STUDIES IN CHROMIUM COMPLEXES

by

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CONTENTS

SUMMARY.

In this work physical and analytical methods have been used to investigate the potassium salts of certain dioxalato chromium (III) complexes.

The solid potassium salts of the trioxalatochromiate and the cis and trans dioxalatodiaquochromiates together with a salt corresponding to potassium dioxalatosulphatoaquochromiate were prepared. The mono- and dihydroxo derivatives of the cis and trans dioxalatochromiates were also obtained in aqueous solution. The methods of preparation and analysis used are described.

Spectrophotometric absorption curves obtained on solutions of these salts using a Beckman Spectrophotometer are in agreement with results of previous workers, and the new absorption curve obtained from a solution of the solid cis dioxalatodiaquochromiate salt shows that it is pure and gives additional proof of the completeness of the trans - cis isomerisation.

Potentiometric titrations were carried out on solutions of the above salts at 8°C., and corrections applied for a blank KOH titration under similar conditions of ionic strength and temperature. The titration curve of the cis dioxalatodiaquochromiate was in agreement with that obtained on an aged solution of the trans salt. The two pK values of the cis and trans isomers of the dioxalatodiaquo salt, corresponding to the acidic dissociation of the two water molecules bound to the complex, were calculated from the titration curves. The pK_1 values were identical for both the *cis* and *trans* isomers, but the pK_2 values showed considerable difference, and in the opposite direction to that expected. These pK values were determined at varying ionic strengths and the corresponding thermodynamic constants obtained by extrapolation to zero ionic strength. The results have been discussed in relation to the molecular structure of the salts and the ratio of the "effective dielectric constants" for the two isomers has been calculated.

A potentiometric titration curve obtained on a solution of the dioxalatosulphatoaquochromiate complex has thrown some doubt on the number of complex-bound aquo groups per molecule and suggests it is a mixture of complexes. An aqueous solution of the salt decomposes with time, and it has been shown spectrophotometrically that the addition of potassium nitrate decreases this decomposition rate. During decomposition a point is reached when added benzidine hydrochloride does not cause the precipitation of benzidine sulphate. This phenomenon has been studied by analytical means and the effect of added potassium nitrate noted. Some suggestions that may account for the above have been given.

In order to follow up some reaction kinetics involving changes in extinction coefficients, the performance of several colorimeters was investigated. The Beckman Spectrophotometer, without special attachments, was not sufficiently sensitive at the low chromium concentrations used. The theory of a Differential Photoelectric

Absorptiometer, together with details of its design, construction, expected performance and results of attempted standardisations have been given; the readings given by this instrument were not sufficiently reproducible to warrant its use in the kinetic studies. The Evelyn Colorimeter was then investigated and, by modifications in technique, it was found that this instrument was sufficiently sensitive for it to be used in the study of the formation of the trioxalatochromiate ion from potassium cis dioxalatodiaquochromiate and potassium oxalate.

The kinetics were studied under two conditions; in the first, the ionic strength was varied by varying the concentration of the reactants, and in the second the concentration of reactants was maintained constant and the ionic strength adjusted by the addition of varying quantities of potassium nitrate. The results of the latter experiments conform to the Brønsted - Bjerrum relationship, and it was found, in agreement with similar conclusions adduced by Burley, that reaction occurs between two singly charged negative ions. The former series however, gave results that showed considerable deviation from the Brønsted-Bjerrum equation at the lowest concentrations, which indicate that the reaction might be one of the third order involving hydrogen ions - the reaction being inhibited by the formation of these ions.

Values of the Energy of Activation and the Frequency Factor were computed by applying the Arrhenius Equation to the data from the second kinetic series. This

plot was not linear if the results at the highest temperature were taken into account, and activation energies were calculated by the method of least squares firstly by considering a linear relationship and secondly by including all experimental points : these results have been discussed. The collision number and probability factor were also calculated by applying the collision theory to the data.

The kinetic results were then considered on thermodynamic grounds and the change in free energy, entropy of activation, and change in heat content were derived for various temperatures.

A physical interpretation of the reaction mechanism in terms of the Collision Theory and the thermodynamical method of Absolute Reaction Rates has been attempted.

CHAPTER I

INTRODUCTION

Chromium salts, as also those of aluminium, iron and zirconium, find extensive use as tanning agents. All these metals have a coordination number of six, being capable of forming complex ions in which six neutral molecules or anions are associated with the metallic ion.

A good discussion of chromium coordination compounds is given by Merry (1). From time to time various theories as to why these salts tan and the mechanism of the tanning process have been put forward by different workers. Of these theories, the more generally accepted ones are those involving the formation of coordination complexes between the protein and the metallic ion or complex. Stiasny (2)(3) first applied the Werner Coordination theory (4) to chrome tanning, and suggested that the oxygen of the carbonyl groups and the nitrogen of the amino or peptide groups coordinate either directly with the central chromium atom or with a group in the chromium complex.

Gustavson (5)-(9) has put forward numerous views, the later ones favouring the formation of an internal complex salt involving the carboxyl and amino groups. The theory of Küntzel and Reiss (10) has much to recommend it, and later workers have suggested mechanisms based on much the same lines. Briefly, it involves entry of the carboxyl groups of the collagen into the chromium complex in a manner analogous to complex formation with anions of organic acids, followed by the formation of links with the basic group in the adjacent polypeptide chain.

Shuttleworth (11), has consistently put forward the theory that the chromium atom coordinates directly on to the ionized carboxyl groups of the protein side chains. For a recent paper (12), he has adduced evidence in support of these views, and has drawn the following conclusions :

"1. Collagen protein, being able to satisfy its coulombic forces internally, does not bind chromium complexes by coulombic attraction of single electrovalent links unless reinforced by other bonds. Nor is the charge as such, the determining factor as to whether or not a complex will coordinate with the carboxyl groups of resin or protein.

2. Residual valence forces must be regarded as of minor importance in chrome tanning, capable of fixing chromium under favourable conditions, but not able to impart the high thermal stability characteristic of chrome tanned leather.

3. Further evidence confirms the view that amino groups of the types found in collagen protein do not coordinate appreciably with basic chromium complexes in dilute aqueous solution under the conditions of chrome tannage.

4. The chief mechanism of chrome tannage is coordination of chromium to the carboxyl groups of protein side chains. This reaction is not determined by the charge on the complex, but by the number and stability of the groups occupying the available coordination positions on the chromium atom. The charge is one of several factors influencing ligand stability.

5. The number of occupied coordination positions is important owing to the stepwise drop in ligand affinity which is also influenced by the type of ligand.

6. The ability of protein carboxyl groups to displace other ligands from chromium complexes is shown to be inversely related to the dissociation constants of the ligands, which explains why chromium formate complexes tan while chromium acetate complexes do not. The additional stability conferred by ring forming polydendate ligands and the high chrome fixation imparted by non ring forming polydendate ligands can also be anticipated from this interpretation of chrome tannage."

For present theories to be improved and extended, more fundamental knowledge of the properties of coordination compounds and complex formation is required; particularly of those of chromium.

There are several methods available, mainly physical ones, for the study of these complexes. Shuttleworth (13) has used conductimetric methods at normal and low temperatures.

Burley (14) studied dioxalatochromiate systems using spectrophotometric and potentiometric titration methods and covered much important new ground.

Ion exchange methods have been used on chromium complexes (12) (15), and recent attempts combining electromigration methods with chromatography have met with some success (16) (17).

The chemistry of the chromium salts is rather complex, but the two greatest advances in our knowledge of the chemistry of the transition elements were the postulation of Werner's Coordination Theory and the concept of bond hybridisation developed by L. Pauling and others using the method of wave mechanics.

The chromic ion has six hybrid bonds, called the sp^3d^2 bonds. These six bonds are directed towards the corners of some regular configuration. X-ray diffraction studies performed on cobalt and other elements that exhibit sp^3d^2 hybridisation show that the six bonds are directed towards the corners of a regular octahedron. Until recently, no such X-ray studies had been made on chromium since complex chromium compounds suitable for X-ray studies were not obtained as unmixed crystals. Werner (18) studied the potassium trioxalatochromiate complex and resolved it into its optical isomers, and suggested it had an octahedral configuration. This was criticised by Britton (19) and others, but Werner's original work has been confirmed by several workers and the rates of racemisation measured. (20)(21)(22)(23). Samples of potassium trioxalatochromiate and potassium trans dioxalatodiaquochromiate, prepared in these laboratories by Burley, have been studied by X-ray diffraction methods at the National Physical Laboratory, Pretoria. Work on the trioxalate is understood to have been completed whilst the complete crystal structure of the trans dioxalatodiaquochromiate has been elucidated (24). It was found, as expected, that the chromium atom in these complexes forms six coordination bonds directed towards the corners of an octahedron. As is seen in Fig. 3, the angle formed between the two oxygen atoms of the oxalate group with the chromium atom is not quite 90°. It is to be expected that the oxalate group, being in the form of a ring, is under a certain amount of strain thus causing a departure from a right angle. This then, is the first direct proof that the bonds in chromium complexes are directed towards the corners of a regular octahedron.

The oxalate group is coordinated fairly strongly to the chromium atom which accounts for the stability of the trioxalatochromiate complex. By using this dioxalatochromiate system, there are only two coordination positions available for most substitutions and for studies on the mechanisms of coordination reactions and other properties of the complex ions, the dioxalato diaquo salt is particularly convenient. Accordingly, following Burley, this salt was used for the present studies. It was hoped that by study of this relatively simple system some more information could be obtained on the mechanism of coordination.

The three main aspects of Burley's work that have been followed up were : (a) further potentiometric studies, carried out on both the cis and trans salts of potassium dioxalatodiaquochromiate; (b) the re-investigation of the kinetics of the formation of the trioxalatochromiate ion; this time at lower ionic strengths and (c) further investigation of the decomposition of a dioxalato sulphato chromiate complex, mainly by analytical methods.

The cis dioxalatodiaquochromiate and oxalate ions react in equimolar proportions to form the trioxalatochromiate ion. This reaction involves a change in extinction coefficients: from that of the cis dioxalate to that of the trioxalate, potassium oxalate having no measurable absorption in solution at the wavelengths used. This change in extinction coefficient is sufficient to enable the progress of the reaction to be measured on a spectrophotometer.

In investigating the reaction using a Beckman Spectrophotometer, Burley (14) used a single chromium concentration, so chosen as to give the best accuracy on the instrument. The ionic strength of the solutions (μ) was varied by the addition of potassium nitrate. The range of ionic strengths covered was from $\sqrt{\mu} = 0.177$ to 0.4, the chromium content being kept constant at about 0.008 Molar. The velocity constants at the various ionic strengths and at several temperatures were then calculated from the spectrophotometric data, and the results were used to find the charge of the ions taking part in reaction, and to calculate the experimental energy of activation and the frequency factor.

Burley (14) found that two singly charged negative ions took part in the reaction. This was of great interest as it showed that the dioxalate ion, $[Cr(C_2O_4)_2(H_2O)_2]^-$ and the binoxalate ion, $(COO)_2H^-$ must react and not the dioxalate ion and oxalate ion $(COO)^=$ as might be expected.

The evidence for the above conclusions was as follows : When the logarithm of the observed velocity constants (k) were plotted against $\sqrt{\mu}$, a straight line with a slope of + 1 was observed. According to the Brønsted-Bjerrum equation,

$$\log k = \log k_o + 2\,A\,Z_A Z_B \sqrt{\mu},$$

the constant A is very nearly 0.50 at normal temperatures and on substitution in the above equation it can be seen that the product $Z_A Z_B$ of the charges on the ions gives the slope of the line.

This interpretation of the reaction has its limitations : the ionic strengths used might be considered rather too high to warrant the use of the simple Brønsted-Bjerrum equation and subsequent extrapolation to zero ionic strength in the plot of the logarithm of the velocity constant against the square root of the ionic strength.

It might have been that the slopes of the lines obtained were fortuitous and that this slope may have been a limiting value for higher ionic strengths. It was thought to be possible, that at dilutions where the Debye-Hückel relationship holds, the slope might be + 2 and not unity, showing that the oxalate ion is involved in the reaction.

On these grounds, it was decided that the reaction required further investigation at lower ionic strengths. The Beckman Spectrophotometer, without special attachments, is not very sensitive at these lower chromium concentrations so that the investigation of the reaction requires the building of a more sensitive spectrophotometer or colorimeter.

The investigation of the dioxalato sulphato chromiate complex by Burley led to the result that at a stage in its decomposition, no sulphate was precipitated on the addition of benzidine hydrochloride to the solution, in spite of there being free sulphate in solution. This requires further investigation in an effort to explain this phenomenon.

CHAPTER II

PREPARATION, ANALYSIS AND PROPERTIES OF SOME CHROMIUM COMPLEXES

1. PREPARATIONS AND PROPERTIES OF CHROMIUM COMPLEX SALTS

All through this work, frequent mention is made of several complex chromium salts. They have been prepared by previous workers, but for convenience the brief preparation, purification, and the results obtained are given here. Analytical methods are described in detail at the end of this section.

(a) Potassium Trioxalatochromiate (25)(26). $K_3[Cr(C_2O_4)_3]3H_2O$

19 g. of potassium oxalate were dissolved in about 50 ml. water. To this solution were added 23 g. of potassium oxalate and 55 g. of oxalic acid hydrate in about 100 ml. water. Effervescence occurred and when this subsided, the solution was boiled down to a small volume and allowed to crystallise.

The reaction is :

$$K_2Cr_2O_7 + 7H_2C_2O_4 + 2K_2C_2O_4 \longrightarrow 2K_3[Cr(C_2O_4)_3]3H_2O + 6CO_2 + H_2O$$

The dark green crystals were filtered off, recrystallised from hot water and dried by standing over calcium chloride. The salt used in investigations was recrystallised three times.

In daylight these crystals were a dark blue-green

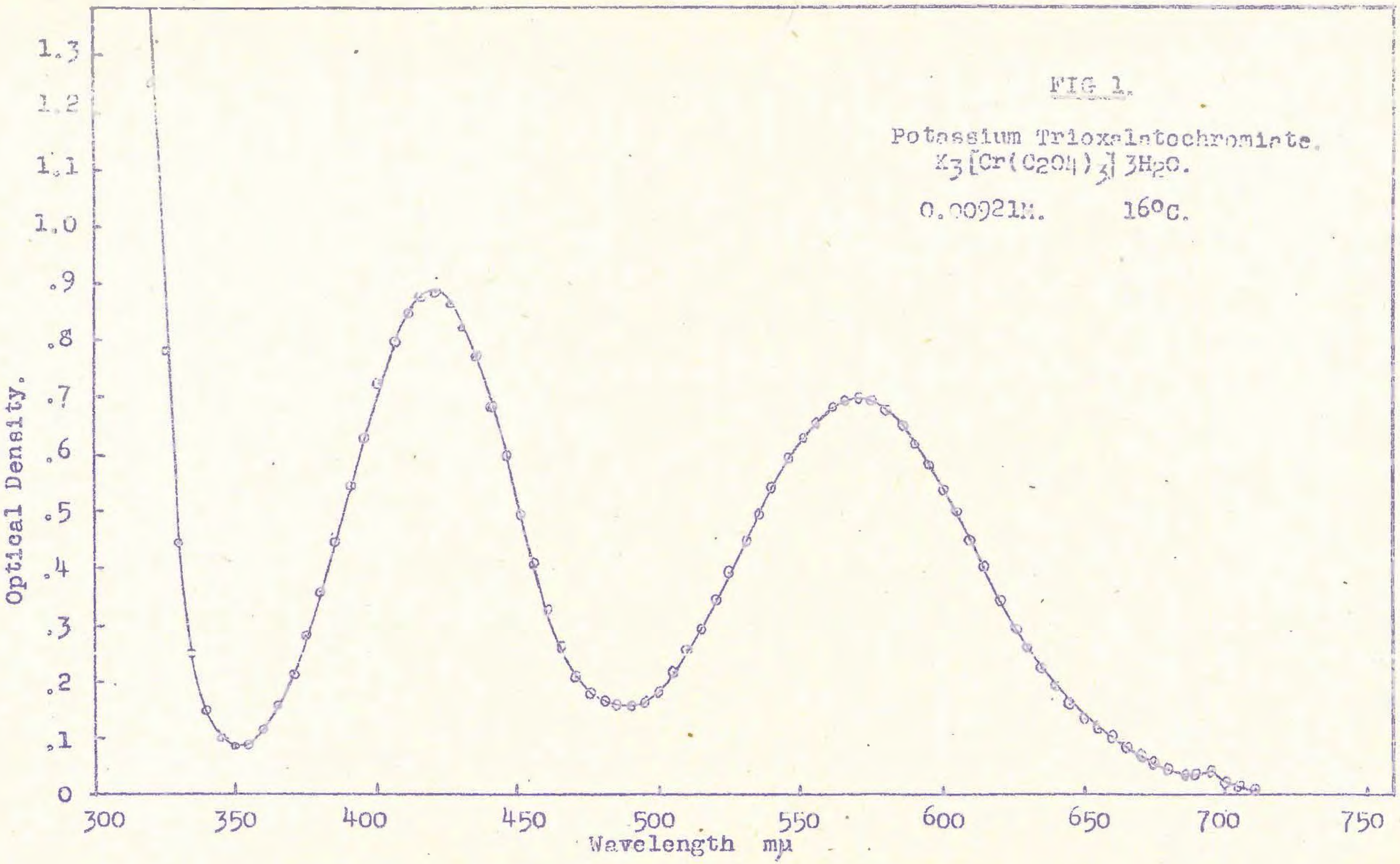


FIG 1.

Potassium Trioxalatochromiate.
$K_3[Cr(C_2O_4)_3]\,3H_2O$.
0.00921M. 16°C.

colour. On drying over sulphuric acid, they lost some of their lustre and appeared more green-red, especially in artificial light.

Theoretical formula. $K_3[Cr(C_2O_4)_3]3H_2O$

	Found	Theoretical
% Cr	10.60	10.68
% K	24.12	24.07
% $(COO)_2$	54.10	54.18

A spectrophotometric curve was performed on a 0.009208M. (0.07% Cr_2O_3) solution of this salt on a Beckman Spectrophotometer. The curve is given in Fig. 1. Maxima were obtained at 420 mμ and 570 mμ in good agreement with Burley (14), (419 mμ and 569 mμ), Theis (27) and Meade (28).

Wavelength	Extinction coefficient
420 mμ	96.2
570 mμ	75.8

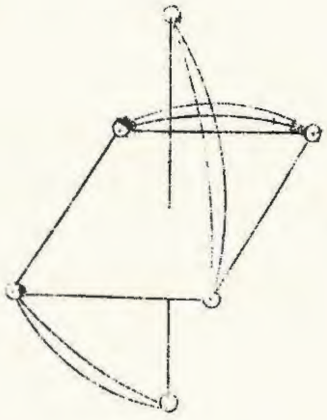
These extinction coefficients are calculated just from the maxima in Fig. 1, and not from a complete Beer's Law relationship.

The salt is neutral and this is shown by Burley's (14) titration curve.

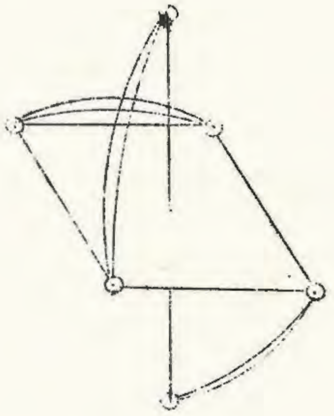
As might be expected, the salt is optically active. Werner (18) resolved the compound into its optical isomers. In 1939 Long (20) investigated the mechanism of the racemisation of the trioxalatochromiate ion in aqueous solution. He used radioactive isotopes of carbon to study the interchange of oxalate between the solution and the trioxalatochromiate ions in solution. He concluded that the mechanism of racemisation does not involve an ionization step, but some sort of intramolecular rearrangement, and suggested that Werner's explanation, i.e. that racemisation might involve the breaking of only one of the bonds with one of the oxalate ions, was the most likely. Similar conclusions have been drawn by Bushra and Johnston (22) who made a study of the rates of racemisation of optically active coordination compounds. The racemisation may therefore be called a tautomerisation, no oxalate ion being free in solution at any time. These investigations also show that the trioxalatochromiate ion is completely stable in neutral solution at temperatures up to 35°C., and at a concentration of about 0.1M.

Another racemisation study has recently been made on potassium trioxalatochromiate by Schweitzer and Rose (23). The effect of mixed organic solvents on the racemisation rate was studied and the rate found to decrease with increasing concentration of the organic component. The experimentally determined energy of activation of the inversion reaction agreed with that found by previous investigators. The complex was resolved by the precipitation of the dextro-isomer with levo-strychnine sulphate. The authors only conclude that the racemisation rate of an inorganic complex is apparently more specific for the complex than for the solvent system. The obvious conclusion is that the racemisation rate decreases when the number of water molecules available is also decreased; here they are replaced by less reactive organic molecules.

As mentioned in the introduction, X-ray diffraction studies are understood to have been completed on the trioxalatochromiate salt, but even apart from this, there is a considerable amount of evidence indicating that the trioxalatochromiate ion has an "octahedral" structure. The two enantiomorphs are therefore :



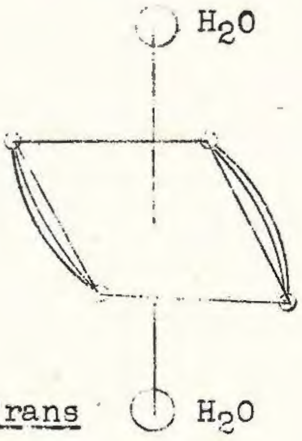
and



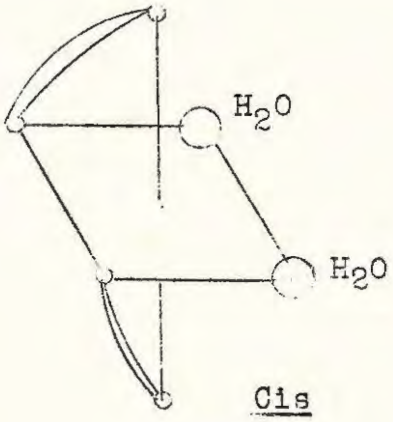
One being dextrorotatory and the other laevorotatory.

(b) The Potassium Dioxalatodiaquochromiates

Chromium compounds containing two oxalate groups per chromium were first prepared in 1842 (29), but their constitution was doubtful. Werner (30) and others (31) showed that the dioxalatodiaquochromiate ion had the formula $Cr\left[(C_2O_4)_2(H_2O)_2\right]^-$ on the newly postulated Coordination Theory. In the course of extensive work on the dioxalato compounds, Werner (32) prepared the two isomeric forms of the dioxalatodiaquochromiate ion : the *cis* and *trans* forms. He suggested they had the following configurations :



Trans



Cis

Their properties, according to Werner, may be summarised as follows :

Potassium *trans* dioxalatodiaquochromiate, $K[Cr(C_2O_4)_2(H_2O)_2]3H_2O$ exists as pinkish crystals which are perfectly stable at room temperature. It does not dissolve readily in the cold but, on boiling, an enormous quantity can be dissolved in water. On subsequent cooling of this solution, the salt does not crystallise out immediately and more than a week may elapse before a small quantity of solid settles to the bottom of the vessel.

The *cis* compound, $K[Cr(C_2O_4)_2(H_2O)_2]2H_2O$, is a pink blue and lighter in colour; it is also very much more soluble in cold water than the *trans* isomer, so that it is difficult to purify satisfactorily by recrystallisation.

Potassium trans Dioxalatodiaquochromiate, $K[Cr(C_2O_4)_2(H_2O)_2]3H_2O$

Werner's (32) method of preparation was used. 450 g. of oxalic acid hydrate were added to about

2 l. of water and heated to boiling. Then 150 g. of powdered potassium dichromate were added cautiously in small portions. Violent effervescence occurred, and when this had subsided, the solution was boiled gently for half an hour and then set aside to crystallise at room temperature. After several days, a small reddish crystalline deposit settled at the bottom of the beaker and small particles were observed floating on the surface of the liquid. The solid was filtered off each day and washed with small quantities of water. The separate portions of solid were combined and the salt purified by dissolving in water containing about 1% strong nitric acid, boiling for half an hour, and allowing to crystallise as before. The nitric acid destroys any trioxalate that might be present (14). The recrystallisation was repeated three times and the final product dried over calcium chloride.

Theoretical formula. $K[Cr(C_2O_4)_2(H_2O)_2]3H_2O$.

	Found	Theoretical
% Cr	14.44	14.56
% K	11.07	10.95
% (C_2O_4)	49.12	49.27

In agreement with Werner, the addition of barium chloride to a freshly prepared saturated solution of the trans salt gave no precipitate. After standing for three days, a small quantity of insoluble fine green powder

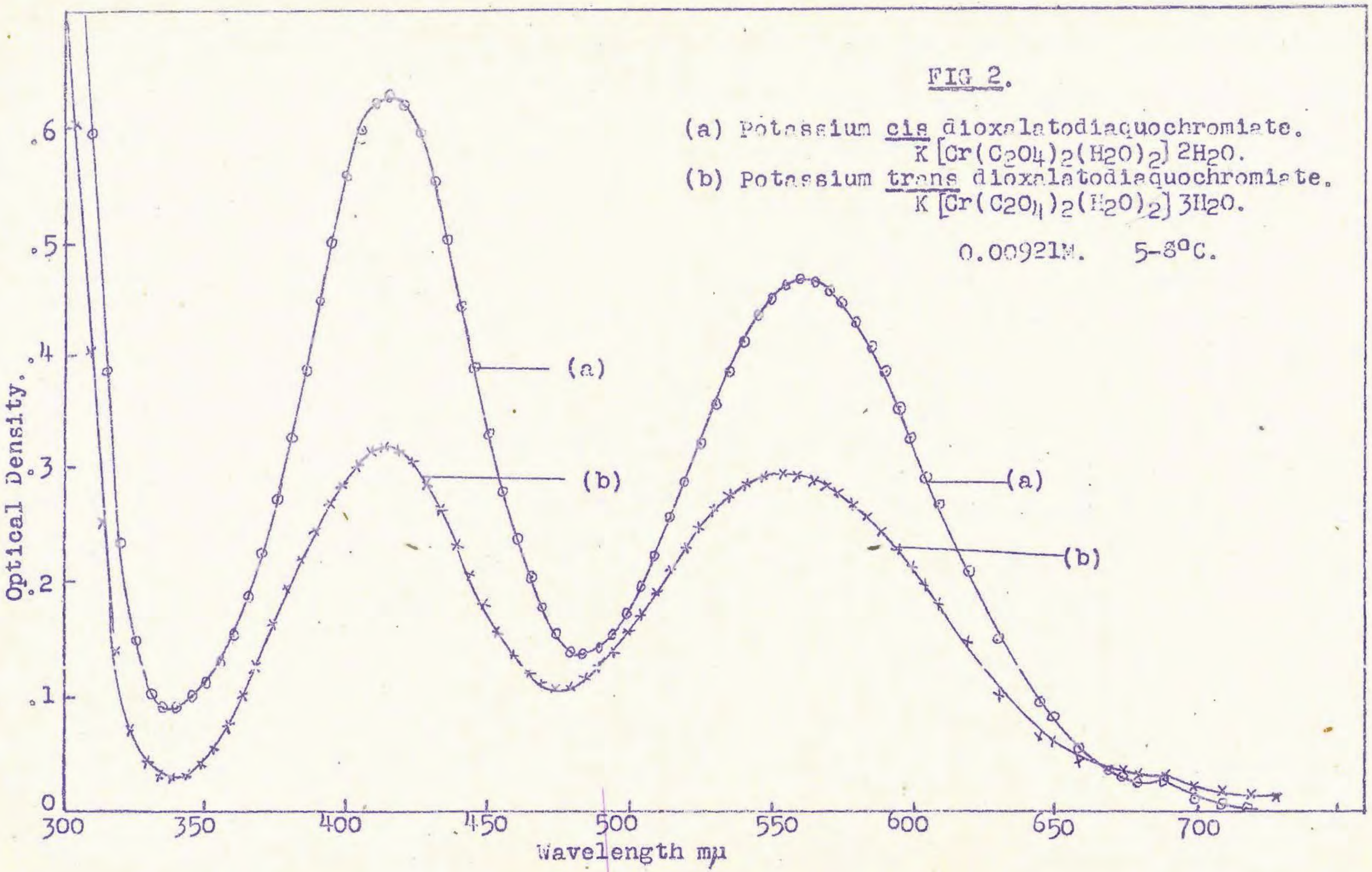


FIG 2.

(a) Potassium cis dioxalatodiaquochromiate.
$K[Cr(C_2O_4)_2(H_2O)_2]\,2H_2O$.
(b) Potassium trans dioxalatodiaquochromiate.
$K[Cr(C_2O_4)_2(H_2O)_2]\,3H_2O$.

0.00921M. 5-8°C.

settled out and, after filtration, it was examined under the microscope. It consisted of green block-like crystals and it is possible that it was the Barium salt of the trioxalate. Also, the addition of potassium iodide and/or potassium bromide to a fresh solution of the trans salt caused the pure trans salt to be precipitated from solution.

A spectrophotometric absorption curve was performed on the trans salt. Fig. 2 (b). The curve could not be measured at room temperature as trans - cis isomerisation occurs too rapidly, but at 5 - 8°C. the rate of isomerisation is very slow, enabling the absorption to be measured. A 0.009208M. solution was prepared by weighing out the pure trans salt and dissolving in cold water. The flask was placed in ice and small portions of the solution removed for readings. Two or three readings were performed on a sample; it was then discarded and a fresh cold portion added to the absorption cell and the readings continued.

The maxima occurred at 416 mμ and 555 mμ. The extinction coefficients were calculated from Fig. 2 (b).

Wavelength	Extinction coefficient
416 mμ	34.4
555 mμ	32.0

A pure sample of the potassium trans dioxalatodiaquochromiate prepared by Burley (14) was sent, together with the trioxalatochromiate, to the National Physical Laboratory, Pretoria. Van Niekerk and Schoening (24) applied the method of double Fourier Series to the X-ray

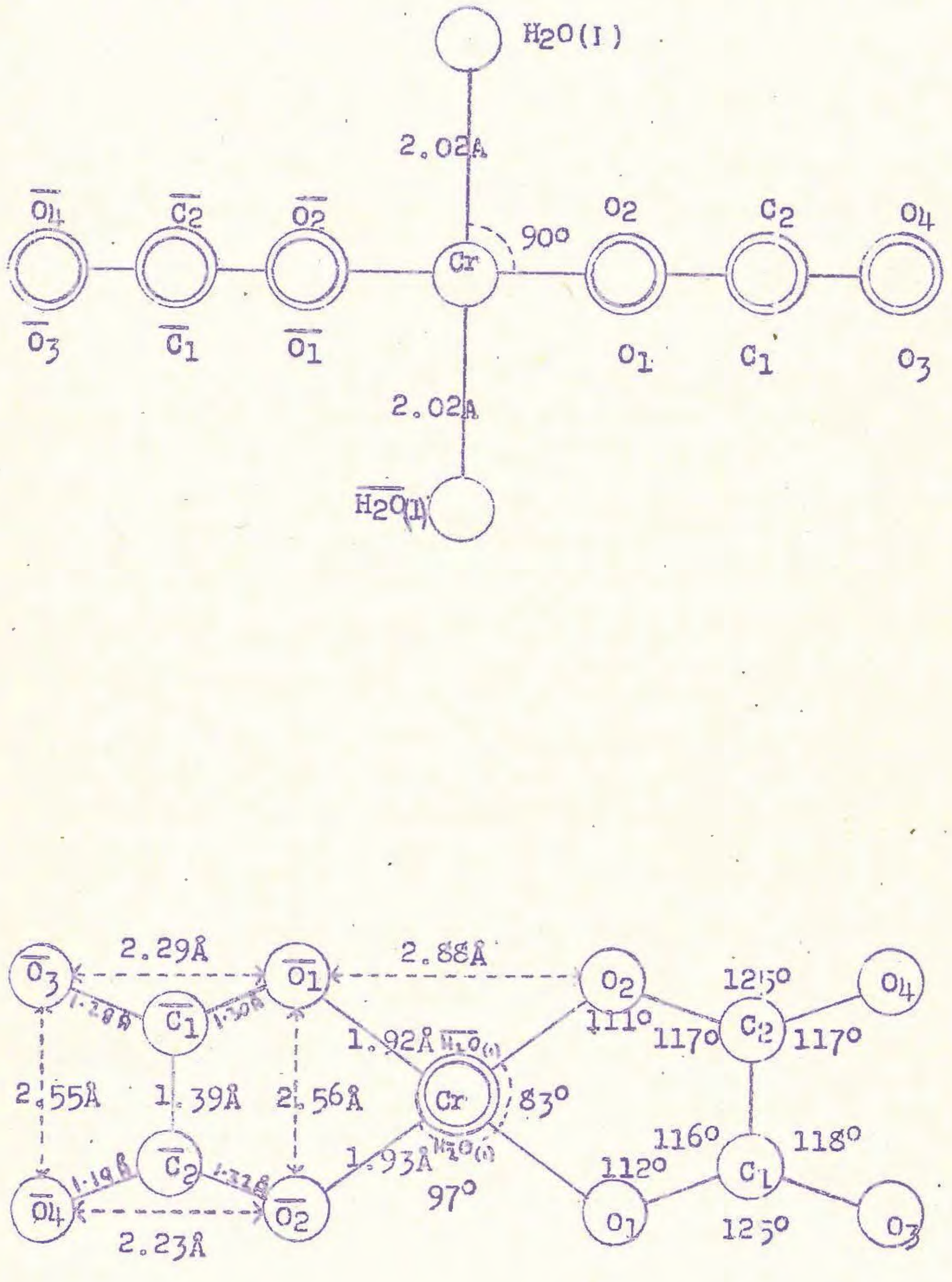


FIG 3.

Dimensions of the complex ion $[Cr(C_2O_4)_2(H_2O)_2]$

diffraction data obtained using this salt. They showed that the chromium atom lies at the symmetry centre of the complex ion, the two oxalate groups lying in a single plane and the two water molecules of the complex ion are perpendicular to this plane. The four oxygen atoms and two water molecules surrounding the chromium atom form an approximate octahedral arrangement. Fig. 3. (Reproduced from ref.(24)). The structure consists of a series of layers, two different kinds of water molecules being mainly responsible for the bonding between adjacent layers. For each formula unit there are two water molecules of the first kind and one of the second kind, so that a complex ion in one layer is linked to complex ions in the next layer by three hydrogen bond bridges through three water molecules.

Potassium cis Dioxalatodiaquochromiate, $K[Cr(C_2O_4)_2(H_2O)_2]2H_2O$

Werner (32) describes two methods of preparation :

(i) 450 g. of crystalline oxalic acid and 150 g. of potassium dichromate are well pulverised. The whole mass is moistened with a few ml. of water and left. After a few minutes a very vigorous reaction occurs, the mass darkening and becoming liquid. This is left to stand and becomes hard on cooling. It is stirred with a little water, filtered under suction and washed once with water and then with alcohol and ether.

(ii) The cis salt may be prepared from the trans form by dissolving 40 g. of this trans salt in 100 ml. of boiling water, warming for an hour on the waterbath, and allowing to cool slowly. A thick layer of violet crystals are formed. They are filtered and washed as before.

Burley (14) attempted to prepare this salt by method (i) but was unable to prepare it in a pure state. He says, "Under certain conditions, which could not be determined, it was found that colloidal particles were obtained on moistening the brown solid in the mortar. These could not be filtered off conveniently".

On carrying out Werner's instructions (i), it was found that there was no need to add water to the pulverised mass, the water of crystallisation of the oxalic acid being sufficient to start the reaction. After cooling, the resultant cis salt set fairly hard. It appeared as a very fine powder and filtration was somewhat slow. However, at no time did it appear as a brown powder, and after filtration and drying, it appeared as lilac coloured lumps; on pulverisation, a lilac powder was obtained.

An attempt was made to obtain this same cis salt, perhaps in a purer state, from the thrice recrystallised trans salt. On following Werner's instructions under method ii), it was found that on slow cooling of the concentrated solution, some sludge appeared which resembled the cis salt, but large amounts of the crystals of the trans salt were visible. It seems that on slow cooling the cis and trans isomers are both present due to the slow formation of the trans form under these conditions.

Rapid cooling of the concentrated solution was achieved by placing the beaker of solution in a mixture of

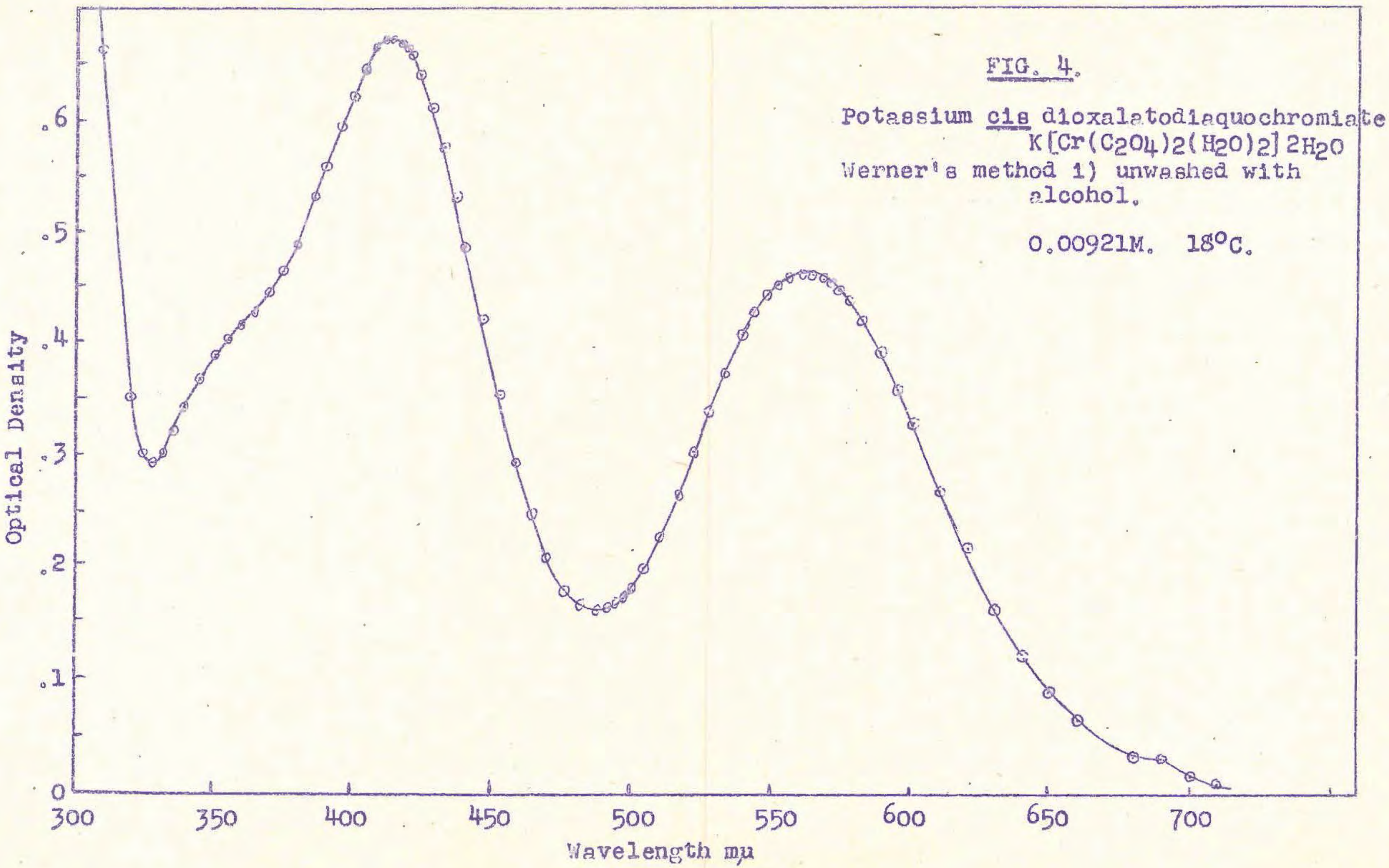


FIG. 4.

Potassium cis dioxalatodiaquochromiate $K[Cr(C_2O_4)_2(H_2O)_2]\,2H_2O$
Werner's method 1) unwashed with alcohol.

0.00921M. 18°C.

dry ice and acetone. This brought down a fine precipitate which was filtered off under suction, washed with alcohol and dried. No sign of <u>trans</u> crystals was visible and later tests confirmed their absence.

The analysis of preparations by both methods (i) and (ii) gave the following results :

Theoretical formula. $K[Cr(C_2O_4)_2(H_2O)_2]2H_2O$

	Theoretical	Found Prep.(i)	Found Prep.(ii)
% Cr	15.34	15.24	15.15
% K	11.53	11.60	11.65
% (C_2O_4)	51.90	52.00	52.10

In both preparations (i) and (ii), the resulting <u>cis</u> salts appeared identical. They were lilac coloured fine powders, much more soluble than the <u>trans</u> form giving blue-red dichroic solutions. The salt becomes green on moistening with alkali. On observing the powder through a microscope, it appeared as an amorphous powder and no signs of crystals were seen at any time. In the absence of crystals, X-ray diffraction patterns are difficult to interpret: as yet, no attempt has been made in this field.

The first preparations by method (i) were left unwashed with alcohol and ether. They appeared identical to later preparations but a spectrophotometric curve did not correspond entirely to a similar curve carried out on a sample of the <u>trans</u> salt aged to the <u>cis</u> isomer. Figs. 4

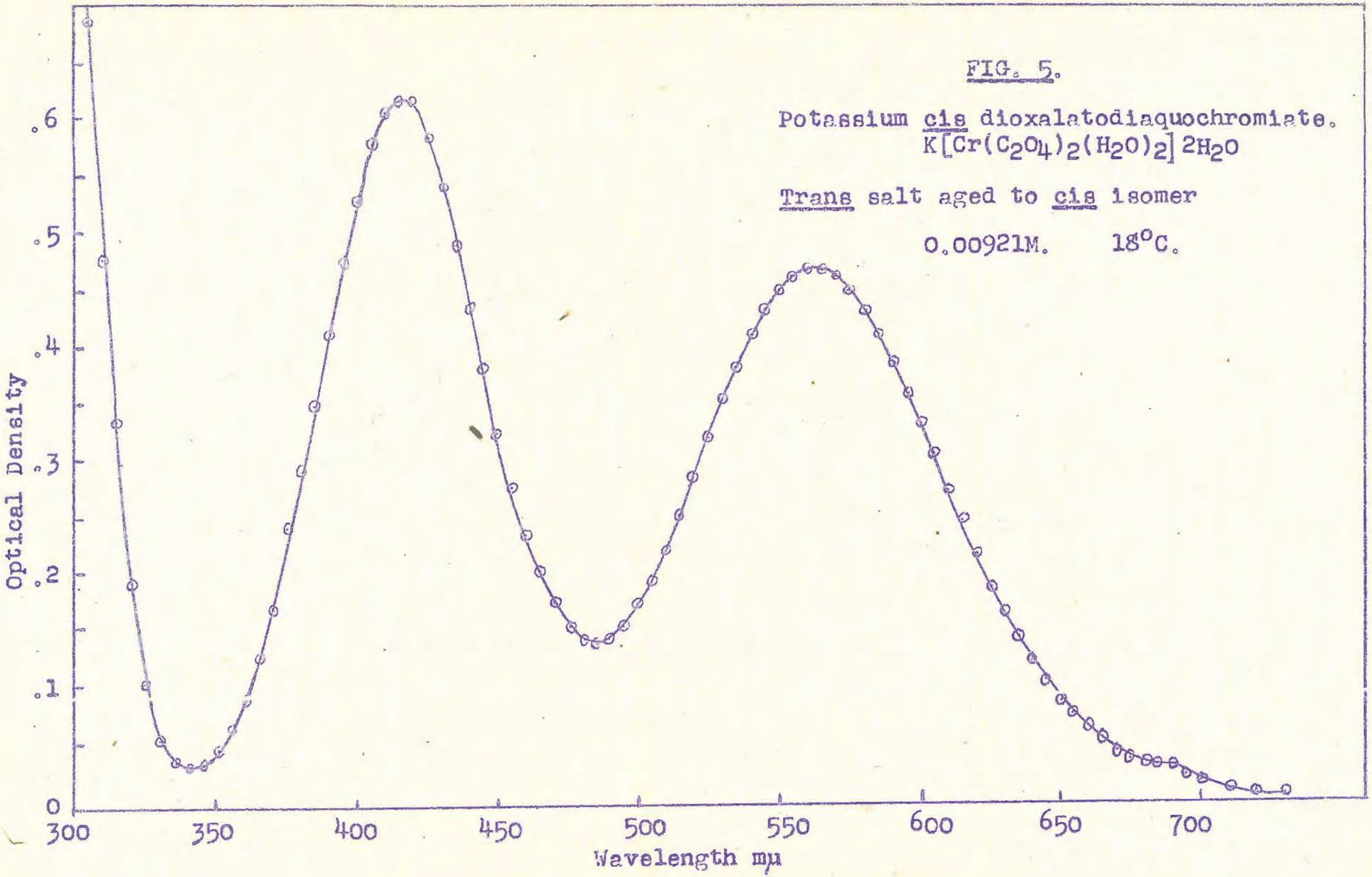


FIG. 5.

Potassium *cis* dioxalatodiaquochromiate.
$K[Cr(C_2O_4)_2(H_2O)_2]2H_2O$

Trans salt aged to *cis* isomer

0.00921M. 18°C.

and 5. The main difference lies in the minimum at 340 mμ. The optical density of the former is considerably higher than in the aged solution and the curve is not smooth. The effect indicates the superposition of another curve, indicating that an impurity is present that absorbs light of this wavelength. A likely impurity is potassium dichromate, some of which may not have been reduced by the oxalic acid. A curve was performed on some potassium dichromate and it was found to absorb all light up to 490 mμ; the density decreased rapidly till at 550 mμ very little light was absorbed. It is therefore probable that a small quantity of potassium dichromate present would have the effect shown in the absorption curve.[*]

A fresh quantity of the _cis_ salt was prepared by method (i), the product being washed with alcohol. An absorption curve of this salt is shown in Fig. 6 and it is identical with the curve of the _trans_ salt aged to the _cis_ isomer, Fig. 5. As a check that no _trans_ salt was present, directly the solution was made up, density readings were taken at the two maxima. Any appreciable quantities of _trans_ salt present would be shown by a lowering of the peaks.

Two separate preparations were made by method (ii). Each appeared identical: analytical results agreed and spectrophotometric curves were identical. One of these curves is shown in Fig. 2 a. Here again, curves were performed on fresh solutions.

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[*] This has since been confirmed by D.R. Cooper using electrochromatographic methods.

