferricyanide couple in analytical work, the adsorptive and hydrolytic properties of the freshly precipitated complexes, their colloid-chemical behaviour and their possible use as membranes of varying degree of selectivity, had all greatly contributed to our knowledge.

More recently thermo-dyanamic properties, viz., heat of solution in water, heat of oxidation, standard free energy, entropy, heat capacity and ratio of force constant to frequencies of iso-structural complex ions had been investigated. Results on photochemistry, manganetic and cryoscopic studies had also been successfully employed to investigate the structure of mixed complexes of Fe(II) and Fe(III).

Inspite of the fact that much has been done during the last twenty years on the physics and chemistry of metal cyanogen complexes, little attention has been paid to the study of reactions involving interaction of organic compounds with cyanogen complexes. A closer review of the chemical literature reveals that the several organic compounds (nitro-nitrosobenzenes, pyridines, quinolines, dyestuff's, vitamines, modified proteins, amino acids and sugars can react with these cyanogen complexes. Investigation on some of the physico-chemical aspects of these types of reactions was, therefore, considered worth undertaking. The following aspects were chosen for study:

(1) Reduction of nitrosobenzene-pentacyanoferrate (II) complex at d.m.e.

(2) Spectrophotometric studies on the composition, stability and kinetics of interaction of hexacyanoferrate (III) with nitrosobenzene in presence of mercuric ions as catalyst.

(3) E^0 of $Fe(CN)_5H_2O^{---} \rightleftharpoons Fe(CN)_5H_2O^{--} + e$ couple and the potentiometric estimation of potassium aquapentacyanoferrate (II).

(4) Polarographic studies on the behaviour of hexacyanoferrate (II), aquapentacyanoferrate (II) and the kinetics of hydrolytic decomposition of hexacyanoferrate (II) in presence of Hg^{++} and Cr^{+++} ions and under the action of ultra violet and white light.

(5) Spectrophotometric studies on the composition, stability, and kinetics of interaction of hexacyanoferrate (II) with 8-hydroxyquinoline 5-sulphonic acid using Hg^{++}, Cr^{+++} and Be^{++} as catalysts.

(6) Polarographic studies on 8-hydroxyquinoline 5-sulphonate pentacyanoferrate (II) complex.

(7) Amperometric titrations of Co(II) with hexacyanoferrate (III) in ammonium citrate and glycine media at pH 9.8 and 8.0 respectively. The reduction of Co(III) binuclear complexes formed in the above reactions at d.m.e.

(8) Amperometric titrations of thiamine (vitamin B_1) with hexacyanoferrate (III) in alkaline medium.

(9) Reduction of bipyridine tetracyanoferrate (II) complex at d.m.e.

(10) Spectrophotometric studies on the compostion and stability of the reaction product obtained by the interaction of pyridine with hexacyanoferrate (II) in solutions. The experimental results and conclusions arrived at are summarised in the proceeding pages.

(1) The reduction of the nitrosobenzene pentacyanoferrate (II) complex at d.m.e.

The reduction of the nitrosobenzene complex of potassium aquapentacyanoferrate (II) at d.m.e. was highly dependent on pH of the medium. Three distinct pH regions were found to exist.

I. In pH rang (1.0 to 4.0) reduction took place giving three waves, first wave arising directly from the dissolution of mercury decreased in height as did the third most -ve wave, where as the second increased. Total wave height remained practically constant (Fig.1(a) curve 1-4 Chapter II Part I). The half wave potential of the second wave was shifted from -0.10 volt at pH 1.15 to -0.30 volt at pH 4.0, where as that of the third wave got shifted from -0.56 volt at pH 1.15 to -0.83 volt at pH 3.0.

II. At pH 5 the height of the second wave decreased (Fig.1(a) curve 5-10). Another more positive wave appeared at -0.06 volt at pH 5.0. The height of which was practically pH dependent.

III. At pH 10.6 the height of the second wave increased again. The half wave potential -0.70 volt. was identical with the free nitrosobenzene (wave(Fig.1 (a), (b) curves 11-13). The results are summarised in (Table 11 page 83).

IV. The simplest curve was observed at pH 4.0 where a single wave diffusion controlled involving a two electron transfer was obtained. The step height was dependent on concentration of complex.

The following scheme for the formation and subsequent reduction of the violet complex has been suggested.

$$Fe^{II}(CN)_5H_2O + C_6H_5NO = (Fe^{II}(CN)_5C_6H_5NO) + H_2O$$

$$Fe^{II}(CN)_5C_6H_5NO + 2H^{+} + 2e = Fe^{II}(CN)_5C_6H_5NHOH \quad \text{(2nd wave)}$$

$$Fe^{II}(CN)_5C_6H_5NHOH + 2H^{+} + 2e = Fe^{II}(CN)_5C_6H_5NH_2 \text{(3rd wave)}$$

(2)(a) Interaction of nitrosobenzene with hexacyanoferrate (III).

The results obtained by spectrophotometric methods are as follows:

I. pH specificity: The rate of the reaction was maximum at pH 8.0. It became quite slow below pH 6.5 while the reaction almost came to a stop in the alkaline range. (Fig.7(a) Chapter II Part I).

II. The pH of the reaction mixture first decreased rapidly and then/increased slowly during the course of the reaction. (Fig.4,5,6 Chapter II Part II).

III. The reaction was found to be highly temperature dependent (Fig.12). The complex obtained at 20°C slowly decomposed at 40°C.

IV. Action of ultra violet or white light for half an hour decomposed the complex.

V. Neutral salts decreased the reaction velocity to a marked extent (Fig.11). In presence of potassium cyanide, the reaction ceased to take place.

On the basis of the above mentioned facts, the following reaction mechemism has been proposed.

$$Hg^{++} + Fe(CN)_6^{---} + H_2O \rightleftharpoons Fe(CN)_5(OH)^{---} + Hg(CN)^{+} + H^{+} \quad (1)$$

$$Fe(CN)_5(OH)^{---} + C_6H_5NO \rightleftharpoons Fe(CN)_5(C_6H_5NO)^{--} + OH^{-} \quad (2)$$

Following the catalytic decomposition of hexacyanoferrate (III).

$$Hg(CN)^{+} + Fe(CN)_6^{---} + H_2O \rightleftharpoons Hg(CN)_2 + Fe(CN)_5(OH)^{---} + H^{+} \quad (3)$$

$$OH^{-} + H^{+} \rightleftharpoons H_2O \quad (4)$$

$$Hg(CN)_2 + 2H_2O \rightleftharpoons Hg^{++} + 2HCN + OH^{-} \quad (5)$$

of these reaction (1) was slow reaction and followed first with a decrease and then a slow increase in pH and was dependent upon both the concentration of Hg^{++} and hexacyanoferrate (III). (2) is a fast reaction representing the formation of the complex $(Fe^{III}(CN)_5C_6H_5NO)$

Reaction (3) represents the catalytic decomposition of $Fe(CN)_6^{---}$ by the cation $Hg(CN)^+$ and should be dependent upon the concentration of $Fe(CN)_6^{---}$, since the variations in O.D. were less marked with varying amount of hexacyanoferrate (III), this reaction should be slow than reaction (1); reaction (4) represent the removal of H^+ions and reaction (5) takes place due to the hydrolysis of hexacyanoferrate (III) (Fig.7 (a,b,c); 9 (a,b); 10 (a,b); Chapter II Part II).

The energy of the activation for the reaction was found to be 5.45 K.cal/molecule.

(b) Composition and formation constant of the complex:

Maximum absorption for the buff coloured complex took place at 560 mμ. Evidence for the formation of only one complex was obtained from the VosBurgh and Cooper's Method (Fig.1(a);1(b) Chapter II Part II). Job's method of continued variation and Molar ratio method (Fig.2 (a,b);3 Chapter II Part II) indicated the existance of 1:1 complex. Formation constant of the complex was found to be 3.611×10^2.

(3) Standard electrode potential of the $Fe(CN)_5H_2O^{---} \rightleftharpoons Fe(CN)_5H_2O^{--} + e$ couple:

Since $Fe(CN)_5H_2O^{---}$ and $K_3Fe(CN)_5\,H_2O^{--}$ were the products of the decomposition of potassium hexacyano ferrate (II) and hexacyanoferrate (III) respectively in the reaction studied above, it was therefore, considered worthwhile to determine the redox potential of the system $Fe(CN)_5H_2O^{---} \rightleftharpoons Fe(CN)_5H_2O^{--} + e$ at different acidities. It was determined employing potential mediator method using ceric sulphate as titrant. The value of E^o was calculated by the relation $E = E^o - \frac{RT}{nF} \log \frac{t}{t_c - t}$, where E is the electrode potential, t_c the amount of titrant added at any particular stage during the titration. The mean value of E^o as determined graphycally (Fig.7 Chapter I Part I) by plotting $\log Fe^{III}(CN)_5H_2O^{---} / Fe^{II}(CN)_5H_2O^{--}$ against electrode potential in presence of sulphuric acid of concentratio 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0N were respectively 0.676, 0.749, 0.762, 0.806, 0.845, 0.866, 0.898 and 0.913 volt.