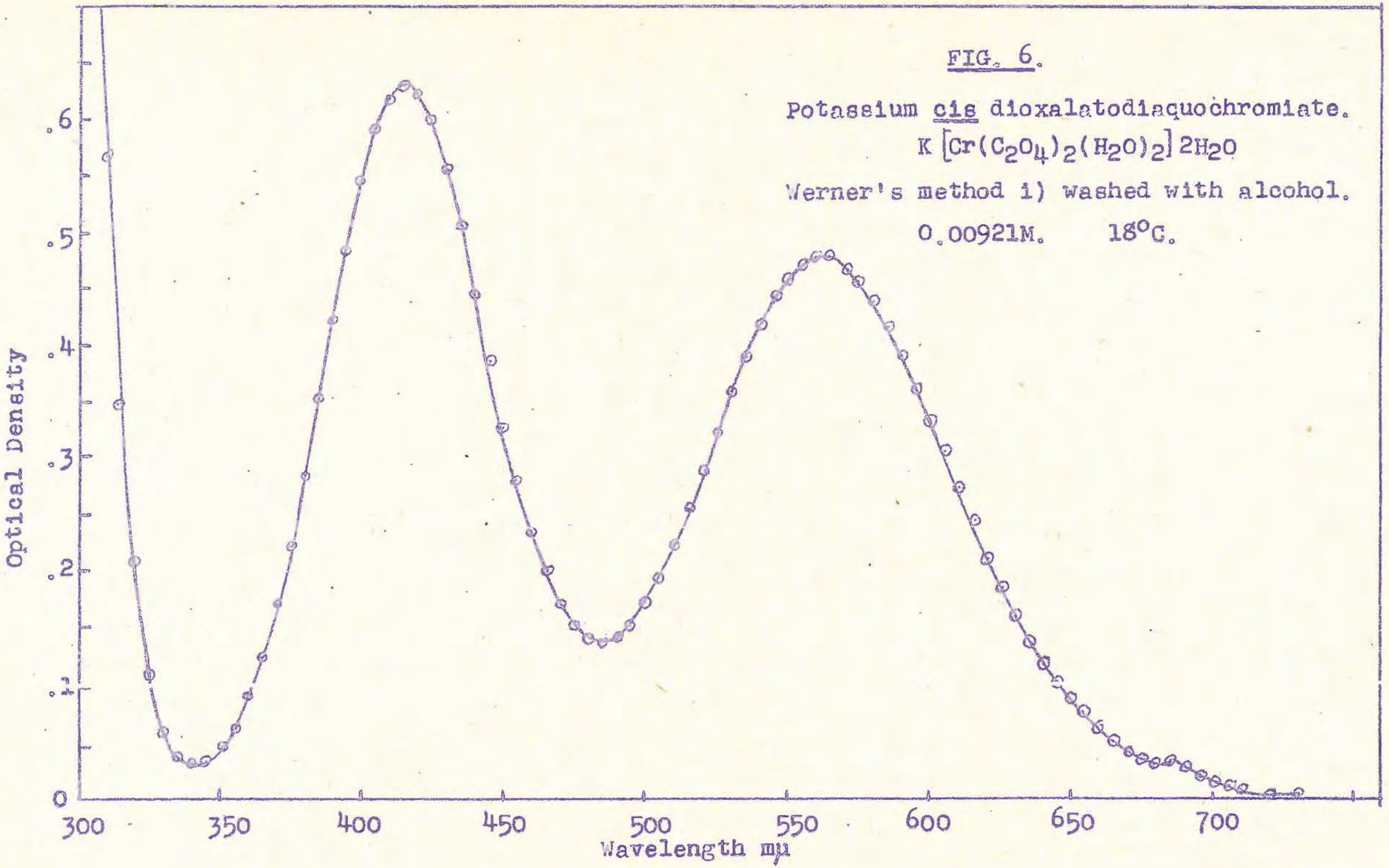

FIG. 6.

Potassium <u>cis</u> dioxalatodiaquochromiate.

K $[Cr(C_2O_4)_2(H_2O)_2]\,2H_2O$

Werner's method i) washed with alcohol.

0.00921M. 18°C.

Thus solutions of potassium cis dioxalatodiaquochromiate may be prepared in three ways :- one from an aged trans solution, and the other two from solid preparations of the cis salt by Werner's two methods. From analytical and spectrophotometric data they appear to be pure.

Wavelength	Extinction Coefficients		
	cis from trans salt	cis salt method (i)	cis salt method (ii)
416 mμ	67.33	68.39	68.61
562 mμ	51.02	52.11	51.02

(c) The Potassium Dioxalatohydroxoaquochromiates

Werner (32) found that the addition of alkali to a solution of either the cis or trans dioxalatodiaquochromiate caused a colour change from pink to green. This is due to the replacement of one or both of the complex water molecules by hydroxyl ions giving the hydroxo complexes :

$Cr\left[(C_2O_4)_2(H_2O)(OH)\right]^{=}$	Dioxalatohydroxoaquochromiate
$Cr\left[(C_2O_4)_2(OH)_2\right]^{\equiv}$	Dioxalatodihydroxochromiate

These two hydroxo complexes may be formed by the addition of first one, and then two equivalents respectively of alkali per chromium. As is later seen in the potentiometric section, these complexes are unstable in solution, rapidly liberating oxalate ion.

To obtain the spectrophotometric curves of both cis and trans hydroxoaquo salts, solutions of cis and trans

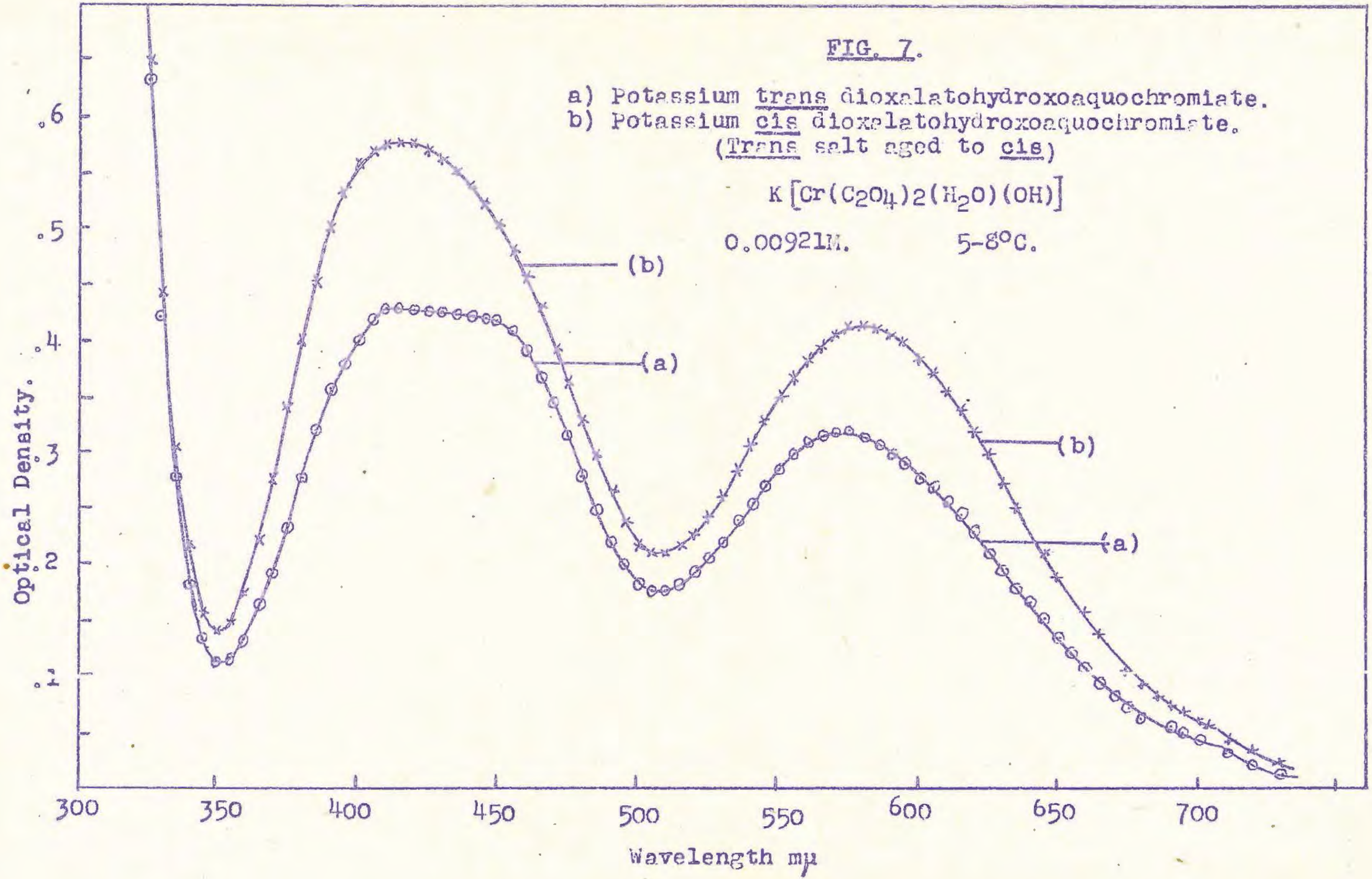

FIG. 7.

a) Potassium trans dioxalatohydroxoaquochromiate.
b) Potassium cis dioxalatohydroxoaquochromiate.
(Trans salt aged to cis)

$K[Cr(C_2O_4)_2(H_2O)(OH)]$

0.00921M. 5-8°C.

dioxalatodiaquochromiates were prepared in the cold (5 - 8°C) and then one equivalent of cold alkali added to each. The flasks were kept in ice and absorption density readings taken on portions that were renewed after every two or three readings. The graphs are given in Fig. 7. It is seen that there still remains a difference in extinction coefficient between the trans and cis hydroxoaquochromiates, but this difference is smaller than for the corresponding trans and cis dioxalatodiaquo salts, the extinction coefficients of the cis hydroxoaquo being lowered and those of the trans hydroxoaquo being raised. The peculiar flattening of the absorption curve maximum between 410 mμ and 450 mμ in the case of the trans salt should be noted. A less pronounced flattening is seen for the cis salt. These effects are presumably due to the presence of two overlapping maxima. While it is tempting to ascribe the development of new maxima to the formation of loose complexes (e.g. as a preliminary to olation), it should be borne in mind that the phenomena occur at the lower frequencies and are thus presumably connected with changes in electron orbitals rather than molecular vibrations. Moreover Burley's data on the olated complex (80% olation) does not show the same displacement as noted here.

(d) Potassium Dioxalatosulphatoaquochromiate

This was prepared as described by Burley (14). To a 50% (w/v) solution of potassium cis dioxalatodiaquochromiate, prepared by weighing a known quantity of the trans salt, dissolving in water and ageing to the cis isomer, an exactly equimolar quantity of pure potassium sulphate was added. After boiling for twenty minutes, the colour of the solution changed from pink to dark green. Burley made several unsuccessful attempts to separate a solid from the cooled solution. Instead, he evaporated the original solution in an air oven at 90°C. for 12 hours, obtaining a dark green glassy solid. This solid was extremely hard and was pulverised with great difficulty.

In this work, the above was repeated, but the mixture of cis salt and potassium sulphate turned a dark green on heating, before the boiling point was reached. It was boiled for twenty minutes, transferred to a porcelain dish and evaporation continued over a steam bath. A dark green viscous liquid resulted and this was dried in an oven at 120°C. for eight hours. A brittle dark green mass remained that was easily broken up and had a crystalline appearance.

This preparation was repeated using the cis dioxalatodiaquochromiate salt prepared as in (b)(ii) above. The results were the same and the two sulphato complexes prepared seemed identical. Further studies on this product are reported in Chapter IV.

2. ANALYTICAL METHODS.

(a) Determination of Chromium

The method used was an adaptation of that of

Smith and Sullivan (33) as modified by Davies and Innes (34) whereby perchloric acid is used to oxidize the chromium and all organic matter present in chrome-tanned leathers. The method is given below :

About 0.2 g. of the chromium compound was accurately weighed into a 300 ml. Kjeldahl flask and about 5 ml. of water added and then 5 ml. of an oxidising mixture. This consisted of 60% perchloric acid and 80% sulphuric acid in the volume ratio of 2 : 1. For compounds containing reactive organic groups, 10 ml. of strong nitric acid was also added.

The mixture was heated, gently at first and then more strongly, until oxidation occurred, i.e. when the solution turned from green to yellow. Heating was continued for a further two minutes only; the flame was removed, a long thistle-funnel was placed in the neck of the flask and 10 ml. of distilled water added all at once, the stem of the funnel directing the cold water on to the hot solution. A further 40 ml. of water was added and the mixture boiled for ten minutes to expel chlorine. After cooling, the contents were titrated against standard ferrous ammonium sulphate solution (N/20) using n-phenylanthranilic acid as indicator.

An alternative oxidant is ammonium persulphate (35). About 0.2 g. of the chrome salt is weighed out and 2 ml. of concentrated sulphuric acid added together with 2 g. of ammonium persulphate, 10 ml. of N/10 silver nitrate and 300 ml. of water. The contents are boiled for ten minutes, during which the trivalent chromium is oxidised. The cooled solution may be titrated against ferrous ammonium sulphate as above or 10 ml. of a 10% potassium iodide solution added and after standing in the dark for 3 to 5 minutes, the liberated iodine is titrated against N/10 sodium thiosulphate using starch as indicator.

The perchloric acid method was standardised on "A.R." Potassium Chrome Alum and the results are shown in Table I a. It will be seen that the mean result is about 1% low.

In another standardisation, weighed amounts of oxalic acid and potassium dichromate were taken, corresponding to the amounts required for the formation of the dioxalatodiaquochromiate salt. Aliquots of these solutions were analysed by the same method and the results are given in Table I b; they again are a bit low (about 1%).

In a third standardisation, an aliquot of standard potassium dichromate solution was taken and treated with excess oxalic acid. It was then oxidized in the usual manner and titrated. Another aliquot of potassium dichromate solution was left untreated and titrated directly. The titration ratios of the treated and untreated aliquots are given in Table I c. The difference in titration ratios is about 0.9%. This perchloric acid oxidation method seems reliable and fairly good precision is obtained. As the results appear to be consistently 1% low in chromium, due allowance must be made in interpreting the analytical data in terms of empirical formulae.

TABLE I (a)

Chromium Potassium Sulphate. $CrK(SO_4)_2.12H_2O$

Theoretical % Cr	Found % Cr
10.41	10.32 10.31 10.33 10.29

TABLE I (b)

Mixture of potassium dichromate and oxalic acid.
$K_2Cr_2O_7$ and $(COOH)_2.2H_2O$

Calculated g. Cr	Found g. Cr
.02639	.02612
.02781	.02757
.02679	.02668

TABLE I (c)

ml. of ferrous ammonium sulphate required by 20 ml. of potassium dichromate (0.997N). (a) with no oxalic acid added and (b) after addition of oxalic acid.

(a) No oxalic acid added	(b) Oxalid acid added
20.05 ml.	19.80 ml.
20.02 "	19.92 "
20.05 "	19.85 "

TABLE II (a)

Potassium oxalate $(COOK)_2$

Calculated % K	Found % K
42.44	42.42 42.41 42.43

TABLE II (b)

Mixture of potassium dichromate and oxalic acid.
$K_2Cr_2O_7$ and $(COOH)_2.2H_2O$

Calculated g. K	Found g. K
.01999	.02063 .02040 .02116
.02110	.02207 .02167 .02190
.02038	.02051 .02087 .02068

Analyses using ammonium persulphate as oxidant gave results of higher chrome values but the precision was not so good as the above method.

(b) Determination of Potassium

About 0.3 g. of the compound was weighed out and about 3 ml. of "A.R." 60% perchloric acid added followed by 5 ml. of water. The mixture was evaporated gently to dense fumes and then allowed to cool. 10 ml. of absolute alcohol (saturated with potassium perchlorate) was added and, after standing for an hour or two, the precipitate was filtered through a tared sintered glass crucible. The precipitate of potassium perchlorate was weighed after drying for one hour at 140°C. During evaporation, care was taken to remove the flame before the chromium present had become oxidised to dichromate. In cases where oxidation did occur, erratic results were obtained.

This method cannot be used in the presence of sulphate.

The method was standardised by analysing some "A.R." potassium oxalate for potassium, the results appear in Table II (a). This gives excellent results in the absence of chromium.

A known mixture of oxalic acid and potassium dichromate was taken (the proportions being those required for the formation of the dioxalatodiaquochromiate), and the potassium content determined. Table II (b). With chromium present the results tend to be a bit high.

(c) Determination of Oxalate

About 0.3 g. of the salt was accurately weighed out, dissolved in 100 ml. water, and an excess of 40% sodium hydroxide added. The solution was boiled until the precipitate of chromium hydroxide flocculated; it was set aside for a while, filtered, and the precipitate washed thoroughly. The filtrate was acidified with SO_2-free 50% sulphuric acid, some excess being added, and the solution was then titrated against standard potassium permanganate in the usual manner.

(d) Determination of Sulphate

This determination only applies to the one sulphato salt prepared and the method is discussed in full in the chapter dealing with this complex. (See page 69).

3. SUMMARY.

Potassium trioxalatochromiate, potassium *trans* and *cis* dioxalatodiaquochromiates and potassium dioxalatosulphatoaquochromiate have been prepared as solid salts and the methods of preparation given.

Spectrophotometric absorption curves have been performed on solutions of these salts using a Beckman Spectrophotometer; the curves are in agreement with previous workers (14). The solid preparation of the *cis* dioxalato salt has been shown to give an absorption curve identical to that of the *cis* salt obtained by ageing a solution of the *trans* salt; this also proves that the *trans* - *cis* isomerisation goes to completion.

The analytical methods by which the salts were analysed have been given, together with standardisations on known salts. The actual analyses of the chromium complexes have been recorded.

CHAPTER III

POTENTIOMETRY

1. INTRODUCTION.

Potentiometric measurements provide evidence which cannot always be obtained by other means concerning the nature of acidic and basic groups present in complex ions.

Such methods have been employed by a number of workers in studies on chrome complexes. In particular, mention may be made of Stiasny (36) who observed the changes in electrode potentials and pH induced by varying the ionic environment of chromium chloride and chromium sulphate solutions, and who used this technique in order to study hydrolysis and ageing phenomena of these and other chromium salts. Britton (19) and Atkin and Chollet (37) employed the potentiometric technique, the former on a chromium dioxalato complex and the latter in a study of the hydrolysis of chrome alum.

Although Britton (19) concluded from the titration curve of potassium dioxalato chromiate that this salt was an addition compound, Burley (14) has established from the titration curve of the red dioxalato salt that it behaves normally as a difunctional acid. However, although Burley calculated the "titration" constants, these do not correspond to the true thermodynamic dissociation constants since no allowance was made for the activity factors. Moreover, Burley subsequently established from his kinetic studies that the trans dioxalatodiaquo complex ion isomerises to the cis form, and it is probable that his data refer to the latter. During the above-mentioned kinetic studies, Burley also found there was no change in the pH of the solutions before and after isomerisation. It may therefore be assumed that there is no difference between the dissociation constants of the two isomers. However, according to Bjerrum (38), the molecular configuration and the distance between the charges have considerable effect on the dissociation constants; in the case of the cis and trans dioxalatodiaquochromiates, where there is a marked difference in the position of the ionisable groups, this effect should be noticeable. Kirkwood and Westheimer (39) have modified Bjerrum's theory by taking into account the effect of the dielectric constant between the charges. It would therefore be of great theoretical interest to investigate these dissociation constants and to determine whether there is any difference between those of the trans and cis salts.

With this object in view, potentiometric titrations on the cis and trans dioxalatodiaquochromiate salts were carried out. However, comparison of the dissociation constants is not strictly valid unless the effect of ionic strength is taken into consideration. At zero ionic strength the values of the "titration" constants are equal to those of the true thermodynamic dissociation constants, and it is possible to obtain these true dissociation constants by application of the Debye-Hückel theory of electrolytes and extrapolation to zero ionic strength.

2. "TITRATION" CONSTANTS

The chromium complexes under investigation are really tribasic acids existing at the end-point of the first (strong acid) stage. For all practical purposes, these complexes can be considered as normal dibasic acids.

The treatment of the theory of the neutralisation of a dibasic acid is fairly standard, but for the sake of clarity in later calculations, it is given below.

Consider the acid H_2A which is capable of ionising in aqueous solution according to :-

$$H_2A \rightleftharpoons H^+ + HA^- \quad \ldots\ldots\ldots\ldots\ldots (3.1)$$

$$HA^- \rightleftharpoons H^+ + A^= \quad \ldots\ldots\ldots\ldots\ldots (3.2)$$

The "titration" constants K_1 and K_2 are given by :

$$K_1 = \frac{h\ a_1}{[H_2A]} \quad \ldots\ldots\ldots\ldots\ldots (3.3)$$

$$K_2 = \frac{h\ a_2}{a_1} \quad \ldots\ldots\ldots\ldots\ldots (3.4)$$

Where h is hydrogen ion activity $= [H^+]\ f_H$,

f_H being the activity coefficient.

Also, $a_1 = [HA^-]$

$a_2 = [A^=]$,

the square brackets indicating concentrations in gram. ions per litre.

For all solutions, the total concentration C of acid H_2A is given by :

$$C = [H_2A] + a_1 + a_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (3.5)$$

If a solution of this acid, having a molar concentration C is titrated with an alkali solution, say NaOH, then at any stage during the titration, the solution as a whole must be electrically neutral, whence :

$$[Na] + [H] = [OH] + a_1 + 2a_2 \quad \ldots\ldots\ldots \quad (3.6)$$

Also for an aqueous solution :

$$h.oh = K_W \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.7)$$

where K_W is the ionic product of water.

Now, using equations (3.3) to(3.7), an equation can be derived showing how the hydrogen ion activity h varies with the addition of alkali. For convenience ($[Na] + [H] - [OH]$) is replaced by Na_1

Thus from (3.5) and (3.6)

$$\frac{Na_1}{C} = \frac{a_1 + 2a_2}{[H_2A] + a_1 + a_2}$$

and from (3.3) and (3.4)

$$\frac{Na_1}{C} = \frac{hK_1 + 2K_1K_2}{h^2 + hK_1 + K_1K_2} \quad \ldots\ldots\ldots \quad (3.8)$$

or $$Na_1 h^2 = K_1h(C - Na_1) + K_1K_2(2C - Na_1) \quad .. \quad (3.9)$$

In this derivation it has been assumed that no large changes in volume occur during titration with alkali. This was the case, approximately 0.5 N alkali being used.

The constants K_1 and K_2 for these weak dibasic acids have been calculated graphically from the pH curves. The method is due to Atkin (40), the derivation being as follows :

Let α be the degree of neutralisation of the acid H_2A at a point during titration; α is defined as :

$$\alpha = \frac{\text{amount of alkali added up to this point (in equivalents)}}{\text{total acid present (in moles per litre)}}$$

i.e. $\alpha = Na/C$

Then if $[H]$ and $[OH]$ are small with respect to $[Na]$

$$\alpha = Na_1/C$$

From (3.8)

$$\alpha = \frac{hK_1 + 2K_1K_2}{h^2 + hK_1 + K_1K_2} \qquad \text{...........} \; (3.10)$$

In order to obtain K, two points are selected on the titration curve, equidistant from the midpoint of neutralisation (i.e. at $\alpha = 1$). This point corresponds to the neutralisation of the first stage of the acid. Let the hydrogen ion activity at the two points selected be h_1 and h_2 (the hydrogen ion activity is calculated from the pH's at these points), and let the degree of neutralisation at h_1 be α. Then that at h_2 will be $(2 - \alpha)$.
Then from (3.10)

$$\alpha = \frac{K_1h_1 + 2K_1K_2}{h_1^2 + K_1h_1 + K_1K_2} \qquad \text{...........} \; (3.11)$$

$$\text{and } (2 - \alpha) = \frac{K_1h_2 + 2K_1K_2}{h_2^2 + K_1h_2 + K_1K_2} \qquad \text{...........} \; (3.12)$$

These can be solved for K_1 giving :

$$K_1 = \frac{\alpha h_1 - (2 - \alpha)\, h_2}{(1 - \alpha)} \qquad \text{...........} \; (3.13)$$

K_2 is obtained by substituting the value of K_1 in either of the above equations.

Thus to find K_1 and K_2, the quantities Na, C, h_2, h_1 and α are obtained from the graph. The method has the advantage that a large number of points can be chosen for h_1 and h_2 so that the values of K_1 and K_2 are averages of many values.

3. EVALUATION OF "TITRATION" CONSTANTS OF THE DIOXALATO-DIAQUOCHROMIATE COMPLEX.

Although the dioxalato complex is really a tribasic acid, the first stage of dissociation is similar to that of a strong acid. The dioxalato ion, $[Cr(C_2O_4)_2(H_2O)_2]^-$ can however be regarded as a dibasic acid. That the same procedure can be employed in evaluating the constants can be shown for the general case of a tribasic acid as follows, where the first dissociation stage is not necessarily that of a strong acid.

Let a' = concentration of $[Cr(C_2O_4)_2(H_2O)_2]^-$
a'' = " " $[Cr(C_2O_4)_2(H_2O)OH]^=$
a''' = " " $[Cr(C_2O_4)_2(OH)_2]^{\equiv}$

By definition, the "Titration" constants are ;

$$K_1 = \frac{ha''}{a'} \qquad \ldots\ldots\ldots\ldots\ldots (3.14)$$

$$K_2 = \frac{ha'''}{a''} \qquad \ldots\ldots\ldots\ldots\ldots (3.15)$$

Where h is the activity of the hydrogen ions.

Also by definition :

$$C = a' + a'' + a''' \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3.16)$$

Where C is the total concentration,

and for electrical neutrality :

$$Na_1 = [Na] + [H] - [OH]$$
$$= a' + 2a'' + 3a''' \quad \ldots\ldots\ldots\ldots\ldots \quad (3.17)$$

From (3.14) and (3.15) we have,

$$a' = \frac{h^2 a'''}{K_1K_2} \qquad \text{and} \qquad a'' = \frac{ha'''}{K_2}$$

$$\text{Now} \quad \alpha_1 = Na_1/C \quad = \frac{a' + 2a'' + 3a'''}{a + a'' + a'''}$$

$$= \frac{h^2/K_1K_2 + 2h/K_2 + 3}{h^2/K_1K_2 + h/K_2 + 1}$$

$$\alpha_1 = \frac{h^2 + 2K_1h + 3K_1K_2}{h^2 + K_1h + K_1K_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3.18)$$

Whence it follows that

$$\alpha_1 - 1 = \frac{K_1h + 2K_1K_2}{h^2 + K_1h + K_1K_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3.19)$$

If we take the degree of neutralisation as measured from the end point of the first (strong acid) stage, then

$$\alpha = \alpha_1 - 1$$

$$\text{or} \qquad \alpha = \frac{K_1h + 2K_1K_2}{h^2 + K_1h + K_1K_2} \quad \ldots\ldots\ldots\ldots \quad (3.20)$$

Hence, in spite of the dioxalatodiaquochromiate complex being a tribasic acid existing at the end point of the first strong acid stage, the same procedure given for a dibasic

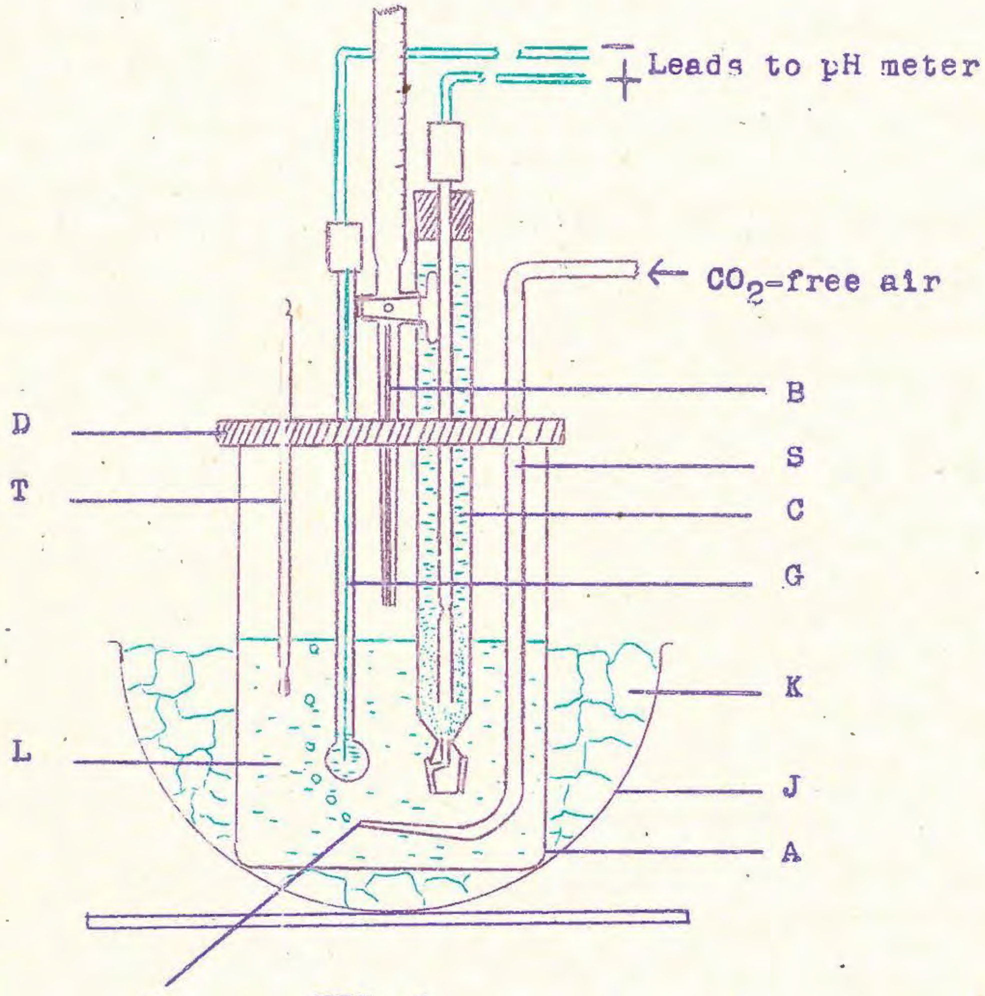

FIG. 8.

pH meter - electrode assembly.

A	250ml.Pyrex beaker.	G	Glass electrode.
J	Dish.	C	Calomel electrode.
K	Ice.	S	Air-bubbler tube.
L	Titration solution.	N	Air-bubbler nozzle.
D	Beaker Cover.	B	Microburette.
T	Thermometer.		

The microburette used was Grade A. NPL.

The water used in the making up of the chrome solutions and alkali must be pure and free from dissolved carbon dioxide. Ordinary distilled water was redistilled from a pyrex still and collected whilst warm. Before use a stream of CO_2-free air was bubbled through the water for twelve hours to remove the last traces of carbon dioxide.

The alkali was "A.R." KOH. A normal solution was prepared using CO_2-free water and kept in an aspirator lined with paraffin wax; a soda lime trap was fitted to this aspirator. For the titrations, smaller quantities of approximately 0.5 N KOH were prepared from this solution as required before each series of titrations and kept in a smaller paraffin wax-lined bottle. The 0.5 N solution was standardised just prior to the titrations being carried out and renewed for the next series of titrations.

"A.R." nitric acid was made up to be about 0.5 N and used for the acid titrations. The acid was standardised at frequent intervals.

5. PROCEDURE

The required amount of pure chromium salt to give a 0.009208M. solution in respect to chromium was weighed out directly into the beaker. The pH meter was allowed to warm up and was then standardised using the standard buffers. Then 100 ml. of CO_2-free distilled water was added to the chromium salt in the beaker and the salt dissolved. The electrodes were immersed in this

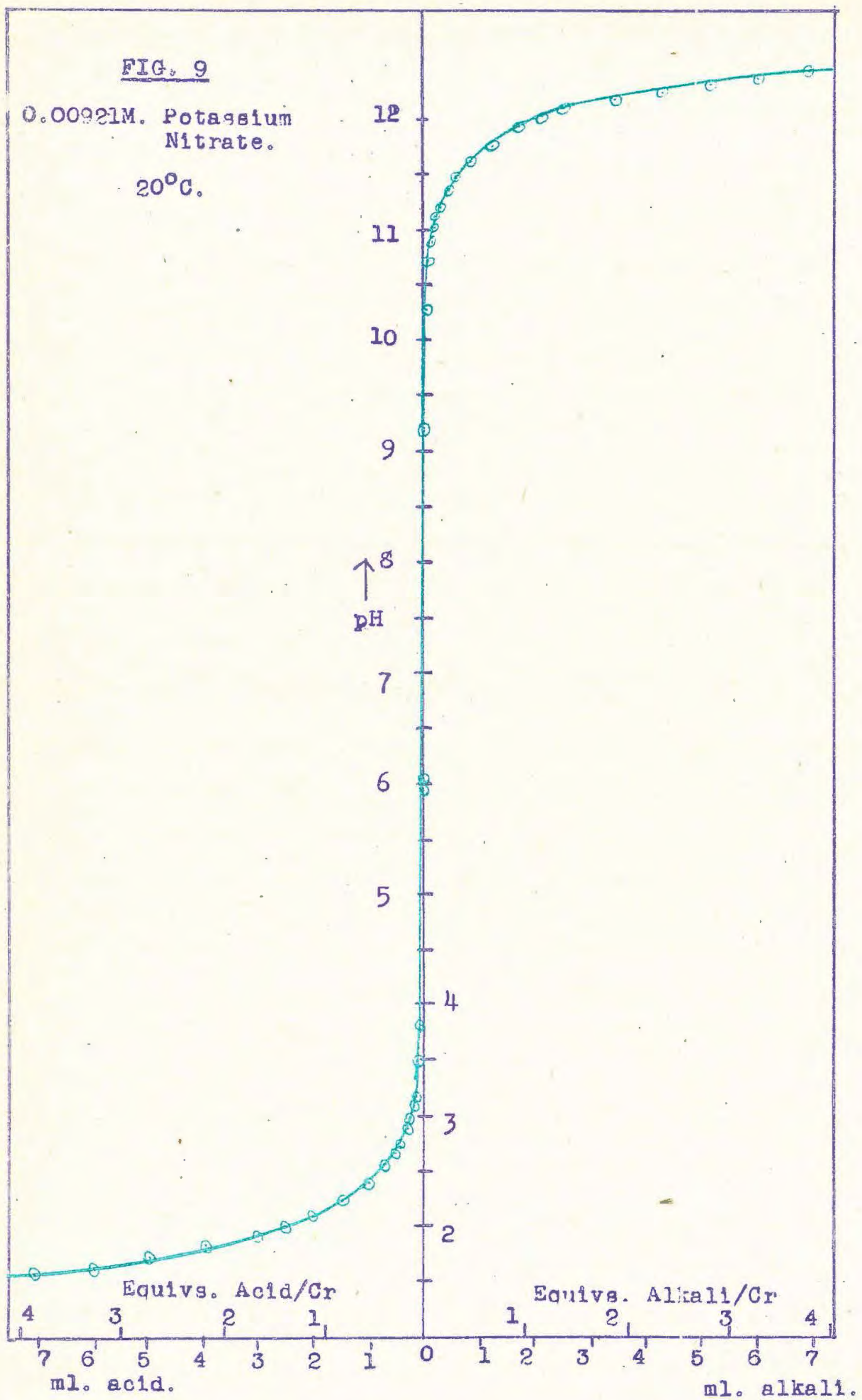

FIG. 9

0.00921M. Potassium Nitrate.

20°C.

solution, the beaker was covered and the titration carried out as rapidly as possible. After each addition of acid or alkali, the solution was stirred by the air bubbler, sending a stream of CO_2-free air bubbles through the solution. By adjusting the nozzle N, efficient stirring of the solution was ensured and the CO_2-free air also helped keep the solution free of any atmospheric carbon dioxide during titration.

Most of the titrations had to be performed at low temperatures in order to prevent trans - cis conversion, decomposition and olation. The titration beaker was placed in a dish J, containing melting ice and, with the even addition of alkali or acid at regular intervals, the temperature of the titration solution was maintained at 5 - 8°C. When low temperatures were used, the temperature compensator of the pH meter was set to this temperature and the necessary corrections made to the pH values of the standard buffers using the temperature coefficients given in section 4 of this chapter.

A preliminary titration was performed on a neutral salt. Fig. 9 shows the titration curve of 0.009208M. potassium nitrate at 20°C. The number of ml. of acid or alkali added have been converted to equivalents of acid or alkali per mole of salt. This curve follows the usual strong acid-strong base curves with a pH increase from 3 to 10 in the region of stoichiometric neutrality. The curve refers to a titration carried out with the ordinary glass electrode up to pH 9. The special "Alki" electrode was then installed, restandardised at pH 9.2, and the titration completed. This electrode was found to be a trifle unsteady but, more important, it took several minutes to settle down to equilibrium. This time lag is serious in the case of these complex chromium salts as decomposition is likely to occur during titration and speed is essential if decomposition is to have no effect on the titration curves. The "Alki" electrode is therefore unsuitable for titrations of these complexes. The titration of the neutral potassium nitrate salt was repeated using the ordinary glass electrode throughout. The points plotted in Fig. 9 are those given by the glass electrode. The actual readings are recorded in Table A8 of the Appendix where also the readings obtained using the "Alki" electrode are recorded. It can be seen that the differences between the readings using the two electrodes are very small and may be ignored.

In these titrations, KOH was used in preference to NaOH, so that readings could be taken up to high pH's of 11 to 12 without potentials being set up between the soda in the glass of the electrode and the titrating solution. This probably accounts for the good results obtained with the glass electrode at high pH's.

The KOH solution used in this titration was carefully standardised against "A.R." potassium hydrogen phthalate. The phthalate was dissolved in CO_2-free water and the KOH added from a microburette, the pH being recorded after each addition. On approaching the end point, the alkali was added drop by drop and the increase in pH recorded for each drop added. This pH increase per drop reaches a maximum at the end point. On an average, each drop was equivalent to 0.03 ml. and the amount of alkali added up to the end point was calculated. For comparison, other quantities of phthalate were titrated against the KOH usinga 50ml. Grade A NPL burette and phenolphthalein as indicator. Extra precautions were taken such as using CO_2-free water and fitting the burette with a soda lime trap. The results obtained agreed well with the potentiometric standardisation.

Normality of potassium hydroxide :

	By Potentiometric Method		By Titration using phenolphthalein
	.4390		.4392
	.4387		.4385
	.4391		.4388
mean	.4389 N	mean	.4388 N

The nitric acid was standardised against the standard KOH above using phenolphthalein, and this checked by titration of the acid against borax using methyl orange as indicator. The results were in good agreement.

All future standardisations of alkali were consequently done by titration against potassium hydrogen phthalate and those of acid against borax.

As most of the pH titrations were conducted at lower temperatures, another alkali titration was performed

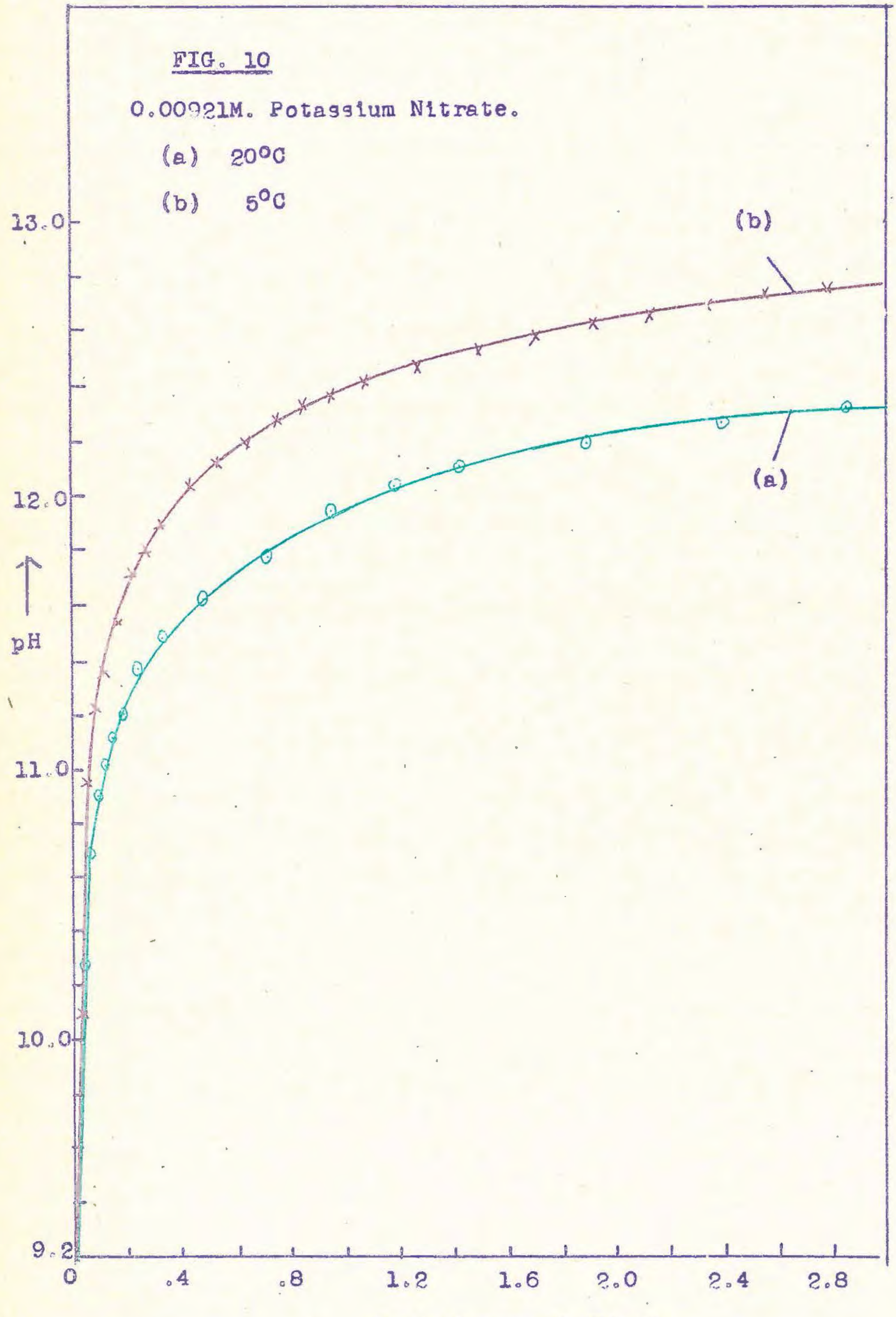

FIG. 10
0.00921M. Potassium Nitrate.
(a) 20°C
(b) 5°C
(b)
(a)
13.0
12.0
11.0
10.0
9.2
pH
0
.4
.8
1.2
1.6
2.0
2.4
2.8
Equivalents of Alkali.

on 0.009208M. potassium nitrate at 5 - 8°C. This, together with an enlarged curve from Fig. 9 is shown in Fig. 10. In these graphs the pH rises rapidly until at about pH 11.5 the curve flattens out and there is only a small increase in pH for each equivalent of alkali added. In the later curves of the chromium salts, after the addition of two equivalents of alkali, the curve also flattens out at approximately pH 12. At the end of the titration the curve should continue to rise to pH 14 but, due to the salt effect seen in Fig. 9 and 10, the pH remains almost constant. These chromium salt titration curves should therefore be corrected for blank KOH titrations carried out on conductivity water under the same conditions of ionic strength and temperature from the data obtained from Fig. 10. These number of equivalents of alkali were subtracted from the values obtained for the titration curves of the chromium salts, giving a corrected curve above pH 9. The correction is very little until approximately pH 11 is reached, when the corrected curve approaches asymptotically the line drawn at two equivalents of alkali per chromium, showing the end of the titration.

6. EXPERIMENTAL TITRATION CURVES OF CHROME COMPLEXES.

(a) Potassium cis Dioxalatodiaquochromiate

Fig. 11 shows the results of acid and alkali potentiometric titrations on solutions of the cis salt. This salt was the solid prepared by Werner's method (ii) (See page 16). From the shape of the curve above pH 6, it

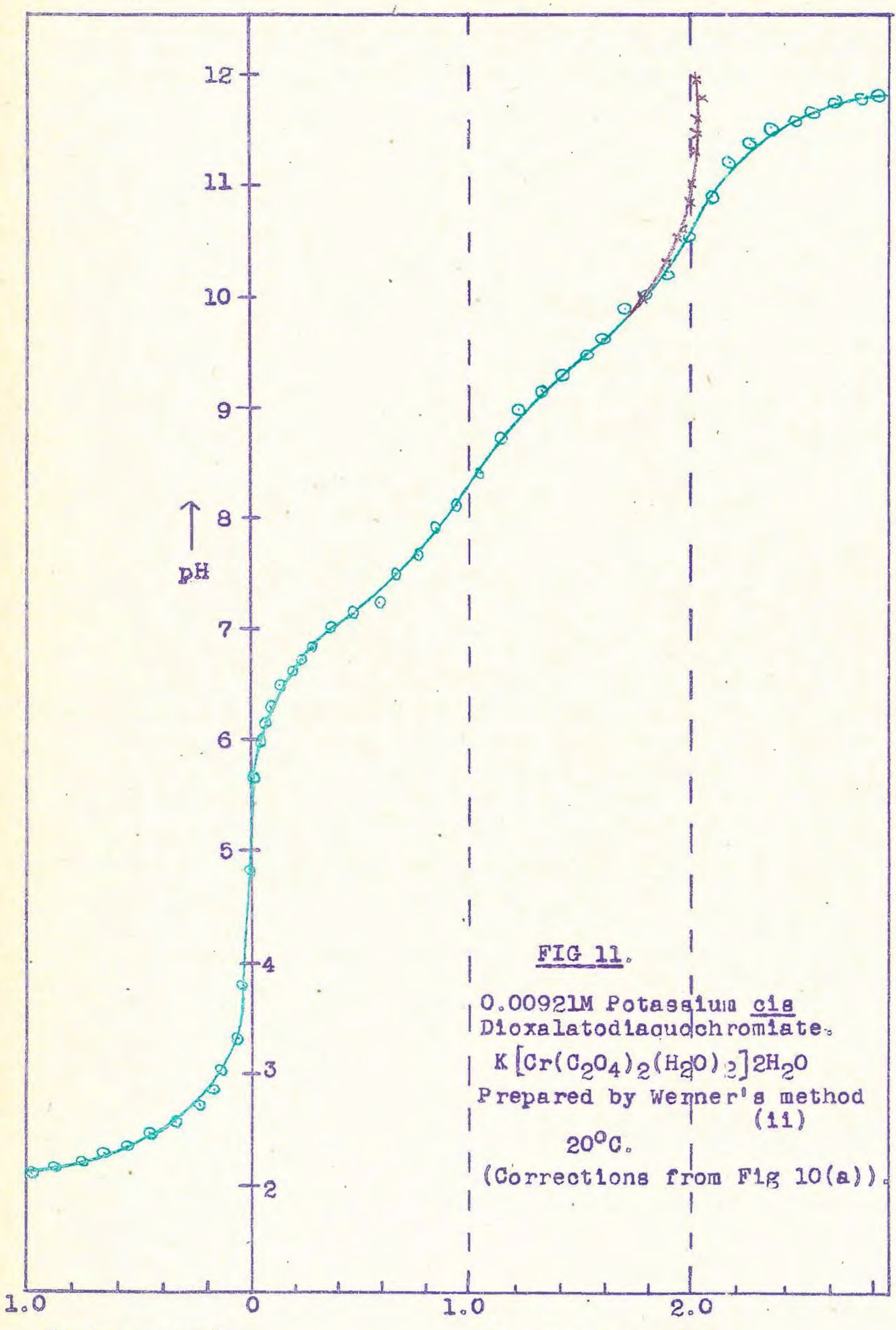

FIG 11.