The value of E^o in the neutral medium was also determined employing Kolthoff's method (page 29). The value of E^o was found by plotting the measured value E of the mixtures (containing equimolecular mixtures of aquapentacyanoferrate (II) and ferrate (III) in the ratios 1:1, 10:1 and 1:10) (Fig.5 Chapter 5 part I) against the under root of ionic strength ($\sqrt{\mu}$) and extrapolating the straight line portion of the curve to zero ionic strength. The values came out to be -0.4120 Volt with 1:1 and 10:1 mixture while with 1:10 mixture it was -0.4130 Volt.

(b) <u>Potentiometric estimation of potassium aquapentacyanide:</u>

The use of various oxidants for the estimation of aquapentacyanoferrate (II) (in 4N sulphuric acid) leads to the following conclusions:

(1) Titrations between potassium permanganate and aquapentacyanoferrate (II) gave good results over a wide concentration range. The change in potential at the equivalence point was 0.285 V.

(2) Titrations between ceric sulphate and aquapentacyanoferrate (II) gave better results in comparision to potassium permanganate. The rise in potential at equivalence point being 0.45 V. (Fig.1,2,3 Chapter I Part I).

(3) Estimations with potassium dichromate were not successful and the error was greater than 1 per cent (Fig.4).

(4) Anodic waves of hexacyanoferrate (II), aquapentacyanoferrate (II) and polarographic studies on kinetic of hydrolytic decomposition of hexacyanoferrate (II).

Anodic waves of potassium hexacyanoferrate (II) and aquapentacyanoferrate (II) were realised at d.m.e. over a wide pH range (1.2 to 11.45). In 0.1M sodium fluoride at pH 4.0 potassium hexacyanoferrate (II) oxidised reversibly and a diffusion controlled step $E_{\frac{1}{2}}$ at + 0.32 V. was obtained. Step height was dependent on concentration (0.025×10^{-2}M to 0.25×10^{-2}M), (Fig.1(A, B,C Chapter I part II, Table 1 page 44), (Fig.2A curve 4).

The behaviour of potassium aquapentacyanoferrate

(II). It also gave a reversible diffusion controlled wave in 0.1M sodium fluoride and potassium nitrate at pH 4.0 but the $E_{\frac{1}{2}}$ value differed considerably ($E_{\frac{1}{2}}$ = +0.15V. Vs S.C.E.). The step height was also dependent on concentration (Fig.2B curve 4).

Mixture containing 0.1×10^{-2}M hexacyanoferrate (II) and aquapentacyanoferrate (II) gave two distinct waves with respective $E_{\frac{1}{2}}$ values mentioned above (Fig. 7 at pH 4.0 in 0.1M sodium fluoride.

Results on the kinetics of hydrolytic decomposition of hexacyanoferrate (II) have been discussed. Kinetics studies were carried out at a potential of +0.4 V. (plateau of the hexacyanoferrate (II) was in the potential range + 0.38 to 0.40 V.) The following information could be made available.

(1) Ultraviolet light, white light, Hg^{++} and Cr^{+++} decomposed hexacyanoferrate (II) to the same product, viz., aquapentacyanoferrate (II).

(2) The catalytic action of ultraviolet light was greater than that of white light and that of 0.1×10^{-4}M Hg^{++} was greater than that of the same concentration of Cr^{+++} At 60th minute current decreased to 30.37, 24.44, 8.14 and 5.3 per cent with ultraviolet, white light mercuric chloride and chromic chloride respectivel (Fig.9) at 30°C.

(3) The decomposition of hexacyanoferrate (II) was found to be of first order, the mean values of rate

constants at temperatures 30°, 40°, 50°C were 2.406×10^{-3}, 3.37×10^{-3}M and 10.086×10^{-3}M. The temperature coefficient and energy of activation were found to be 1.403 and -6.411 K.cal./molecule (Fig.11(a) Table 13,14,15 Chapter I part II).

(5) (a) Spectrophotometric studies on the interaction of hexacyanoferrate (II) and 8-hydroxyquinoline 5-sulphonic acid:

The results of spectrophotometric studies and variations in pH for the reaction can be summarised as given below:

(1) At room temperature no reaction between 8-hydroxyquinoline 5-sulphonic acid and hexacyanoferrate (II) appeared to take place when the reactants were mixed as such.

(2) In presence of small amounts of Hg^{++}, Cr^{+++} and Be^{++} the reaction between hexacyanoferrate (II) and 8-hydroxyquinoline 5-sulphonic acid was found to be catalysed and after a lapse of few hours an olive green colour was developed.

(3) The reaction was found to be pH dependent, and reaction velocity was maximum at pH 4.0. The reaction markedly decreased in neutral solutions and almost completely stopped in alkaline solutions. (Fig.7,8,9,10 Chapter III Part I).

(4) The pH of the various reaction mixtures increased slowly during the course of reaction. Concentration of both the reactants accelerated the rate of increase

of pH. The effect of concentration of 8-hydroxyquinoline 5-sulphonic acid was more pronounced (Fig.5,6a,b).

(5) The reaction velocity was found to be dependent on the concentration of both the reactants as well as the catalysing ions. (Fig.11a,b).

Summing up the above facts the following probable reaction mechanism was proposed. Let Q represents the molecule of 8-hydroxyquinoline 5-sulphonic acid and Hg^{++} as catalyst.

(I) $Hg^{++} + Fe(CN)_6^{4-} \underset{H_2O}{\rightleftharpoons} (FeCN)_5^{---} + Hg(CN)^+$

(II) $Fe(CN)_5H_2O^{3-} + Q \rightleftharpoons Fe(CN)_5Q^{3-} + H_2O$

(III) $Hg(CN)^+ + Fe(CN)_6^{4-} \rightleftharpoons Hg(CN)_2 + Fe(CN)_5^{3-}$

(IV) $Hg(CN)_2 + 2H_2O \rightleftharpoons Hg^{++} + 2HCN + 2OH^-$

Of these reaction (I) is slow and depends upon the concentration of Hg^{++}(or Cr^{+++} and Ba^{++}) ions, while (II) is a fast reaction representing the formation of $(K_3Fe(CN)_5Q)$ and is dependent on the concentration of 8-hydroxyquinoline 5-sulphonic acid. Reaction (III) represents the catalytic decomposition of hexacyanoferrate (II) by $Hg(CN)^+$ and is dependent on the concentration of hexacyanoferrate (II). The stoichiometric reaction (II) and catalytic reaction (III) seem to proceed simultaneously. Reaction (IV) takes place due to the hydrolysis of potassium cyanide.

(b) Composition and formation constant of the complex:

Maximum absorption for the alive green complex took place at 425 mμ although a small peak was also obtained at 575 mμ. But the Job's method of continued variation, slope and Molar ratio methods at both the wavelengths confirmed the existance of only 1:1 complex. Formation constant of the complex was found to be 25.3x 10^3 (Fig.1,2,3,4 Chapter III Part I).

(6) Polarographic studies on 8-hydroxyquinoline 5-sulphonate pentacyanoferrate (II):

Reduction of 8-hydroxyquinoline 5-sulphonic acid and its complex with aquapentacyanoferrate (II) (8-hydroxyquinoline 5-sulphonate pentacyanoferrate (II)) at d.m.e. had been investigated in the pH range 1.0 to 11.0 8-hydroxyquinoline 5-sulphonic acid gave main reduction step (I) over the entire pH range. This was preceeded by an ill defined reduction step (II), which became distinct above pH 6.0. Besides another reduction setep (III) was also realized in the pH range 9.0 to 11.0 in the borax and sodium hydroxide buffer. The $E_{\frac{1}{2}}$ and i_d values for step (I) and (III) were highly dependent on pH as well as on the buffers used. The half wave potential values for the main reduction step (I) was in accordance with the expression $E_{\frac{1}{2}} = -(0.965+0.015\ pH)$ in pH range 1.0 to 4.0 in sodium acetate and hydrochloric acid buffers (Table 25, 26, 27 Chapter III Part II).

8-hydroxyquinoline 5-sulphonate pentacyanoferrate (II) complex was also found to be reduced over a wide pH range (1.0 to 12.0), giving two reduction steps (I) and (II). The $E_{\frac{1}{2}}$ and i_d values of step (I) were highly dependent on pH and composition of buffers etc. The expressions $E_{\frac{1}{2}} = -(0.972+0.02\text{pH})$; $E_{\frac{1}{2}} = -(0.92+0.1\ \text{pH})$ and $E_{\frac{1}{2}} = -(1.33+0.11\ \text{pH})$ were found to hold good for the dependence of $E_{\frac{1}{2}}$ on pH in sodium acetate and hydrochloric acid buffer (pH 1.0 to 4.0), in disodium hydrogen phosphate and citric buffer (pH 5.0 to 7.0) and in borax buffer (pH 9.0 to 11.0) respectively. Unlike the 8-hydroxyquinoline 5-sulphonic acid step (III) was not realized for the complex (Table 25,26,27). The results in both cases have been explained on the basis of formation of the dihydroderivatives and are represented by the equations as given on page 194-195.