0.00921M Potassium *cis* Dioxalatodiaquochromiate.
K$[Cr(C_2O_4)_2(H_2O)_2]2H_2O$
Prepared by Werner's method (ii)
20°C.
(Corrections from Fig 10(a)).

is obvious that the dioxalatodiaquochromiate ion is weakly acidic. Two end points can be seen, corresponding to 1.0 and 2.0 equivalents of alkali per chromium respectively.

These two end points correspond to the titration of the two aquo groups of the dioxalatodiaquochromiate ion to form the mono and di-hydroxo derivatives.

$$\mathrm{Cr}\left[(C_2O_4)_2(H_2O)(OH)\right]^{=}$$

and $$\mathrm{Cr}\left[(C_2O_4)_2(OH)_2\right]^{\equiv}$$

In a further experiment, a solution of the <u>trans</u> dioxalatodiaquochromiate was prepared and allowed to convert to the <u>cis</u> isomer by slight warming and standing. An alkali potentiometric titration was performed on this solution at room temperature (18°C.). The curve obtained was exactly the same as in Fig. 11 (and has not therefore been reproduced), showing that the solution on which Burley (14) performed the titration was that of the <u>cis</u> isomer and that the <u>cis</u> salt prepared by Werner's method (ii) gave a curve identical to what is known to be a pure <u>cis</u> dioxalatodiaquochromiate solution.

The curve shown in Fig. 11 has been corrected for the blank KOH titration at similar ionic strength and temperature, the data being obtained from curve (a) in Fig. 10. It is seen that the end point is reached very nearly at two equivalents of alkali.

Burley calculated the acid constants for his <u>cis</u> titration curve by the method outlined in section 2 of this

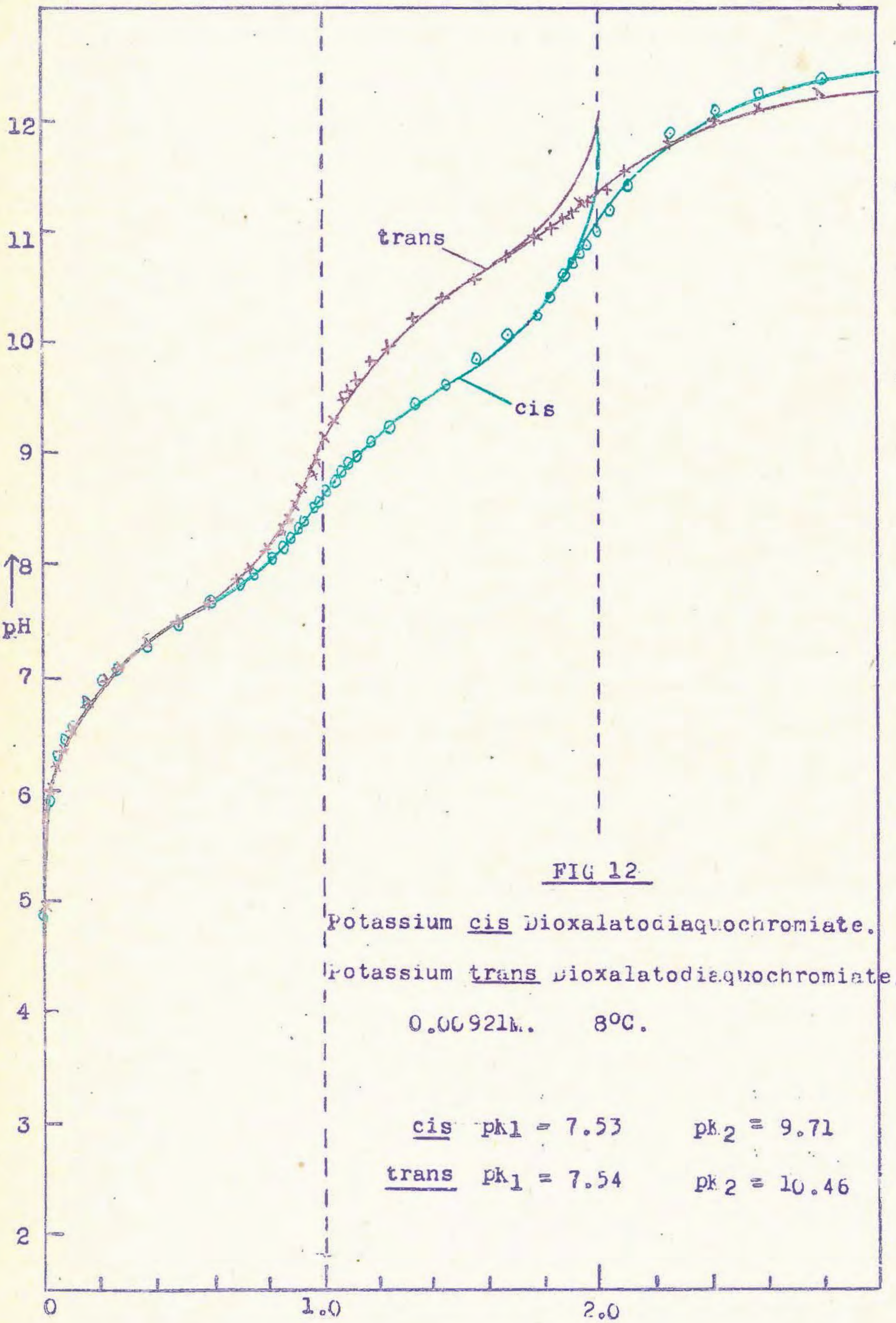

FIG 12

Potassium *cis* Dioxalatodiaquochromiate.

Potassium *trans* Dioxalatodiaquochromiate.

0.00921M. 8°C.

cis $pK_1 = 7.53$ $pK_2 = 9.71$

trans $pK_1 = 7.54$ $pK_2 = 10.46$

chapter; his results for room temperature (18 - 20°C.) are :

$$pK_1 = 7.09$$
$$pK_2 = 9.45$$

Since in the case of the other chrome salts, decomposition and/or conversion is rather rapid at room temperature similar curves were obtained at lower temperatures. Thus a fresh alkali potentiometric titration was performed on the solid cis salt at 8 °C. The curve is shown in Fig. 12. Here the pK values are different due to the lower temperature. The values obtained by the graphical method are as follows :

$$\left.\begin{array}{l} pK_1 = 7.53 \\ pK_2 = 9.71 \end{array}\right. \quad \underline{\text{cis}} \text{ salt at } 8^{\circ}\text{C.}$$

The constants are of course the "titration" constants and not the true thermodynamic constants.

(b) Potassium trans Dioxalatodiaquochromiate

It was not possible to perform this titration at room temperature due to the occurrence of trans - cis conversion. Fig. 13 shows the acid and alkali titration curves for this salt at 8°C. The general form of the curve is similar to that of the cis salt obtained at the same temperature, but after pH 8 the trans curve is higher than that of the cis. There are end points at 1.0 and 2.0 equivalents of alkali respectively, denoting the formation of the mono and di-hydroxo derivatives. The alkaline section of this

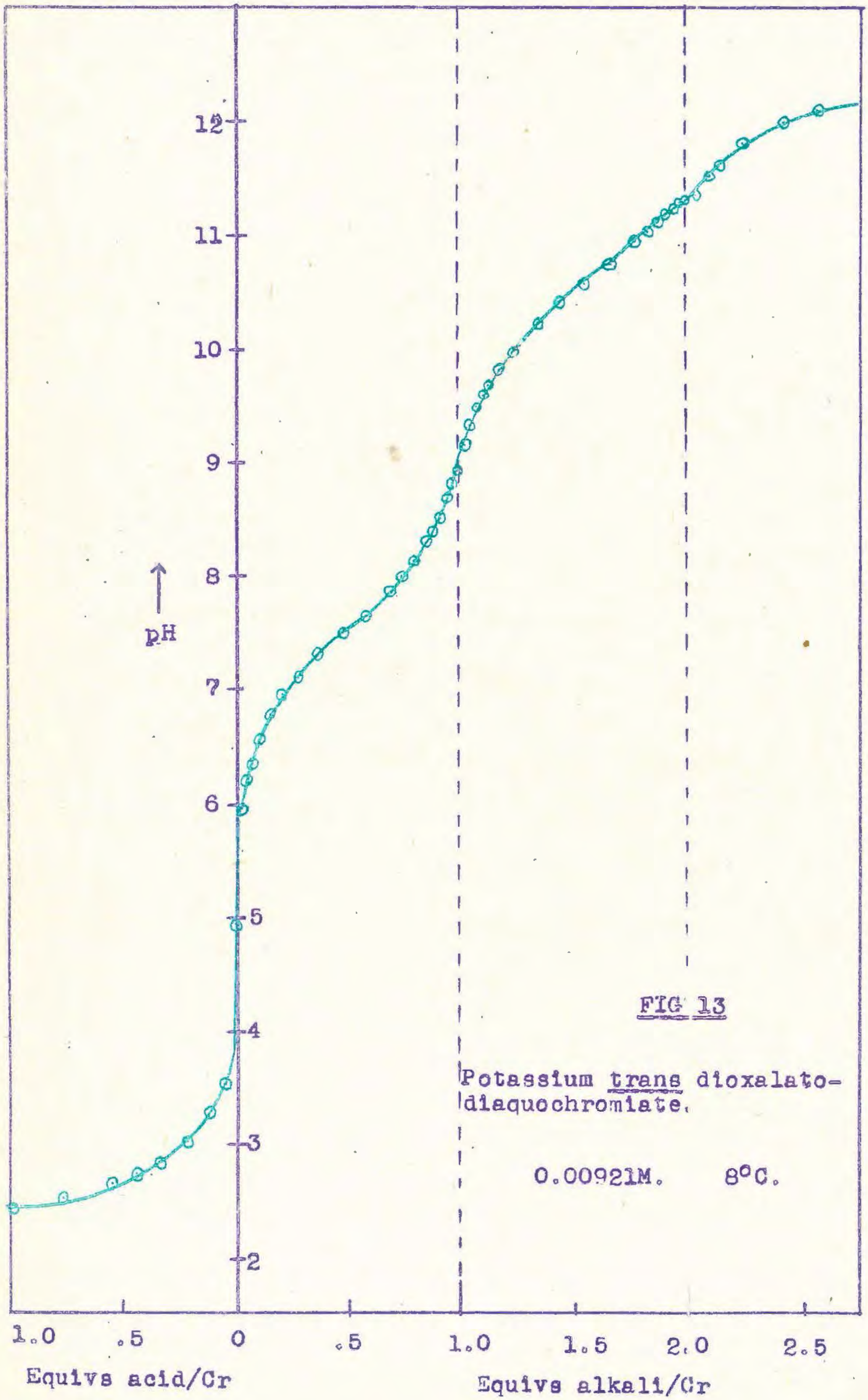

FIG 13

Potassium *trans* dioxalato-diaquochromiate.

0.00921M. 8°C.

curve has been reproduced in Fig. 12 enabling comparison with the similar cis curve to be made. Both curves are corrected for the blank KOH titration from curve (b) Fig.10.

In Fig. 12 it is seen that the curves for the trans and cis salts are identical up to approximately pH 8, giving equal pK_1 values for both forms of the complex ion. After this the curves diverge and only meet again after the completion of the titration at about pH 12. The pK_2 value for the trans salt is somewhat higher than the corresponding constant for the cis salt. The values of the "titration" constants expressed on the pH scale are :

$$\left.\begin{array}{l} pK_1 = 7.54 \\ pK_2 = 10.46 \end{array}\right. \quad \text{\underline{trans} salt at } 8^{\circ}C.$$

(c) Hysteresis

It is evident that misleading interpretations of the data on the dioxalatodiaquochromiate salts are obtained if oxalate ions are liberated during titration. On the other hand, decomposition of this type is readily detected by immediate back-titration following the forward titration. The liberation of free oxalic acid and possibly of carboxyl groups from the complex should be indicated by a change in the shape of the titration curve, particularly in the region below pH 6. Hysteresis of this kind has already been observed by Burley when a solution of cis dioxalatodiaquochromiate was back-titrated after the addition of three equivalents of alkali per chromium. Burley ascribed the effect to the instability of the dihydroxo ions and concluded that the forward titration curve truly represented the titration of the complex-bound aquo groups. It was considered however, that further confirmation on this point should be sought and, with this end in view, the experiments described below were performed.

Initially back-titrations were performed on the cis and trans dioxalatodiaquochromiates at 8°C. after 1.0, 1.5 and 2.0 equivalents of alkali had been added. The alkali was added in one lot and back-titration commenced immediately. In this way it was hoped to prevent any decomposition of the mono and di-hydroxo complex ions. Although slight hysteresis was noticeable, it was far less than that obtained by Burley.

It would appear therefore that Burley's explanation adequately accounts for the facts, and the larger hysteresis observed by him can be ascribed to the fact that his titrations were conducted at room temperature, as against 8°C. in the present work; and also because his titrations would have taken longer to perform, since he did not adopt the procedure described above.

Some of the hysteresis is very likely due to the fact that when the solution was back-titrated, it had a higher ionic strength than initially. According to the Debye-Hückel theory, the effect of increasing the ionic strength would be to lower the pH. The effect of varying the ionic strength was investigated in the following manner :

Alkali potentiometric titrations were performed at 8°C. on both the cis and trans salts at double ionic strength, the latter being controlled by the addition of potassium nitrate, but the chromium concentration was maintained at 0.00921M. It was found that in the case of the cis salt there was very little difference between the two curves. There was a slight lowering of the pH at the higher ionic strengths, but at no point did this exceed 0.1 pH units. For the trans salt this difference was slightly greater, probably due to slight trans - cis isomerisation occurring. Even in this case, however, the pH was lowered only by a very small amount on doubling the ionic strength.

The slight hysteresis observed on back-titration with acid is therefore mainly due to decomposition of the hydroxo complexes formed. As is to be expected, this decomposition is likely to be more rapid at higher temperatures. (18 - 20°C.).

After back-titration with acid, the green colour of the solution due to the formation of the hydroxo complexes disappeared and the solutions turned pink once more. This shows that the reaction is reversible and the dioxalatodiaquo salt can be regenerated. After exactly neutralising the alkali added with acid, the extinction coefficients were measured and found to correspond to those of the cis dioxalatodiaquochromiate solution at 419 and 560 mμ, showing that the resulting solution was that of the cis salt.

(d) Evaluation of the Thermodynamic Dissociation Constants

A study was carried out in order to determine the nature of the variation of the pK_1 and pK_2 values with ionic strength for the cis and trans dioxalatodiaquochromiates.

Fairly accurate values of pK_1 and pK_2 are obtained from the potentiometric titration curves by recording the pH at 0.5 and 1.5 equivalents of alkali per chromium respectively. Accordingly, values of pK_1 and pK_2 were obtained by measuring the pH of solutions at the half neutralisation point for each stage of the dissociation of the complex ion. The concentration of the cis and trans salts was the same throughout, namely 0.00921M. The ionic strength was varied by the addition of increasing quantities of potassium nitrate. The procedure was as follows :

Amounts of cis and trans dioxalatodiaquochromiates were weighed into separate beakers. The amounts corresponded to 0.00921M. solutions of the cis and trans salts when 100 ml. of water was added to each. To all except one beaker for each series, were added varying amounts of potassium nitrate. When the pH was to be measured, 100 ml. of CO_2-free water was added to the beaker and the contents rapidly dissolved, the beaker being kept in ice. After the contents had dissolved, the required amount of alkali was added to give 0.5 or 1.5 equivalents of alkali per chromium and the pH measured (8°C.), the mean of three readings being recorded. In calculation of the ionic strength, the amount of alkali as well as the amount of potassium

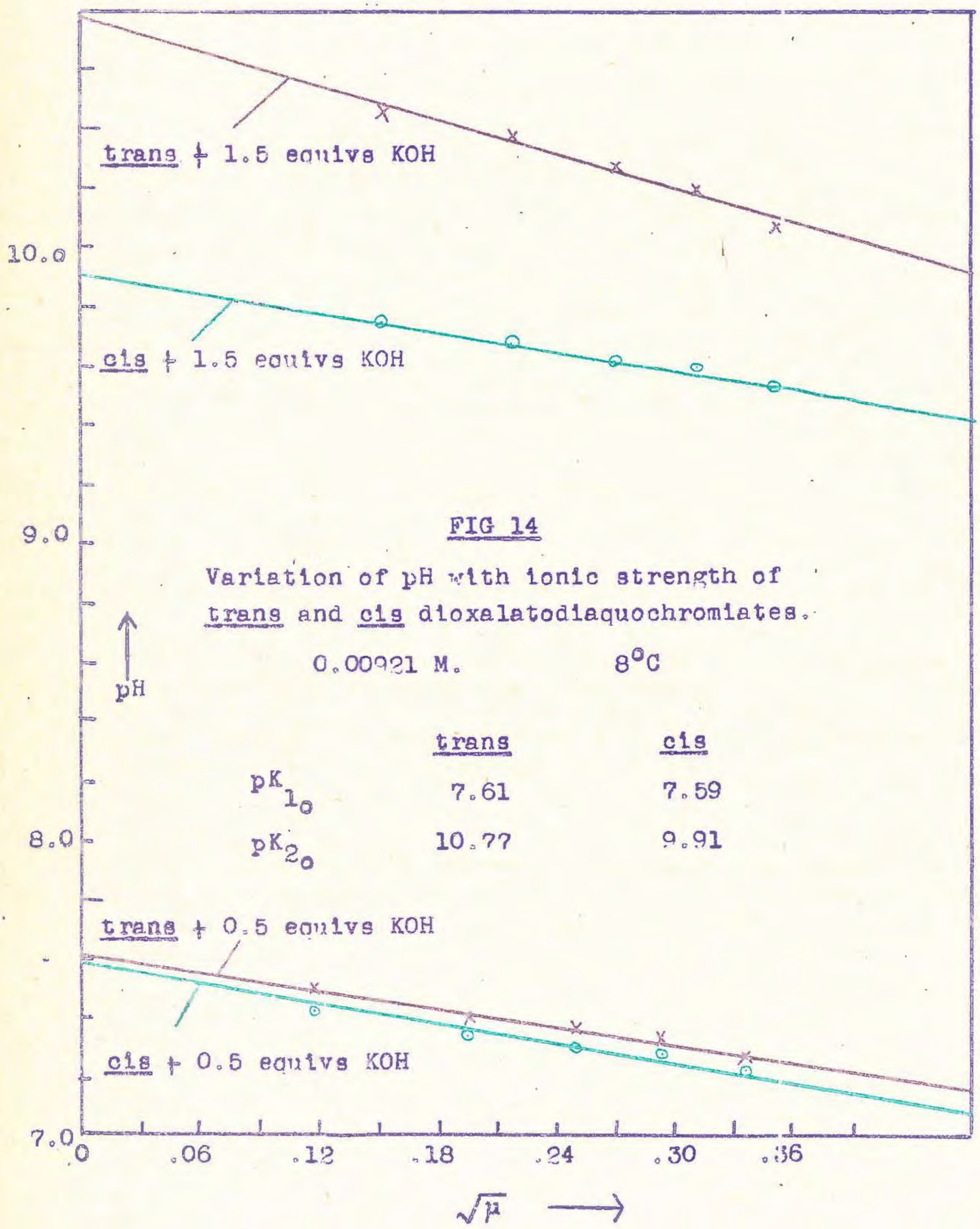

FIG 14

Variation of pH with ionic strength of trans and cis dioxalatodiaquochromiates.

0.00921 M. 8°C

	trans	cis
pK_{1_0}	7.61	7.59
pK_{2_0}	10.77	9.91

nitrate added must be taken into account. The pH values so obtained have been plotted against the square root of the ionic strength. See Fig. 14. The values of the slopes were first obtained from the data in Table A 15 of the Appendix by the method of least squares, then the lines in Fig. 14 were drawn to correspond to these slopes.

It is seen that the pK_1 values for both the cis and trans salts lie very close together whilst the pK_2 values differ considerably. The pK values do not appear to vary greatly with ionic strength and the relationship appears to be linear. The pK_1 and pK_2 values for both salts have been calculated for zero ionic strength and the values obtained are as follows :

pK^o values at $\mu = 0$ and 8°C.

	cis dioxalatodiaquochromiate	trans dioxalatodiaquochromiate
pK_1^o	7.59	7.61
pK_2^o	9.91	10.77

(e) Discussion

The table of dissociation constants above shows that the first dissociation constants of the cis and trans complex ions appear to be identical but that there is a significant difference in the second dissociation constants, which also follows from the curves of the two complex salts in Fig. 12. Now, apart from theoretical considerations, it is an experimental fact that for the simple symmetrical dibasic carboxylic acids in an homologous series, the closer the distance between the carboxyl groups, the greater is the value of Δ pK (defined as $pK_2 - pK_1$). Moreover, in these acids, it is generally the case (43) that with a decrease in the distance between the polar groups, pK_1 is lowered relatively whereas pK_2 is frequently increased in value relative to the pK value for a single carboxyl group. It is remarkable therefore that in the present system the pK_1 values should have been found to be identical, despite the difference in distance between the charges.

Bjerrum (38) has shown that the ratio of the dissociation constants of a long chain dibasic acid, corrected for the statistical factor, can be calculated in an approximate manner if due account is taken of the electrostatic interaction of the charged groups.

The statistical correction follows from the fact that in the case of a dibasic acid anion carrying a double negative charge, there are two equivalent positions for recombination with protons, while a singly charged ion has only one position.

The first and second dissociation constants, as ordinarily defined, are related to the constants K_1' and K_2' for the separate removal of the hydrogen ions by the relation (43) :

$$K_1 = K_1' + K_2'$$

$$K_2 = \frac{K_1'K_2'}{K_1' + K_2'}$$

Whence it follows that $K_1/K_2 = 4$, if no electrostatic effects are involved.

In the more general case, i.e. for a polybasic acid, the j'th dissociation constant K_j, is given by (44) :

$$K_j = \frac{(n - j + 1)}{j} \; K^o$$

Where j = 1, 2, ... n, and n is the maximum number of equivalent proton positions, while K^o is a constant.

$$\text{Accordingly} \; \frac{K_j}{K_{j+1}} = \frac{(j + 1)(n - j + 1)}{j(n - j)}$$

Thus for a dibasic acid, n = 2, j = 1.

and $K_1/K_2 = 4$.

The electrostatic effect is considered by Bjerrum (38) to be due to the attraction for the remaining protons by the free charge produced through ionisation of an acid group. In the case of dibasic acids whose carboxyl groups are fairly far apart, the ratio K_2/K_1 may be accounted for completely by the statistical effect and the electrostatic effect.

The electrostatic effect has been derived by Bjerrum (38) in an approximate manner by calculating the electrostatic interaction from a consideration of the coulombic interaction of two point charges at a distance r apart.

If for a dibasic acid $n = pK_2 - pK_1 - 0.60$, then Bjerrum showed that :

$$n = \log_{10} e^{\varepsilon^2 N/RDTr} \quad \text{..........} \quad (3.21)$$

Where ε is the charge of the electron

N is Avagadro's Number

D is the dielectric constant of water

R is the Gas constant

T is the absolute temperature

r is the distance between the charge and the hydrogen atom on the other polar group in the singly charged ion.

Two important assumptions are made in this derivation :

(i) That the value of n (the total effect of ionisation on the dissociation number) originates exclusively from the electrostatic effect.

(ii) The ordinary dielectric constant of water at the working temperature is appropriate in the calculation.

Bjerrum himself states that the calculation is only theoretically permissible when numerous water molecules are present between the charges whose mutual effect is to be derived. Some of his results show however, that empirically the procedure is permissible when the distances between the charges are only of molecular size.

A modification of Bjerrum's theory was put forward by Kirkwood and Westheimer (39) who calculated the "effective" dielectric constant D_E between the two charged positions, this value varying with the angle subtended by the points and the centre of the molecule, considered spherical. In their derivation, the dielectric constant of the molecule

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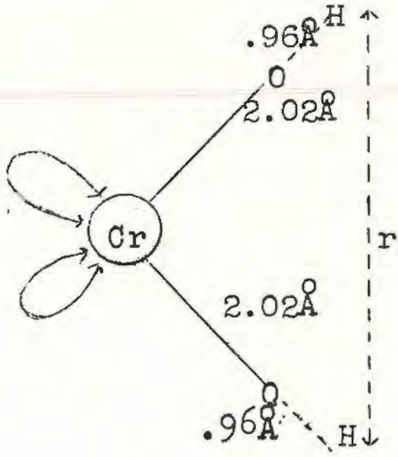
itself was taken to be 2.00, this value being considered reasonable for the aliphatic chain in a dicarboxylic acid. Since for a chromium complex ion it would not be justifiable to employ this value, and in the absence of data from which a reasonable value can be derived, the values for D_E recorded by Kirkwood and Westheimer cannot be employed in the modified equation :

$$n = \log_{10} e^{\varepsilon^2 N / R D_E T r} \quad \text{..........} \quad (3.22)$$

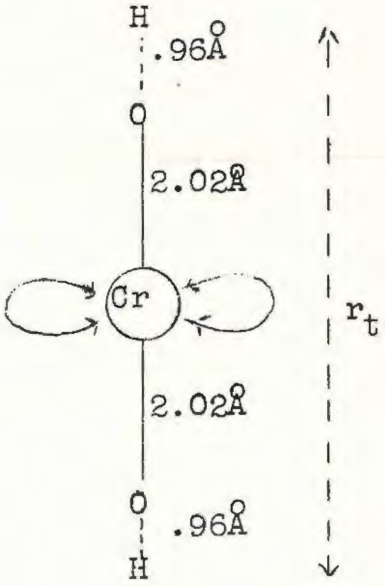
for the present case.

Nevertheless, in terms of the spatial configuration of the atoms in the trans and cis isomers, it should be at least possible to estimate the relative effective dielectric constants for the two complex ions.

Consider the cis and trans isomers of dioxalatodiaquochromiate with both complex bound water molecules ionized.



cis



trans

Following Kirkwood and Westheimer (39), the proton-oxygen bond has been shown as an extension of the bond joining the oxygen atom to the central atom. This therefore does not represent the true geometrical picture since the oxygen valencies subtend a solid angle of 105° (45) but nevertheless, bearing in mind that free rotation is possible, this simplification may be valid as a means of calculating the average interprotonic distance. The figure of 2.02 Ångstrom units for the Cr - O distance has been taken from Van Niekerk and Schoening's (24) data (See Fig. 3), and the O - H distance as 0.96 Ångstrom units (46). From the diagram the interprotonic distances r_c and r_t for the <u>cis</u> and <u>trans</u> ions respectively are calculated to be 4.14 Å and 5.96 Å. From the pK values recorded on p. 48 we have, correcting for the statistical effect :

$$n_c = \Delta pK_c - 0.6 = 1.88$$
$$n_t = \Delta pK_t - 0.6 = 2.56$$

From equation (3.22) it follows that :

$$\frac{nc}{n_t} = \frac{D_{Et}\ r_t}{D_{Ec}\ r_c}$$

Whence

$$\frac{D_{Et}}{D_{Ec}} = \frac{n_c\ r_c}{n_t\ r_t}$$

$$= \frac{1.88 \times 4.14}{2.56 \times 5.96} = 0.51$$

The effective dielectric constant when the centre of the complex chromium atom lies between the charged groups (trans complex) would thus appear to be lower than when the centre of the complex lies outside the line joining the two proton positions (cis complex).

What physical significance can be attached to this finding is a moot point since it should be borne in mind that the effective dielectric constant is only a "conventional" dielectric constant in order that the relationship may be expressed in the form of Bjerrum's original equation. Presumably the difference is due to differences in polarisability and electron resonance for the two forms, or what Bjerrum has referred to as the "rest effect". This effect appears to be so powerful that despite the further distance between the charged groups in the trans salt, their mutual interaction is greater than that in the cis complex ion.

Since further consideration would involve a detailed exposition of Kirkwood and Westheimer's method, it is not proposed to take the subject further in the present work.

7. SUMMARY.

Potentiometric titrations have been performed on solutions of the cis and trans dioxalatodiaquochromiates, mostly at $8^{o}C$. The titration curve obtained from a solution of the solid cis salt was in agreement with a similar curve obtained by ageing a solution of the trans salt, thus furnishing further proof of the composition of the solid cis salt.

The pK_2 values of the cis and trans salts were found to differ and values of pK_1^o and pK_2^o were obtained by plotting pK_1 and pK_2 values, determined at different ionic strengths, against the square root of these ionic strengths and extrapolating to infinite dilution.

The theories of Bjerrum and Kirkwood and Westheimer have been considered in relation to the ΔpK^o values obtained. The ratio of the "effective" dielectric constants, D_{Et}/D_{Ec}, for the two forms was found to be 0.51 and this result has been discussed.

CHAPTER IV.

THE POTASSIUM DIOXALATOSULPHATOAQUOCHROMIATE COMPLEX.

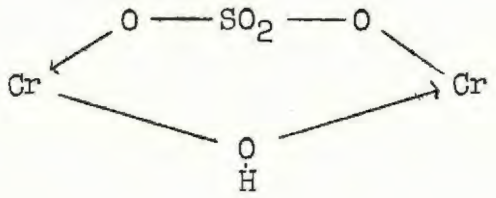
1. INTRODUCTION.

Solutions of chromium sulphate salts are used in tanning processes and a considerable number of investigations have been made on various complexes.

The colour changes undergone by chrome alum and chromic sulphate solutions were remarked upon as long ago as the end of the last century. In 1934 Atkin and Chollet (37) studied the hydrolysis of chrome alum solutions and interpreted their results in terms of Werner's coordination theory. The colour change in solutions of chrome alum from violet to green on long standing or boiling were found to be due to the penetration of free sulphate ions into the complex, where they displace water molecules and become coordinated on to the chromium atom. It was also found that an increase in concentration of the solutions led to more sulphate entering the complex after boiling, and Atkin and Chollet derived an empirical relation between the initial concentration of chrome alum and the proportions of sulphate entering the complex after boiling the solution.

Atkin (47) has also recorded the following interesting phenomenon : a commercial chrome liquor, containing excess sodium sulphate, and which yielded a heavy precipitate of benzidine sulphate when treated with benzidine hydrochloride, was diluted with saturated potassium chloride, and it was then found that no precipitate was produced on adding benzidine hydrochloride. The effect of the potassium chloride was to drive all free sulphate ions into the chromium complex, including those originally associated with the sodium ions.

Atkin (47) suggested that when sulphate enters the complex it results in a dimer :

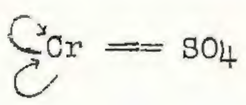


Eva Mitchell (48) concluded that in an 87% dehydrated chrome alum prepared by her, the molecular unit consists of four chromium atoms, two dimers being joined together by an olated hydroxyl group.

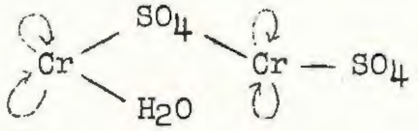
The oxalato complexes appear to be more stable than the sulphato complexes, so that investigations of the latter are more difficult especially as these olate readily (49).

Most past investigators have considered chrome alum or chrome sulphate, in which each of the six coordination positions are available for substitution by sulphate. Burley (14) considered it desirable to attempt an investigation commencing with the <u>cis</u> dioxalatodiaquochromiate, in which only two positions are available for coordination, the remaining four being blocked by oxalate. By leaving only two positions free, it might be possible to ascertain whether sulphate can coordinate using both positions, or whether only one is used, an aquo group being attached to the second.

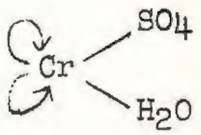
Three main configurations are possible :



(a)



(b)



(c)

In conjunction with analytical evidence it should be possible to ascertain from potentiometric data which of these forms are present, on the assumption that only the complex bound aquo groups titrate in the region pH 6 - 10. In preliminary work on this point Burley found approximately 0.8 moles. complex bound aquo groups per Cr atom.

In this chapter Burley's work has been continued and an attempt made to explain certain phenomena by analytical determinations as well as by spectrophotometric and potentiometric means.

2. PREPARATION OF THE COMPLEX.

Following Burley (14) the potassium dioxalatosulphatoaquochromiate salt was prepared by the addition of an equimolar quantity of potassium sulphate to a solution of cis dioxalatodiaquochromiate and evaporation to dryness as described on page 21. In the present work a glassy solid was also obtained but it was brittle and pulverised easily after heating at 120°C. for some hours, unlike Burley's product which was reported to be very hard.

On viewing the salt through a microscope, it was found that it consisted of solid glass-like green particles which did not appear to be crystalline. Further heating up to 170°C. caused no decrease in weight. On heating above 250°C., the powder puffed up and became light green in colour, this powder then giving a yellow solution. This heating evidently causes oxidation of the chromium to the dichromate. Chrome alum also oxidises at about this temperature. Similar results were reported by Burley.

It is considered that during the heating at 120°C., most of the dioxalatodiaquochromiate complexes have their co-ordinated water molecules displaced by sulphate. Burley reasoned that the absence of free dioxalato salt in the heated product was established by the fact that when the former is heated under similar conditions, it yields a dark green glassy solid only sparingly soluble in cold water, in contrast to the product obtained on heating in the presence of potassium sulphate, which dissolved fairly easily in cold water to give a bright green solution.

3. ANALYSIS.

Analysis for chromium and oxalate recorded by Burley led him to assign the empirical formula : $K_3\left[Cr(C_2O_4)_2(SO_4)(H_2O)\right]$ to the product.

The potassium dioxalatosulphatoaquochromiate prepared by the author did not appear to be completely stable in regard to its water content and was therefore analysed for chromium and oxalate after being dried under different conditions;

(a) Directly after drying in an air oven at 120°C. for several hours.

(b) After keeping over sulphuric acid in a desiccator for several days.

(c) After keeping over calcium chloride in a desiccator, also for several days.

Method of Drying	Experimental	Theoretical for $K_3[Cr(C_2O_4)_2(SO_4)(H_2O)]$
	% Cr	% Cr
a) Heated at 120°C.	11.40	
b) Conc. sulphuric acid	10.83	11.32
c) Calcium chloride	10.62	
	% C_2O_4	% C_2O_4
b) Conc. sulphuric acid	38.15	38.33

Since the analytical method employed leads to results for chromium which tend to be low rather than high, (see p. 24), the value obtained in (a) above appears to have some significance and suggests that under these conditions the proportion of complex bound H_2O is less than 1 mole/mole Cr. Thus a chromium content of 11.4% corresponds to 82% of the water that should be present on the basis of the formula assumed.

As will be shown later, this is in agreement with the potentiometric titration data where it appears that not

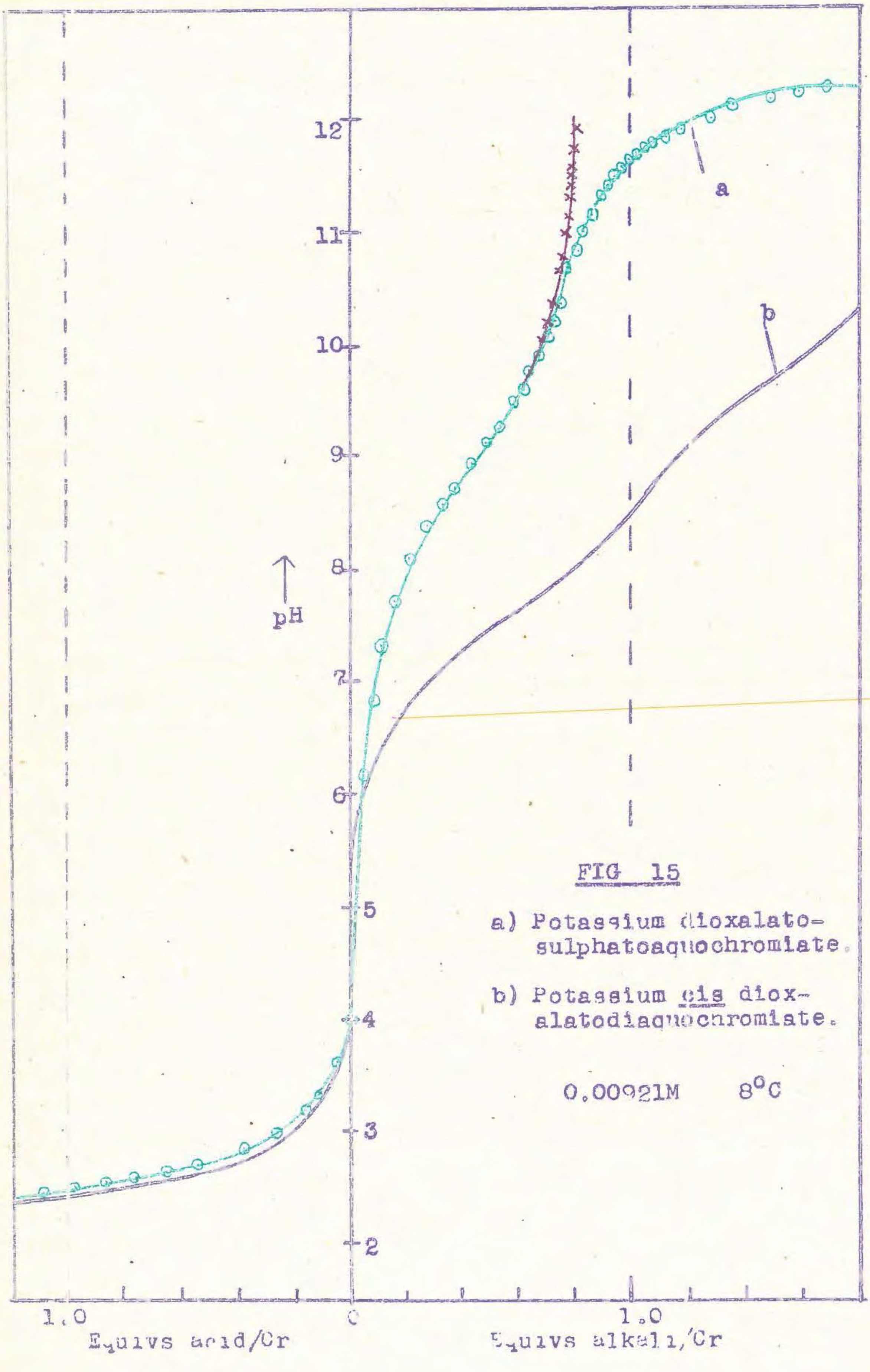


FIG 15

a) Potassium dioxalato-sulphatoaquochromiate.

b) Potassium *cis* dioxalatodiaquochromiate.

0.00921M 8°C

more than 0.8 moles of complex bound H_2O are present per mole of Cr (see Fig. 15).

4. POTENTIOMETRIC INVESTIGATIONS

In aqueous solution the dioxalatosulphatoaquochromiate salt decomposes to the dioxalatodiaquochromiate ion and free sulphate. For a titration curve to be obtained, the solution must be freshly prepared and kept at a low temperature. Fig. 15 shows the acid and alkali titration curves. There is only one end point occurring in the region of one equivalent of alkali per mole of chromium, showing there is only one titratable aquo group in the molecule. The shape of the curve is also consistent with a single acid group titrating over the range pH 6.0 - 10.5. Burley (14) obtained titration curves at different time intervals on this complex: the first curve, obtained on a fresh solution, was very similar to that shown in Fig. 15 but on increasing the time of standing prior to titration, his curves gradually approached that of the *cis* dioxalatodiaquo complex. The titration curve shown in Fig. 15 is in agreement with Burley's. It has been corrected for the blank KOH titration from Fig. 10(b). This correction shows the end of the titration to occur at 0.8 equivalents of alkali and not at one equivalent as expected; this was also observed by Burley. This suggests that the empirical formula $K_3[Cr(C_2O_4)_2(SO_4)(H_2O)]$ assigned to this complex may be incorrect and it is possible the salt is a mixture of two or more sulphate complexes giving an average value of 0.8 coordinated water molecules.

Burley concluded that there was a moderately strong acid present at low temperatures which decomposed as the temperature rose. However this acid must have been present in very small amounts as it does not show appreciably on the titration curves. The present curve is consistent with 0.05 equivalents of strong acid per chromium.

If due allowance be made for 0.05 equivalents of strong acid, there would appear to be 0.75 moles of complex bound aquo groups per mole of chromium. If, therefore, the product were homogeneous, the molecule would require not less than four chromium atoms associated with three aquo groups.

Since all the coordination positions would be occupied in a dimer, it appears that a molecule containing four chromium atoms is out of the question. Accordingly it must be concluded that the product is a mixture of at least two complex salts. Since only monomers and/or dimers can be present, the data could be accounted for in terms of structures (a), (b) and (c) on page 58. Thus one mole of (a) with three moles of (c), or alternatively one mole of (b) with two moles of (c) would yield an average composition in agreement with the analytical results. Other combinations involving all three simultaneously are possible but it does not appear to be a simple matter to distinguish between the different combinations from the data at hand. Nevertheless, the apparent constancy of composition is worthy of comment.

5. SPECTROPHOTOMETRIC STUDY OF THE DECOMPOSITION OF THE SULPHATO COMPLEX.

Burley (14) found that a solution of the dioxalatosulphatoaquo complex was unstable, decomposing with time into the dioxalatodiaquo salt and potassium sulphate. He found that over an interval, the peaks of the spectrophotometric curves of the freshly prepared solution shifted and coincided with the peaks given by the pure dioxalatodiaquo complex. By attempting to determine the progress of this decomposition quantitatively from absorption data, it was necessary to assume that the sulphato solid dissolved at low temperature to give a solution containing no dioxalatodiaquochromiate ions and that equations based on Beer's law were applicable to the solution during the decomposition. Both these assumptions are reasonable.

The percentage sulphato complex (C_s) at any instant is given by :

$$C_s = \frac{(D - D_d)}{(D_s - D_d)} .100\%$$

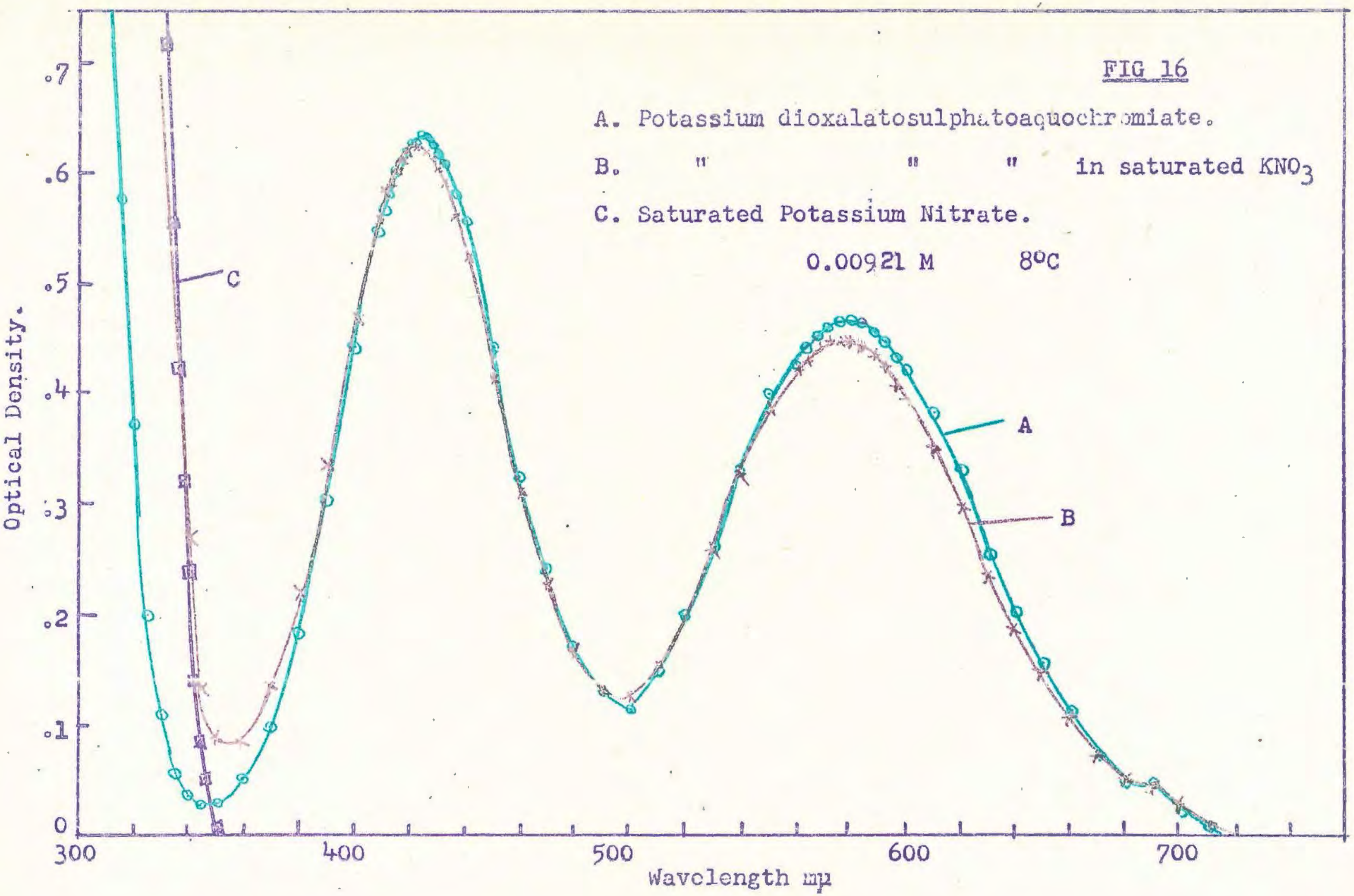
where D is the density of the decomposing solution at any instant.

D_d is the density of pure dioxalatodiaquochromiate.

D_s is the density of pure sulphato complex at low temperatures,

all these densities being measured at a fixed wavelength. By plotting the % sulphato complex present against time, Burley obtained a graph showing the rate of decomposition of the sulphato complex with time; the decomposition was

FIG 16


A. Potassium dioxalatosulphatoaquochromiate.
B. " " " in saturated KNO_3
C. Saturated Potassium Nitrate.
0.00921 M 8°C
A
B
C
Optical Density.
0
.1
.2
.3
.4
.5
.6
.7
300
400
500
600
700
Wavelength mμ

apparently not exponential.

It was decided to investigate the effect that a neutral salt such as potassium nitrate may have on the decomposition of this complex.

Firstly, a complete spectrophotometric curve was obtained from a 0.00921M. solution of the sulphato complex at about 8°C., the cold solution in the absorption cell being frequently renewed from a flask of solution kept in ice. This curve is shown in Fig. 16 curve A. It is seen that the two maxima occur at different wavelengths to the dioxalatodiaquochromiate complex.