(7)(a) Amperometric titrations of Co(II) with hexacyanoferrate (III) in glycine and ammonium citrate media. Reduction of the resulting complexes at d.m.e.

Amperometric titrations of Co(II) with hexacyanoferrate (III) have been reported in the medium of ammonium citrate at pH 9.8 and in the medium of glycine at pH 8.0 Co(II) concentration of the order of 0.5×10^{-5} M with error less than ± 1 per cent could be determined in both the media. Several fold concentration of metals, like Cu(II), Ni(II), Mn(II), Cr(III), Ce(III) and V(V) did not interfere in its determination. (Table 2,3,4,5 Chapter IV part I).

The binuclear complex formed in the medium of ammonium citrate was found reduce in two steps with one and two electron transfer waves respectively. Both the waves were well defined and diffusion controlled. In the glycine medium also two reduction steps were realized but the first reduction step was not well defined. The effect of Cu(II), Ni(II), Mn(II), Cr(III), Ce(III) and V(V) on these reduction steps had been discussed.

The reduction of Co(II) and resulting Co(III) glycine complexes in buffers of different compositions in various supporting electrolytes in pH range 8.0 to 11.0 was also investigated. Two diffusion controlled irreversible reduction steps in each case w-ere obtained. Second reduction step was well defined in all the buffers and electrolyte used, but the first reduction step became comparatively more defined in 0.066M sodium fluoride, 0.33M glycine at pH 8.0 and in 0.133M calcium chloride and 0.53M glycine from pH 9.0 to 11.0.(Table 1 8_A etc. Chapter IV part I).

(b) <u>Amperometric titrations of thiamine (vitamine B_1) with hexacyanoferrate (III):</u>

Redox amperometric titrations of vitamine B_1 with hexacyanoferrate (III) were carried out in alkaline medium at -0.35V. (because hexacyanoferrate (III) gave a diffusion current at zero applied potential with limiting value of the current was in the potential region -0.25 to -0.4V. while thiamine did not give a wave under these conditions).

Small quantities of thiamine even when present upto 2.43 mgs per 100 ml could be easily determined in direct (thiamine in the cell) and reverse (hexacyanoferrate (III)in cell) titrations with error less than ± 0.5 per cent. Method was also extended to determine the small quantities of vitamine B_1 in multivitamine tablets and Eupeptin syrup, with fairly good accuracy. Various results are summarised in (Table 7 page 242).

8-Polarographic behaviour of bipyridine tetracyanoferrate (II) complex:

Reduction of the complex over a wide pH range (2.0 to 12.0) at d.m.e. was investigated.

In the pH range 2.0 to 8.0 a catalytic hydrogen wave, in different buffers of same pH values was realized. The $E_{\frac{1}{2}}$ of the wave was dependent on both composition and pH of the buffers. Increase in pH together with a shift of $E_{\frac{1}{2}}$ to more -ve side, a decreased in the wave height to a marked extent took place. The height of this wave was also dependent on the concentration of the complex. Curves of the type of Langmuir Isotherm (Fig.1,2,3(A,B),8 Chapter IV)part II) were obtained, On plotting concentration of the complexagainst limiting value of the current at pH 3.0 and 8.0 in sodium acetate hydrochloric acid and disodium hydrogen phosphate and citric acid buffers respectively.

In addition to catalytic wave a reduction wave in the pH range (6.0 to 8.0) in all the buffers was realized. The electrode process was diffusion controlled and the wave height was dependent on concentration (Fig.4, 5 Chapter V Part II). $E_{\frac{1}{2}}$ of this wave was independent of pH and the same value of $E^{\frac{1}{2}}$ (-0.85V.) was obtained in pH range 6.0 to 8.0.

In pH range 9.5 to 11.0 in borax and sodium hydroxide buffer a kinetic character of the wave was exhibited.

For the existance of the catalytic hydrogen wave at the dropping mercury electrode the following scheme was suggested.

$$K_2Fe(CN)_4(C_5H_5N)_2 + 2H_2O \rightleftharpoons K_2Fe(CN)_4(C_5H_5N^+H)_2 + 2OH^- \quad (1)$$

$$K_2Fe(CN)_4(C_5H_5N^+H)_2 + 2e \rightleftharpoons K_2Fe(CN)_4(C_5H_5N)_2 + 2H$$

$$2H \rightleftharpoons H_2 \quad (2)$$

Since the complex according to equation (1) was in equilibrium with free base, therefore, the height of the wave decreased with increase in pH. Eventually no wave was obtained at pH 12.0 or in 0.1M sodium hydroxide.

In the pH range 9.5 to 11.5 in borax and sodium hydroxide buffer the existance of kinetic wave was probably due to the recombination of the complex with hydrogen ions as represented by the equation (1).

(9) Composition of the complex formed with the interaction of hexacyanoferrate (II) with pyridine:

Maximum absorption for the complex took place at 400 mμ (Fig.1,2 Chapter V part I) and information of only one complex was obtained from VosBurgh and Cooper's method. Job's method of continued variation and molar ratio methods (Fig.3,4 Chapter V part I) confirmed the existance of 1:2 hexacyanoferrate (II) pyridine complex formation constant of the complex was found to be 2.686×10^2.

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LIST OF PUBLICATIONS:-

(1) Electrometric studies on Potassium aquapentacyanide Part I-Standard Potential of Ferroaquapentacyanide^{3-}/ Ferriaquapentacyanide^{2-} couple and the estimation of aquapentacyanide.(Indian Journal of Chem; 4, 106-108(1966)).

(2) Electrometric studies on potassium aquapentacyanide Part II. The reduction of the nitrosobenzene complex at dropping mercury electrode.(J.Electroanal.Chem; 11 467-471 (1966)).

(3) Amperometric titrations of Co(II) with hexacyanoferrate (III) in ammonium citrate and glycine media. The reduction of the resulting complexes at d.m.e. (Communicated, J.Talanta).

(4) Polarographic estimation of uranium (VI) at d.m.e. (J. electroanal. Chem; in press).

(5) Polarographic studies on 8-hydroxyquinoline 5-sulphonate pentacyanoferrate (II) complex (Ready for communication to J. electroanal. Chemistry).

(6) Polarographic estimation of Zerconium (IV) using Eriochrom Black T (E.C.B.T.) in alkaline medium. (Communicated to J. Polarographic society).

J. ELECTRO-ANALYTICAL CHEMISTRY (IN PRESS)

Polarographic estimation of uranium (VI) at droping mercury electrode in phosphoric acid:

by

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Herasymenko (1) first of all carried out the polarography of uranyl ion in neutral and weakly acidic medium and concluded that it was reduced successively in three steps from uranium (VI) to (V) to (IV) and then to (III). These results were confirmed by Harries and Kolthoff (2). In 0.01 to 0.02M hydrochlorid acid two reduction steps corresponding to uranium (VI) to uranium (V) and then to uranium (III) were reported. But only the first reduction step could be of some analytical importance. The interference of even of large amounts of ferric ions was eleminated as originally recommended by Strube (3). It was reduced to the ferrous state by warming the solution with 2.0M hydroxylamine hydrochloride at 50°C for 10 minutes. The fact that the reduction of either uranyl ion or uranous ion catalyzes (4) the reduction of nitrate ion was utilized by Herris and Kolthoff (2) for determination of traces of uranium down to about $3x10^{-7}$M, but difficulty was that the catalysed limiting current of nitrate ions, was not directly proportional to the uranium concentration. But the procedure was followed with the empirical caliberations of various known uranium concentrations, using supporting electrolyte, comprising of 0.005M potassium nitrate, 0.5M potassium chloride and 0.05M hydrochloric acid.

Besides these investigations, Orlemann (5), Kaus, Nelson and Johnson (6), Kritchevsky and Hindmann (7) and Ballenger (8) also carried out polarography of uranium under various conditions of pH and supporting electrolytes. In the present communication the reduction of uranium (VI) had been reported in the medium of phosphoric acid in presence of several electrolytes. The effect of various cations, Tl(I), Ag(I),Ni(II), Co(II), Fe(II), Cu(II), Mn(II),Cd(II), Hg(II), Pb(II), Sn(II), Zn(II), Cr(II), Fe(III), Ce(III), Bi(III), Al(III) Cr(III), Zr(III), Ce(IV), Sn(IV), V(IV), Th(IV), Hf(IV), V(V), Mn (VII) on its reduction also constitutes a part of the paper.