1st maximum	424 mμ
2nd maximum	580 mμ

These are in agreement with the maxima found by Burley. A complete spectrophotometric curve was obtained on another solution of the sulphato complex of the same chromium content but almost saturated with potassium nitrate. The curve is shown as B in Fig. 16. It is seen that there is very little difference in the curves, especially at the first peak. The effect of KNO_3 appears to be to shift the curve slightly towards that of the dioxalatodiaquo complex, except below 350 mμ, where the difference between the two curves is accounted for by the effect of the nitrate ion. The curve for a pure solution of saturated potassium nitrate is shown in curve C Fig. 16. From these curves it appears that a similar product to that prepared by Burley was being investigated and that a concentrated potassium nitrate solution has

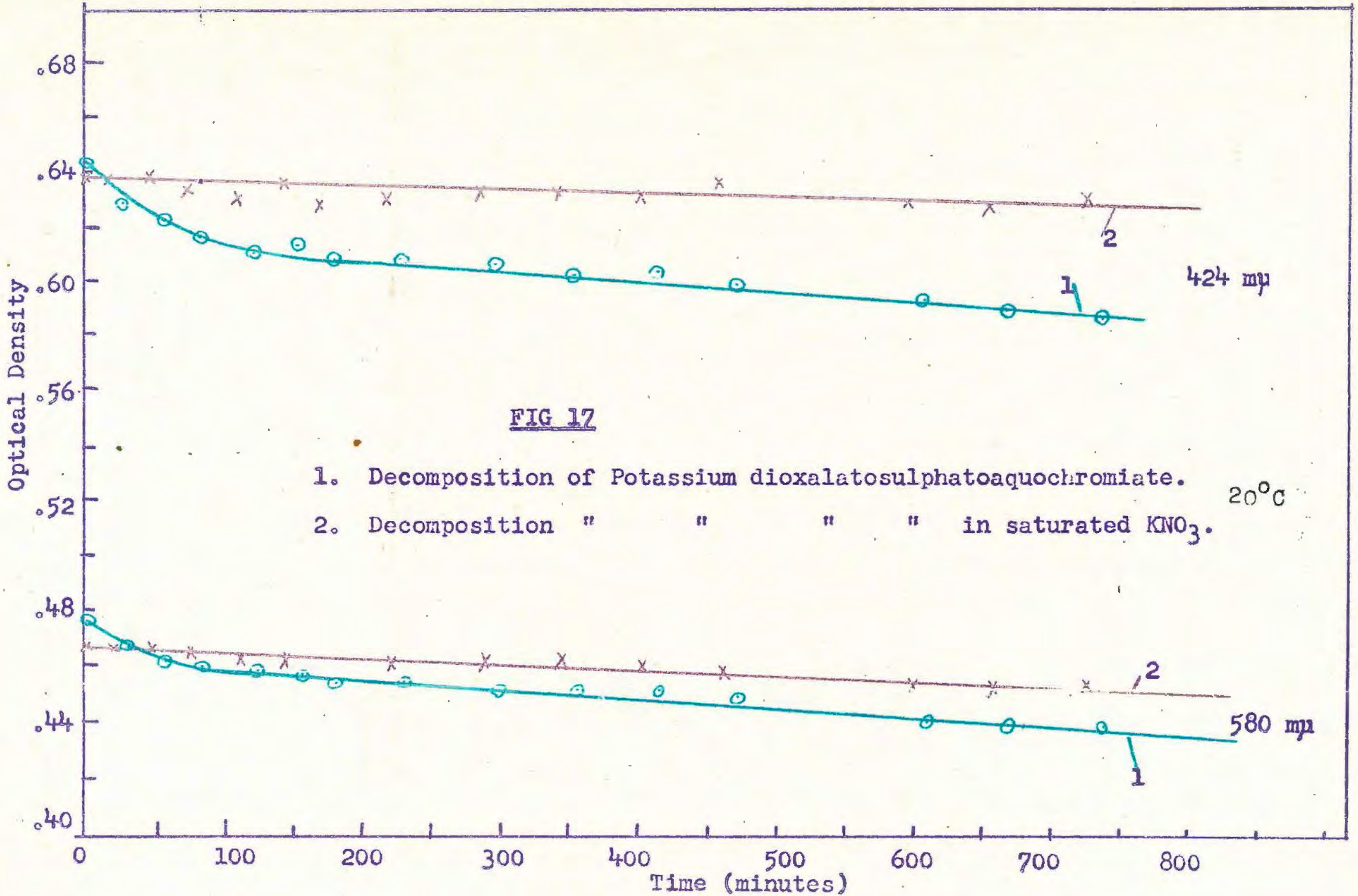


FIG 17

1. Decomposition of Potassium dioxalatosulphatoaquochromiate.

2. Decomposition " " " " in saturated KNO_3.

little effect on the maxima at 424 mμ and 580 mμ. The decomposition of the complex may therefore be measured in aqueous and in potassium nitrate solutions at these wavelengths.

The effect of the neutral salt was studied as follows :

Two solutions of 0.00921M. sulphato complex were made up, one in distilled water and the other in almost saturated potassium nitrate solution. Both these solutions were placed in a thermostat at 20°C. At various time intervals, portions of these solutions were removed and their optical densities measured at 424 and 580 mμ on the Beckman spectrophotometer. The results have been plotted in Fig. 17.

It appears from the spectrophotometric data that decomposition in the presence of KNO_3 is considerably retarded. In view of this, it was decided to investigate this decomposition further by analytical means.

6. ANALYTICAL STUDY OF THE DECOMPOSITION OF THE SULPHATO COMPLEX.

A. INTRODUCTION AND PRELIMINARY INVESTIGATION.

Burley (14), in attempting to analyse this complex for sulphate, found that the amount found present varied with the age of the solution. On making sulphate determinations at various times, he found the initial "apparent" sulphate content to be greater than the theoretical amount.

However, this SO_4 value diminished with time until a period was reached when the sulphate value was very nearly zero. After this "minimum point", the value rose again to the theoretical amount.

In view of the difficulties in accounting for this phenomenon, it was considered desirable first of all to confirm it, and secondly to ascertain the extent to which the "minimum point" is affected by external conditions. Thus, if the decomposition of the sulphato complex were to be ascribed to hydration effects, it might be expected that in concentrated salt solutions, its stability would be enhanced; if so, the "minimum point" would occur, if at all, later than in the case of the pure aqueous solution under comparable conditions.

A preliminary qualitative investigation was carried out as follows :

(a) To a series of boiling tubes 5 ml. aliquots of a freshly prepared solution of the sulphato complex were added. At specified (successive) time intervals, reckoned from the time when the solid was first dissolved, 5 ml. of benzidine hydrochloride solution was added to each of the tubes in turn and the result recorded. In the first tube a copious precipitate was formed; it was flocculent and light green in colour, unlike the characteristic colourless crystals of benzidine sulphate. With succeeding tubes the quantity of precipitate gradually diminished, till at 400 minutes the addition of benzidine hydrochloride failed to cause any precipitation whatsoever. For solutions which had been standing for periods longer than 400 minutes prior to the addition of reagent, a precipitate was again apparent, until after 800 minutes there was a bulky precipitate once more. However, the appearance of the precipitate after the "minimum point" seemed much the same as that of normal benzidine sulphate.

The sulphate derivative in solution at its "minimum point" gives no precipitate *even if some potassium sulphate is added after the benzidine hydrochloride*. Eventual precipitation only occurs when the volume of K_2SO_4 added is about three times that of the volume used initially. Potassium sulphate and benzidine hydrochloride solutions alone give an immediate precipitate as also does a mixture of solutions of dioxalatodiaquochromiate, potassium sulphate and benzidine hydrochloride.

(b) To a freshly prepared solution of the sulphato complex with some KNO_3 added, benzidine hydrochloride was added. It was found that if the potassium nitrate concentration was low (about equal to that of the sulphato complex), immediate precipitation occurred. If, however, the concentration of KNO_3 is increased to nearly saturation, no precipitate appears on the addition of benzidine hydrochloride. The precipitate produced in the presence of little or no KNO_3 can even be made to dissolve by the addition of excess nitrate. The addition of benzidine to a mixture of the sulphato complex, KNO_3 and K_2SO_4 causes no precipitation of the familiar benzidine sulphate. The above repeated with dioxalatodiaquochromiate in place of the sulphato complex did cause the precipitation of benzidine sulphate.

Burley claims that with a fresh solution at 5°C. in water alone, the addition of benzidine hydrochloride caused all of the chromium to be precipitated with the benzidine complex, leaving a clear colourless filtrate.

This result could not be confirmed in the present work, even at temperatures in the vicinity of 0°C. It was found that more chromium did come down at the lower temperatures but never at any time was the filtrate completely colourless. However, the phenomenon of the "minimum point" is remarkable in that at this stage considerable decomposition of the complex must have occurred (shown by Burley's spectrophotometric studies), and there should be considerable quantities of free sulphate present in solution.

The acid section of a potentiometric titration curve performed by Burley at the "minimum point" behaves like a mixture of potassium sulphate and dioxalatodiaquochromiate and the alkali titration shows that a large percentage of the dioxalatodiaquochromiate was titrating, although the decomposition had not gone quite to completion.

The results of the benzidine sulphate method are therefore in disagreement with the spectrophotometric and potentiometric evidence. From this evidence, it would be expected that as the solution of the complex commenced to decompose, the quantity of benzidine sulphate precipitate would gradually increase until at complete decomposition the theoretical sulphate content would be reached.

As regards the effect of potassium nitrate, it would appear that an almost saturated solution of KNO_3 not only decreases the decomposition rate of the sulphato complex, but prevents the initial formation of the benzidine sulphato chromiate complex as illustrated by the absence of a precipitate even in the initial stages.

The initial precipitate obtained when benzidine hydrochloride was added to a freshly prepared solution of the sulphato complex was seen to contain some chromium by its green colour, and its appearance was not identical with that of benzidine sulphate. When this precipitate was filtered off and the % SO_4 determined by titration with caustic soda, a sulphate value in excess of that theoretically possible was obtained (Burley). This was quite possible as the chromium contained in the precipitate would form chromium hydroxide with the NaOH, thereby increasing the titration ratio.

Analytical Determination of Sulphate.

It was proposed to analyse the decomposing solution at time intervals and so determine the following :

(i) "Apparent sulphate" present, including any chromium precipitated with the benzidine sulphate.

(ii) The percent chromium left remaining in the filtrate and

(iii) The true percent sulphate in the precipitate after any chromium present had been removed.

Before commencing these studies it was necessary to establish a suitable analytical method for the determination of sulphate in the presence of anionic chrome salts. Details of these investigations are given below :

A benzidine hydrochloride solution was prepared as follows : 15 g. of pure benzidine was added to 50 ml. of concentrated HCl and heated. When all had dissolved, the solution was made up to one litre with distilled water.

To 20 ml. of the chrome solution under test, containing about 0.1% Cr_2O_3, 20 ml. of benzidine hydrochloride solution was added and the mixture left to stand for exactly one minute. The solution was then filtered by suction using a 1½ inch diameter Buchner funnel and a Whatman No. 42 filter paper. The precipitate was washed with 10 ml. portions of distilled water, and then washed into a porcelain dish with a jet of distilled water from a wash-bottle. Any portions of the paper containing precipitate that could not be removed with a jet of water were torn off and added to the porcelain basin, the funnel also being washed out. Water was added to the precipitate in the dish and the benzidine sulphate hydrolysed by boiling. The liberated sulphuric acid was titrated with standard N/10 NaOH at the boil, phenolphthalein being used as indicator.

The solubility of benzidine sulphate and benzidine hydrochloride in hydrochloric acid solutions has been studied by Meldrum (50). The conditions here however, are well within the limits and benzidine sulphate is only very slightly soluble.

A.R. K_2SO_4 was taken and analysed for sulphate by the above method. The results are as follows :

Theoretical % SO_4	Found % SO_4
	54.73
55.1	54.69
	54.71
	54.71

These are in good agreement with Burley's analysis (54.7% SO_4) but cannot be considered completely reliable as in this standardisation no chrome was present.

A trial run of the determination of sulphate in the presence of chromium was carried out on some A.R. potassium sulphate. Amounts of K_2SO_4 were accurately weighed out into small beakers, water was added and after the solid was in solution, the sulphate was precipitated as benzidine sulphate in the usual way. After filtering, washing, and transferring the precipitate into a porcelain dish, some dioxalatodiaquochromiate was added. This was to make conditions as near as possible to the actual determination when chromium comes down with the precipitate. Excess NaOH was added, the chromium hydroxide filtered off and washed, the filtrate acidified and the sulphate reprecipitated.

K_2SO_4

Theoretical % SO_4	Found % SO_4
	53.40
55.1	53.29
	53.32
	53.33

The results are slightly low, but appear consistent. Using this method throughout, the results obtained are comparable.

The final procedure decided on was as follows :

An exact aliquot of the sulphate solution under observation was pipetted into a beaker and a similar aliquot of benzidine hydrochloride added. After standing for one minute the mixture was filtered and washed, the washings being collected together with the filtrate. The precipitate was washed into a porcelain basin as usual and titrated with standard caustic soda at the boil. The titration value at the end point was noted, giving a value for the "apparent % SO_4". Excess caustic soda was then added, ensuring the complete precipitation of any chromium as the hydroxide. After the solution had cooled, this precipitate together with the free benzidine base that came out of solution on cooling, were filtered off and the residue well washed. The filtrate was made just acid to phenolphthalein by the addition of HCl, and the SO_4 present precipitated by the addition of a fresh quantity of benzidine hydrochloride.

This second precipitation of the sulphate was filtered, washed and titrated against NaOH as before. The titration value so obtained gave the "true % SO_4" exclusive of any chromium.

The filtrate containing the unprecipitated chromium was carefully washed into a Kjeldahl flask and evaporated down to about 10 ml.The percentage chromium was determined by the usual perchloric oxidation method, extra quantities of perchloric and nitric acids being added to oxidize the benzidine hydrochloride present.

B. TIME STUDIES

A thermostat was set operating at 24.7°C. Flasks of distilled water and A.R. benzidine hydrochloride solution were suspended in the bath and allowed to equilibriate. At zero time a weighed amount of the solid sulphato complex was washed into a volumetric flask using the water at 25°C. and made up to the mark. The solution was transferred to a dry flask which was then immersed in the waterbath. At recorded intervals of time, exact portions (25 ml.) of the chrome solution were pipetted out and 25 ml. of benzidine hydrochloride solution (25°C.) added. After standing for one minute, any precipitate formed was filtered off and the sulphate and chromium determined as described above.

The above experiments were performed on a solution of potassium dioxalatosulphatoaquochromiate of strength 0.00921M. at 24.70°C. The percentage SO_4 and Cr obtained

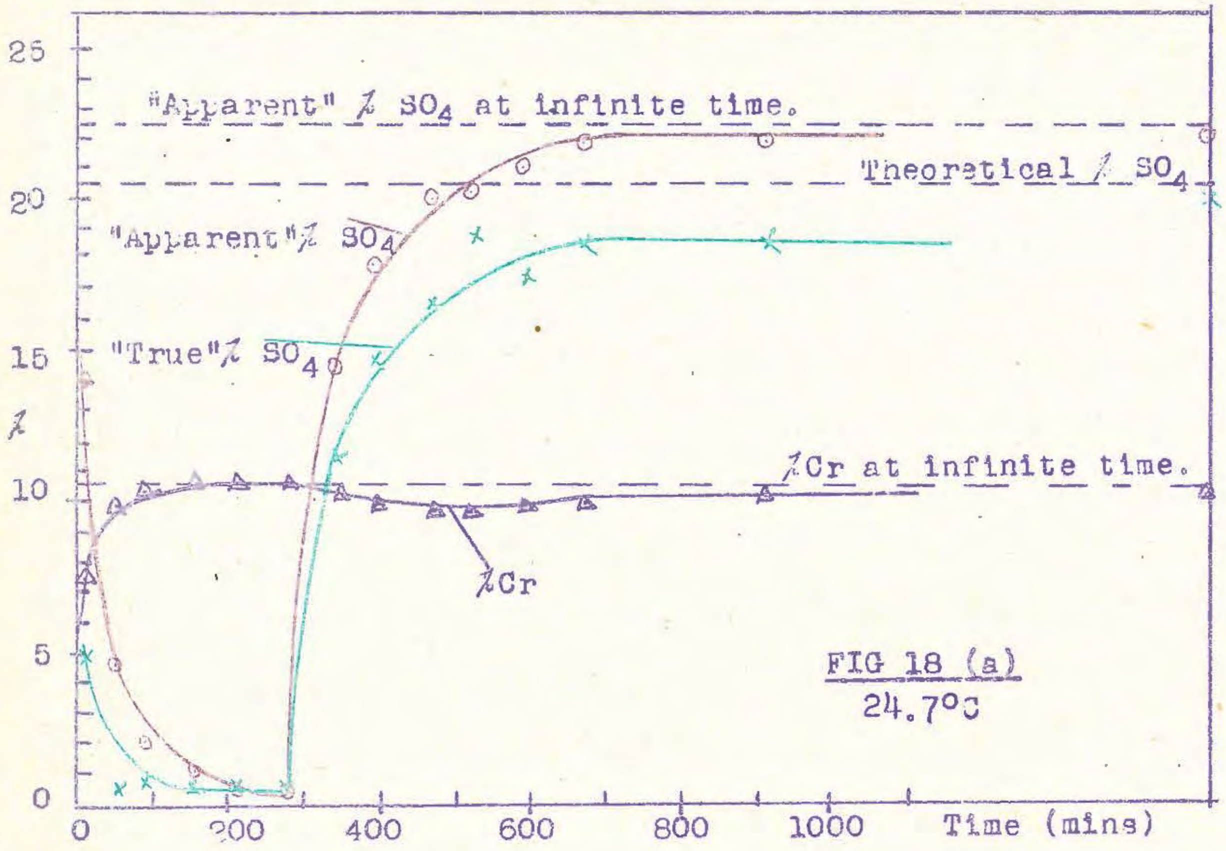


FIG 18 (a)
24.7°C

Decomposition of the Sulphate Product.

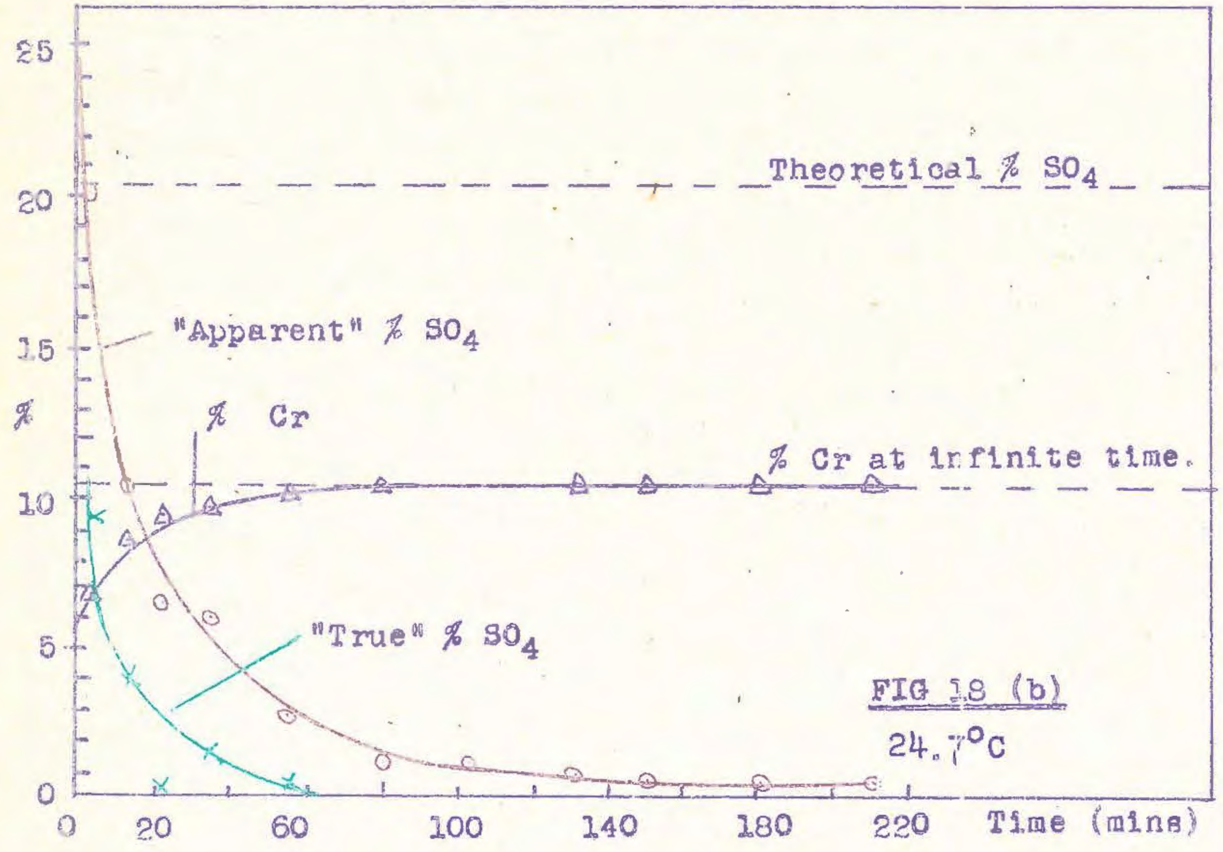


FIG 18 (b)
24.7°C

have been plotted against time and the results shown in Fig. 18 (a). In order to obtain the final analytical figures for Cr, "apparent % SO_4" and "true % SO_4", the remaining solution was allowed to stand for several days. This solution was then analysed for Cr and the sulphate values should coincide but, owing to losses in the reprecipitation, the "true % SO_4" was found to be 2% lower than the theoretical value. The theoretical value (20.9%) lies approximately midway between the "apparent" and "true" values. The higher figures for the "apparent" value at "infinite" time are most likely due to some hydrochloric acid being absorbed on the filter paper.

It is seen that, unlike Burley's results, the first sulphate determinations do not give greater values than the theoretical one, alhtough this would seem possible at lower temperatures. These first SO_4 values are not entirely due to precipitated chrome as is shown by the "true SO_4" graph. However, in view of the discrepancies between the figures at "infinite" time, too much significance cannot be attached to these differences. A definite "minimum point" occurs at about 250 minutes, no precipitate being visible when the benzidine hydrochloride was added. After the "minimum point", the sulphate content rises steeply until the values approach those given at infinite time.

It is seen that initially some chromium was present in the precipitate, the filtrate containing less chrome than was weighed out. This chrome value however, soon approaches the theoretical value and remains fairly constant thereafter.

This series of experiments was repeated on another fresh chrome solution, the intervals between readings being shorter. This was partly as a check on the preceeding results and partly to study the first part of the decomposition more closely.

The results are given in Fig. 18 (b). They are in agreement with the previous set of results and show the approach to the minimum point more clearly. The percentage "true sulphate" decreases rapidly, whilst that of the "apparent sulphate" is not so rapid. The "apparent sulphate" precipitate does not contain any chromium after about 80 minutes; after this time the sulphate value is low and is most probably due to acid being absorbed on the filter paper.

A third series of experiments were attempted on a solution of the sulphato complex made up in almost saturated potassium nitrate solution. At first no initial precipitate appeared on addition of benzidine hydrochloride but later, when a precipitate did appear, it was very bulky and unlike the previous precipitates. On filtration and washing, nearly all this precipitate dissolved. The titration ratios for "apparent sulphate" were very erratic and no reliance could be placed on them. Unfortunately the KNO_3 appeared to interfere with the analytical procedures because when a sulphate determination was carried out on "A,R." K_2SO_4 in the presence of saturated KNO_3 and some dioxalatodiaquochromiate, the following results were obtained :

Theoretical % SO_4	Found % SO_4
55.1	60.2
	68.9
	60.7

However, after each precipitation, the percentage Cr in the filtrate was determined. The KNO_3 did not interfere with the actual titration value for Cr, but caused considerable frothing and "bumping" during oxidation. The values obtained appeared to be reliable and determinations performed on the solution, after decomposing for several days, corresponded to the final values obtained for the other two series. The chromium content of the filtrate was constant throughout within the limits of experimental error. The mean value was slightly less than that obtained for total % Cr on the solution but not enough to be significant.

The following qualitative statements may be made on these determinations in the presence of saturated potassium nitrate :

(i) For a period of about 150 minutes after making up the solution there was no precipitate of any sort when benzidine hydrochloride was added to the solution.

(ii) After a period of about 150 minutes, a definite precipitate started to appear. This precipitate was not formed instantaneously, but took at least 1½ minutes to form completely. When aliquots of the solution were taken at later intervals and benzidine hydrochloride added, it was found that as the time increased, so did the quantity of precipitate increase, until after about 300 minutes, the quantity appeared much the same each time.

(iii) The titration ratios for sulphate were very near zero for the first 150 minutes, after this they increased in rather an erratic fashion. These values can be taken as an indication that after the first 150 minutes there is SO_4 present in the precipitate. This ratio is not due to precipitated Cr, as these values remain constant.

(iv) The precipitate formed had a coarse appearance and, judging by its colour, contained no Cr. This was borne out by the analytical results obtained for the Cr content of the filtrate. Although some of the precipitate appeared coarse, the distinctive benzidine sulphate precipitate was also present. On filtration and subsequent washing with cold water, some of the precipitate dissolved. It is possible that this might have been crystals of potassium nitrate or some soluble benzidine nitrate complex.

The three solutions on which the above experiments were performed were kept for several weeks and then their extinction coefficients were measured at 419 and 560 mμ. The values of the extinction coefficients were very near to those of pure dioxalatodiaquochromiate at these wavelengths, showing that complete decomposition to the dioxalatodiaquochromiate had occurred.

7. DISCUSSION

Before proceeding further, it would be as well to summarize the properties and behaviour of the sulphato derivative as obtained from the foregoing sections :

(i) On heating equimolar portions of the dioxalatodiaquochromiate complex and potassium sulphate, a product is obtained possessing properties differing from those of the original ingredients.

(ii) The product obtained is easily soluble in water, but decomposes in aqueous solution with the elimination of the sulphate ion to give the original constituents - namely, dioxalatodiaquochromiate and sulphate.

(iii) Titration and other evidence indicates that the sulphato derivative may be a mixture of complexes, each of which contains complex bound sulphate; no free sulphate ions appear to be present in the freshly prepared solution. The average proportion of complex bound aquo groups appears to be somewhat less than one (possibly 0.75 to 0.8) moles per mole of chromium.

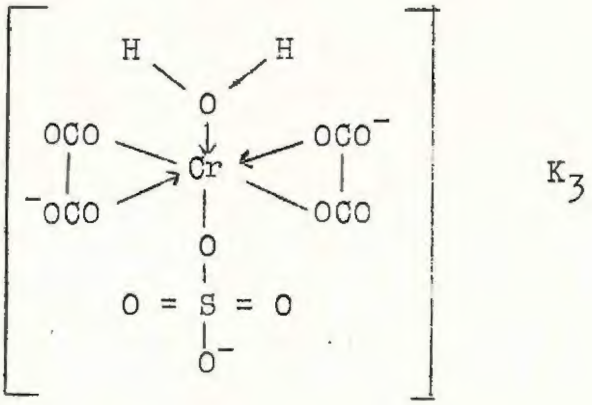
(iv) One or more of the anionic chromium complex products present in the freshly prepared solution has an insoluble benzidine salt.

(v) During ageing of the solution, the proportion of ions precipitatable by benzidine hydrochloride appears to diminish until a point is reached when no precipitate is obtained on the addition of benzidine hydrochloride reagent. Beyond this point normal benzidine sulphate is brought down free from chromium.

(vi) In the presence of a large excess of potassium nitrate, the first stage appears to be inhibited and the time at which the "minimum point" is reached is also shortened. The subsequent precipitate of benzidine sulphate is normal.

(vii) It has been established that the precipitate thrown down prior to the "minimum point" contains appreciable quantities of chromium.

From analytical data, the empirical formula of the product would appear to be close to $K_3\left[Cr(C_2O_4)_2(SO_4)(H_2O)\right]$. One complex with this formula is :

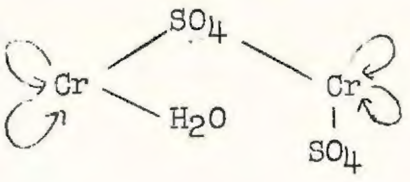


(I)

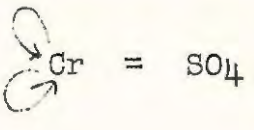
For this complex to exist, there must be evidence for the presence of a single coordinated water molecule and a sulphato group coordinated by one position only.

Evidence for a complex possessing a single aquo group acting as a weak acid, even weaker than the dioxalatodiaquochromiate, has been obtained from the potentiometric data. (Note : It appears particularly significant that the shape of this curve is that characteristic of a single acid group; note also that the approximate pK value lies midway between the pK_1 and pK_2 values pertaining to the first and second dissociation constants of the complex bound aquo groups in the dioxalatodiaquo complex ion). These data also indicate that less than one equivalent of this acid was present per Cr, Burley finding this amount to vary with temperature. The analytical figures for chromium determinations performed directly after preparation of this complex tend to confirm that only about 0.8 mole of aquo groups is present.

Other possible structures are :



and



(II)

(III)

A mixture containing 75% of (I) and 25% of (III) would give an average of .75 moles of complex bound aquo groups per chromium. It appears that even a singly bound sulphato group is rather unstable and hence compound (III) with a doubly bound group would appear to be even more unstable.

Another possibility is that the derivative consists of equal proportions of (I) and (II). The former contains one aquo group per Cr and the latter 0.5 groups per Cr. A combination of these two would give an average of 0.75 aquo groups per Cr.

Neither of these possibilities account for the observations (v) and (vi). It appears that one of the constituents present has an insoluble benzidine salt. From the phenomenon of the "minimum point", this complex possessing an insoluble benzidine salt must decompose to a further complex (x). This complex (x) gives no precipitate with benzidine and then in turn decomposes to give the dioxalatodiaquo ion and free sulphate. Two objections to the conception of complex (x) are that, in order to agree with Burley's spectrophotometric data, (x) would have to have the same spectrophotometric properties as the dioxalatodiaquochromiate ion. It should be noted also that the acid titration curve at the "minimum point" shows the presence of free sulphate ions despite the fact that a precipitate is not thrown down by benzidine hydrochloride at this point. Also, as no sulphate is precipitated at the "minimum point" even when potassium sulphate is added to the solution, the sulphate ions added would have to coordinate instantaneously to (x) to prevent precipitation. These possibilities do not seem likely. It may be considered that complex (x) exists as the structure shown by (III), giving no precipitate with benzidine and then decomposing after the minimum point. The previous two objections to (x) are still valid in this case and in addition, it seems unlikely that a single coordinated sulphate group would change over to a double coordinated one (which is less stable) and then finally liberate the doubly bound SO_4 and coordinate to singly bound water molecules to form the dioxalatodiaquo complex. It appears therefore, that the phenomenon is more likely related to the "salting-in" effect.

Recently Barnes and others (51) in studying the potential of a complex osmium cell in the presence of electrolytes, have noted that some complexes with a chelate group can be stabilised with a high concentration of electrolyte as can also the optical stability of enantiomorphous forms of the tris (1 : 10 - phenanthroline) nickel ion. These phenomena are consistent with the view that the stability of complex ions in solution is partly dependent upon electrostatic environment.

Similarly it is extremely likely that the solubility of sparingly soluble salts (in this case benzidine sulphate) is connected with the local environment.(See for example a discussion of the "salting-in effect." (52)).

Thus it might be that the absence of benzidine sulphate precipitate at the "minimum point" is due to the ionic atmosphere of the solution at this point. The effect of changing the electrical properties of the solution, as was done by the addition of excess KNO_3 is to prevent initial precipitation as well. Presumably after the "minimum point" the ionic environment has altered sufficiently to enable the sulphate to be thrown out of solution in increasing quantities.

The results of the investigations described in this section seem to confirm without doubt the results obtained by Burley and it would appear that his conclusions are essentially correct. It must be admitted however, that the latter unusual phenomenon in connection with the "minimum point" cannot be completely explained without further work on the problem.

8. SUMMARY

A dioxalatosulphato compound was prepared that corresponded analytically to $K_3[Cr(C_2O_4)_2(SO_4)(H_2O)]$. A solution of the compound was found to decompose to form dioxalatodiaquo and sulphate ions.

Potentiometric titration curves, however, indicated that the product might have been a mixture of complexes, each containing complex bound sulphate but possessing a mean 0.75 to 0.8 moles of complex bound aquo groups per mole of chromium. It also appeared that there were no free sulphate ions present in the freshly prepared solution.

A spectrophotometric curve of a freshly prepared solution of the sulphato product was obtained. It was found that the addition of large concentrations of potassium nitrate to this solution had little effect on the curve, but it decreased the decomposition rate of the sulphato product.

It was found that on allowing a solution of the sulphato product to stand, and on determining the sulphate present by the benzidine hydrochloride method at successive intervals, a considerable initial precipitate appeared, but after 200 minutes no precipitate was visible. After longer periods this precipitate reappeared. The effect of potassium nitrate was to prevent initial precipitation, and to shorten the period to the point where a precipitate again appeared. These phenomena were investigated by analytical means, the amounts of sulphate and chromium being determined at intervals during decomposition.

Attempts have been made to account for the unusual behaviour of the salt by postulating the formation of an intermediate complex, but it was inconsistent with spectrophotometric data. It is possible that the effects observed are due to the electrical properties of the solution and that the addition of potassium nitrate influences the properties sufficiently to prevent initial precipitation by benzidine hydrochloride.

CHAPTER V.

INSTRUMENTATION.

INTRODUCTION.

In working with highly coloured solutions, use may be made of colorimetric methods of investigation. Spectrophotometric curves obtained on solutions of some complex chrome ions have already been described, and further aspects of colorimetry as applied to chromium complexes are given in this section.

The relationships between the incident light falling on a coloured solution and the light transmitted by the solution are based on two elementary laws : Lambert's Law, which deals with the variation in the light absorption of a solution as the thickness is varied, and Beer's Law, which gives the relation between the absorbing power of a solution and its concentration.

Both laws are best summarised by the equation :

$$L = L_o.10^{-kcl} \quad \ldots\ldots\ldots\ldots \quad (5.1)$$

where L_o is the intensity of the incident monochromatic light and L is its intensity after passing through a solution of thickness "l" containing an absorbing substance of concentration c. k is the extinction coefficient and is constant for a given substance at a given wavelength.

L/L_o is the transmission of the solution. It is often more convenient to use the optical density (D), which is defined as :

$$D = \log_{10} L_o/L \quad \ldots\ldots\ldots\ldots \quad (5.2)$$

From (5.1)

$$D = kcl \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5.3)$$

If the transmission T is measured as a percentage,

$$D = 2-\log_{10} T \quad \ldots\ldots\ldots\ldots\ldots \quad (5.4)$$

In the kinetics to be studied in the present work, one of the essentials is to be able to work at low ionic strengths. This means a decrease in the chromium concentration. For maximum accuracy, the transmission should be in the region of 30 - 50% (53). The suitability of the Beckman Spectrophotometer for such work is discussed in the next section, but it was not found possible to use the instrument.

The design and construction of a differential photoelectric absorptiometer using barrier-layer photo-cells is described. Unfortunately certain difficulties were met with in calibration and operation of this instrument and further investigations must be carried out before it can be recommended for accurate work.

An Evelyn colorimeter using a single barrier-layer photo-cell was actually used, with some modifications, in the kinetic studies. A description of the instrument and its operation is given in section III of this chapter.

PART I.

THE BECKMAN QUARTZ SPECTROPHOTOMETER.

The Beckman Quartz Spectrophotometer model DU was used for all absorption curves given in this work.

The principle of operation of this instrument is given below :

A light source, either from a tungsten filament or an ultra-violet lamp, gives a steady beam which is reflected on to a quartz prism. By rotation of this prism, the wavelength of the emergent beam can be varied. The beam passes through a variable slit and then through a glass cell containing the test solution. The transmitted light impinges on a phototube, and the electrical changes occurring in this phototube due to the action of light are amplified. The output is balanced by a potentiometer circuit, and the potentiometer scale is graduated to give directly both the transmission of the solution and its optical density.

The electrical circuit is supplied by dry cells and a high capacity six volt accumulator; it includes variable resistances for standardising the galvonometer circuit and for adjustment of the sensitivity. "Corex" and silica absorption cells are provided for the complete range of wavelengths (230 to 1000 mμ). The cells, up to four at a time, are placed in a holder where each cell in turn can be brought into the path of the light beam. The "light path length" of each cell is recorded on that cell. The slit width regulates the width of the spectral band passing through the cells; the band width varies with wavelength owing to diffraction effects. The slit width also controls the sensitivity of the instrument.

The Beckman Spectrophotometer has widespread uses and, because it is a standard model, results are comparable. A number of reports on the instrument have been published (54)(55)(56) and it is generally agreed that, although readings on a particular instrument are almost exactly reproducible, differences of the order of 1% in the optical density reading of a given solution may be expected between different instruments. It appears generally, that greater precision is attained when the absorbance of the standard is raised. Hiskey and others (57) have compared the performance and accuracy of three commercial instruments, one of which was the Beckman model DU. They concluded that in practice the best results are obtained at maximum sensitivity and at the highest absorbance values of the reference standard which may be obtained without absorption law deviations.

Many analytical determinations have been carried out using this instrument, the determination of chromium and manganese in steel and ferroalloys (58) being one example. Details regarding this instrument and its operation may be found in a recent paper (59).

The two greatest advantages of the Beckman Spectrophotometer are its selection of monochromatic light and the stability and sensitivity of its electrical circuit. These give rise to reproducible readings and easy standardisation.

However, the absorption cells of this instrument are only 1 cm. thick and, for dilute solutions, very low transmission values are obtained. This could be overcome by using special attachments designed to provide longer light paths through the solution. As, however, the necessary attachments were not available, this instrument could not be considered for use in the previously mentioned kinetic studies.

PART II.

DIFFERENTIAL PHOTOELECTRIC ABSORPTIOMETER.

In view of the Beckman Spectrophotometer not being suitable for these particular kinetic studies, it was decided to construct a highly sensitive photoelectric absorptiometer incorporating a pair of barrier-layer photocells.

The principles and properties of photo-cells are described below and various circuits using these cells are given and discussed. The construction of the instrument is described and the results of attempted standardisations recorded.

1. BARRIER-LAYER PHOTOELECTRIC CELLS

(a) General Principles and Properties

Barrier-layer type photoelectric cells consist of an iron base plate on one side of which is deposited a thin layer of pure selenium. This layer is covered by a very thin transparent metal layer which in turn is surmounted by a metal ring. Connections are made to this ring and to the metal base plate. When light impinges on this surface, it must be able to penetrate the first transparent metallic layer. Electrons are released on the surface of the selenium by this light action and they travel across the "barrier layer" to form a negative charge on the top of the transparent metal layer. This negative charge is collected by the metallic ring. A potential is thus set up by the action of light between the collecting ring and the base plate.

The photo-cells obtained for the colorimeter were manufactured by Evans Electroselenium Ltd., Harlow, England. The general properties described apply to all selenium photo-cells, but characteristics quoted apply specifically to the "E.E.L." photo-cells, and it cannot be taken for granted that other makes of photo-cells have similar characteristics.

The output of selenium photo-cells is related to both the effective cell area and the intensity of illumination. The relationship is not linear but depends on the external load resistance. In Fig. 19 is reproduced a graph

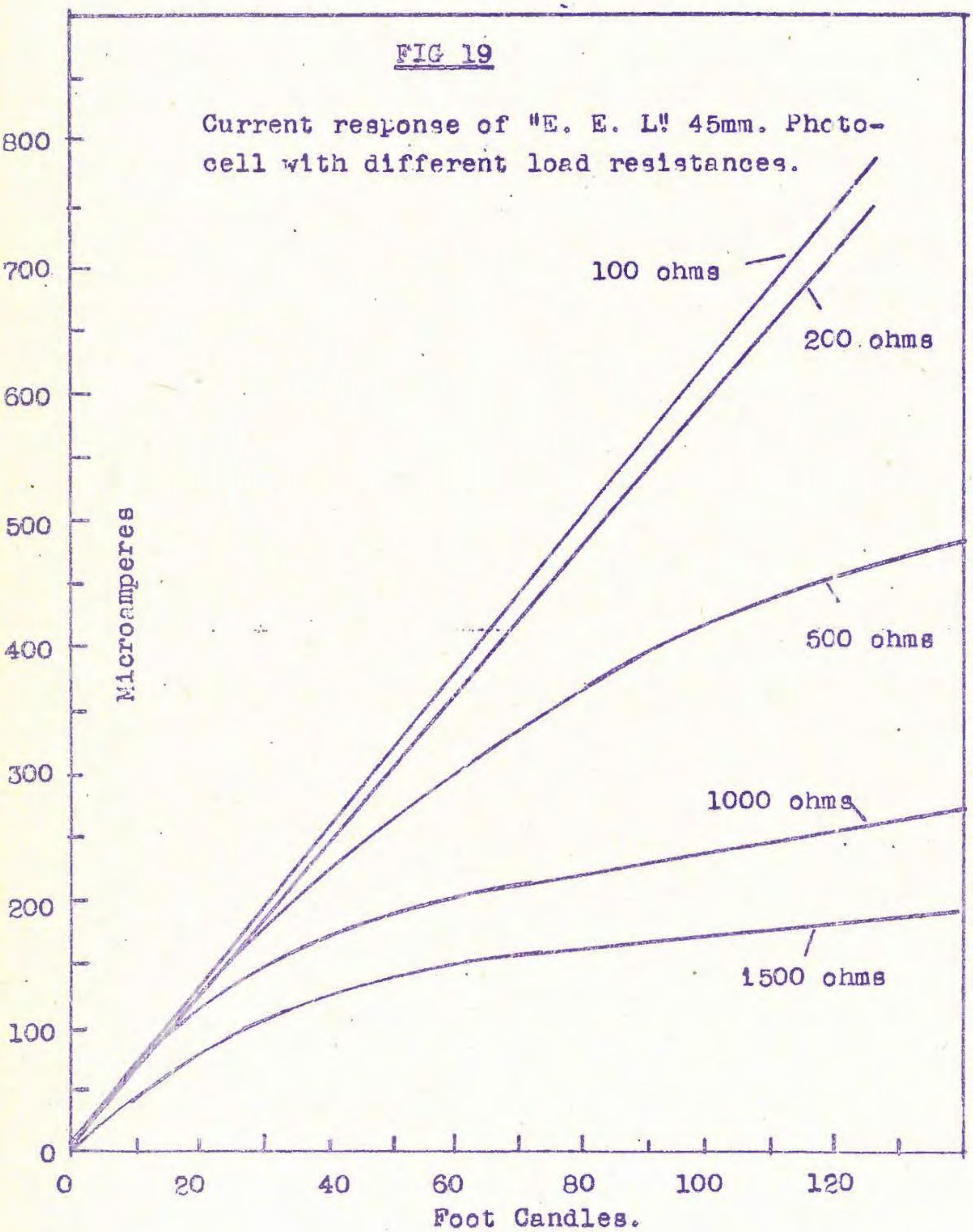


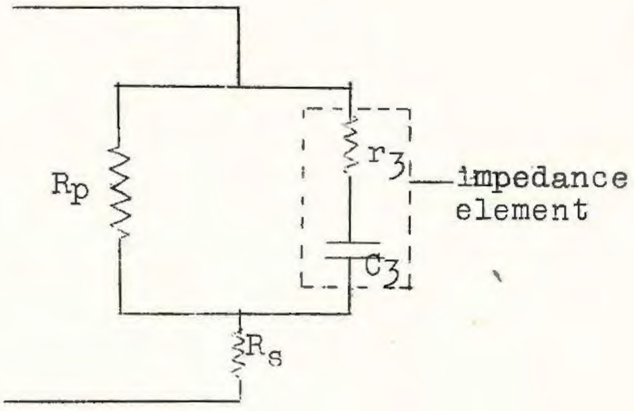
FIG 19

Current response of "E. E. L." 45mm. Photo-cell with different load resistances.

given for a 45 mm. "E.E.L." photo-cell. With 100 ohms external load, the output is almost linear at both high and low illuminations. At 200 ohms, there is linear response only up to about 150 foot-candles; at higher resistances the response is non-linear at even lower illuminations. For a smaller photo-cell, the output for the same illumination range would be less, but with like resistances linearity would extend further. Conversely, with a larger photo-cell and the same illumination/resistance conditions, non-linearity in the response curve would occur earlier.

Romain (60) has shown that the internal leakage path in the photoelectric cell may be regarded as consisting of three conductances. (i) A conductance which is constant for a given cell, (ii) a conductance which is directly proportional to the illumination of the cell, (iii) a conductance which is directly proportional to the total internal leakage current in the cell.

Wood (61) developed the equivalent circuit of a blocking-layer photo-cell. It is represented simply as follows :



Where Rp is the parallel resistance of the cell, Rs is the series resistance and r_3 and C_3 are the resistance and capacity of the impedance element. He found that the phase angle of the impedance element remained constant as the frequency was varied. Light and variable daily factors had little effect on Rs. However Rp was found to decrease under illumination, as is to be expected with selenium.

Romain observed large daily variations in Rp, presumably caused by variable factors such as temperature and humidity.

The effect of an increase in temperature is to decrease the internal resistance of the photo-cell. If the cell is kept at constant temperature, its working should not be affected, but it is inadvisable to subject the photo-cell to temperatures higher than 50°C.

Selenium photo-cells are fairly robust: as reported by the manufacturers of "E.E.L." photo-cells, a cell was shortcircuited and exposed to an illumination of 500 foot-candles for 1000 hours and, after cooling and testing, not more than 3% variation was reputed to occur. The photo-cells show fatigue effects and Wood (61) observed that recovery in the dark (or at decreased illumination) took at least 10 minutes but 80% recovery occurred in the first minute.

(b) Circuits

Single photoelectric cells are in use in a multitude of simple colorimeters, reflectometers, photometers, etc. They provide for easy manipulation and give fairly reliable results for routine measurements. However, they suffer from fatigue, temperature and other effects, and must therefore be compared against some standard before each reading. Several circuits have been put forward incorporating two of these photocells working on a differential principle.

(i) Voltage-Balancing Circuits

This type of circuit consists of two photo-cells coupled together; the two positive terminals being joined and the two negative ones joined. See Fig. 20 (a). One of these couplings is broken by the insertion of a galvonometer.

Here, the open circuit voltages are balanced by a variation in light intensity until the meter reading is zero. This simple series-opposing circuit was first used by Lange (62) and many modifications have been applied (63). Wood (64) has described and analysed this circuit. For these cells, the current output I is proportional to the intensity of the incident light L.

$$I = kL$$

where k is a constant representing the total generated current per unit light intensity.