EXPERIMENTAL

Apparatus:

A Heyrovsky PL-55A polarograph operated manually was employed using a pye-sclamp galvanometer in the external circuit. The polarographic cell and the reference electrode (S.C.E.) were kept immersed in a thermostatic bath maintained at 25 ± 0.1°C purified hydrogen was used for deaeration. A Fischer capillary with a droptime of 3.42 second in 2.0M phosphoric acid, 0.133M potassium chloride and 1.334×10^{-3}M uranyl nitrate at a potential of -0.4V. (at a height of mercury meniscus of 54.7 cm. from the tip of capillary), was used. The weight of one drop was 0.00404 gm.

Reagents:

All reagents were of A.R. quality. The solutions of required concentrations of phosphoric acid, uranyl nitrate, different electrolytes and soaps (cetyl trymethyl ammonium bromide, nonidate P-40 used as maximum suppressor with some electrolytes) were prepared in double distilled water. The solutions of various metal ions were prepared by respective standard methods.

The polarograms for the solutions in several sets of different conditions, given below, were recorded

1. To determine the effect of phosphoric acid concentration on the reduction of uranyl nitrate, solutions containing 6.66x10^{-4}M uranyl nitrate, 1.33x10^{-1}M potassium chloride and phosphoric acid ranging from 0.667 to 4.0M were prepared.

2. In order to study the relationship between i_d and concentration of uranyl nitrate, solutions containin 1.334x10^{-3}M to 2.867x10^{-5}M uranyl nitrate in 1.33x10^{-1}M potassium chloride and 2.29M phosphoric acid were prepared (from 2.0M to 4.0M of phosphoric acid single, reversible, diffusion controlled, one electron transfer wave was obtained).

3. With a view to determine the uranium in presence of metal ions. Solutions containing 2.0M phosphoric acid, 1.33x10^{-1}M potassium chloride, 1.334x10^{-3}M uranyl nitrate in presence of equal concentrations of various cations, mentioned earlier were prepared. Parallel

solutions of the metal ions separately under similar conditions were also prepared for comparison:

4. To study the reduction of uranium in phosphoric acid alone and in other electrolytes, solutions were prepared, which contained 1.334x10^{-3}M uranyl nitrate, 2.0M phosphoric acid and either of the electrolytes, lithium chloride, sodium chloride, calcium chloride, barium chloride (2.66x10^{-1}M), potassium nitrate, sodium flouride (each 2.0x10^{-1}M) potassium chlorate and potassium sulphate (each 1.0x10^{-1}M), solutions containing 1.334x10^{-3}M uranyl nitrate 2.0M phosphoric acid were also made saturated either with calcium chloride or barium chloride.

5. Several solutions to study the effect of concentration of these electrolytes were prepared comprising of 2.0M phospheric acid, 1.334x10^{-3}M uranyl nitrate and increasing amounts of either of the electrolytes, lithium chloride, sodium chloride, calcium chloride, barium chlotide, (o.66x10^{-1}M to 4.0x10^{-1}M potassium nitrate, sodium fluoride (0.33x10^{-1}M to 2.0x10^{-1}M), sodium sulphate and potassium chlorate (0.166M to 1.0x10^{-1}M). The effect of concentration of uranyl nitrate (1.334x10^{-4}M to 2.0x10^{-3}M) was also studied in the above supporting electrolytes. In case of potassium chlorate and sodium fluoride as supporting electrolytes 0.01% Nonidate p-40 and 0.01% cetyl trymethyl ammonium bromide soaps respectively, were used as maximum suppressor. Polarogram in presenc

of Cr(II) was recorded under a thin layer of distilled kerosine oil.

RESULTS AND DISCUSSION:

From the current voltage curves it was realized that the uranyl nitrate was found to reduce reversibly ($E_{\frac{1}{2}}$ -0.14V) in 2.0 to 4.0M phosphoric acid and 0.666×10^{-1}M potassium chloride. The electrode process was completely diffusion controlled with one electron transfer (results were confirmed by Logrithmic analysis and mercury pressure). Unlike the studies of Herasymenko; Kolthoff and Harris (loc.cit) other reduction steps (Uranium +6 to +4 to +3 or +6 to +3) could not be realized. It was probably due to the discharge of hydrogen at d.m.e. in phosphoric acid. The wave height was dependent on concentration and it was found possible to determine the concentration of uranium (VI) upto 10^{-6}M.