The condition of balance will occur at equal light intensities L_1 and L_2 only if the product kRp for one cell has the same value as for the other. The Rp values for selenium cells differ widely even under the same conditions and the Rp value for a single cell shows fatigue effects and varies considerably from day to day due to temperature, humidity and other variations. At balance in this null-point method, each cell is effectively on open circuit, and the whole electron current, I, must leak back internally through Rp. The values of Rp are lowered by these high internal leakage currents and the sensitivity of balance is thereby diminished.

These variations in Rp prevent linearity in the relation between the current (Ig) through the galvonometer and the light intensity difference, $L_1 - L_2$.

(ii) Current-Balancing Circuits

This type of circuit has been analysed both by Wood (64) and Brice (65). The essential circuit is shown in Fig. 20 (b). The terminals of opposite polarity from the two cells are connected together, with the meter in parallel with the cells. At balance each cell is furnishing its full short circuit current, the currents through Rp in each cell being quite small. Variations in the value of Rp are found to have little influence on the meter current. If the load resistance (galvonometer resistance) Rg is kept small compared to Rp, the whole difference between the photo-currents I_1 and I_2 is obtained for the galvonometer current Ig and the galvonometer gives a reading proportional to the difference between the two light intensities for two

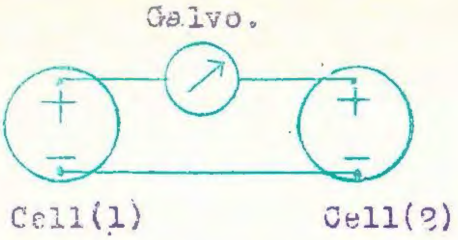


FIG. 20 (a)

Voltage-balancing Circuit

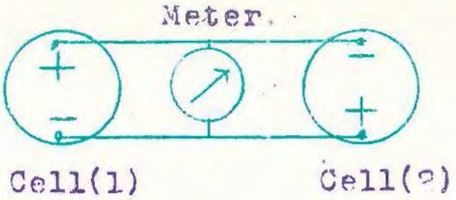


FIG. 20 (b)

Current-balancing Circuit.

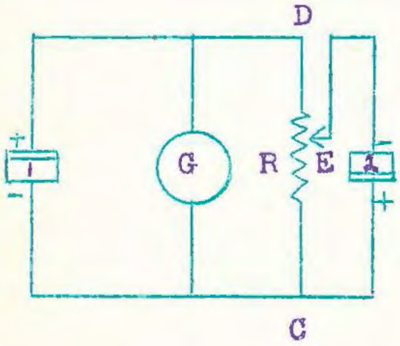


FIG. 21 (a)

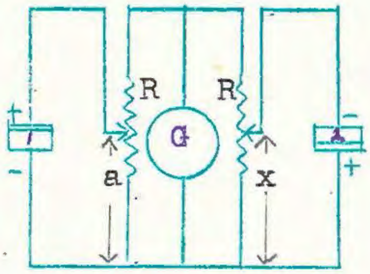


FIG. 21 (b)

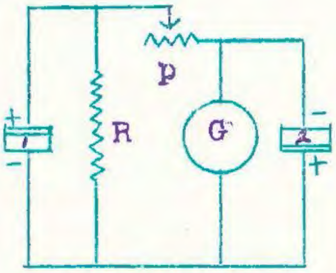


FIG. 21 (c)

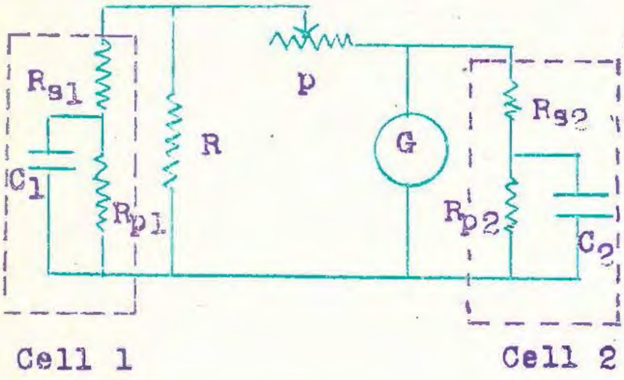


FIG. 22 (a)

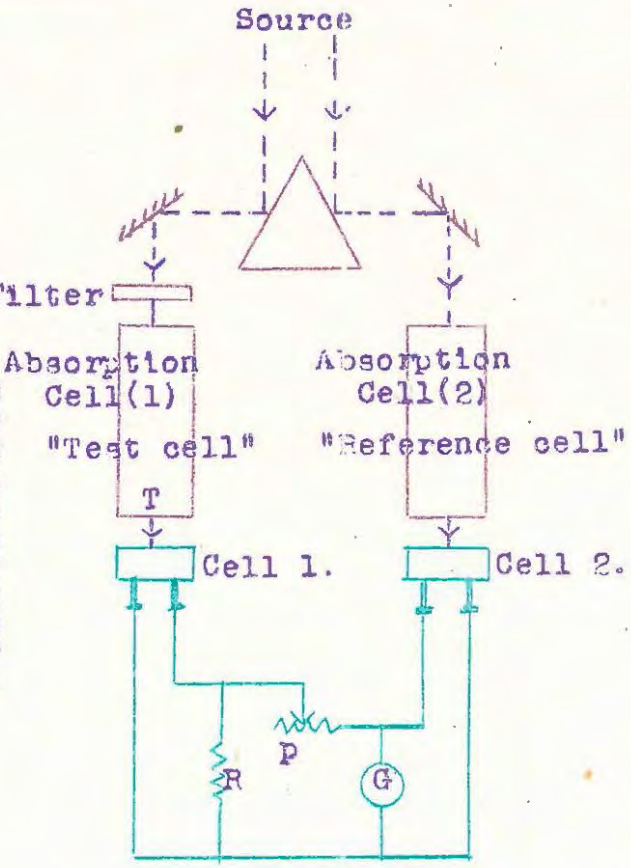


FIG 22 (b)

cells with equal values of k.

If, however, this circuit is used to give direct readings on the galvonometer scale, the conditions for compensation for source fluctuations are given only when the transmittance is unity. The circuit thus only has perfect compensation when not in use!

By using a null point balancing method, the compensating feature is retained. The circuit may be balanced either by optical compensation or by electrical compensation. The former method is used in the Speckker Absorptiometer by means of an iris diaphragm placed in the path of one of the light beams, the diaphragm being calibrated directly in units of transmission or density. The latter electrical compensation method is described and analysed in the following pages.

As a means of balancing the circuit when $L_1 \neq L_2$, resistances in the form of potential dividers may be placed across each cell. Various circuits employing these resistances are shown :- Fig. 21 (a),(b) and (c).

The circuit (a) has been fully analysed by Brice (65). The internal series resistances R_{s1} and R_{s2} of cells 1 and 2 are small compared to the internal parallel resistances R_{p1} and R_{p2}, and are practically constant. The primary electron currents I_1 and I_2 crossing the blocking-layers are believed to be exactly proportional to the intensity. The fractional part of the resistance R across cell 2 is F, where F = CE/CD. If matters are arranged so that when F = 1, i.e. the variable contact is at D, the circuit is identical to that of Wood with a shunt R across the galvonometer. If a scale reading is arranged so that when F = 1, the scale reads 100, then when F is equal to some fraction, the scale reading will represent this fraction as a percentage. On placing a sample of transmission T in the path of the light beam falling on cell 1, the galvonometer deflects and balance is restored by adjusting the value of F to give no deflection. Using a close approximation, Brice showed that :

$$T = F$$

Thus the scale will indicate transmission if the resistance of the potentiometer-rheostat is small compared to the internal parallel resistance R_{p2} of the "compensating" photo-cell 2, and if the internal series resistances of both photo-cells are small compared with their internal parallel resistances. Brice showed that the maximum relative error, $(F - T)/T$ in the scale reading F, occurs when $F = \frac{1}{2}$, and that the maximum difference or scale error $F - T$ occurs when F is approximately $2/3$.

The optimum conditions for this circuit are the use of monochromatic light and a low light intensity. When used under these conditions, the performance of this compensating circuit becomes practically independent of all the internal electrical characteristics of the blocking-layer photo-cells except the proportionality of the true primary blocking-layer current with intensity of illumination.

Circuit Fig. 21 (b) is a variation of (a) containing a potential divider across each photo-cell. It is described by Muller (66). The analysis given by Brice applies equally to this circuit. The settings of the resistances parallel to the photo-cells are given by a and x. At balance the two opposing currents through the galvonometer are equal and :

$$x = Ta$$

x, the slide wire setting, is therefore directly proportional to the transmittance. If the initial adjustment is so arranged that, when $T = 1.0$, x is set at its maximum value, R, and a is varied until balance is established, then all successive values of T will be given by x directly. When electrical balance is established, the arrangement is independent of source fluctuation.

Circuit Fig. 21 (c) is yet another variation of the current-balancing type. A fixed resistance R is placed across cell 1 and a variable resistance p is placed in series with the galvonometer. This circuit was decided on for the photoelectric absorptiometer to be built.

Circuit (c) is given in greater detail in Fig. 22 (a) and shows the electrical section in which the equivalent circuits of the two cells are enclosed in dotted lines. Fig. 22 (b) shows the diagramatic arrangement of the light source and absorption cells in relation to the photo-cells.

R_{s1} and R_{s2}, the series resistances of the photo-cells are small compared to the internal parallel resistances R_{p1} and R_{p2}. (For "E.E.L." photo-cells, R_p is about 30,000 ohms in the dark). It may also be taken that R_{p1} and R_{p2} are much greater than R and G respectively, where G is the resistance of the galvonometer.

Therefore $R_{s1} \ll R_{p1}$ and $R_{s2} \ll R_{p2}$

$R \ll R_{p1}$ and $G \ll R_{p2}$

Some of the characteristics of the circuit illustrated in Fig. 22 (a) are given in detail in the following discussion :

Let I_1 and I_2 be the currents crossing the cells 1 and 2 respectively; then the e.m.f's. E_1 and E_2 of the cells 1 and 2 are given by :

$$E_1 = I_1 \frac{R(p + G)}{R + p + G}$$

and

$$E_2 = I_2 \frac{G(R + p)}{R + p + G}$$

Let I_g' be the current passing through the galvonometer due to cell 1 (clockwise).

Let I_g'' be the current passing through the galvonometer due to cell 2 (anticlockwise).

$$I'_g = \frac{E_1}{p + G} = I_1 \cdot \frac{R}{R + p + G} \qquad \text{and}$$

$$I''_g = \frac{E_2}{G} = I_2 \cdot \frac{R + p}{R + p + G}$$

Taking the current going clockwise as being positive, the nett current through the galvonometer I_g, is given by :

$$I_g = I_g' - I_g'' = \frac{I_1 R - I_2 (R + p)}{R + p + G} \quad \ldots(5.5)$$

Now I_1, the current across cell 1, is proportional to the light intensity L_1 falling on an effective area A_1 of that cell.

Thus : $I_1 = K_1 L_1 A_1$

Similarly : $I_2 = K_2 L_2 A_2$

and : $\frac{I_2}{I_1} = \frac{K_2 L_2 A_2}{K_1 L_1 A_1} = KT$

since $T = \frac{L_2}{L_1}$

K being a constant for the two cells and
T is the transmission of the sample placed in the path of photo-cell 1.
From (5.5) therefore,

$$\frac{I_g}{I_1} = \frac{R - KT (R + p)}{R + p + G}$$

At electrical balance, $I_g = 0$

$$R = KT (R + p)$$

The transmission of a standard solution T_s placed in the path of cell 1 is therefore

$$T_s = \frac{1}{K} \cdot \frac{R}{R + p_o}$$

Where p_o is the setting of p giving balance for the standard solution.

Similarly : $T_x = \frac{1}{K} \cdot \frac{R}{R + p}$

Where T_x is the transmission of an unknown solution in place of T_s, and p is the new setting giving balance.

The Relative Transmission is given by :

$$\frac{T_x}{T_s} = \frac{R + p_o}{R + p} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5.6)$$

If matters are so arranged that

$$p_o = 0$$

Then $T_s = 1$

Equation (5.6) then simplifies to

$$T = \frac{R}{R + p} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5.7)$$

An instrument built using a pair of photo-cells as described above should be a useful and very sensitive device for measuring differences in transmission of samples of solutions placed in the path of one of the cells.

The arrangement of the light source is shown in Fig. 22 (b). A single beam is split into two equal parts, each one shining on a single cell. When electrical balance is obtained, such as during readings, the arrangement should be independent of source fluctuations. This is the case as may be seen by differentiating the expression for the nett current through the galvonometer given by equation (5.5).

If cell 1 has a sample of transmission T placed in its light path, the current I_1 given by this cell is :

$$I_1 = kTL$$

And for cell 2 with no sample placed in its light path,

$$I_2 = kL$$

Where k is a constant, and L is the source intensity.

From equation (5.5) :

$$I_g = \frac{kLR - kLT\ (R + p)}{R + p + G}$$

Let

$$C = k/R + p + G$$

$$\therefore I_g = CLR - CLT\ (R + p)$$

$$\therefore \frac{dI_g}{dL} = CR - CT\ (R + p)$$

for

$$\frac{dI_g}{dL} = 0$$

$$R = T\ (R + p)$$

or

$$T = \frac{R}{R + p} \qquad \ldots\ldots\ldots\ldots (5.8)$$

Therefore, any fluctuations due to variations in the light source are at a minimum when $T = R/R + p$, and this is precisely the condition when electrical balance is obtained during a measurement.

It is of interest at this point to calculate the relative error in T.

Considering the original circuit;

From equation (5.5) :

$$I_g = I_1 . \frac{R}{R + p + G} - I_2 . \frac{R}{R + p + G}$$

At balance when $I_g = 0$

$$T = \frac{I_2}{I_1} = \frac{R}{R + p_o}$$

Where p_o is the setting of p at balance with the sample of transmission T in place.

At any other setting of p ($p \approx p_o$)

$$\begin{aligned} I_g &= I_1 \left[\frac{R}{R + p + G} - T . \frac{R + p}{R + p + G} \right] \\ &= I_1 \left[\frac{R}{R + p + G} - \frac{R}{R + p_o} . \frac{R + p}{R + p + G} \right] \\ &= \frac{I_1 R}{R + p + G} \left[1 - \frac{R + p}{R + p_o} \right] \\ &= \frac{I_1 R}{R + p + G} . \frac{(p_o - p)}{R + p_o} \end{aligned}$$

If $\frac{p_o - p}{R + p_o}$ is small, we can write this as $\frac{\partial p}{R + p_o}$

But at balance, since $T = \frac{R}{R + p_o}$

Whence :
$$-\frac{\partial T}{T} = \frac{\delta p}{R + p_o}$$

Hence :
$$-I_g = \frac{I_1 R}{R + p + G} \cdot \frac{dT}{T}$$

or
$$\frac{-dT}{T} = \frac{(R + p + G)}{R} \cdot \frac{I_g}{I_1}$$

If the smallest detectable deflection on the galvonometer scale is x mm. and the sensitivity of the galvonometer is σ μA/mm.

$$I_g = \sigma x$$

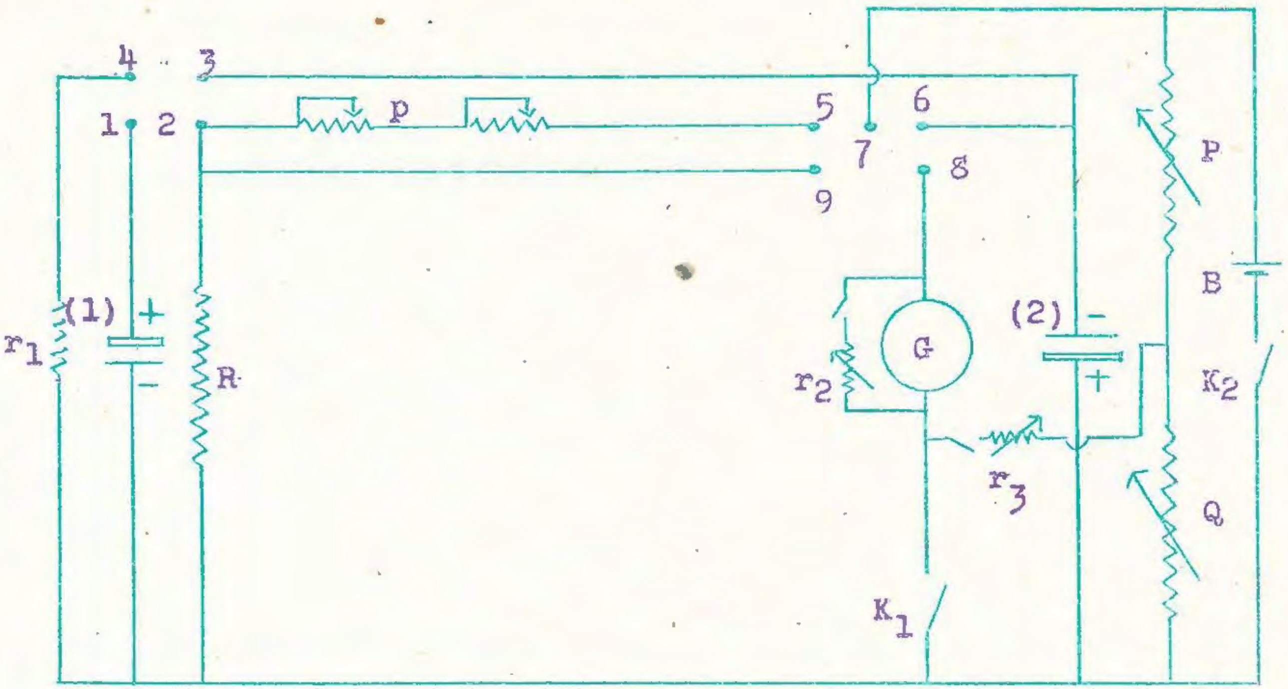
Whence :
$$\frac{-dT}{T} = \frac{R + p + G}{R + I_1} \sigma x$$
$$= \frac{\sigma x}{I_1} \left[\frac{1}{T} + \frac{G}{R} \right] \quad \ldots\ldots\ldots (5.9)$$

Hence G σ must be as small as possible relative to R in order to minimise the relative error in T at any given balance position.

2. DIFFERENTIAL PHOTOELECTRIC ABSORPTIOMETER

(a) Electrical Circuit

A photoelectric absorptiometer built on the design shown in Fig. 21 (c) must have the values of R and p known fairly accurately. For good reproducability, p should be an accurately wound rheostat with good contacts. An ordinary variable resistance may be used, however, pro-



Cell Circuit (Switch in "Cells In" position).
Contacts: 1 - 2; 5 -6 - 8.

Bridge Circuit (Switch in "Batteries In")
Contacts: 1-3-4; 5-7; 8-9.

K_1 Galvonometer Key.
K_2 Battery Key.
P Decade Resistance Box.
Q Resistance Box.
R 185.5 ohms.
p 500 ohm variable resistance.
(1)&(2) Photoelectric Selenium Cells.
G Galvonometer.
r_1 12 ohms.
r_2 5000 ohms.
r_3 5000 ohms.
B 2 volt accumulator.

FIG. 23

Electrical Circuit of Differential Photoelectric Absorptiometer.

vided that at any setting its resistance can be measured, the contact resistances being included in this measurement.

The incorporation of a Wheatstone Bridge circuit, with R and p forming two of its arms, into the photo-cell circuit enables the value of p to be measured at any setting.

The full circuit is shown in Fig. 23. The resistances R, p, P and Q form the four arms of the Wheatstone bridge. On making electrical contact between the points 1 - 2, and 5 - 6 - 8, the circuit reverts back to the original shown in Fig. 21(c). When the above contacts are broken, and the following made : 1 - 3 - 4; 5 - 7; 8 - 9, and the galvonometer series resistance is switched in, the Wheatstone Bridge circuit comes into operation.

Contact between points 1, 3 and 4 is necessary in order to short the photo-cells to earth potential through the low resistance r_1. A shunt was placed across the galvonometer to protect it during balancing of the circuit; at final balance it was switched out of circuit. A series galvonometer resistance was necessary to make contact from the galvonometer to the join of P and Q when using the bridge circuit; the resistance was cut down to zero for final balancing.

This circuit enables the photo-cells to be balanced by an electrical null-point method and the value of the resistance required to bring about balance can then be determined by a switch over to the bridge circuit.

The construction of this instrument and the components used will now be described.

The electrical section apart from the photo-cells, was mounted in a box with a dial panel. The variable resistance p was divided into two sections, one coarse and one fine. The former was a 500 ohm radio rheostat fitted with a graduated "Perspex" dial and the latter consisted of a vulcanite disc whose periphery was grooved to hold a resistance wire. The dimensions were so chosen that when mounted, the arc of movement constituted a resistance of 1 ohm; a "Perspex" dial, divided into 100 equal parts, was mounted on this disc.

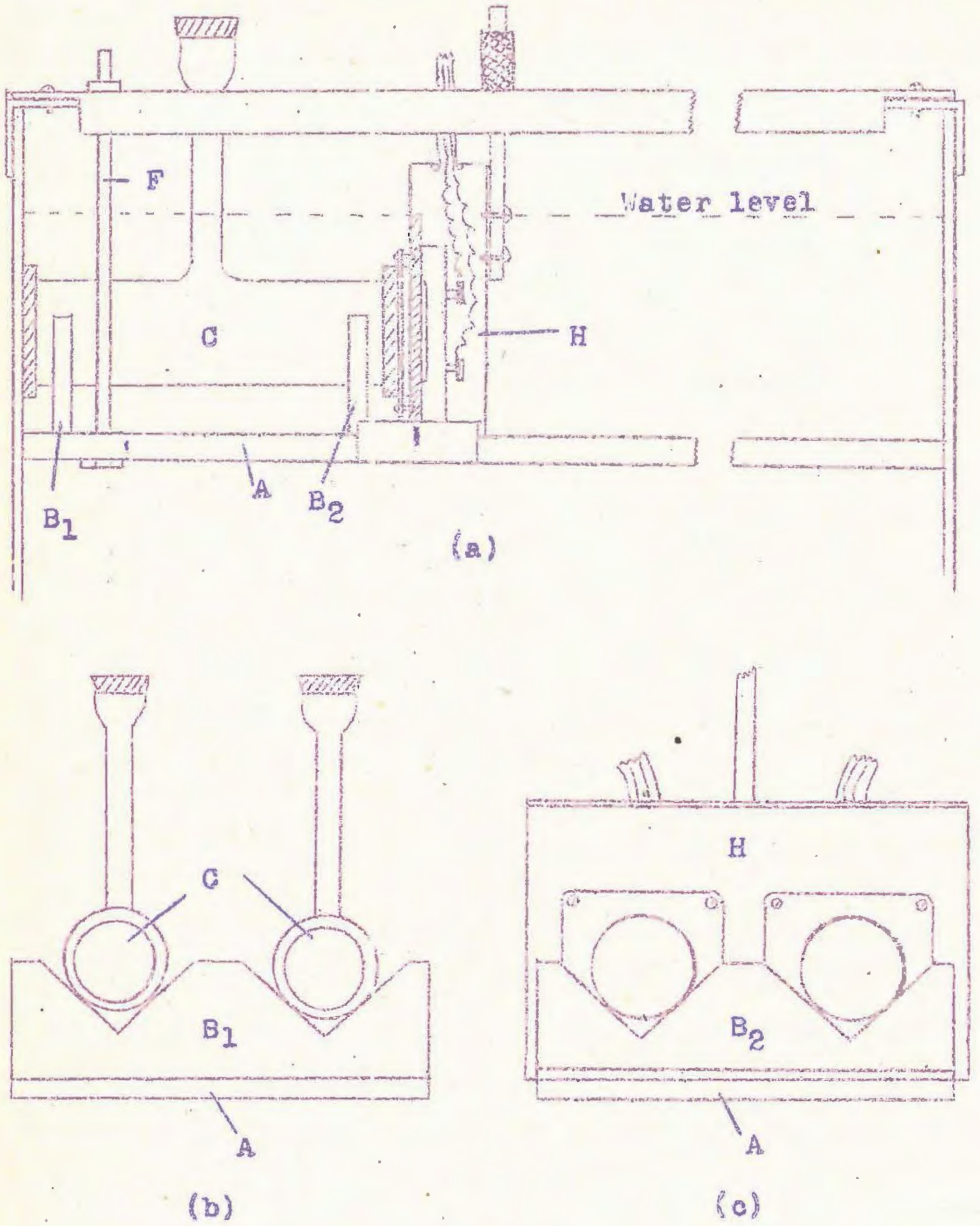
R consisted of two 100 ohm variable porcelain radio resistors joined in series. P was a "Cambridge Instrument Co." low inductance decade resistance box of range 0.1 to 10,000 ohms. A "Leeds and Northrup" shunt of total resistance 10,000 ohms was used as Q having contacts giving 1, .1, .01, .001, and .0001 fractions of the total resistance.

To change the circuit from the photo-cell arrangement to the bridge one, several contacts must be made and broken. Using separate switches for each contact is inconvenient and risks damaging the galvonometer and photocells. Mercury switches were devised that changed all the necessary contacts in one movement. These switches were made by blowing three glass envelopes, sealing nine platinum contacts into the glass, and adding clean mercury before sealing. They were attached to a frame whose position could be moved by a lever, this lever constituting the main switch. The platinum contacts were soldered to a series of copper rivets; long flexible leads led from the rivets to a fixed terminal bank from which lead stouter wires to the other components. These flexible leads were necessary due to the large arc of swing of the mercury switch.

The remainder of the circuit was wired using heavy 10 gauge copper wire, rosin-cored solder being used throughout. External connections to the photo-cells and resistance boxes were made through thumb terminals.

A box-type galvonometer was employed; its nominal sensitivity was 0.0069 microamps. per mm., its resistance was 1,203 ohms and its period was a short one of 2.4 seconds. This resistance was high for the type of circuit used. In the section dealing with the calculation of the relative error in T (page 102), it is seen that G must be as small as possible relative to R. Unfortunately no short period galvonometer of low resistance was available, so the one described above had to be used. The pointer in this galvonometer was a light spot shining on a ground glass scale fitted to the housing.

In order to increase the sensitivity of this galvonometer, the ground glass scale was removed and the light spot refocussed on a longer scale placed 2 metres from the position of the original one. This scale was 50 cms. long as compared to the original 10 cm. scale, and the sensitivity of the galvonometer was thereby increased



(a)

(b)

(c)

FIG. 24

(a) Plan.
(b) Section through B_1
(c) Section through B_2

A Supporting platform.
B_1 & B_2 Cell supports.
C Absorption cells.
H Photo-cell housing.
F Supporting rods.

DIFFERENTIAL PHOTOELECTRIC ABSORPTIOMETER to 0.00138 microamps. per mm.

(b) General Arrangement

The general layout of the instrument embodies the same principles as are used in most colorimeters; namely : a light source, a light filter, absorption cells, and photoelectric cells as shown in Fig. 22 (b). Both absorption cells and photocells were kept at constant temperature by immersion in a water-bath. By allowing the reaction to take place in one of the absorption cells, and filling the other with some standard, continuous readings may be taken without removing and cooling any samples.

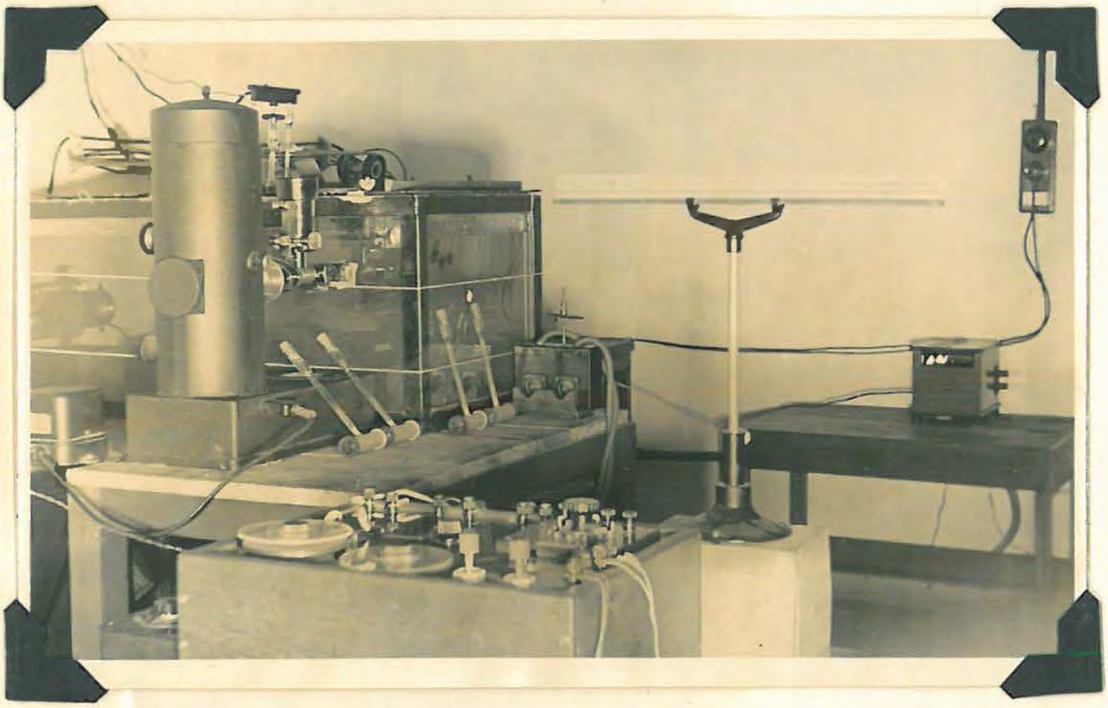
A general view of the arrangement is given in Fig. 24. The method of supporting the absorption cells and photo-cell housing in the water was to suspend a platform (A) in the thermostat. Attached to the platform was a V-block (B_1) which supported one end of the absorption cells (C), the other end of the cells being supported by a second V-block (B_2) attached to the photo-cell housing (H). This housing was a separate unit containing the photo-cells and could be made to run freely along the length of platform A, and could also be clamped in any position along it. The platform fitted exactly across the inside of the tank and was suspended by four rigid brass rods (F). The levelling of the platform was adjusted by nuts on the ends of the brass rods.

The distance apart of the two V-cuts in each of the blocks B_1 and B_2, the distance apart of the centres of the photo-cells and that of the two emergent light beams, were all made to correspond.

The light source chosen was a 100 watt bulb fitted into a Zeiss Ultraphot and giving an intense parallel beam. A binocular combination was placed in the path of the emergent beam, splitting the beam into two parallel ones, the distance apart of which could be adjusted over a small range so as to shine directly on the centres of the two photo-cells mounted side by side. The two emergent beams were not quite of the same intensity; this was rectified by placing an iris diaphragm in the path of the stronger beam. The diaphragm also enabled the instrument to be balanced at any electrical setting, thereby altering its range. A light filter was placed in the path of the beam that passed through the sample solution.

Absorption Cells and Photo-cells

In measuring the transmittancies of very dilute solutions, the light paths through these solutions should be made fairly long, enabling transmission readings of about 40% to be obtained. Longer light paths were obtained by making special absorption cells. These were constructed from one inch diameter soda glass tubing; 10 cm. lengths of this tubing were cut and the ends ground smooth and level. A side arm was attached midway along the length of the tube. Plane soda glass ends for the cells were made by grinding 1 in. discs out of a photographic plate. The discs were



Differential Photoelectric Absorptiometer
with Absorption Cells and Photo-cell
Housing Removed from Water Bath.

cemented to the cell ends using Dow Corning 2103 Silicone Resin by heating to about 250°C., under pressure. This resin had good bonding properties at first, but after ageing, these properties decreased somewhat and occasionally end discs had to be re-cemented in position. The external surfaces of the cells were silvered, except for the end discs, and the silver protected with aluminium paint. Protective rubber rings were placed over the ends of each cell, projecting $\frac{1}{4}$ inch beyond each end.

The most convenient arrangement was to shine the light beams through the glass-walled thermostat, the light then passing through the absorption cells placed in the thermostat, and finally impinging on the photo-cells. The photo-cells can either be placed directly behind the absorption cells, or outside the tank on the opposite side to the light source. Owing to the width of the glass tank obtained, the latter alternative involves the passage of the light beams through a considerable depth of water after emerging from the absorption cells. The divergence of the beams over this depth of water and the likelihood of the water becoming easily dirtied, make the first alternative preferable. A brass housing was therefore constructed for the photo-cells so they could be mounted directly behind the absorption cells in the thermostat. A separate window in the housing was provided for each photo-cell and these cells were clamped against the windows with a circle of sponge rubber in between acting as a cushion. The leads from the photo-cells were encased in rubber tubing to protect them from moisture.

Thermostatic Control

The waterbath used was a plate glass aquarium tank of 35 gallons capacity. The water was circulated by a paddle wheel and heated by two 1000 watt immersion heaters.

Temperature control was effected by a toluene-mercury thermo-regulator fitted with a "Sunvic" proportioning head and which controlled a "Sunvic" type E.A.2.T. electronic relay. One of the heaters was operated off this relay and it was sufficient to maintain the temperature constant up to values of 40°C. For higher temperatures, the second heater, coupled through an energy regulator, was used in conjunction with the first one. The energy regulator was adjusted to maintain the average temperature of the bath a few degrees lower than the temperature actually required, and the necessary heat for the remaining few degrees was given by the heater operated through the thermo-regulator. A change in the setting of the energy regulator results solely in a change of ratio of time "on" to time "off" and this ratio determines the ambient temperature of the water bath. The regulator, working on a definite cycle, is independent of the cycle set up by the electronic relay, but generally the two regulators settle down to an out of phase movement. Even when both start heating together, there is no noticeable extra temperature variation due to the fact that the periods of heating are relatively short and the capacity of the water bath is large.

The temperature was maintained constant to within ± 0.05°C. for temperatures above 50°C and better control, ± 0.03°C., for temperatures below 50°C.

(c) Operation of the Photoelectric Absorptiometer.

R, the fixed resistance in the electrical circuit must be known accurately before any readings can be taken. It was found possible to measure this resistance as it stood in the circuit without having to remove it. This is an advantage as any resistances due to connections and soldering are included in the value obtained. Connections were made as follows :

The main switch was placed in the "Cells In" position; i.e. the contacts being made to bring the photo-cell circuit into operation. The resistance P remained in position but a lead was taken from one of the contacts of P to one of the galvonometer contacts. Neither photo-cell was connected but across the terminals leading to cell 1 was placed a resistance S, together with a switch to bring it in or out of circuit. The battery was not connected to its usual terminals, but placed between one of the connections to S and the contact on Q common to P. By making these alterations, the circuit in Fig 24a) is completed. This constitutes a Wheatstone Bridge Circuit, the Resistance R (with which S can be connected in parallel) forming the unknown arm.

The procedure was as follows :

Q was set to a convenient value and then p was placed on a selected setting. S consisted of a resistance box and its resistance was made to correspond with the value chosen for p. The bridge circuit was balanced by adjusting the value of the decade box P to give no galvonometer deflection. This value of P was recorded. The shunt S was then switched out of circuit and, with the setting of p and Q remaining as before, P was adjusted to give a new value for balance.

If Pi is the decade box reading for balance when S is in circuit,

and Po is the decade box reading for balance when S is out of circuit,

then R is given by : $$R = \frac{Pi - Po}{Po} . S$$

Readings of Pi and Po were taken for each setting of p and S, and R calculated in each case, the reading being recorded in Table A 16 of the Appendix. The mean value for R was found to be 185.50 ohms.

It is seen from the readings that poor values of R were obtained for low dial settings. It appears that the rheostat is rather inaccurate at these low resistances and in later work low values of p were avoided. One explanation is that when there is only a short section of resistance wire in the circuit, the heating effects are much more noticeable.

R having been determined, the circuit was again connected in the usual manner.

Some precautions taken before any readings were made are given below:

The absorption cells were filled with distilled water, placed in the thermostat and allowed an hour to attain the working temperature. The photo-cells, in their housing, were always placed in position in the thermostat 24 hours before any measurements were made. The flasks containing the various standard solutions and mixtures were immersed in the water bath for several hours before they were required. When a reading was to be taken on a solution, the water was emptied from the absorption cell and the cell rinsed out three times before being finally filled with the solution. Care was taken to ensure there were no bubbles trapped in the absorption cell and the cell was always filled completely and corked. This prevents condensation at the top of the side arm, which alters the concentration.

Solutions placed in the absorption cells must be at the working temperature, as otherwise small air bubbles form inside the cells and an expanding solution is liable to break the corked absorption cell.

In spite of the precautions taken in the filling of the cells, after standing for some hours in the waterbath, a few small bubbles often did appear.

At intervals during readings, the cell windows and photo-cell housing windows were carefully cleaned with tissue for, in spite of every effort made to keep the water in the bath clean, small deposits were formed on the cell windows after several hours.

The actual operation of the instrument is described below; the term "Reference cell" applies to the absorption cell containing the standard solution, and "Test cell" to the one containing the reacting solution.

The two cells, having been filled with their respective solutions, balance is obtained thus : The main switch is set to the "Cells In" position, the galvonometer shunt is set to minimum sensitivity, and the galvonometer series resistance switched out of circuit. The galvonometer key is depressed and the light spot of the galvonometer brought to its zero position on the scale by adjustment of p. The galvonometer shunt is switched out of circuit, thereby giving maximum sensitivity, and final balance obtained with p. If for this standardisation a certain setting of p is required, then p is set on this value, the galvonometer key depressed, and the spot brought to zero by adjusting the iris diaphragm.

To take a reading on a solution under investigation, the test cell is filled with this solution and replaced in position. Balance is obtained as described above by adjusting p. To measure this value on the Wheatstone Bridge Circuit, the setting of p is left unchanged, and the switch set to the "Batteries In" position. The galvonometer shunt is set to minimum sensitivity, and the galvonometer series resistance is switched into the circuit and set to its maximum resistance; Q is set at a convenient ratio, the Battery key is depressed and P, the decade resistance box,

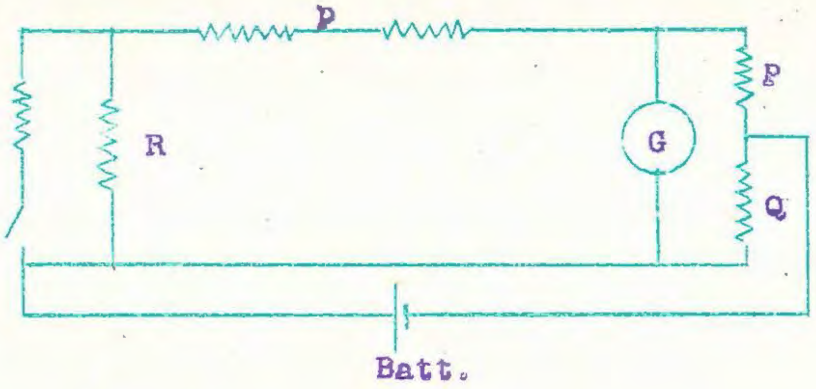


FIG 24 (a)

Circuit for the Determination of R

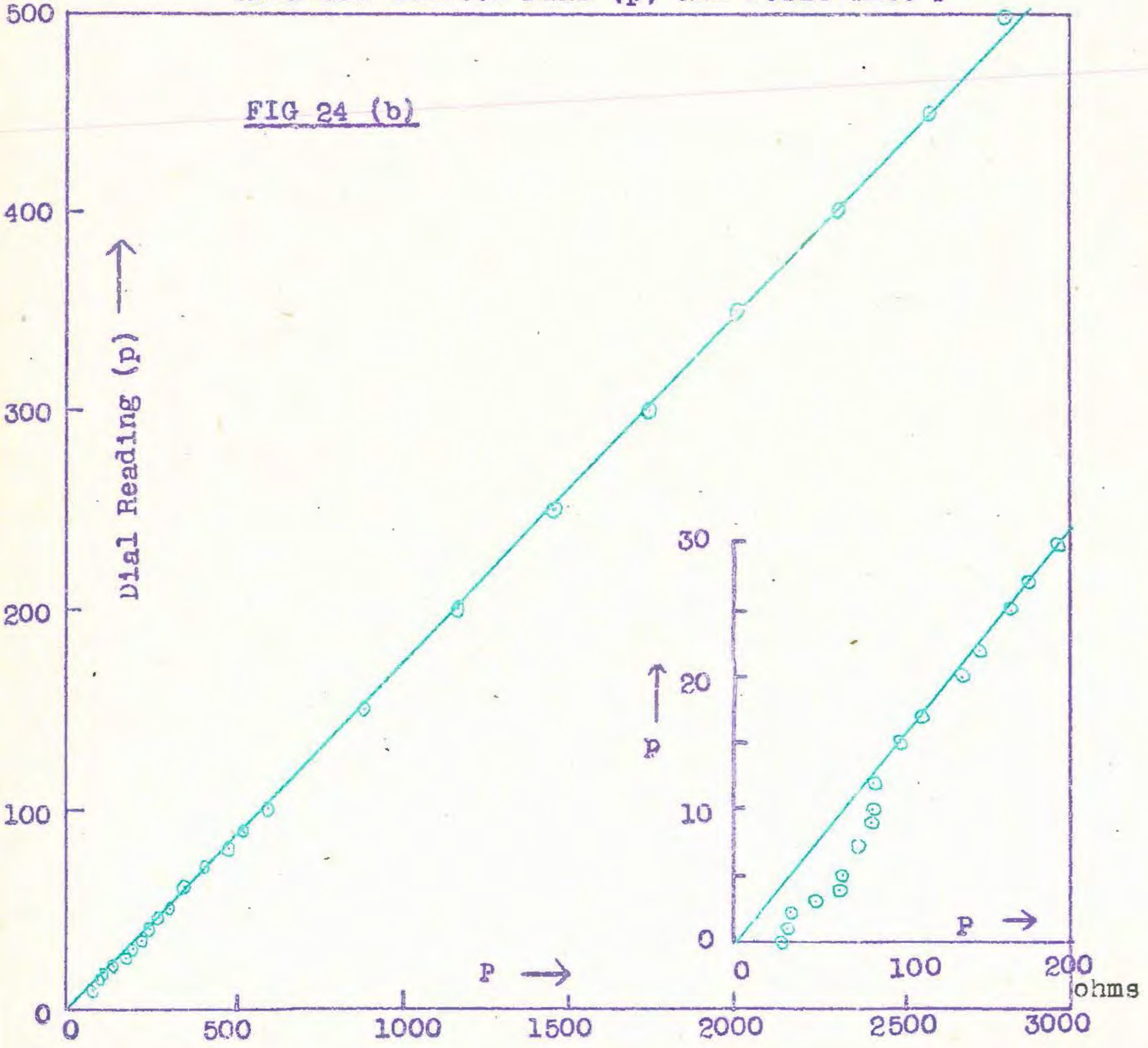

Relation between Dial (p) and resistance P

FIG 24 (b)

adjusted to give no galvonometer deflection. The value of the series galvonometer resistance is decreased to a minimum, the galvonometer shunt is brought to maximum sensitivity, and final balance obtained with P.

Matching of Absorption Cells

In spite of the care taken in making all the absorption cells the same length, it was found they did not all transmit the same amount of light. To match the cells, a spot of resin mixed with a pigment was placed on each window and allowed to harden. All four cells were filled with the same standard solution, one being placed in the reference position. The remaining three were placed successively in the test position, and pieces of resin chipped off until all gave the same reading of P at balance. One of these three cells was placed in the reference position and the fourth tube made to give the same reading as the other two. As a final check, the tubes were interchanged in the two positions without any difference to the reading of P.

Relation between Dial Reading (p) and Decade Resistance (P) at Balance.

Provided that the resistance p is not too inaccurately wound, the value of P required for balance should vary linearly with the setting of p.

Accordingly the switch was set in the "Batteries In" position and the values of P for balance measured for different settings of p. The dial readings were plotted against the values of P, as shown in Fig. 24(b) and the readings taken are recorded in Table A17 of the Appendix.

The readings were repeated some days later, and good agreement found between both sets. The graph was a good straight line except for values of the dial setting below 20. The experiment was repeated on two occasions for dial values up to 30; both these sets of readings were found to be erratic, showing that low values of p should not be used. Erratic readings in this region of the scale have previously been noted in the determination of R.

This shows that the windings on the 500 ohm rheostat are fairly regular and that the resistance increases linearly except for values below 20 ohms.

Therefore the substitution of P for p in transmission calculations may be made without destroying the relationship of p to T.

Calculation of Optical Density

The transmission T is given by :

$$T = \frac{R}{R \div p}$$

$$\text{or} \qquad \%T = \frac{R \times 100}{R + p}$$

From the Wheatstone Bridge circuit at balance :

$$\frac{P}{Q} = \frac{p}{R}$$

R is fixed, the value of Q thereby determining the value of P.

It has been shown above that $p \propto P$

Then T may be written as : $T = \frac{Q.\ 100}{Q + P}$

This value of T is purely dependent on the solution in the reference cell and the setting of the iris diaphragm; its value is relative and has no absolute meaning.

From the Beer-Lambert Law :

$$D = kcl$$

k = extinction coefficient

c = concentration

l = length of cell

These cells were 10 cms. long,

$$\therefore 10\ D = \log 100 - \log T$$

D = optical density

T = % transmission

$$\text{i.e. } 10\ D = 2 - \log T$$

(d) Beer's Law and Selection of Filter

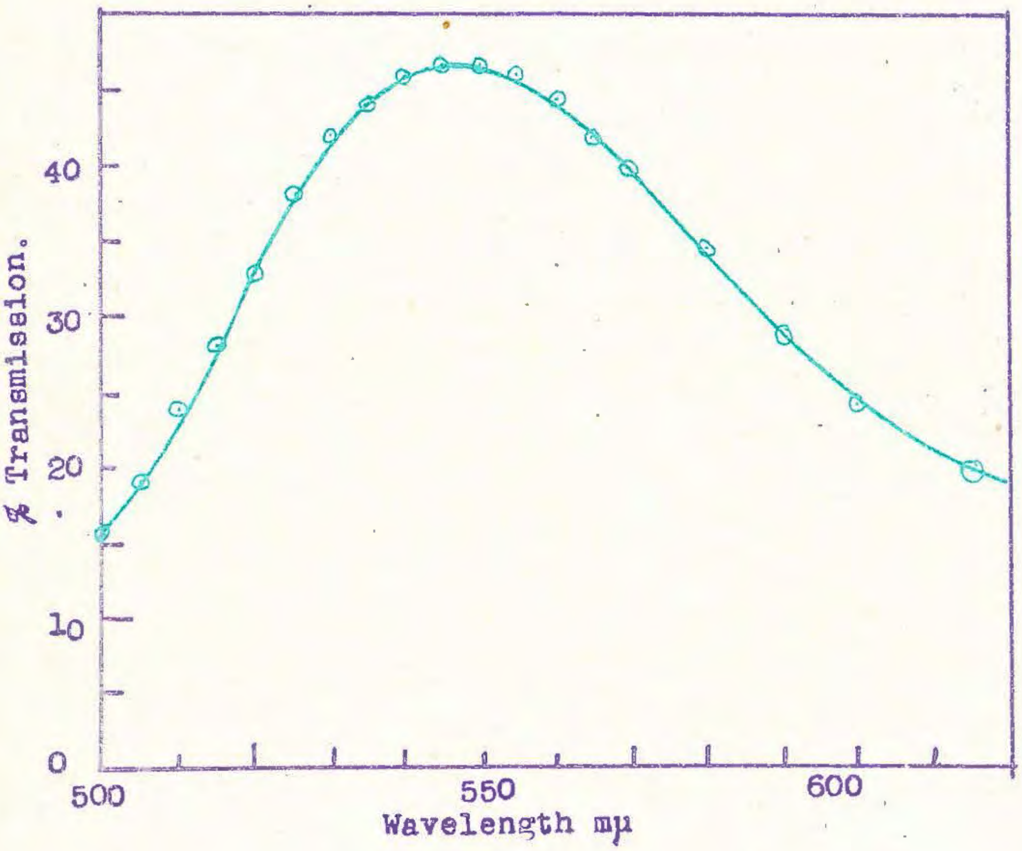
Both potassium trioxalato and potassium dioxalatodiaquochromiates obey Beer's Law remarkably well. Using the Beckman Spectrophotometer at a constant wavelength to measure the optical density of solutions at varying concentrations, good straight lines were obtained on plotting optical density against concentration.

In barrier-layer cell photometers, the usual method of selecting the required wavelength is to pass the light beam through a glass or gelatin light filter. Glass filters are more robust if slightly less selective.

Selenium photo-cells have their greatest spectral response in the red region of the spectrum, "E.E.L." photocells having maximum sensitivity at 550 millimicrons. The

FIG 25

Transmission Curve of Green Glass Filter.



absorption curves of the potassium trioxalato and potassium dioxalato chromiates show that both these have maxima at nearly the same wavelengths, namely 420 and 565 millimicrons. For the selenium photo-cell absorptiometer therefore, the second peak at 565 mμ is the most suitable at which to work.

A special interference filter, passing light of a very narrow band peaking 560 mμ and made by Barr and Stroud, was obtained. This should have been ideal but had to be discarded for the following reasons. These types of filters, despite their high selectivity, give a total intensity that is very low (66). In addition to the low intensity, an incandescent tungsten filament is rather deficient in light of the wavelength required so that, taken together, the intensity of light reaching the photo-cells is too small to give adequate galvonometer deflections.

This Barr and Stroud filter was replaced by a glass one. The transmittance curve of this filter was plotted using the Beckman Spectrophotometer and air as a "blank"; see Fig. 25. Its transmittance reaches a peak at 547 mμ and is far greater than that of the interference filter. The transmitted band is rather wide but as the maximum does occur in the vicinity of the required wavelength, it was used in the apparatus.

Beer's Law curves for both trioxalate and dioxalate were obtained using both the above-mentioned filters. With the interference filter in place over the entrance to the test cell, the reference cell had to be

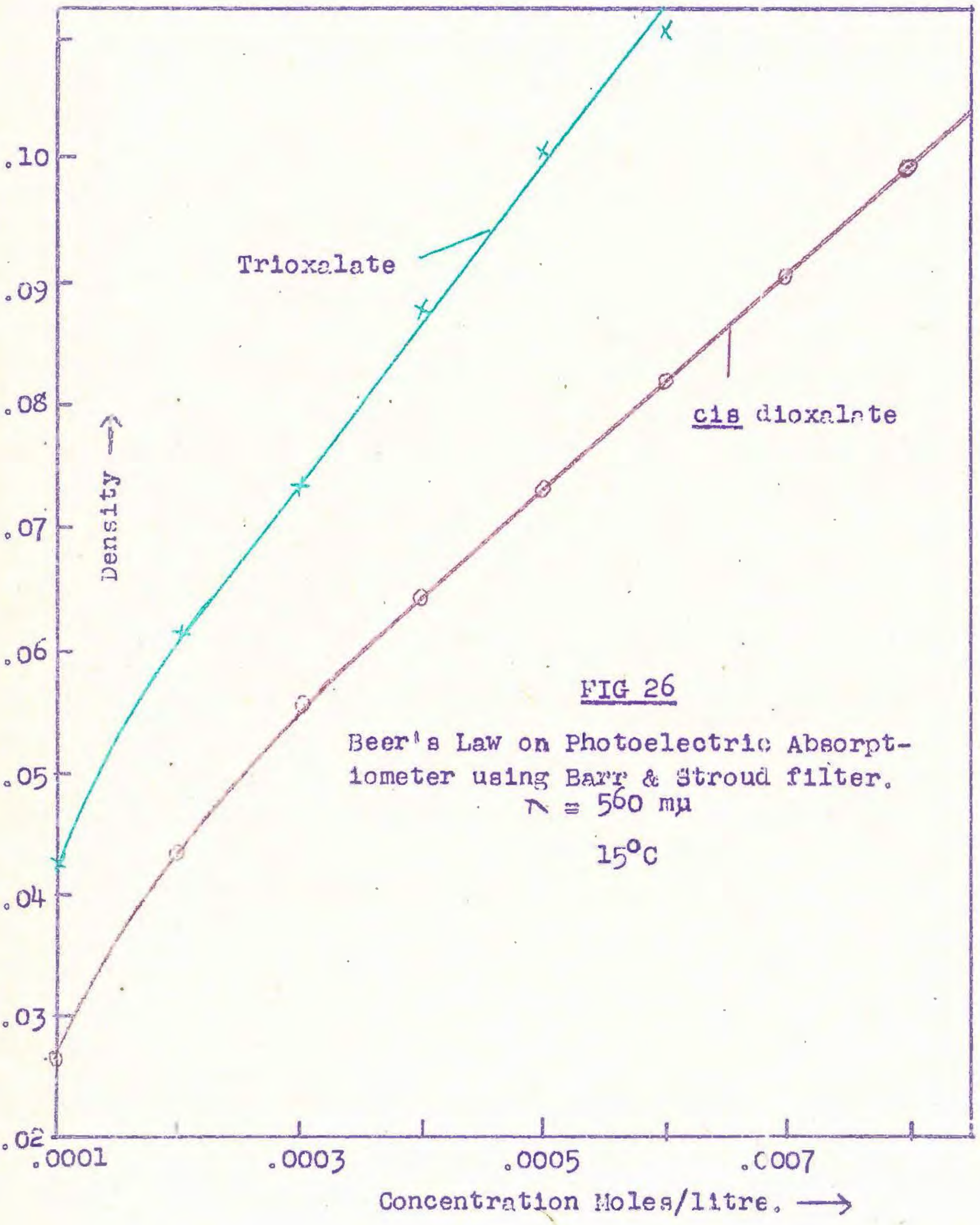


FIG 26

Beer's Law on Photoelectric Absorptiometer using Barr & Stroud filter.
λ = 560 mμ
15°C

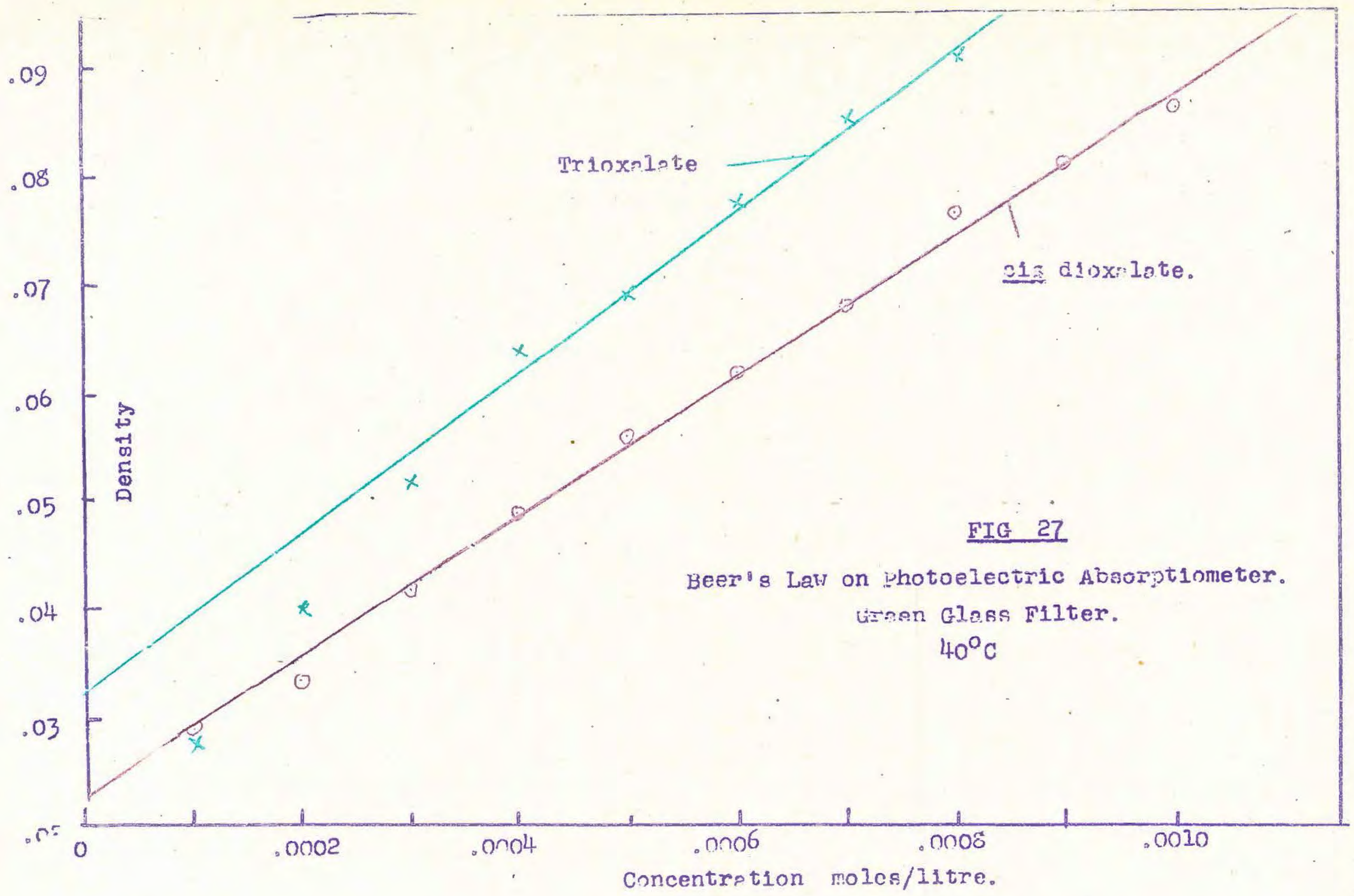


FIG 27

Beer's Law on Photoelectric Absorptiometer.
Green Glass Filter.
40°C

filled with .01M trioxalate before balance could be obtained with water in the test cell. On using the green glass filter, both cells were filled with water. Solutions of varying concentrations were placed in the test position and the densities recorded. After each reading, the test cell was replaced by the one containing water and the instrument zero checked.

The graphs obtained are shown in Figs. 26 and 27, and give fairly good straight lines over the limited concentration range of 0.0003M to 0.0009M. There was little response below this concentration, the density of the solutions being very close to that of water. Although the interference filter gave a good straight line, its use was discontinued as it decreased the sensitivity of the instrument to a great extent. The good results were most likely due to its selectivity.

Thus it appeared that the sensitivity of the instrument was sufficient for it to be used for the study of reaction kinetics at low concentrations.

(e) Standardisation Curves.

(i) General

Due to a rather wide transmission band on the green glass filter, the concentration range over which Beer's Law was strictly applicable, was rather limited. In order therefore to be able to determine the amounts of trioxalate and dioxalate present together in the reaction tube at any time, a standardisation curve must be drawn at each concentration used.

A suitable concentration is selected and solutions of dioxalate and trioxalate made up at this concentration. The two solutions are mixed in varying proportions, the chrome concentration remaining constant throughout, and the resultant optical density plotted against the percentage composition. As both these solutions obey Beer's Law, the combined effect should be to give a straight line, the density increasing as the percentage trioxalate present increases.

Providing a good straight line is obtained, and that the graph is reproducible, then on performing kinetic runs at the same concentration, and measuring the optical density at any time, the percentage trioxalate formed at that time can be read from the standardisation curve.

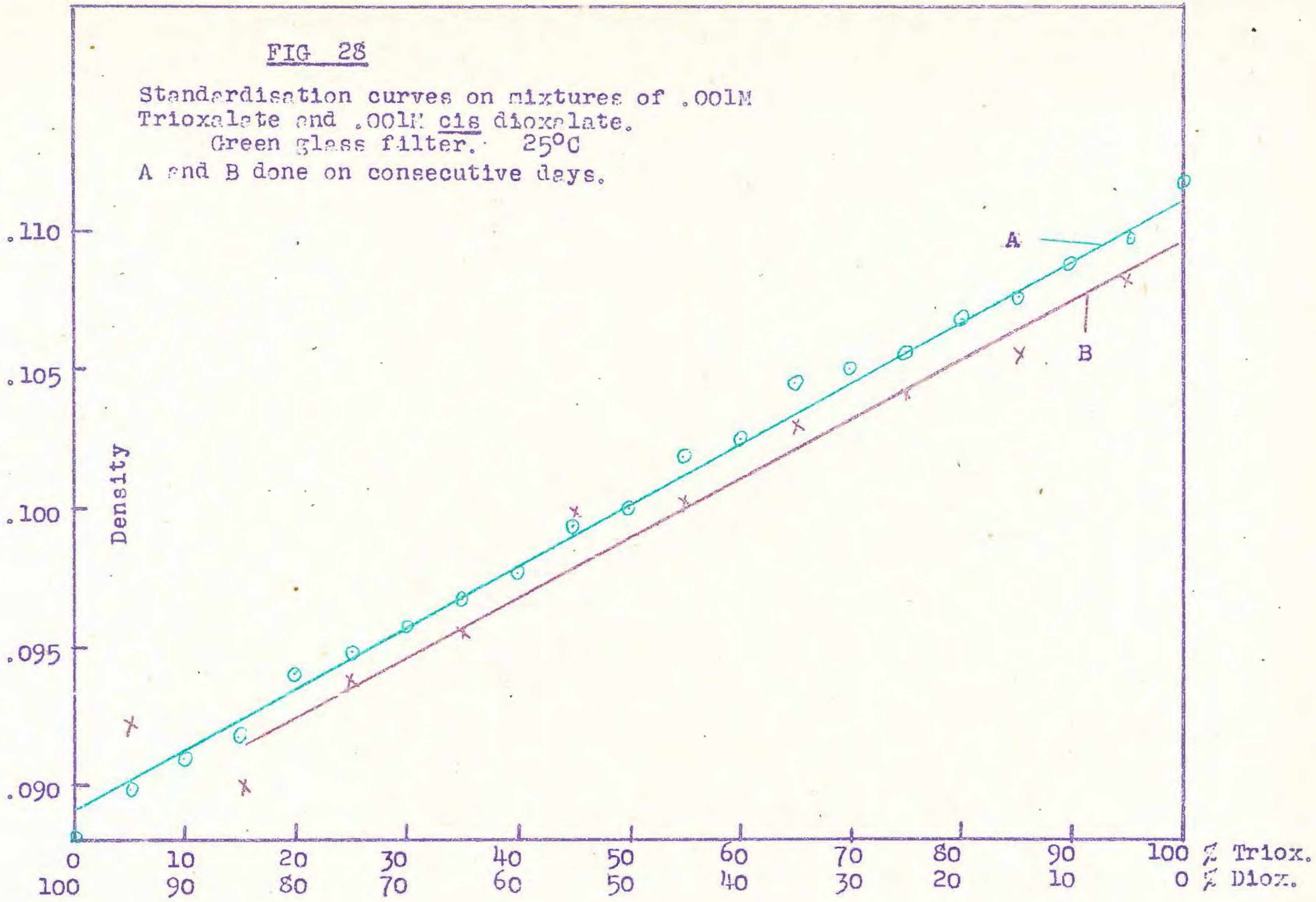
By using this standardisation method, the necessity of knowing the absolute density is done away with. The reference solution must, of course, be noted and the dial setting at which the instrument was balanced must be recorded. Then, provided the instrument gives reproducible readings, the kinetic readings can always be referred to the original standardisation curve.

(ii) Standardisation Method 1.

0.001M. solutions of potassium trioxalato and potassium dioxalatodiaquo chromiates were made up and a series of solutions having varying proportions of the two

FIG 28

Standardisation curves on mixtures of .001M Trioxalate and .001M cis dioxalate.
Green glass filter. 25°C
A and B done on consecutive days.



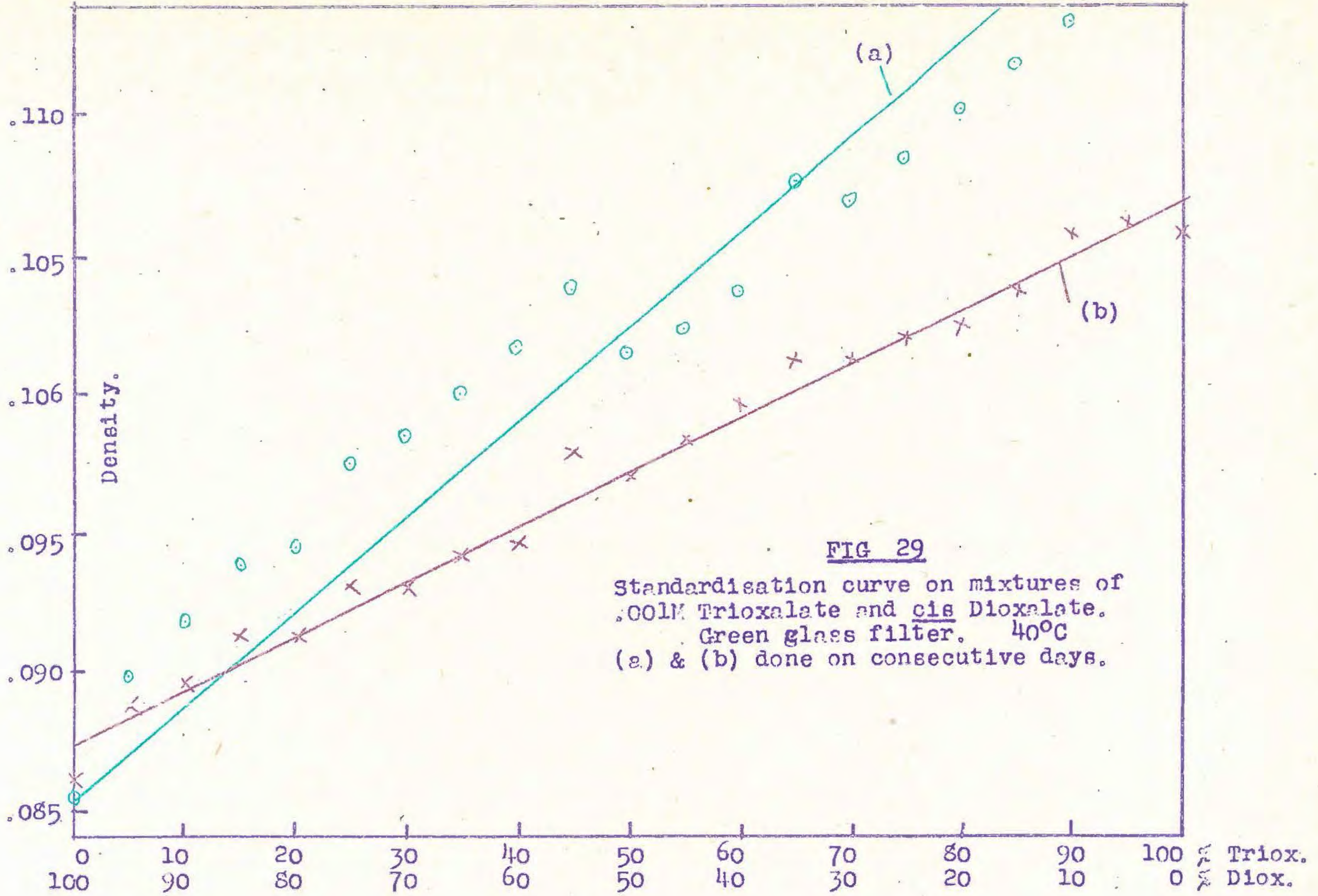


FIG 29

Standardisation curve on mixtures of .001M Trioxalate and cis Dioxalate. Green glass filter. 40°C
(a) & (b) done on consecutive days.

complexes, but with the same chrome concentrations, were prepared.

The optical densities of these solutions were measured, the standardisation of the instrument being carried out using water as a blank. A standardisation performed at 25°C. is shown in Fig. 28. Lines A and B represent two standardisations carried out on different days. These curves do not coincide and show that the instrument gave results that were not reproducible.

The working temperature of the thermostat was raised to 40°C., and the standardisation repeated. The results are shown in Fig. 29, the lines A and B were also obtained on different days. These lines are very erratic and, as above, are not reproducible.

It appears then, that by this method of standardisation, graphs are obtained which are not straight lines and it is impossible to reproduce the same graph from day to day.

(iii) Standardisation Method 2.

A fresh standardisation was performed on 0.0005M solutions at 40°C. In this case the reference cell was filled with standard 0.0005M trioxalate solution and the test cell contained a 50/50 mixture of 0.0005M trioxalate and 0.0005M. dioxalate. With these solutions in place, the instrument was standardised on a dial reading of 250 by adjustment of the iris diaphragm. The 50/50 mixture was replaced by other known mixtures, all 0.0005M in respect to

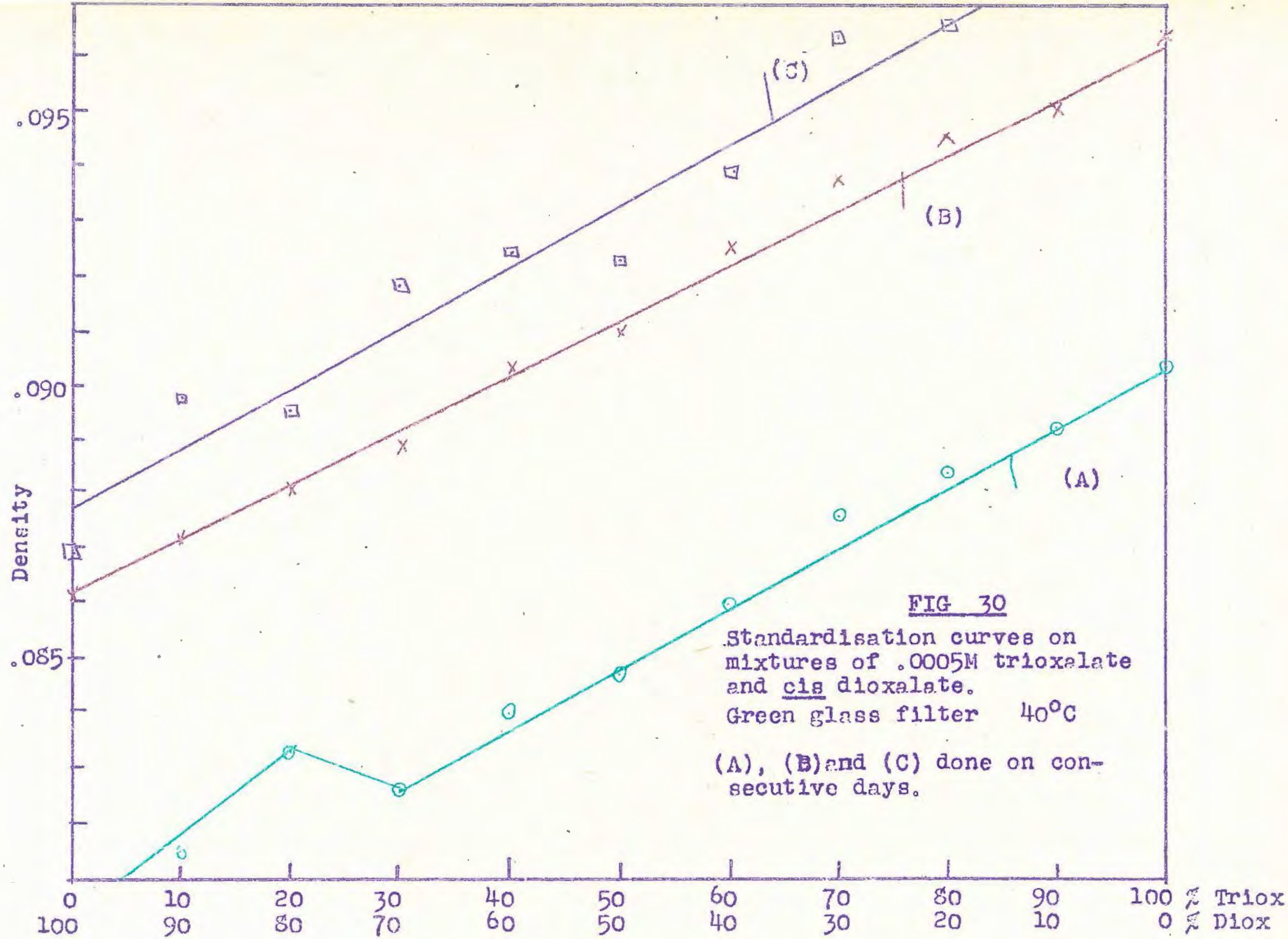


FIG 30

Standardisation curves on mixtures of .0005M trioxalate and *cis* dioxalate.
Green glass filter 40°C

(A), (B) and (C) done on consecutive days.

Cr, and their densities measured. After each reading the 50/50 mixture was replaced in the test position and the standardisation checked. It was found that some drifting of this standard setting occurred for each reading. The instrument was therefore restandardised after each reading. This standardisation on the centre of the dial prevents any irregularities due to the minimum or maximum values of p and any errors due to non-linearity of response are diminished.

Three curves are shown in Fig. 30. The temperature was 40°C. and the curves were obtained on three consecutive days. The lines are nearly parallel, but the density values vary considerably for each standardisation. Since the instrument was standardised each time on the same 50/50 standard mixture, this point at least should be common to each graph. However, this was not the case and the instrument therefore varies from day to day even on a standard setting.

(iv) Standardisation Method 3.

All the absorption cells were re-matched as described previously. One cell was filled with distilled water, placed in the reference position, and labelled A_O. The test cell B was first filled with 100% 0.0005M. dioxalate solution - designated by $B_{100/O}$, the dial set at 200 and the diaphragm adjusted to give balance; this constituted the first standardisation.

Solution $B_{100/O}$ was replaced by solution $B_{90/10}$ representing 90% 0.0005M. dioxalate and 10% 0.0005M. tri-

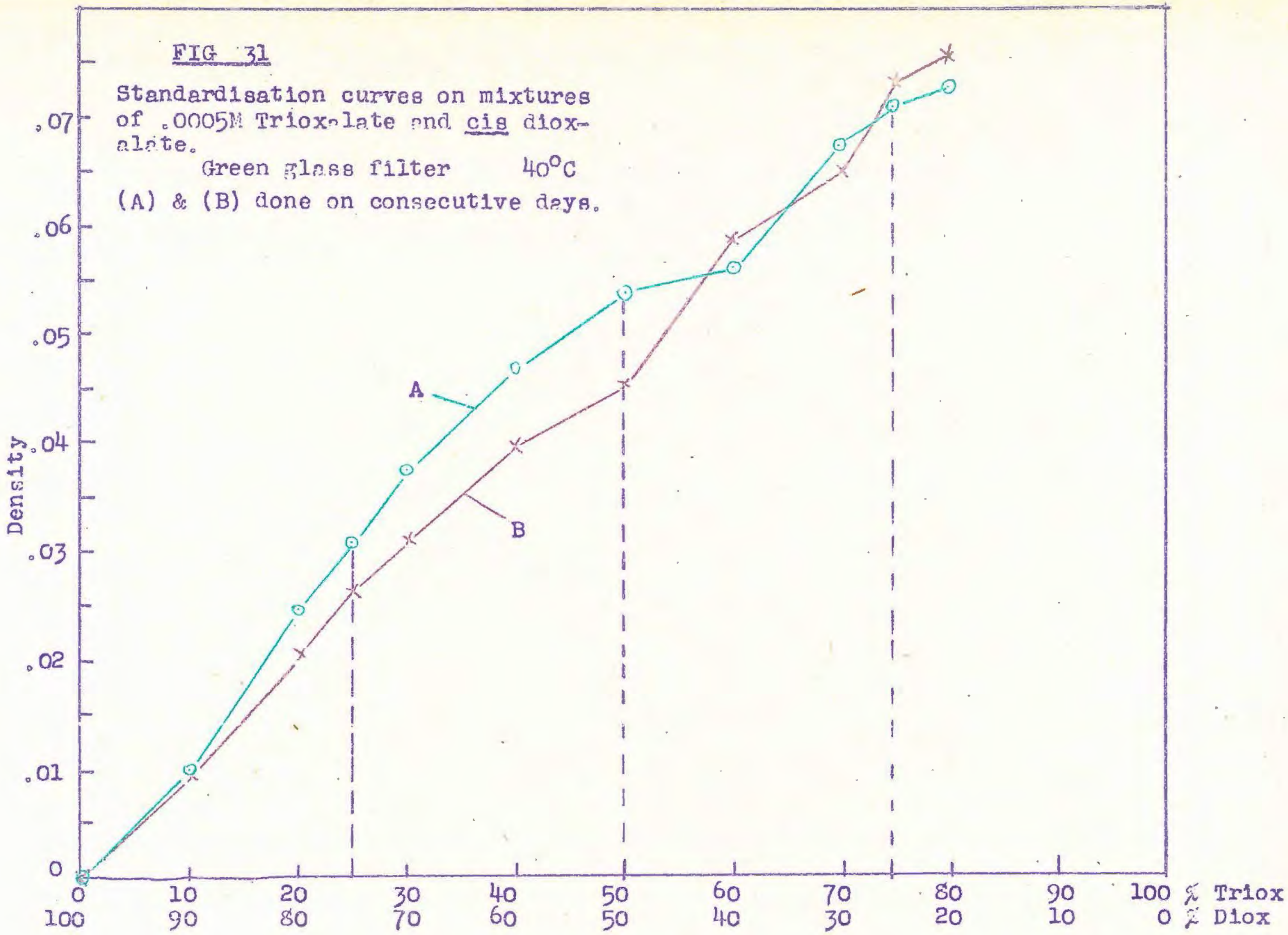


FIG 31

Standardisation curves on mixtures of .0005M Trioxalate and cis dioxalate.
Green glass filter 40°C
(A) & (B) done on consecutive days.

oxalate; the density of this solution was measured. This solution was followed by solutions $B_{80/20}$ and $B_{75/25}$, their densities also being measured and recorded.

At this point the instrument was restandardised by leaving solution $B_{75/25}$ in the test position and replacing reference solution A_0 by A_1, so chosen that balance was again obtained at a dial reading of 200 without the iris diaphragm being altered. From this setting, the densities of solutions $B_{70/30}$, $B_{60/40}$ and $B_{50/50}$ were measured. At $B_{50/50}$ the instrument was again standardised on a dial reading of 200, a fresh solution A_2 replacing A_1. The fourth and last standardisation was done at $B_{25/75}$.

The object of the frequent restandardisations was to use as small a portion of the resistance p as possible for the readings, thereby relying more on a set of standard solutions than on the instrument.

For the calculation of results, the value of P + Q was recorded and its logarithm taken as corresponding to an arbitrary density, the total additive density being recorded after each standardisation. The graphs obtained from these results are shown in Fig. 31. Curve B is a repitition of A obtained a day later. Even with this method the curves are not coincident at the three standardisation points, although they must of necessity agree at the first reading, where D is made equal to zero in each case.

This standardisation method, although better than the previous two methods, did not give sufficiently constant results to be considered for kinetic work.

3. DISCUSSION

The principle of using two blocking-layer photo-electric cells to measure the difference in light intensities falling on the photo-cells is sound. The circuit described by Brice (65) has been used in both standard and research colorimeters and is capable of giving accurate results for small differences in illumination of the photo-cells.

The instrument described was constructed because, as has been shown, the Beckman Spectrophotometer, without special attachments, was unsuitable, and an instrument was needed that possessed high sensitivity at high chrome dilutions.

The modifications made to the instrument were to enable continuous readings of solution densities to be made whilst reactions were in progress. This required an arrangement whereby the reaction was allowed to proceed in the actual absorption cell on which readings were taken. As the temperature of reaction must be maintained at a constant value, conditions were arranged so that the absorption cells were kept at constant temperature by immersion in a thermostatically controlled water bath.

It has been shown that the transmission is given by $T = R/R + p$. R is fixed, but the value of p must be known for every setting at which a reading is recorded. An accurately and linearly wound potentiometer with extremely good sliding contacts was unobtainable, but, provided the value of p can be determined for any setting, then any potentiometer will suffice. The most convenient way of determining the value of p is to incorporate a Wheatstone Bridge into the circuit so that, after obtaining balance with p, its exact value, including contact resistances, can be measured directly afterwards.

The use of mercury switches for changing the circuit minimises any errors due to faulty contacts and it is hardly possible for the erratic readings obtained during standardisation to be caused by faults in the wiring and contacts.

A possible source of inaccuracy is variation occuring in the resistances, especially p, due to heating effects. The 2 volt accumulator is only used in balancing the Wheatstone Bridge circuit; during balancing, especially at first when the circuit is far off balance, considerable currents may pass through the resistances. These currents, if present, cause heating of the resistances thereby altering their values. As is to be expected, for low values of p a shorter length of resistance wire is in circuit, and heating effects are likely to be greater over this short length of wire. It is probable that the inaccuracies already mentioned for low values of p are partly due to this heating effect.

It was unfortunate that the photo-cells had to be placed in the water bath. The glass windows of the photo-cell housing easily became dirtied, and occasionally bubbles formed on these windows. As the increased temperature was common to both photo-cells, the relative working of these cells is probably unaffected. However, the humidity effect is likely to be considerable and this might have affected the working of the cells.

By placing the absorption cells directly in the water bath, they were maintained at constant temperature, but, here again, the ends of the cells easily become dirtied and bubbles formed or trapped on these ends interfered.

Some modifications that might make for improved working are as follows :

The absorption cells could be made with detachable screw-on ends, to enable them to be cleaned easily, and the length of the tube encased in a brass jacket, through which water from the thermostat could be circulated. The photo-cells could then be mounted directly behind these brass-jacketed absorption cells without having to be placed in the thermostat. Higher temperatures could then be used without the photo-cells being affected.

A galvonometer of high sensitivity and low resistance (20 - 50 ohms) would be better suited to the circuit; also, in order to comply with the requirements of the Brice circuit, a galvonometer with a low critical damping resistance of about 100 ohms should be used. This would enable the intensity of the light source to be increased whilst still obtaining linearity of response.

A better quality resistance in place of p might be a slight advantage.

As has been shown, without improvement of the instrument, the standardisation methods attempted do not yield results constant enough for any reliance to be placed on them for accurate kinetic work. Some of the modifications suggested could not be made as they require expensive and unobtainable equipment.

PART III

THE EVELYN PHOTOELECTRIC COLORIMETER

1. INTRODUCTION

The Beckman Spectrophotometer and the Differential Photoelectric Absorptiometer have both been discussed and investigated in relation to the study of kinetics at low chromium concentrations. The former instrument was found to be unsuitable for these studies, and the latter had to be rejected owing to unsatisfactory behaviour.

It was decided that one of the most important aspects of Burley's work (14) which required further investigation, was the kinetics of the formation of the trioxalatochromiate ion. This then, being one of the main objects of this work, was more important than the continuation of construction and investigation of the previously mentioned photoelectric absorptiometer, especially without improved equipment.

Evelyn Colorimeter.

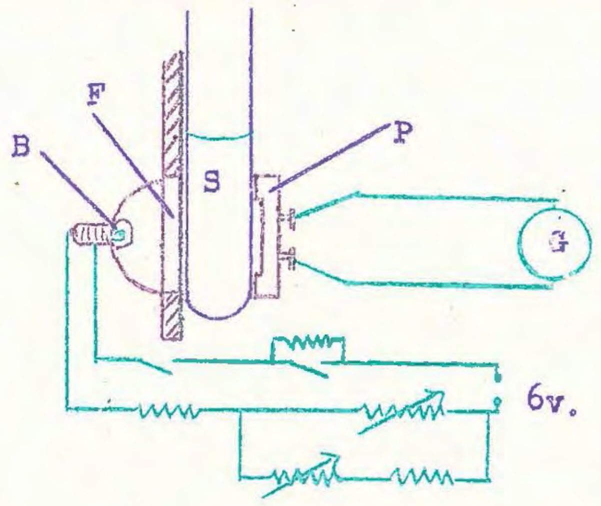


FIG 32

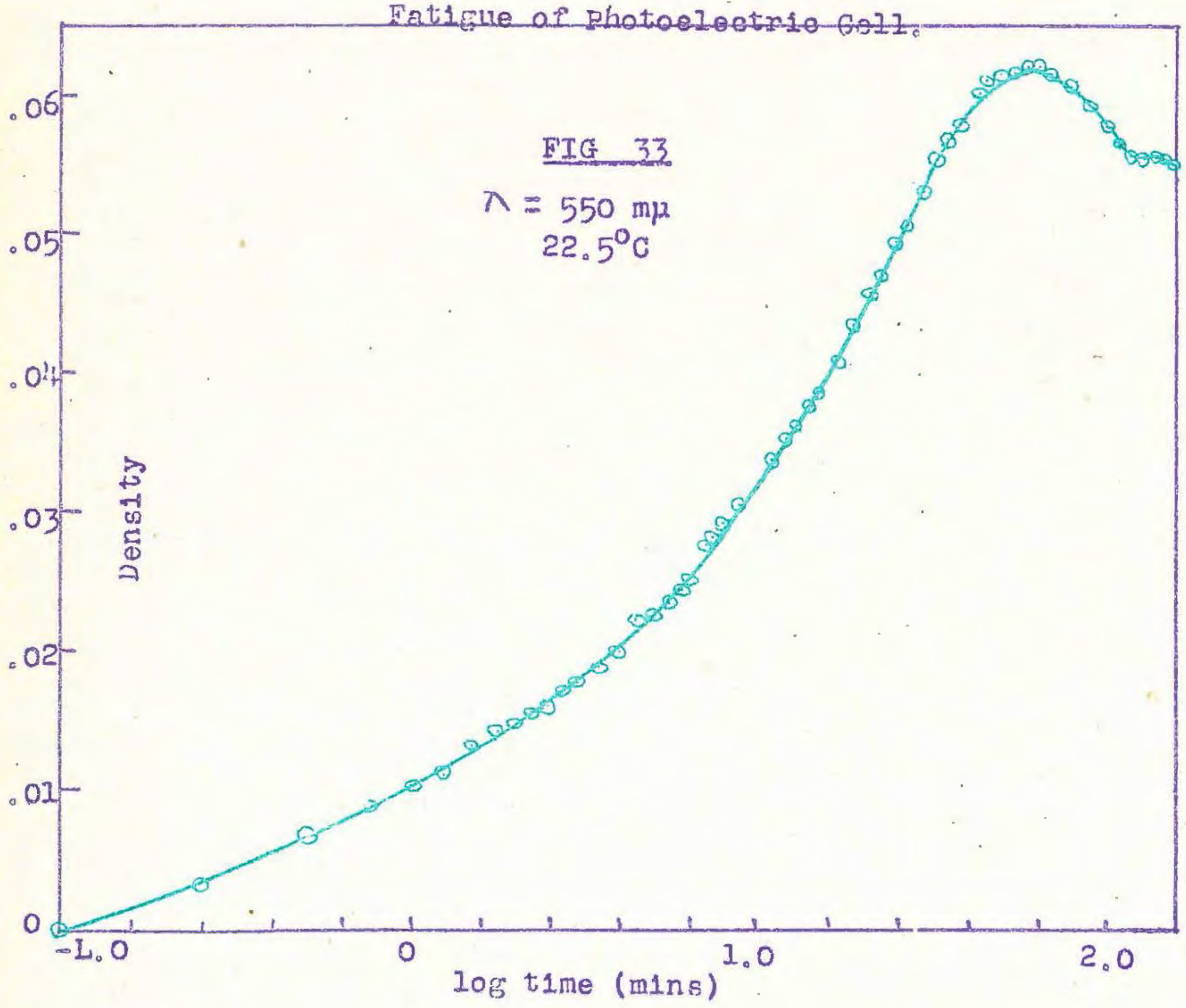

Fatigue of Photoelectric Cell.

FIG 33

A standard commercial model, the Evelyn Photoelectric Colorimeter was therefore investigated with a view to using it for kinetic studies. This instrument is described, together with the modifications in technique required for the study of kinetics, in this section.

(a) Principles of Operation.

The Evelyn Colorimeter is a relatively simple instrument employing a single barrier-layer photoelectric cell in conjunction with a light source and optical filter. The instrument is described by its designer K.A. Evelyn (67). The bibliography of the colorimeter appears to be concerned entirely with colorimetric determinations of a biochemical nature, and no mention is made of its use in kinetic studies.

A diagrammatic representation of the instrument, together with the simple circuit, is shown in Fig. 32. A high capacity six volt accumulator sends a steady current through a small bulb B. The light from this bulb shines through an optical filter F, then through the sample solution contained in a tube S, and finally impinges on the photo-cell P. This photo-cell is connected in a circuit of low resistance and produces a current whose magnitude is accurately proportional to the intensity of the light beam; the proportionality only holds provided the intensity is low. By connecting a galvonometer in the circuit, the deflection produced is therefore directly proportional to the intensity of light falling on the photo-cell.

The light intensity is directly controlled by variable resistances in the battery circuit, the resistances being arranged so that one gives coarse and the other fine control. In general the instrument is standardised by placing a tube of water or solvent ("blank") in position and adjusting the intensity of the light source so that the galvonometer deflection is 100 divisions. The"blank" is replaced by the sample in a similar tube and the galvonometer deflection recorded. The sample, being more optically dense than the "blank", registers a smaller deflection than the "blank" (100% transmission) and the deflection is recorded directly as percentage transmission. To express this transmission T, as optical density, D, the relationship: $D = 2 - \log T$ is used.

This value of D cannot be used to calculate true extinction coefficients as the width of the tube is not 1 cm. as in the Beckman Spectrophotometer. However, this logarithmic relationship is sufficient provided it be remembered that the value of D is relative and not absolute.

All photo-cells or tubes are liable to suffer from fatigue, but this has little effect if the instrument is standardised on a known solution before each reading. However, if continuous readings are to be taken, the nature of the fatigue effects must be determined. This was done as follows :

A tube filled with distilled water was placed in the holder; at zero time the colorimeter bulb was switched on, and the galvonometer deflection recorded. The bulb was left lighted for nearly 200 minutes, and the galvonometer deflection noted at intervals throughout this period. The values of T given by the galvonometer were converted to density units (D) and plotted against the logarithm of the time : the result is given in Fig. 33. After about 65 minutes the drift appears to stop, but rather erratic values are obtained.

The effects described above may be due to three causes :

(a) Unsteadiness of the battery voltage.

(b) The warming up of the galvonometer.

(c) Fatigue of the selenium photo-cell.

By standardisation of the instrument before each reading, effects (a) and (b) are eliminated as they are compensated for by increasing the intensity of the light source. The time taken for a reading after the instrument has been standardised is short, and the fatigue effects are hardly noticeable over this small time period. As a check, several readings on the solution are made, standardisation being repeated before each reading. In this way the effects of (c) are almost entirely eliminated.

2. TECHNIQUE

(a) General

The reaction between potassium cis dioxalatodiaquochromiate and potassium oxalate to form the trioxalatochromiate causes the optical density of the solution to increase from that of the dioxalate to that of the trioxalate. The densities of reactants and product are fixed for each concentration and wavelength, and, having prepared both reactants and product in a pure state, solutions of these salts can be used as standards. Potassium oxalate, having no measurable optical density in the region of 560 mμ, does not effect the density readings.

The accuracy of any kinetic measurements will therefore depend on the sensitivity of the instrument in distinguishing between solutions of <u>cis</u> dioxalate and trioxalate at equal chrome concentrations, and at a fixed wavelength. In any instrument, the difference in densities will be most marked for the more concentrated solutions, this difference becoming smaller with increasing dilution, until at zero concentration the values coincide.

The maximum differences in densities are obtained at the wavelengths at which the maxima occur in the absorption curves. A wavelength of 560 mμ, where both complexes show peaks, was chosen due to the greater sensitivity of selenium photo-cells at this wavelength. The Evelyn colorimeter was provided with a set of filters covering a range from 400 - 700 mμ; a filter passing light peaking 565 mμ was chosen. The transmission limits of this filter were recorded as 550 to 585 mμ.

(b) Galvonometer

The galvonometer supplied with the Evelyn Colorimeter was that used in conjunction with the photoelectric absorptiometer previously described. The modifications and changes effected are described on page 106, and apply without change in this instance, as the galvonometer was set up in an identical manner for both instruments.

(c) Separate Reactions

The method of removing aliquots for readings from a relatively large quantity of reaction mixture has certain disadvantages. Any errors made in preparing the solutions affect all subsequent readings and errors are likely to be accumulative. Also, the initial time of mixing is the same for all readings on that run and, for reactions taking about 40 hours, readings must be taken about every 4 hours over long periods.

Accordingly it was decided to make every reading a separate reaction in itself; random errors are confined to one reading only, and each reaction may be started and arrested at individual convenient times. After the initial mixing of the reactants, the tube is stoppered and left to react for a certain period in the water-bath. The tube is not unstoppered again until the reading has been recorded and the contents discarded. By this method the reaction is allowed to proceed with the minimum of interference. This method is inconvenient insofar as generally, only one kinetic run can be in progress at a time; however, it was found possible to overlap the runs by about 24 hours.

This method may seem somewhat tedious, but it was felt that it was warranted by the elimination of certain errors, and improvement in the reliability of results.

(d) Standardisation of Tubes

The cell holder of the Evelyn Colorimeter is built to accomodate 7 × 7/8" absorption test tubes. The tubes provided with the instrument were of a special grade marked "S", and were all of uniform diameter to within close tolerances. However, on comparison, not all the tubes had quite the same transmission, and they should therefore all be standardised before use.

Several dozen of the tubes were taken, any showing obvious visual defects such as scratches and flaws were immediately discarded, the remainder were cleaned thoroughly by standing in warm chromic acid cleaning mixture for 24 hours. After washing and drying, each tube was filled with 20 ml. of distilled water and stoppered. The colorimeter was switched on and allowed to settle down; with the absorption cell holder empty, and the 565 mμ filter in place, the galvonometer spot was adjusted by altering the coarse and fine rheostats until it rested exactly on 50 on the scale. This serves as a standard centre setting and, throughout the standardisation, the spot was kept adjusted to this position with the utmost care. After this setting, one of the prepared absorption cells containing water was placed in the cell holder. The tube was slowly rotated in the holder through one full revolution, and the position of greatest stability of reading determined. At this position a mark was scratched on the lip of the tube so that it coincided with a line drawn on the cell holder. The reading with the tube in this position was recorded. This was done for all the tubes and the mean reading recorded. Any tube whose reading differed by more than 0.1% from the mean was discarded. All tubes, prior to being placed in the cell holder, were carefully wiped free from moisture on the outside and then polished with a clean soft cloth. In all future measurements, the tubes were placed in position so that the two marks coincided, thereby having the same transmittancy to within narrow limits.