Equal concentrations of Tl(I), Ni(II), Co(II), Mn(II), Fe(II), Cd(II), Hg(II), Sn(II), Zn(II), Ce(III), Bi(III), Al(III), Cr(III), Zr(III), V(IV), Ce(IV), Sn(IV), Th(IV), Hf(IV), V(V) and Mn(VI) did not interfere. Cu(II) interfered seriously due to its reduction and pronounce a maxima was realized. Although an appreciable current even at 0.0V (as compared to the polarogram obtained in absence of Fe(III) due to Fe(III) was realized but the height of the wave was almost uneffected. Cr(II) interfered probably due to its oxidation to Cr(III) by uranium (VI). Ag(I) appreciable interfered, a pronounce maxima was also observed. A well defined step of Pb (II) was obtained just after the step of uranium (VI), but no interference was observed.

In presence of only phosphoric acid (absence of electrolyte a pronounced maxima was obtained, which could not be suppressed by methyl red, gelatine and other surface active agents but a highly distorted waves were obtained in their presence. In presence of different concentrations of the electrolytes (lithium chloride, sodium chloride, potassium chloride, barium chloride, calcium chloride potassium nitrate, sodium sulphate) waves obtained were reversible diffusion controlled. The values of $E_{\frac{1}{2}}$ and $i_d/cm^{2/3}t^{1/6}$ in these electrolyts are summarised in table 1. The typical polarograms are shown in Fig.1.

Besides these studies, some interesting facts worth noting are:

(1) Well defined and reversible diffusion controlled waves were realized in 2.0M phosphoric acid and saturated barium chloride but no wave, however, in saturated calciu chloride could be obtained.

(2) In 0.166×10^{-1}M potassium chlorate, 2.0M phosphoric acid a 1.334×10^{-3}M uranyl nitrate pronounced maxima was obtained. The height of which decreased on increasing th concentration of potassium chlorate and reduced completel

in 1.0×10^{-1}M potassium chlorate.

(3) In 2.0M phosphoric acid, 0.666×10^{-1}M potassium chlorate 0.666×10^{-3}M uranyl nitrate a small maxima was obtained, by increasing the concentration of uranyl nitrate, the height of maxima was found to increase.

(4) On increasing the concentration of uranyl nitrate, in potassium chlorate though the value of limiting current was dependent concentration (but not strictly a linear function) but the wave obtained appeared to be irreversible as verified by logarithmic analysis.

(5) Using sodium fluoride as supporting electrolyte also, a pronounced maxima was obtained. It could not be suppressed by gelatine, methyl red and Nonidate p-40 soap, but could be easily suppressed by 0.01 per cent cetyl trimethyl ammonium bromide. Unlike potassium chlorate, the electrode process in sodium fluoride as supporting electrolyte was reversible diffusion controlle Wave height was dependent on concentration of uranyl nitrate.

(Typical polarograms are shown in Fig.2)

TABLE No.1

$E_{\frac{1}{2}}$ and $i_d/ct^{1/6}m^{2/3}$ values in different supporting electrolytes in 2.0M phosphoric acid.

Electrolyte	Concentration	$E_{\frac{1}{2}}$	$i_d/ct^{1/6}m^{2/3}$
XCl	2.66×10^{-1}M	-0.14V.	0.379
LiCl	"	-0.14V.	0.375
NaCl	"	-0.14V.	0.375
$CaCl_2$	"	-0.15V.	0.326
$BaCl_2$	"	-0.15V.	0.316
KNO_3	2.0×10^{-1}M	-0.13V.	0.393
Na_2SO_4	1.0×10^{-1}M	-0.11V.	0.325
NaF	2.0×10^{-1}M	-0.13V.	0.256
$BaCl_2$	Saturated	-0.145V.	0.316

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SUMMARY

Polarographic reduction of uranium (VI) in phosphoric acid has been reported in various supporting electrolytes in phosphoric acid. Single diffusion controlled, reversible one electron transferred reduction step had been obtained almost in all the electrolytes used (except potassium chlorate).

The uranyl nitrate concentration upto the order of 10^{-5}M had been determined with iron less than ± 1 percent. Superiority of the method lies in the fact that large number of cations Tl(I), Ni(II), Co(II), Mn(II), Fe(II), Pb(II), Cd(II), Hg(II), Sn(II), Zn(II), Ce(III), Bi(III), Al(III), Cr(III), Zr(III), Fe(III), V(IV), Ce(IV), Sn(IV), V(V), Th(IV), Hf(IV) and Mn(VI) did not interfere in its determination. No need of reduction of Fe(III) to Fe(II) was required as was done in the polarographic estimation of uranium (VI) proposed by Harris and Kolthoff (2,4).

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