3. BEER'S LAW

Burley (14) showed that both the cis dioxalato and trioxalato chromiates obey Beer's Law over a fairly wide concentration range. Measurements were carried out using the Beckman Spectrophotometer as also were the kinetic measurements.

If standardisation graphs are to be drawn for the Evelyn Colorimeter, it must be known whether Beer's Law is obeyed, and over what concentration range, using this instrument with the 565 mμ filter.

Solutions of both cis dioxalato and trioxalato chromiates of from 0.001M to 0.006M were placed in clean dry absorption tubes. A tube of distilled water, representing 100% transmission, was used as a blank and the other

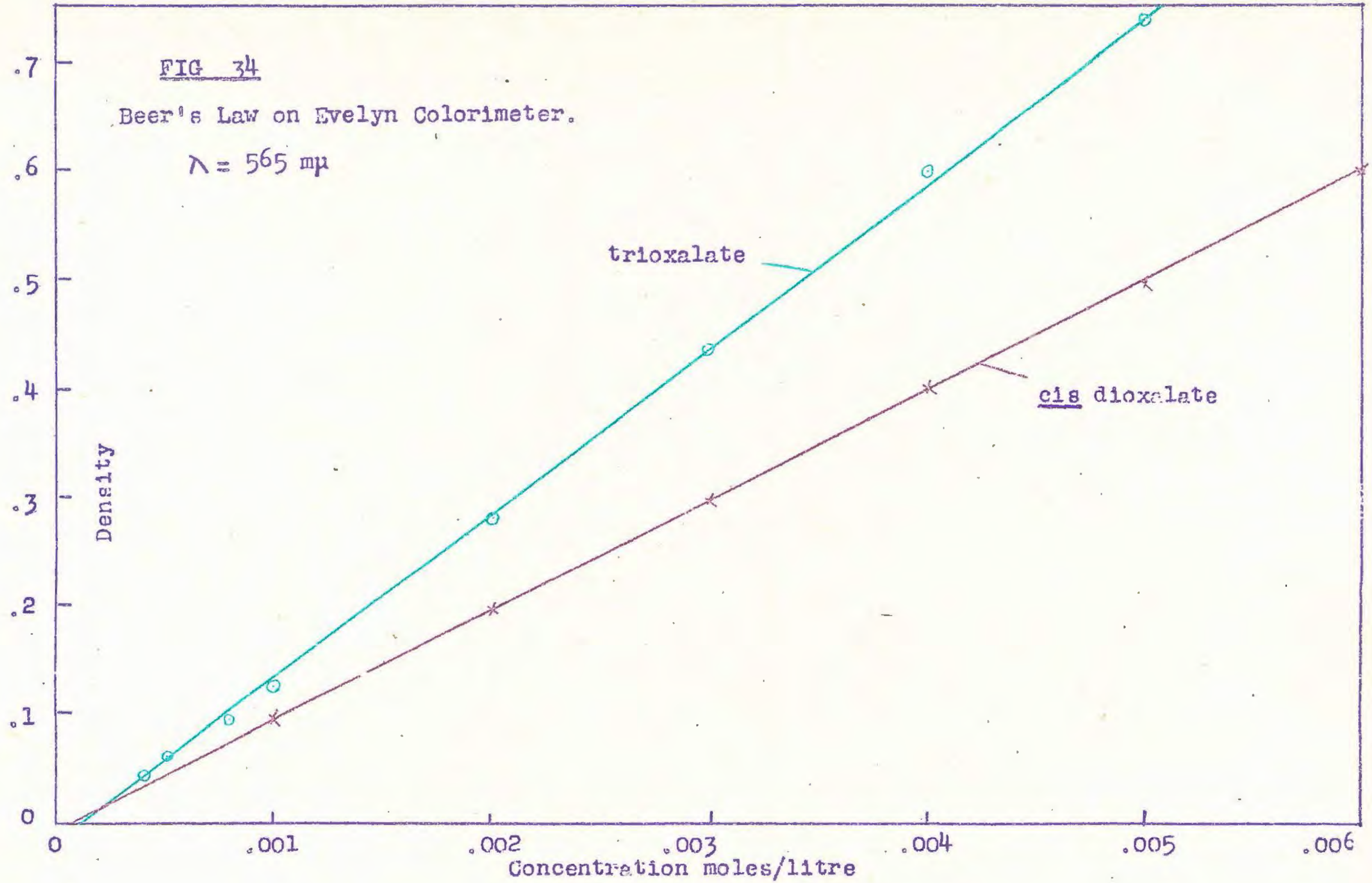


FIG 34
Beer's Law on Evelyn Colorimeter.
λ = 565 mμ
trioxalate
cis dioxalate
Density
Concentration moles/litre
.7
.6
.5
.4
.3
.2
.1
0
0
.001
.002
.003
.004
.005
.006

tubes were compared against this. The optical densities of these solutions were calculated from the transmission readings and plotted against the concentrations. From the graph in Fig. 34, it is seen that good straight lines were obtained for both solutions. This was checked by taking readings on the same solutions at 565 mμ on the Beckman Spectrophotometer; here linearity was also observed. (Burley's graphs were not obtained at a wavelength of 565 mμ).

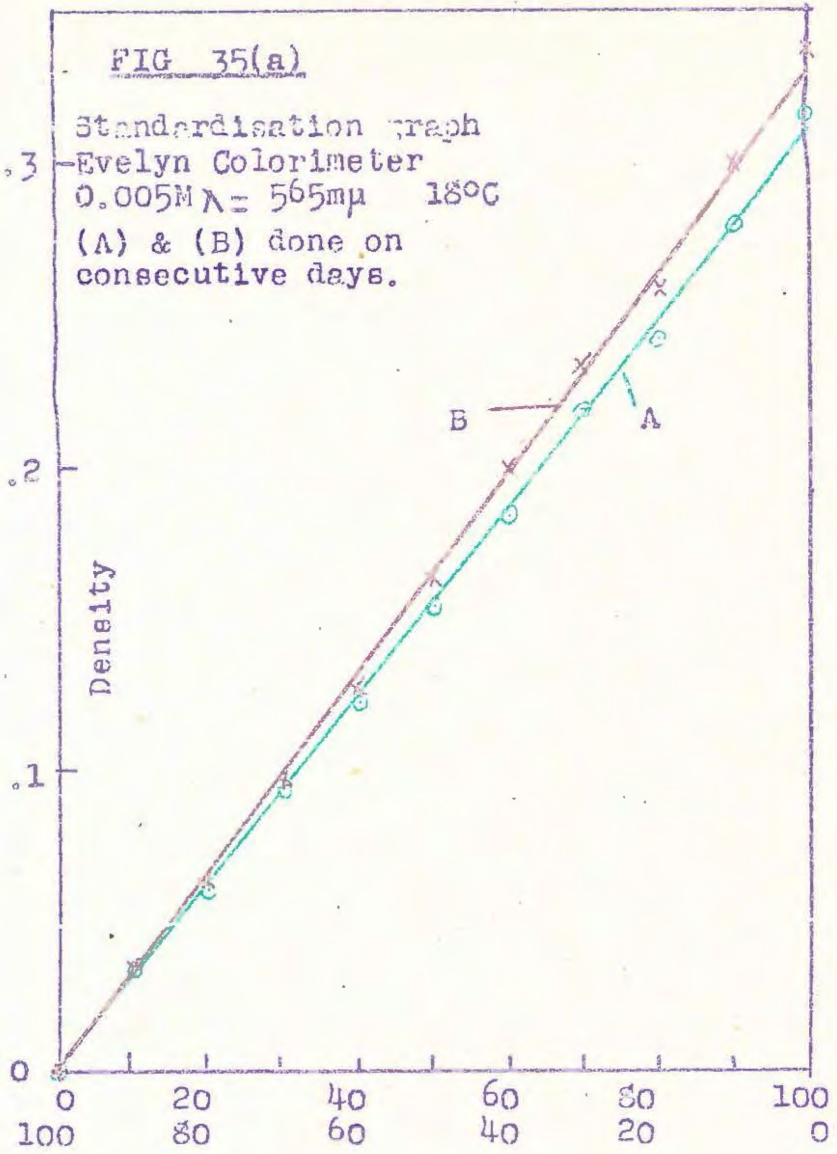
Because of this linear response of the instrument, standardisation graphs can be drawn and, as is seen later, the percentage conversion to trioxalate can be calculated in spite of variations in the slope of the standardisation graphs.

4. STANDARDISATION GRAPHS.

As has been shown, the change occurring during reaction is measurable due to the change in optical density of the solution. The two extreme standard densities are those given by the cis dioxalate and trioxalate solutions, mixtures of these solutions having intermediate density values.

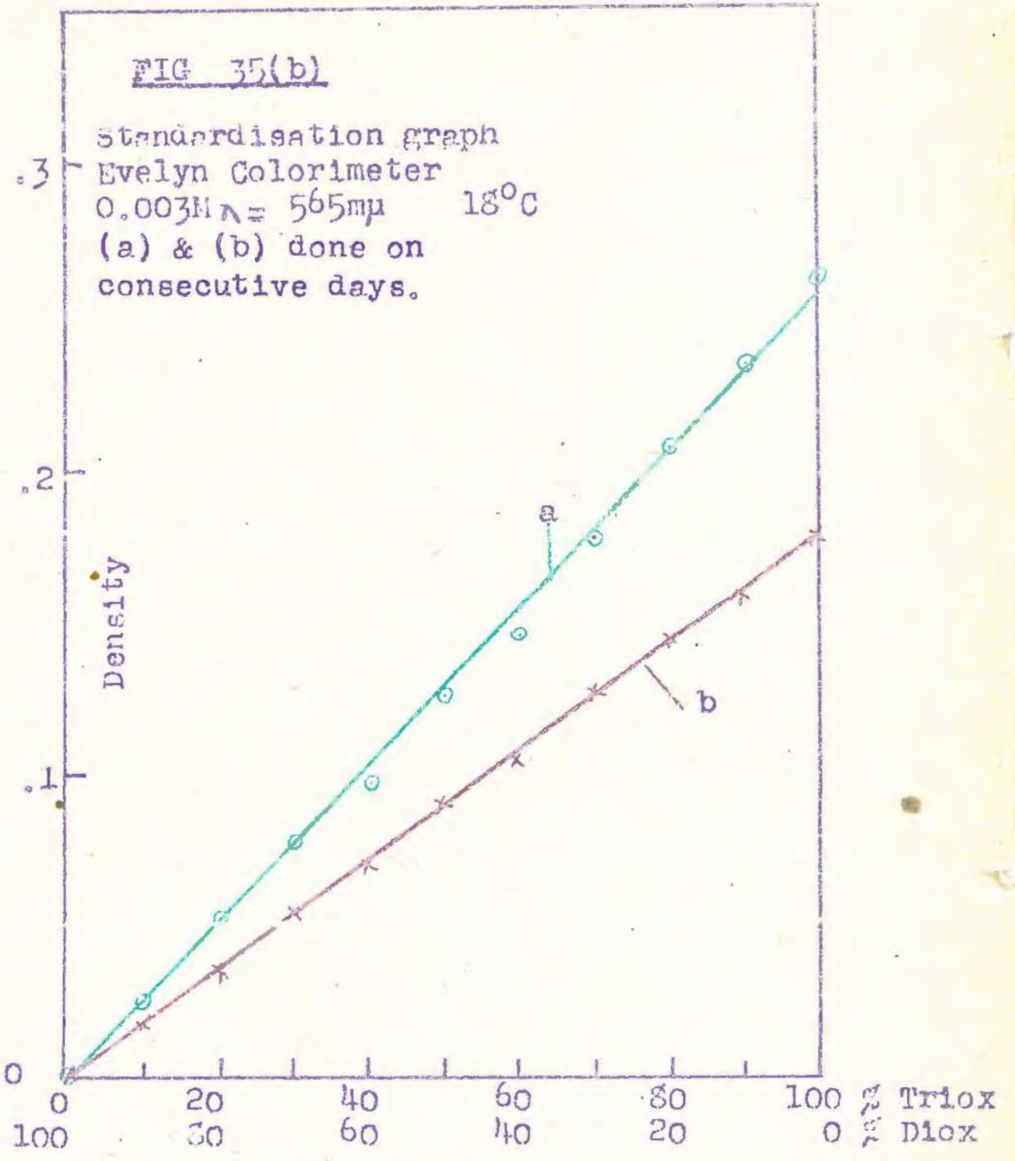
Both the standard solutions obey Beer's Law, and therefore, the resultant densities of mixtures of the two solutions plotted against the percentage composition, should be a straight line. Such graphs, obtained at constant chromium concentrations, serve as standardisation graphs provided the readings obtained are reproducible.

FIG 35(a)



Standardisation graph
Evelyn Colorimeter
0.005M λ = 565mμ 18°C
(A) & (B) done on
consecutive days.

FIG 35(b)



Standardisation graph
Evelyn Colorimeter
0.003M λ = 565mμ 18°C
(a) & (b) done on
consecutive days.

Standardisation graphs were obtained at chromium concentrations of 0.005M and 0.003M. Considering the curves of 0.005M solutions, the procedure was as follows :

A series of absorption cells were taken and varying amounts of 0.005M trioxalate and dioxalate buretted in-to each. The final volume in each tube remained constant (20.0 ml.), and the amounts were arranged so that the trioxalate content increased from 0% to 100%, whilst the dioxalate content decreased from 100% to 0%, the chromium concentration of each mixture remaining constant at 0.005M. All burettings were made with NPL grade A burettes in a constant temperature room.

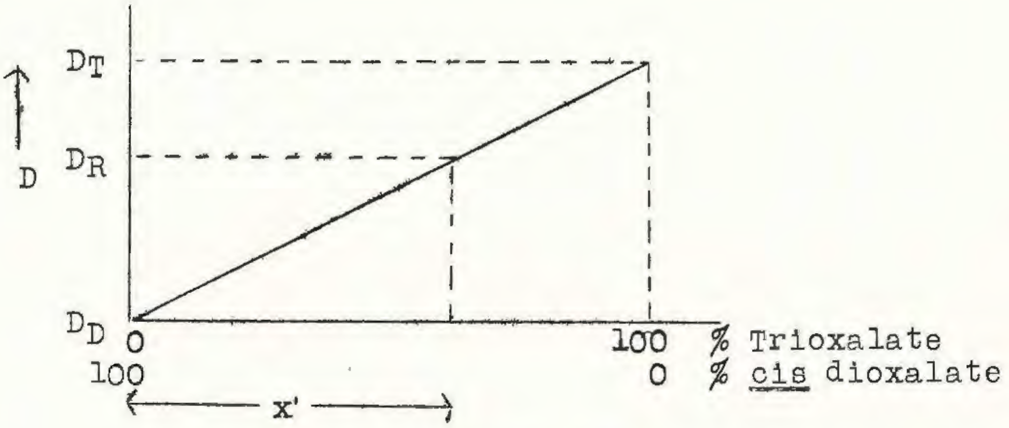
The colorimeter was standardised at 100% transmission with the tube of pure cis-dioxalate in position. A reading was then taken on a tube containing 10% trioxalate and 90% dioxalate; the next tube contained 20% trioxalate and 80% dioxalate, etc., until the transmission of the final tube containing pure (100%) trioxalate was read; the instrument was re-standardised between each of these readings. The transmission readings were converted to optical density values and plotted against the percentage composition. After about 12 hours, the procedure was repeated.

Similar readings were taken on a set of 0.003M solutions; the readings are recorded in Table A 19 of the Appendix and the graphs are shown in Figs. 35 (a) and (b). It is seen that good straight lines were obtained, as expected in view of the agreement with Beer's Law. However, on repitition, these graphs did not have identical slopes although every graph must pass through the origin, as this is the point on which the instrument was standardised. In the first case, the difference of slope between the lines A and B in Fig. 35 (a) is small, but in Fig. 35 (b), there is a considerable difference between the slopes of lines (a) and (b). This difference is most likely due to fatigue effects of the photo-cell, and that the light intensity versus current output relationship for the photo-cell is not linear. In this case the latter reason is probably the most significant, as the method of standardising the instrument is to vary the light intensity.

Therefore, instead of having a fixed standardisation curve for each concentration, the slope of the standardisation curve must be known for each and every reading. It would be impossible to repeat the entire graph for every reading taken but, since the graphs have been shown to be linear, only two points need be fixed in order to calculate the slope of the graph. Standardisation is always carried out on one of these points (100% dioxalate), and the other point may be fixed by recording a reading taken on pure trioxalate solution after each kinetic reading. The procedure in taking a reading during a kinetic run will therefore be as follows :

The instrument is standardised on pure <u>cis</u> dioxalate; the transmission is set at 100%, giving an optical density reading of zero. This density is denoted by D_D. The tube containing the reaction mixture is placed in the holder and its transmission (T_R) recorded; this is calculated in terms of optical density, D_R. Finally the pure trioxalate is placed in the holder, its transmission being T_T, and its optical density D_T. This procedure is repeated for each kinetic reading.

The three values of D obtained are represented in the graph below :



The three points are joined by a straight line, since the previous standardisation graphs all give linear relationships.

D_D represents 0% conversion to trioxalate
D_T " 100% " " "
D_R " x'% " " "

Therefore x' is given by

$$x' = \frac{D_R}{D_T} \cdot 100 \qquad \text{..........} \ (5.10)$$

Hence, by taking one extra reading, (D_T), for each kinetic reading (D_R), x', the percentage conversion to trioxalate, can be calculated directly without having to obtain complete standardisation graphs. If the slope of the graph changes in between readings, then D_T changes proportionately and the correct value of x' is still obtained.

The method of standardising on the two solutions representing pure reactants and pure product is the most obvious one to use. Such a "Transmittance-Ratio" technique has been described by Gridgeman (68), and it has been used and mathematically analysed by several workers (53)(69).

5. DISCUSSION

The Evelyn Colorimeter is sensitive enough to distinguish between solutions of potassium trioxalatochromiate and potassium cis dioxalatodiaquochromiate. The difference between the two readings depends on the wavelength used and the concentrations of the solutions. By using one of the above solutions as a standard instead of water, a marked increase in sensitivity was obtained. The optimum wavelength was found to be 565 mμ, and sufficient differentiation between the densities of the two solutions, to enable kinetic readings to be taken, was obtained using concentrations of 0.001M or higher.

It would appear therefore, that, using the modifications in technique described, and by use of the differential standardisation method, the Evelyn Colorimeter is sufficiently sensitive and reliable to enable a study of the kinetics of the formation of the trioxalatochromiate ion to be made.

SUMMARY

In order to follow up certain kinetic studies

involving the formation of the trioxalatochromiate ion from cis dioxalatodiaquochromiate and potassium oxalate, three instruments were investigated.

The general principles of the Beckman Spectrophotometer Model DU have been given and the reasons for its unsuitability in the present case discussed.

The theory of a Differential Photoelectric Absorptiometer, together with details of its expected performance, design, construction, operation and standardisation, have been given. Results of attempted standardisations have been recorded, and the possible reasons for its failure to give reproducible results are discussed.

A description of the principles and operation of the Evelyn Colorimeter is given, together with modifications and techniques in operation and standardisation required, in this case, for the kinetic studies. It appears that the kinetics under consideration can be satisfactorily studied using this instrument.

CHAPTER VI.

THE KINETICS OF THE REACTION BETWEEN POTASSIUM cis DIOXALATODIAQUOCHROMIATE AND POTASSIUM OXALATE IN AQUEOUS SOLUTION

1. INTRODUCTION

As has been shown in the previous chapter, the Evelyn Colorimeter is sufficiently sensitive for concentrations as low as .001M in chromium and, by the method of standardisation described, it was used to follow the kinetics of the reaction between potassium cis dioxalatodiaquochromiate and potassium oxalate.

Burley (14) studied this reaction and found it to be of the second order. The reaction is :

cis dioxalatodiaquochromiate ion + oxalate ion → trioxalato-chromiate ion + water .... (6.1)

Let the initial concentrations of the reactants cis dioxalate and potassium oxalate be a and b respectively at time $t = 0$.
Let the concentration of the product be x at time t.
For a second order reaction, the rate of reaction is proportional to the concentrations of the two molecular species :

$$\frac{dx}{dt} = k_2(a-x)(b-x) \quad \text{..........} \quad (6.2)$$

or

$$\frac{dx}{(a-x)(b-x)} = k_2 dt$$

where k_2 is the velocity constant.
Integration being performed by the method of partial fractions, we have :

$$k_2dt = \frac{1}{a - b}\left[\int\frac{-dx}{a - x} + \int\frac{dx}{b - x}\right]$$

$$k_2dt + A = \frac{1}{a - b} . \ln\frac{a - x}{b - x}$$

The boundary condition is $x = 0$ at $t = 0$, so that,

$$A = \frac{1}{a - b} . \ln\frac{a}{b}$$

Whence $$k_2t = \frac{1}{a - b} . \ln\frac{b(a - x)}{a(b - x)}$$

When the two initial concentrations are made equal, i.e. $a = b$, then (6.2) becomes

$$\frac{dx}{dt} = k_2(a - x)^2$$

or $$\frac{dx}{(a - x)^2} = k_2dt$$

On integration,

$$\frac{1}{(a - x)} = k_2t + B$$

at $t = 0$, $x = 0$,

thus $$B = \frac{1}{a}$$

and $$k_2t = \frac{1}{(a - x)} - \frac{1}{a} \quad \text{...........} \quad (6.3)$$

the dimensions of k_2 being time^{-1}. $\text{concentration}^{-1}$.

Rearrangement of equation (6.3) gives :

$$\frac{1}{a - x} = \frac{1}{a} + k_2t \quad \text{............} \quad (6.4)$$

On plotting $1/(a - x)$ against t, the graph should be in the form of a straight line, the velocity constant being given by its slope.

When using the Evelyn Colorimeter, it is convenient to express the concentration x of reaction product as a percentage of the initial concentration a. Thus if the percentage conversion to trioxalate is represented by x', equal to 100x/a, equation (6.4) can be put in the form :

$$\frac{1}{100 - x'} = \frac{1}{100} + \frac{k\ at}{100}$$

and the slope of the plot of $1/(100 - x')$ against t is given by ka/100.

Accordingly, $$k = \frac{100\ .\ \text{slope}}{a} \quad \text{..........} \quad (6.5)$$

where a is the initial concentration of cis dioxalato complex ion and potassium oxalate, expressed as moles/litre, and t is measured in minutes.

2. EXPERIMENTAL.

Two sets of kinetics were studied : one on equimolar mixtures of potassium cis dioxalatodiaquochromiate and potassium oxalate at various concentrations, and the other on a fixed equimolar concentration of the reactants, the ionic strength being varied by the addition of increasing quantities of potassium nitrate.

(a) Preparation of Solutions

(i) Potassium cis dioxalatodiaquochromiate. The solid trans dioxalatodiaquochromiate salt was used in preference to the solid cis isomer, as it was considered to be purer. 0.01, 0.008, 0.006, 0.004, and 0.002 Molar solutions were prepared by weighing out the required amounts of the trans salt, dissolving in distilled water, and allowing to age to the **cis** form. These solutions were used for the first kinetic series mentioned above.

For the second kinetic series, a quantity of 0.006 Molar cis dioxalatodiaquochromiate solution was prepared in the same manner.

(ii) Potassium trioxalatochromiate. 0.005, 0.004, 0.003, 0.002, and 0.001 Molar solutions of this salt were prepared for the first series of kinetics, and a quantity of 0.003M solution for the second series.

(iii) Potassium oxalate. Solutions of concentrations 0.01, 0.008, 0.006, 0.004 and 0.002 Molar were prepared from A.R. potassium oxalate for the first kinetic series and several flasks of 0.006M solution for the second series. To each of these latter flasks were added calculated quantities of A.R. potassium nitrate to increase the ionic strengths.

For the first kinetic series the ionic strengths obtained by mixing equimolar quantities of the cis dioxalate and potassium oxalate solutions were $\sqrt{\mu} = 0.1414$, 0.1265, 0.1095, 0.0894, and 0.0633.

In the second kinetic series, the lowest ionic strength was that of equal quantities of 0.006M solutions of cis dioxalato and potassium oxalate, $\sqrt{\mu} = 0.1095$. The quantities of potassium nitrate added to the other flasks of potassium oxalate gave ionic strengths corresponding to $\sqrt{\mu} = 0.1916$, 0.2480, 0.2936, and 0.3333 when mixed with equal amounts of 0.006M cis dioxalate.

The flasks containing the mixtures of potassium oxalate and nitrate were sterilized before being filled with the solutions, and when filled, they were kept in a refrigerator. This was to prevent the growth of bacteria which was observed when the solutions were kept at room temperature. Before kinetic runs, aliquots of these cold solutions were removed, allowed to attain the controlled temperature of the room (22.2°C.) and then 10 ml. portions were pipetted into the tubes in the usual manner.

The potassium oxalate used was found to be not less than 99.8% pure, as indicated by titration against potassium permanganate standardised directly with A.R. sodium oxalate.

Optical density measurements were made on solutions of potassium oxalate and nitrate of the concentrations used, and it was found that these solutions had no measurable density at 565 mμ.

The chromium solutions used were very stable as was shown by repeating some transmission readings after they had stood for several months - the readings were in agreement.

(b) Procedure

For a complete kinetic run, the following procedure was adopted :

To eleven matched absorption tubes were added exactly 10.0 ml. of a cis dioxalate solution of double the required concentration, and 20 ml. of trioxalate solution of the required concentration was added to a twelfth tube.

10.0 ml. aliquots of potassium oxalate solution of the same concentration as the cis dioxalate solution, were added to ten boiling tubes; to an eleventh tube was added 10.0 ml. of distilled water.

Storage and pipetting were done in a constant temperature room (22.2°C.), the same NPL Grade A pipette being used throughout and full drainage time was allowed for in each case.

The tubes were tightly stoppered and all, except the one containing trioxalate, suspended in the water bath and given at least an hour in which to attain the working temperature.

The contents of a tube containing dioxalate and those of the tube containing distilled water were first mixed; the absorption tube containing this mixture was the one used for standardisation of the instrument, the contents of this tube after mixing, being of the same concentration as the trioxalate. The other tubes containing cis dioxalate were mixed with the potassium oxalate solutions in the same way, and the time at which mixing occurred was recorded. The absorption tubes, now containing 20 ml. of reaction mixture, were immediately replaced in the water bath and allowed to react at the working temperature. Each tube was immersed right up to the stopper, as it was found that condensation occurred on the inside walls of the tubes projecting above the level of the water in the bath; this condensation caused concentration changes which led to erratic results. If the tubes were not completely clean inside, condensation occurred in spite of full immersion of the tubes.

After a suitable period had elapsed, a tube was removed and cooled in cold water, the time being recorded. After cooling, the outside of the tube was immediately dried and polished and its transmittancy measured.

For this measurement the instrument was standardised on 100% transmission with the tube of cis dioxalate in place; the reading of the reaction mixture was then recorded and also that of the trioxalate solution. These readings were repeated at least three times, the cis dioxalate solution being used to standardise the instrument each time, and the mean of the readings was recorded. The densities of the reaction mixture and the trioxalate, D_R and D_T respectively were calculated ($D = 2 - \log \%T$), and the percentage conversion to trioxalate, x', calculated as previously described. The values of $1/(100 - x')$ were plotted against time, t.

The second order curves for the first set of kinetics with no potassium nitrate added, are shown in Figs. 36 to 40. A set of five concentrations were used for each of five different temperatures; the readings are recorded in Tables A 20 to A 24 of the Appendix, where the first table, A 20 shows in full the transmission readings taken, while the following tables give the calculated densities only.

As is seen later (Fig. 45), this first series of kinetics gave results in disagreement with Burley's. As a check that the method and instrument were not the cause of

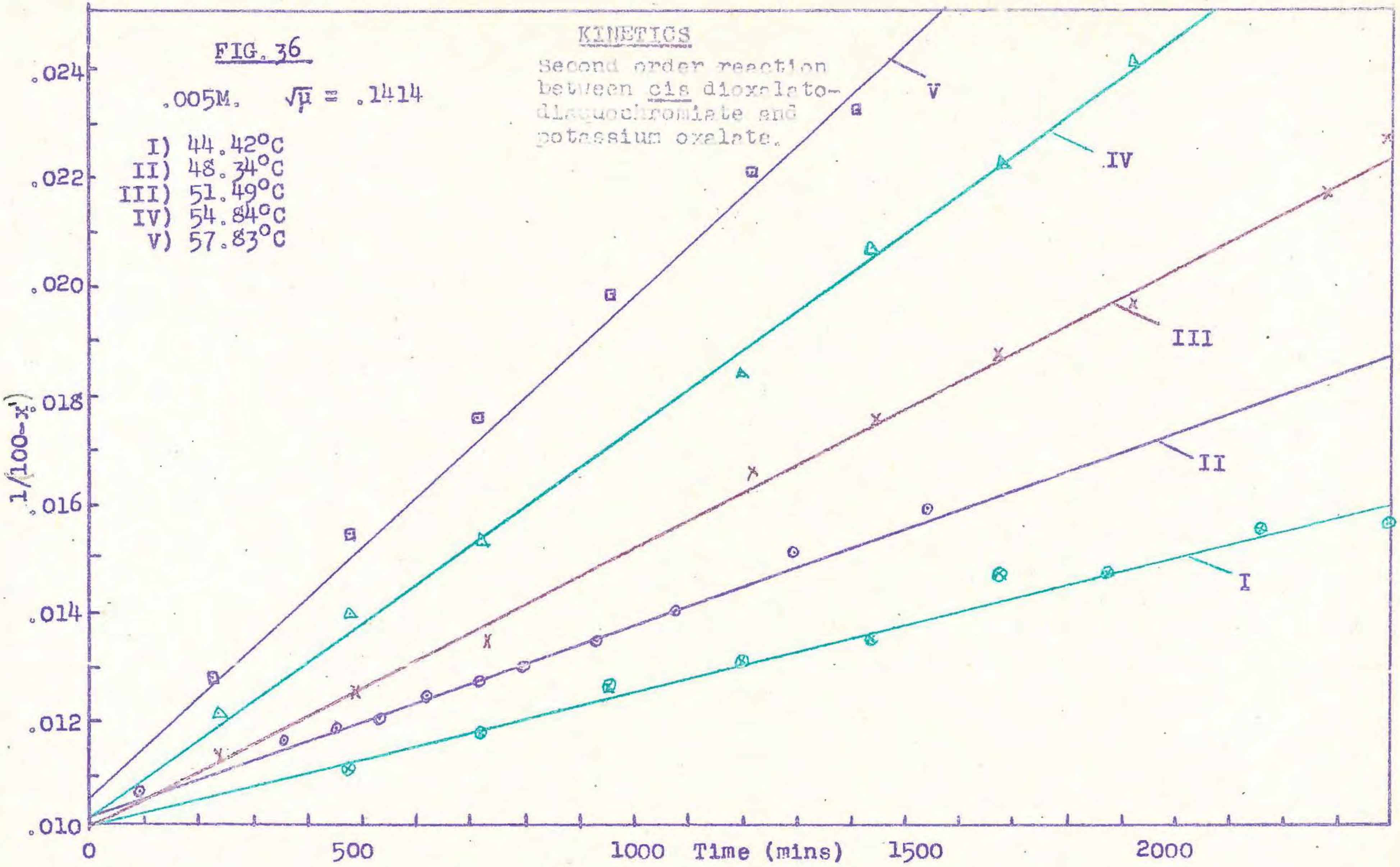


FIG. 36

.005M. $\sqrt{\mu} = .1414$

I) 44.42°C
II) 48.34°C
III) 51.49°C
IV) 54.84°C
V) 57.83°C

KINETICS

Second order reaction between *cis* dioxalato-diaquochromiate and potassium oxalate.

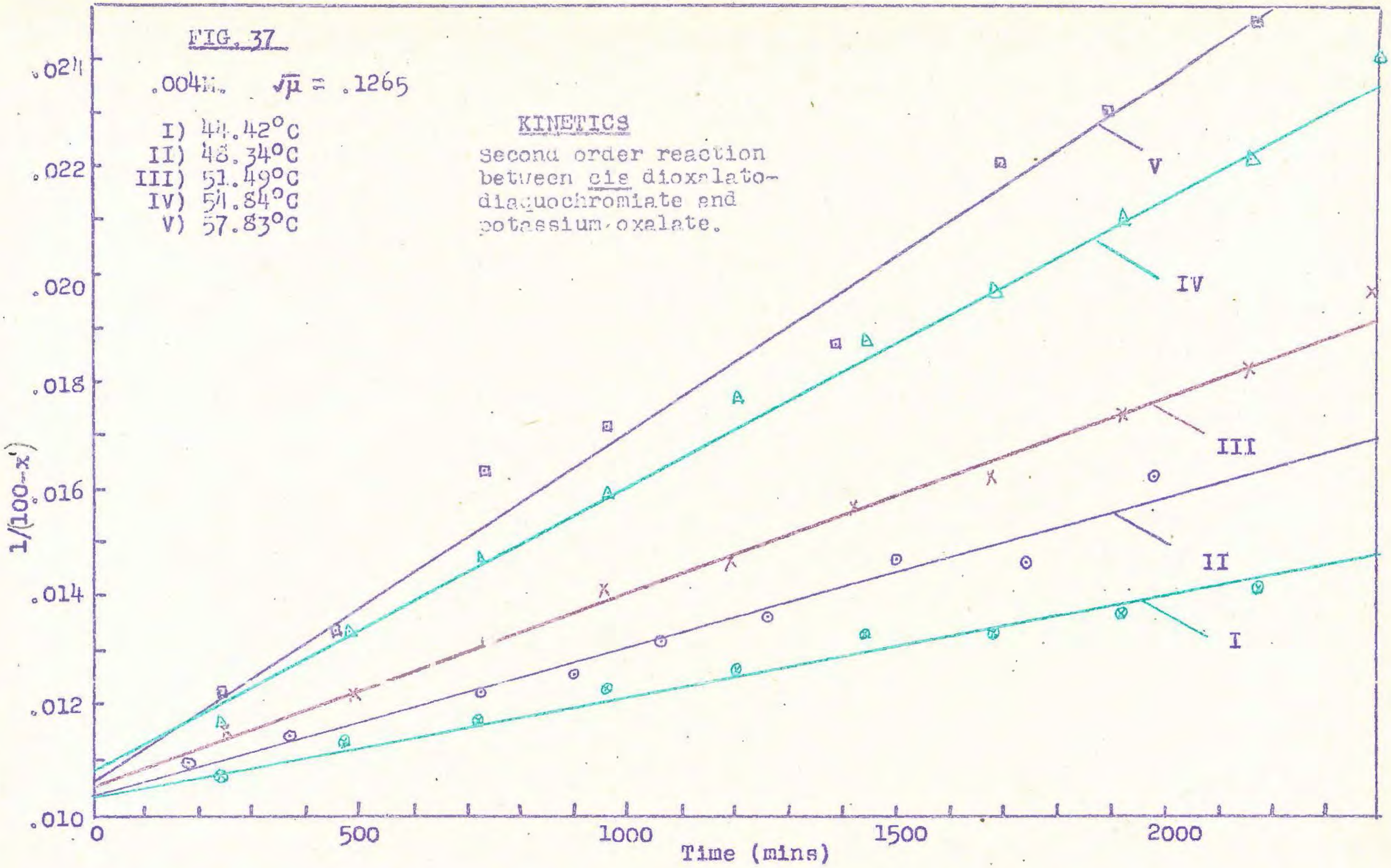


FIG. 37

KINETICS

Second order reaction between *cis* dioxalatodiaquochromiate and potassium oxalate.

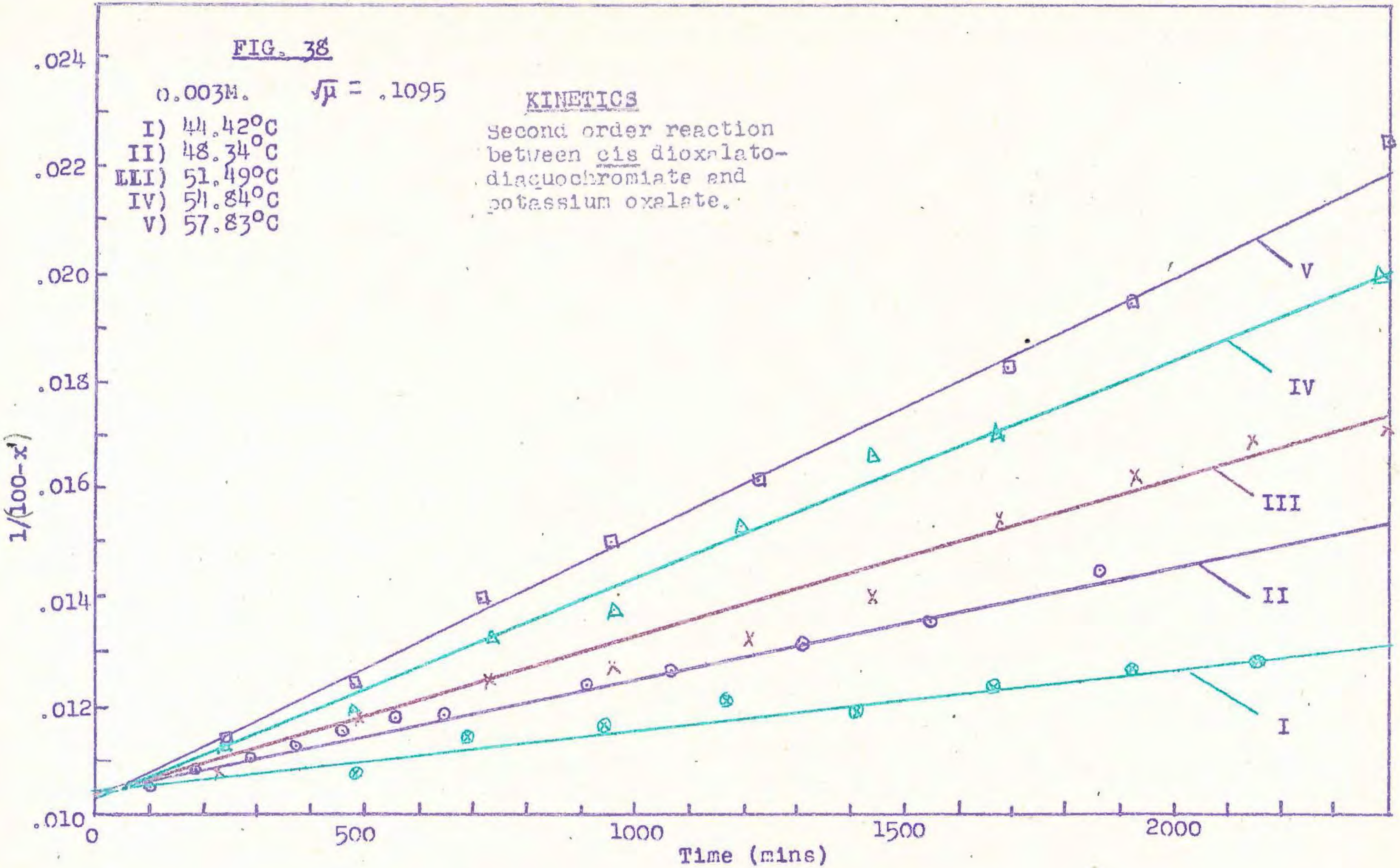


FIG. 38

KINETICS

Second order reaction between cis dioxalato-diaquochromiate and potassium oxalate.

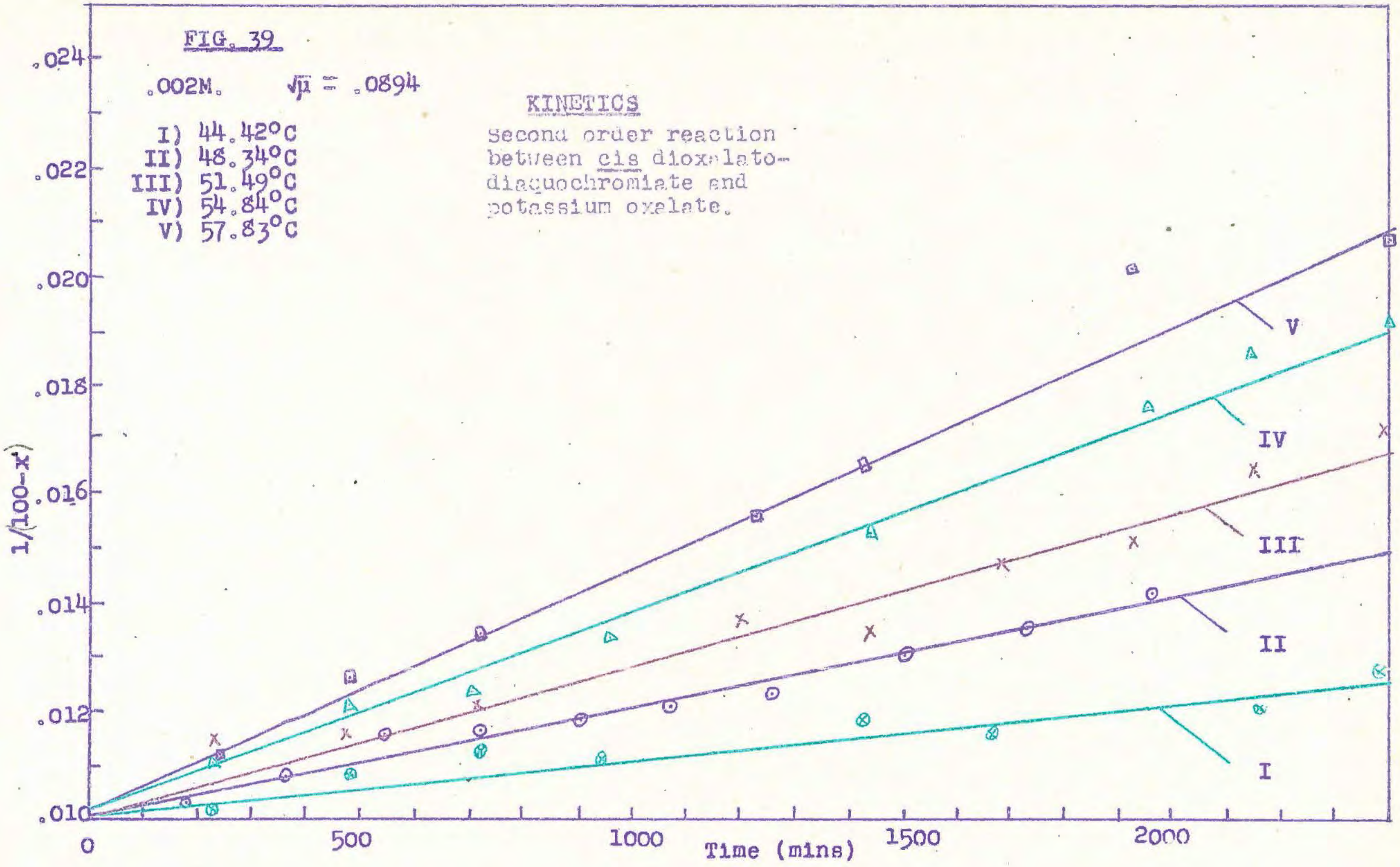


FIG. 39

.002M. $\sqrt{\mu} = .0894$

I) 44.42°C
II) 48.34°C
III) 51.49°C
IV) 54.84°C
V) 57.83°C

KINETICS

Second order reaction between cis dioxalato-diaquochromiate and potassium oxalate.

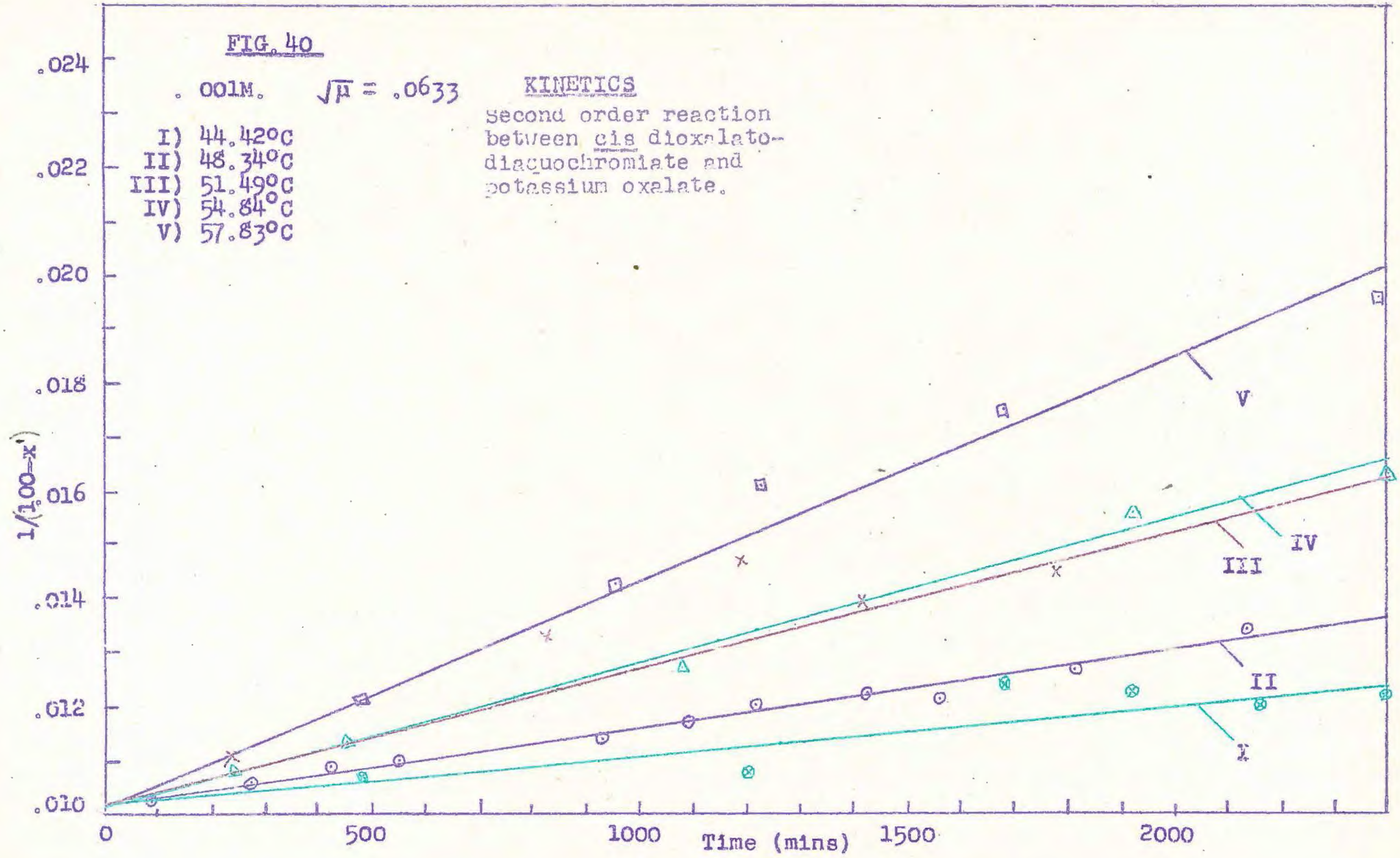


FIG. 40

.001M.
$\sqrt{\mu} = .0633$
KINETICS
Second order reaction between cis dioxalato-diacuochromiate and potassium oxalate.
I) 44.42°C
II) 48.34°C
III) 51.49°C
IV) 54.84°C
V) 57.83°C
V
IV
III
II
I
.024
.022
.020
.018
.016
.014
.012
.010
1/(1.00-x')
0
500
1000
1500
2000
Time (mins)

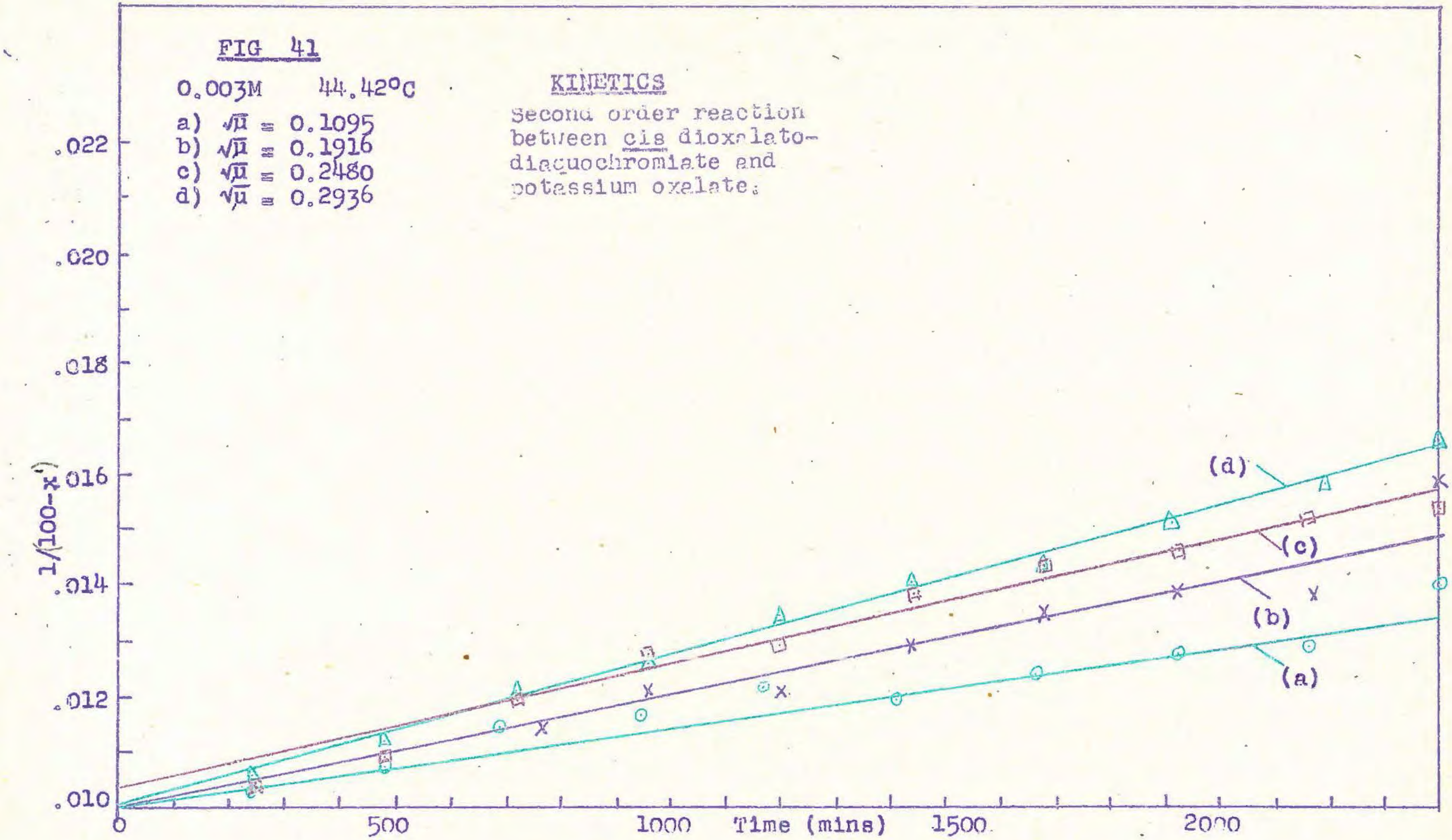


FIG 41

KINETICS

Second order reaction between cis dioxalatodiacuochromiate and potassium oxalate.

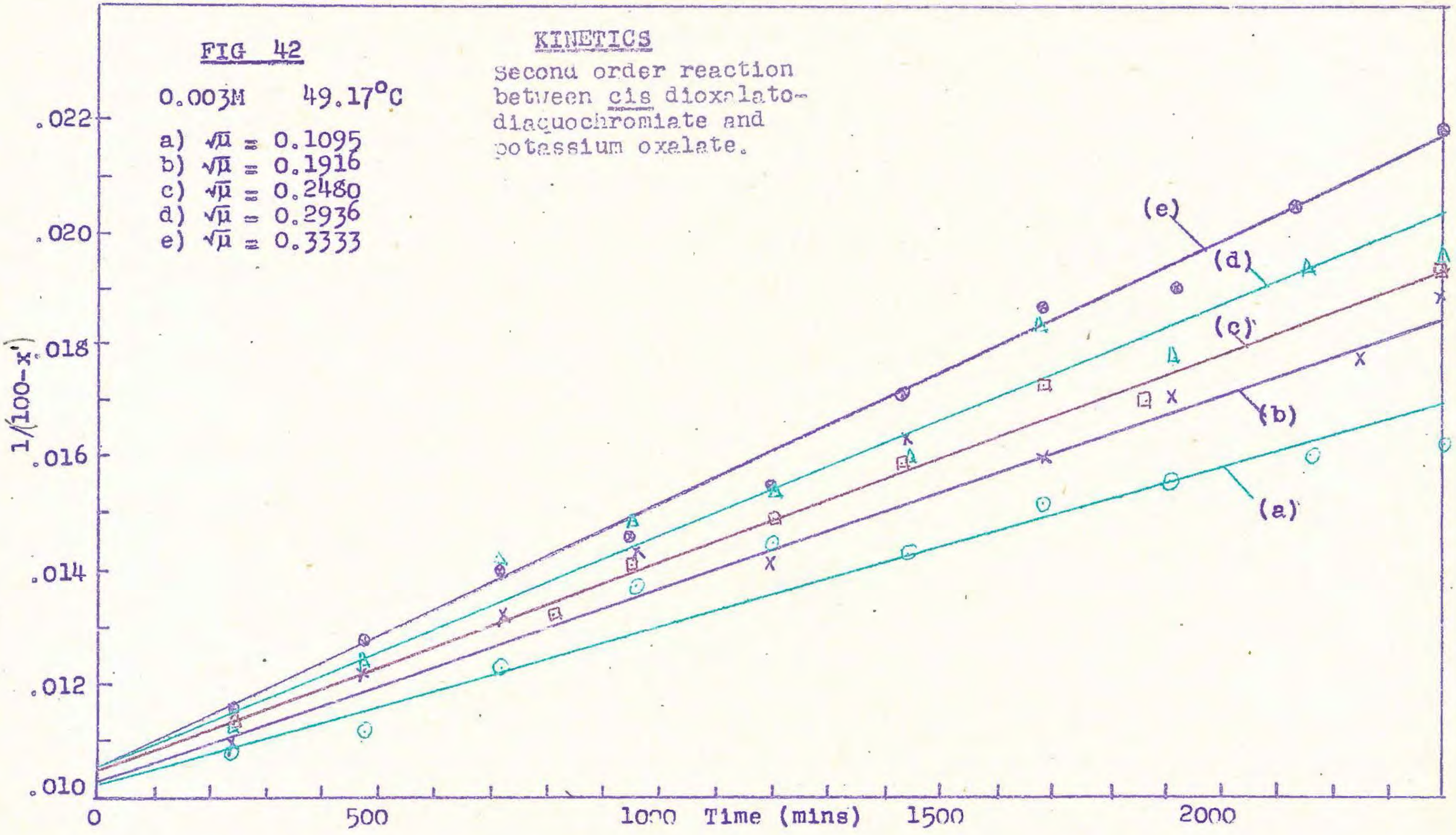


FIG 42

KINETICS

Second order reaction between cis dioxalato-diaquochromiate and potassium oxalate.

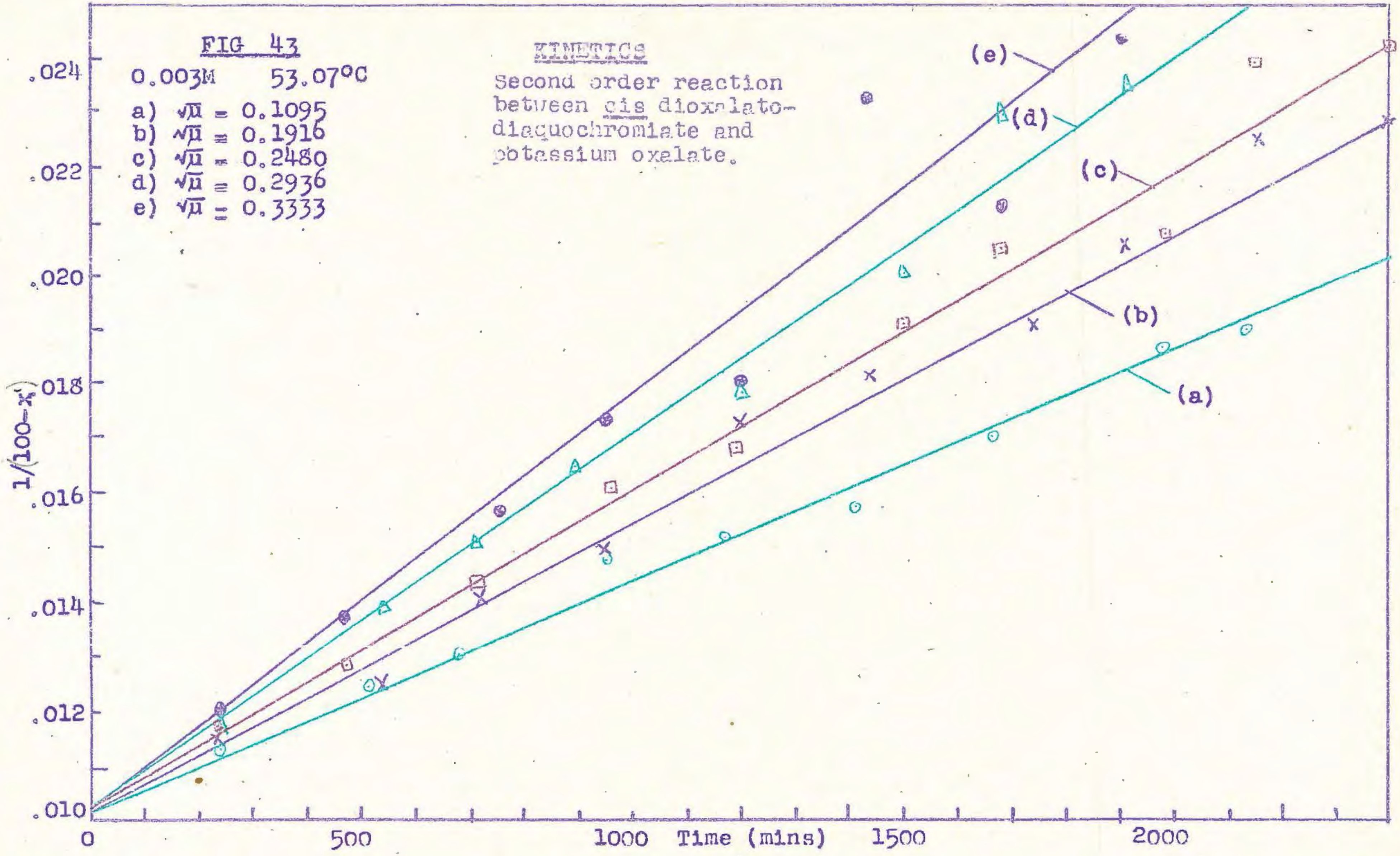


FIG 43

0.003M 53.07°C

KINETICS

Second order reaction between cis dioxalato-diaquochromiate and potassium oxalate.

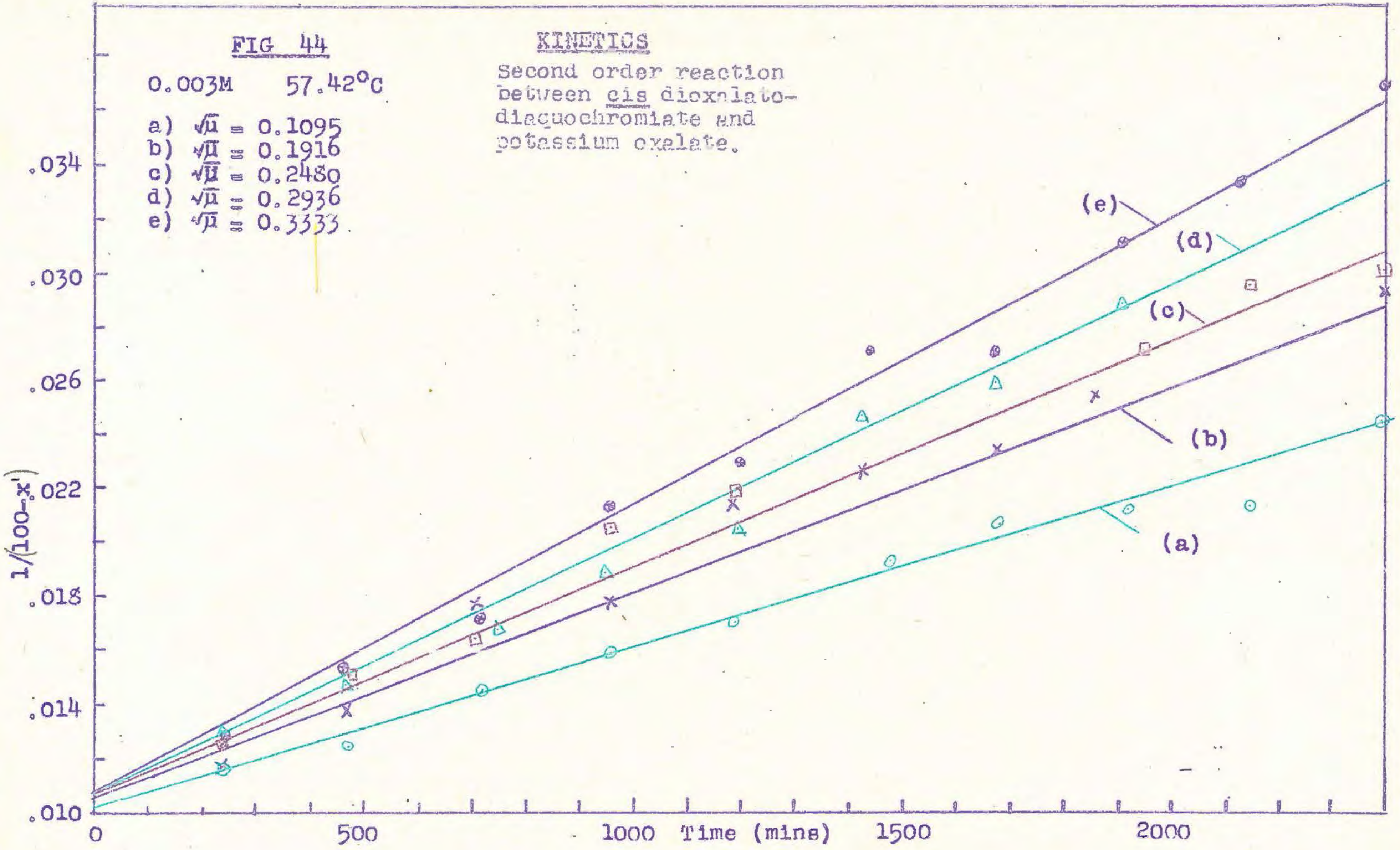


FIG 44

KINETICS

Second order reaction between cis dioxalatodiaquochromiate and potassium oxalate.

these results, a fresh series of kinetics were carried out and, as described above, potassium nitrate was used to increase the ionic strength. It was still possible to work at ionic strengths somewhat lower than those of Burley, and the results are shown in Figs. 41 to 44, and Tables A25 to A28. Here results agreeing with Burley's were obtained. The two sets of results are discussed in later sections.

The water bath temperature was read at intervals throughout the runs, and the mean value recorded. The thermometer used was one recently standardised at the National Physical Laboratory, Pretoria; corrections were to within 0.02°C, and temperatures were read to 0.02°C also.

The ionic strengths were calculated from the definition : $\mu = \frac{1}{2}\Sigma CZ^2$, where C is the concentration of an ion of charge Z.

3. RESULTS

The graphs in Figs. 36 to 44 show that a relationship of the predicted linear form exists, and that the reaction studied was one of the second order. The reaction rate decreases with decreasing concentration; and at higher values of x' the points show some scatter due to the decrease in the difference $D_T - D_R$. The best lines are seen to be those at the higher concentrations and lower temperatures.

For each line the value of the velocity constant k was calculated using the equation :

$$k = \frac{100.\ \text{slope}}{C \times 60} \quad \text{litres. moles}^{-1}.\ \text{secs}^{-1}.$$

The values of k and $\log_{10}k$ at each ionic strength and at each temperature are recorded in Tables A29 and A30 of the Appendix.

A bimolecular reaction follows the scheme :

$$A + B \rightleftharpoons X \longrightarrow \text{Products} \quad \text{...........(6.6)}$$

where A and B are the reactants; X represents the Brønsted concept of a critical collision complex of great instability, whose charge, Z_X, should equal the algebraic sum of the charges on the reactants : i.e. $Z_X = Z_A + Z_B$.

Brønsted and Livingston (70) have shown that the kinetic velocity constant, k, is not a true constant, but is a function of the total salt concentration :

$$k = k_o .\ f_A\ f_B\ /\ f_X \quad \text{...................(6.7)}$$

f_A, f_B and f_X denoting the activity coefficients of A, B and X respectively. Thus k varies proportionately to the "kinetic activity factor", f_Af_B/f_X.

According to the Debye-Hückel theory, the activity coefficient, f, of a given ion may be calculated from the relation :

$$-\ln f = \left[\frac{N^2 \varepsilon^3 (2\pi)^{3/2}}{(DRT)^{3/2}(1000)^{1/2}} \right] Z^2 \sqrt{\mu} \quad \text{...(6.8)}$$

where Z is the valence of the ion under consideration

μ is the ionic strength

N is Avogadro's number

ε is the electronic charge

D is the dielectric constant of the medium

R is the gas constant

T is the absolute temperature.

The factor in parenthesis contains universal constants only and may be denoted by the symbol A.

Equation (6.7) may thus be written in the following form, known as the Brønsted-Bjerrum equation :

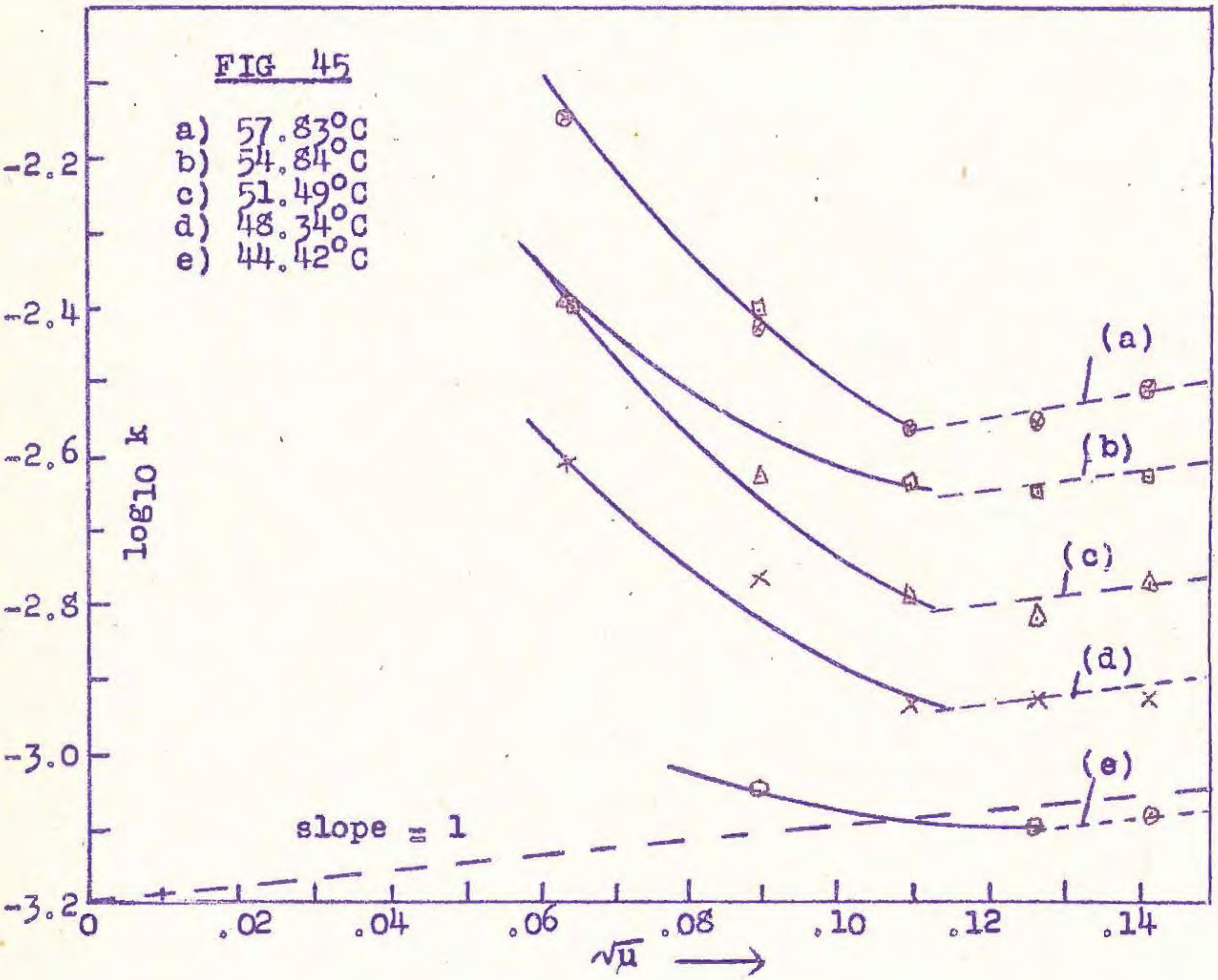
$$\log_{10} k = \log_{10} k_o + \frac{2A\ Z_A Z_B}{2.303} \sqrt{\mu} \quad .....(6.9)$$

Since the term 2A/2.303 has a value of about unity at 25°C, the plot of $\log_{10} k$ versus $\sqrt{\mu}$ should give a straight line of slope very nearly equal to $Z_A Z_B$ and intercept $\log_{10} k_o$, k_o being the value of the velocity constant at zero ionic strength. The linear relationship should hold provided the solutions used obey the conditions of the Debye-Hückel theory.

The upper limit to the value of μ for which this relationship still holds varies considerably with the type of reaction taking place. Livingston (71) has considered the data of five available reactions, and found agreement to values of $\sqrt{\mu} = 0.2$, but at higher ionic strengths, departures from linearity were noted. He points out that satisfactory agreement is also found in certain cases with values of $\sqrt{\mu}$ as high as 0.45 to 0.55. It has been found that in reactions where the intermediate complex is a neutral molecule, the theory may be applied to reactions occurring in much more concentrated solutions (72).

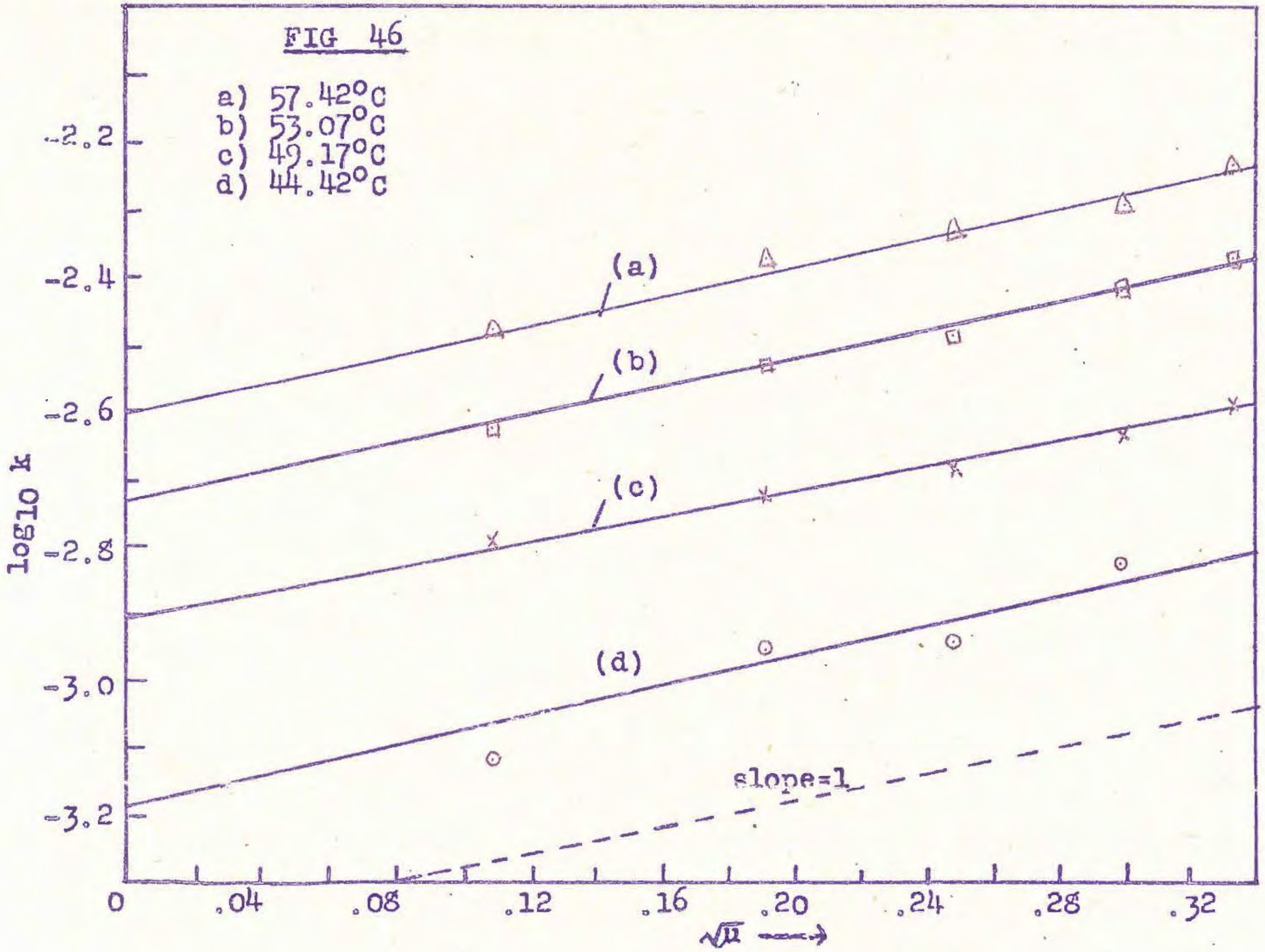
Equation (6.9) has been applied to the data obtained from the two sets of kinetic studies described. Log_{10} k has been plotted against $\sqrt{\mu}$, as shown in Figs. 45 and 46. The former figure refers to the kinetic data with

FIG 45



Variation of velocity constants with ionic strength with no potassium nitrate added.

FIG 46


a) 57.42°C
b) 53.07°C
c) 49.17°C
d) 44.42°C
(a)
(b)
(c)
(d)
slope=1
-2.2
-2.4
-2.6
-2.8
-3.0
-3.2
log10 k
0
.04
.08
.12
.16
.20
.24
.28
.32
√μ →

no potassium nitrate added and the latter one is for the series in which potassium nitrate was used to vary the ionic strength.

The value of the constant A in equation (6.9) is 1.237 at $50^\circ C$ using a value of 69.94 for D, the dielectric constant of the medium (73).

The Brønsted-Bjerrum equation at $50^\circ C$ is therefore :

$$\log_{10} k = \log_{10} k_o + 1.07\ Z_A Z_B \sqrt{\mu} \quad \ldots\ldots(6.10)$$

Thus in the plot of $\log_{10} k$ versus $\sqrt{\mu}$, the slope should be very near to unity if, as Burley found, the product of the charges $Z_A Z_B$ is unity.

Fig. 45 shows the plot for the series in which ionic strength was varied by varying the chromium concentration only. A dotted line of unit slope has been drawn through the three points at the highest chromium concentrations. Even if these experimental points are considered to be reasonably close to the theoretical line, it is evident that the remaining observations at lower ionic strengths apparently follow a different law.

On the other hand Fig. 46, which refers to the series in which the chrome concentration was maintained constant at 0.003M., and the ionic strength varied by means of potassium nitrate, shows that the Brønsted-Bjerrum equation is obeyed over the whole range, the product of the ionic charges being unity. This result is in agreement with Burley's observations made at higher ionic strengths and employing a somewhat different technique.

4. THEORETICAL DISCUSSION

It is apparent, both from the earlier work of Burley and from the results obtained in the present work, that when the chromium concentration is kept constant and the ionic strength is varied with a neutral salt, the Brønsted-Bjerrum equation is applicable, and the reaction appears to be of the type :

$$A^- + B^- \longrightarrow AB^=$$

as indicated by the fact that the product $Z_A Z_B$ is + 1.

This seems to indicate that the rate-determining step in the reaction is the reaction between the binoxalate ion $\left[(COO)_2H\right]^-$ and the dioxalatodiaquochromiate ion $\left[Cr(C_2O_4)_2(H_2O)_2\right]^-$ as originally postulated by Burley. The present data obtained at lower ionic strengths than those employed by Burley, show that the slope of the expected order of unity is not fortuitous.

On this view the non-linear relationship obtained at high dilutions when the chromium concentration is not maintained constant is somewhat disconcerting, since there is no obvious reason why this should be so in terms of the Debye-Hückel theory of Primary Salt Effect. Certain simplifying assumptions have been made however, one of the most important being that the appropriate ionic strength to be used in the Brønsted-Bjerrum equation is the initial ionic strength. If we assume that the principal reaction is between dioxalate ions and binoxalate ions, the ionic strength will vary with time according to the formula :

$$\mu = 2a(2 + x') \text{ .... } (6.11)$$

Where a is the initial concentration of reactants, and x' is the degree of completion of the reaction at any time t.

However if this increase in ionic strength during reaction is to be considered significant, then the effect should be noticeable in the second order curves : the slope would increase with time. All the graphs are linear however, and it is apparent that any changes in ionic strength that might occur are not sufficient to affect the apparent order of the overall reaction over the range of ionic strengths and temperatures used.

Another possibility is that the reaction is actually one of the third order involving hydrogen ions. The concentration of these ions compared with those of the reactants would normally be small at moderate chromium concentration, and hence the effect on the second order curves would not be noticeable. Nevertheless it is conceivable that at high dilutions the hydrogen ions would have sufficient influence on the relation between $\log_{10}$ k and $\sqrt{\mu}$ to cause the loss of linearity seen in Fig. 45.

This follows from the fact that the hydrogen ion concentration of the reacting mixture depends on the ionic dissociation of the reactants, and hence on the dilution of the solutions. It has been shown that the ion that appears to react with the <u>cis</u> dioxalatodiaquochromiate ion is the half-neutralised oxalate ion or binoxalate ion $[(COO)_2H]^-$; the quantity of this ion present in solution will depend on the pH, oxalate ions being present in greater amount as the pH increases.

Considering the equilibria :

$$\begin{array}{ccccc} (COO)_2^{=} & + & H^+ & \overset{K_2}{\rightleftharpoons} & [COO.COOH]^- \\ A-x-B & & h & & B \end{array}$$

and

$$\begin{array}{ccccc} [Cr(C_2O_4)_2(H_2O)_2]^- & \overset{K_1}{\rightleftharpoons} & [Cr(C_2O_4)_2.H_2O.OH]^{=} & + & H^+ \\ D & & A-x-D & & h \end{array}$$

Where A is initial concentration of oxalate

B is concentration of binoxalate

D is concentration of dioxalate

x is concentration of trioxalate formed.

then $K_2 = \frac{(A-x-B)h}{B}$ and $K_1 = \frac{(A-x-D)h}{D}$

$\therefore B = \frac{(A-x)h}{K_2 + h}$ $\therefore D = \frac{(A-x)h}{K_1 + h}$

For a second order reaction the reaction velocity is given by :

$$\frac{dx}{dt} = k_o \; B.D.$$

Where k_o is the true velocity constant.

$$\text{Now } \frac{B}{D} = \frac{K_1 + h}{K_2 + h}$$

$$\therefore D = \frac{K_2 + h}{K_1 + h} . B.$$

$$\therefore BD = B^2 \; \frac{K_2 + h}{K_1 + h}$$

$$= (A - x)^2 . \; \frac{h^2}{(K_1 + h)(K_2 + h)}$$

Here A corresponds to the initial concentration of reactant a in equation (6.3), so we may write :

$$kt = \frac{1}{A - x} - \frac{1}{A}$$

and this is derived for a bimolecular reaction assuming that the initial concentration of the two reactants are equal :

$$\text{i.e.} \qquad \frac{dx}{dt} = k(A - x)^2$$

It is clear therefore, that this velocity constant k is related to the true velocity constant k_0 by a factor BD,

$$\text{or} \qquad k_0 = \frac{(K_2 + h)\ (K_1 + h)}{h^2}\ k \quad .....(6.12)$$

A being maintained constant. h is presumed constant if it is assumed that dh/dt is relatively small, which should be the case since the system is relatively well buffered, although strictly speaking, the activity coefficients must also be taken into account.

The relation between the observed k's at different values of A might therefore be a function of dissociation as reflected by the difference in the initial hydrogen ion concentration. This possibility is shown in Fig. 45, where it is observed that at the higher chrome concentrations, the effect on the slopes is very much less than at the low concentrations where the slope changes rapidly.

Considering Fig. 46, in which the data from the second kinetic series have been plotted, little deviation from a slope of unity is apparent and the Brønsted-Bjerrum relationship is followed. In this case, as the concentration of the solutions is slightly higher, the dissociation effects are likely to be less noticeable and since the initial concentration of the reactants is constant throughout, any deviations due to dilution will equally affect all readings. By having considerable quantities of potassium nitrate present in solution, any changes in ionic strength and dissociation are rendered less noticeable.

The possibility that the results obtained are due partly to the secondary salt effect follows from the above considerations. In both the primary and secondary salt effects, the added electrolyte influences one or more of the factors in terms of which thermodynamic equilibrium is defined. In the case of the secondary salt effect, it is the equilibrium between one of the reactants and a third component, usually a constituent of a weak electrolyte, which is affected. This would be expected to have an effect in the second kinetic series, because the activity coefficients of the reactants decrease with the addition of neutral salts and the hydrogen ion concentration would therefore increase. However, it is this series of kinetics that gave the expected straight lines, and the secondary salt effect can be considered to exert little influence on the reaction with the neutral salt added.

Debye and Brønsted have extended the Brønsted-Bjerrum equation (6.9) for use at higher ionic strengths :

$$\ln K_{obs.} - \frac{A\ Z_A Z_B \sqrt{\mu}}{1 + \overset{o}{a} B \sqrt{\mu}} = \ln K_o - C\mu \ ....(6.13)$$

where A and B are constants depending on the temperature and the dielectric constant of the medium at that temperature and $\overset{o}{a}$ is the mean distance of closest approach of the ions in the solution; K_{obs} and K_o are the observed velocity constants and those at zero ionic strength respectively. This equation was applied to the data obtained in the kinetic studies. The value of $\overset{o}{a}$ was taken as 3×10^{-8} cm. (74) and the constants A and B have been calculated at various temperatures (75). The value of ϕ, representing the second term in equation (6.13) was found to be small (0.06 to 0.03) and the plot of $\log_{10} K_{obs} - \phi/2.303$ against μ gave a result little different from the graphs shown in Fig. 45.

It appears then, that the range of ionic strengths over which the kinetics were conducted were within the limits of the Debye-Hückel relationship as the extended form of the equation for more concentrated solutions made very little difference.

The effects noticed in these kinetic studies are unlikely to be due to departure from the Debye-Hückel theory at the higher concentrations, as the results obtained in these regions are those that conform to the theory.

While it is evident that in the presence of potassium nitrate the Secondary Salt Effect has negligible influence, the departure from the relationship predicted on the Brønsted-Bjerrum theory in the absence of neutral salts

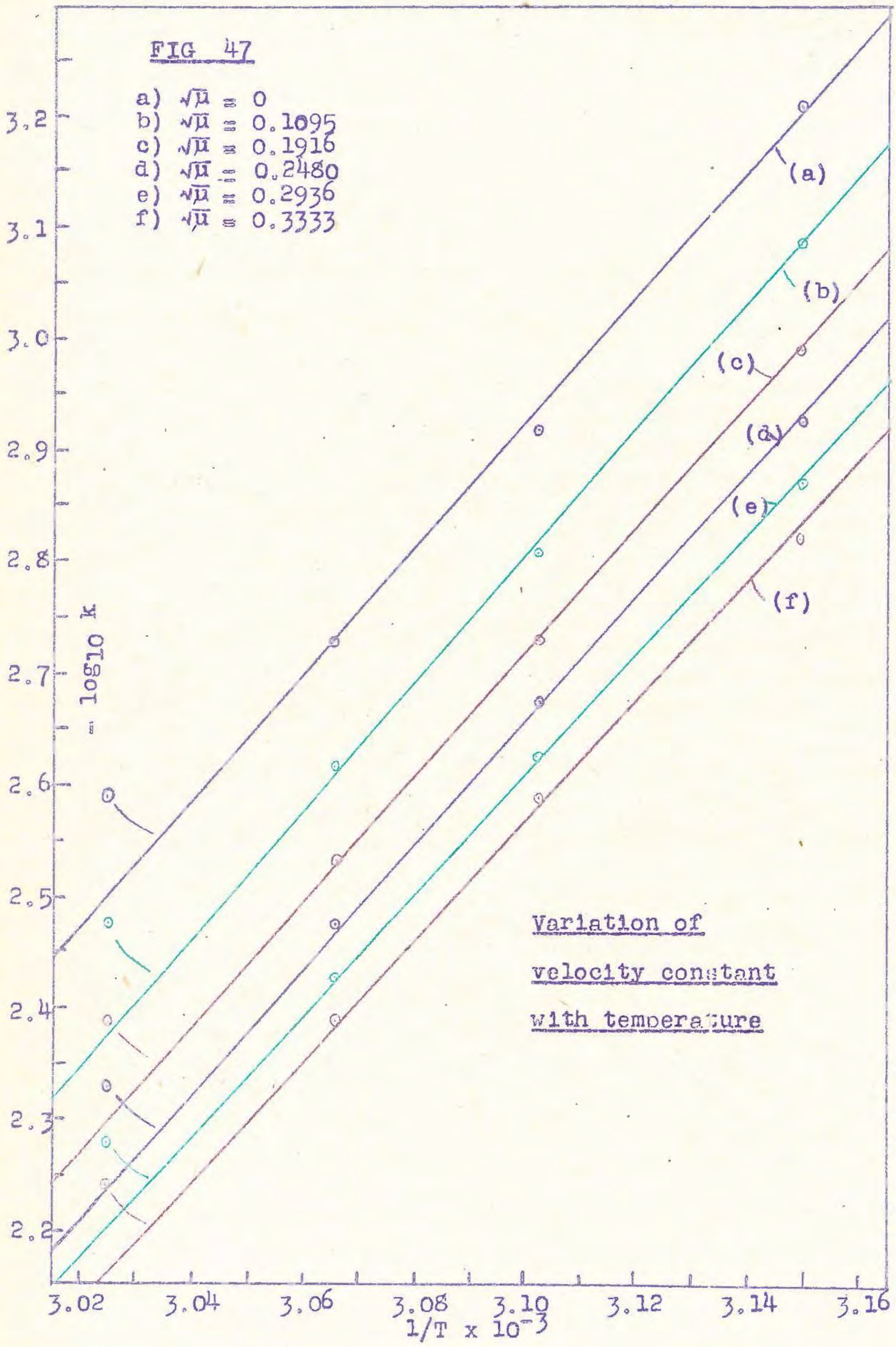


FIG 47

Variation of velocity constant with temperature indicates that the reaction is sensitive to ionic dissociation of the reactants. The phenomenon is thus analagous to acid base catalysis. Since it would be impossible to maintain the pH constant by the addition of buffer salts (which might react with the chromium complex), a quantitative study of the kinetics of the reaction in the presence of an excess of mineral acid would be of interest.

The Arrhenius Equation

The variation with temperature of the velocity constant for a thermal reaction occurring in solution may be expressed by the Arrhenius equation :

$$k = Ae^{-EA/RT}$$

$$\text{or } \log_{10} k = \log_{10} A - E_A/(2.303RT) \quad \ldots\ldots\ldots\ (6.14)$$

E_A is the "Experimental Activation Energy" of the reaction and A is a constant (depending on steric and other factors) known as the "Frequency Factor". T is the absolute temperature and R is the Gas Constant.

To test the applicability of this equation, the values of $-\log_{10} k$ were plotted against $1/T$ for the second kinetic series. The values of $-\log_{10}k_o$, k_o being the value of the velocity constant at zero ionic strength, were obtained by extrapolation from the lines in Fig. 46, and are recorded in Table A30 of the Appendix. The graphs obtained at each ionic strength are shown in Fig. 47.

Agreement with the Arrhenius equation appears reasonable if the points corresponding to the higher temperature are ignored. The appropriate values for the critical increment E_A and for the temperature independent factor A of the Arrhenius equation have been derived graphically from the data for the three lower temperatures and are shown in Table III below for each value of ionic strength.

TABLE III

Values of E_A and A at different ionic strengths

$\sqrt{\mu}$	E_A cals. $mole^{-1}$.	$\log_{10}A$	A
0	2.62×10^4	14.84	6.92×10^{14}
.1095	2.65 "	15.20	15.85 "
.1916	2.58 "	14.73	5.37 "
.2480	2.59 "	14.90	7.94 "
.2936	2.52 "	14.41	2.57 "
.3333	2.59 "	14.98	9.55 "

The values for $\sqrt{\mu} = 0$ have been obtained from the corresponding $\log_{10}k_o$ values derived from Fig. 46. The extent to which these data are subject to purely graphical errors may be gauged from the corresponding values of E_A and A calculated for $\sqrt{\mu} = 0$ by the method of least squares utilising only the three lower temperatures. These values were found to be 26,571 cals. $mole^{-1}$ and 11.92×10^{14} respectively, which should be compared with the figures given for $\sqrt{\mu} = 0$ in Table III above. For the same reaction Burley (14) found $E_A = 30,300$ cals. $mole^{-1}$ and $A = 6.3 \times 10^{21}$, also using graphical methods and assuming a linear relationship.*

The relative independence of A with temperature is indicated by the data in Table IV, where the derived values at different ionic strengths are tabulated for each individual temperature, using the corresponding E_A values calculated from Fig.47.

TABLE IV

Values of A at different ionic strengths and temperatures

$\sqrt{u}$	44.42°C.	49.17°C.	53.07°C.	57.42°C.
0	6.56x10^{14}	6.92x10^{14}	6.76x10^{14}	5.37x10^{14}
.1095	13.27 "	15.42 "	13.71 "	11.27 "
.1916	5.82 "	5.57 "	5.35 "	4.56 "
.2480	7.10 "	7.14 "	6.98 "	5.92 "
.2936	2.92 "	2.53 "	2.65 "	2.19 "
.3333	-	8.99 "	9.10 "	7.41 "

Since it is probable that the curvature observed in Fig. 47 if the higher temperature data are also taken into account is real, it would seem that except for purely empirical purposes limited to the temperature range 44 - 54°C., no real significance can be attached to the values recorded above, except insofar as they might be regarded as maximum values which the "true" parameters of the Arrhenius equation do not exceed.

---

* It seems possible that the results recorded by Burley for A are about 10^4 too high evidently through a computational error from his data in Fig. 32 (14), and the value of 2 x 10^{17} was calculated by the present writer.

If the data for the highest temperature are also included for the purpose of extrapolation, then a closer approach to the "true" values might reasonably be expected since the slope of the best straight line through all four points more nearly approaches the limiting slope of the curve as $^1/T \longrightarrow 0$.

By applying the method of least squares to all four points in Fig. 47 ($\mu = 0$), and still assuming that to a first approximation the Arrhenius equation is valid, the following relationship is obtained :

$$\log_{10} k = 12.7325 - 5055/T \quad \ldots\ldots\ (6.15)$$

The standard deviations of the intercept and slope in the above equation are ± 0.1551 and ± 477.2 respectively, and if these limits are assumed (corresponding to a probability of about 60% of including the "true"value between the fiducial limits set, for two degrees of freedom), the value of E_A may be taken to lie between 23,133 ± 1,782 cals. mole^{-1} and of A between 3.78×10^{12} and 7.71×10^{12}, with a most probable value of 5.40×10^{12}.

It will be noted that these values are considerably less than those previously calculated (or those derived by Burley), and the discrepancy indicates the large uncertainty introduced according to whether or not the data at the highest temperature are used in the calculations. Since on the assumption that the Arrhenius equation is valid there is no justification for omitting the data corresponding to the higher temperature, the revised figures quoted above seem more appropriate to the present case and are used below in comparing the observed specific reaction rate at $\mu = 0$ with the value calculated from theoretical considerations based on the Kinetic Theory of collisions between activated molecules.

The experimental factor $e^{-E_A/RT}$ in the Arrhenius equation may be regarded as a measure of the probability of the occurence of the activated state, or of the fraction of the total number of molecules that possess the necessary activation energy to enable them to react.

The number of molecules that possess sufficient energy for reaction will depend on the collision frequency or collision number Z_c. Assuming that all activated collisions give rise to reaction, we may write :

$$k = Z_o . e^{-E_A/RT} \quad \ldots\ldots\ldots\ldots\ldots (6.16)$$

If for steric or other reasons every collision between activated molecules does not result in reaction, this relationship would be further modified by a factor P, called the "steric" factor. Thus

$$k = PZ_o . e^{-E_A/RT} \quad \ldots\ldots\ldots\ldots (6.17)$$

The collision frequency, or collision number Z_o, is given by the Kinetic Theory equation

$$Z_o = \frac{N_o}{1000} . \sigma^2_{1,2} \left[8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2}\right) \right]^{\frac{1}{2}} \ldots (6.18)$$

which is for gas reactions but may be applied to reactions in solution.

Substituting this value of Z_o in equation (6.17) and taking $k = 1.202 \times 10^{-3}$ at 50°C., the calculated value for P is 72.9, taking E_A to be the value calculated by least squares from the whole of the data (Table A 30), namely 23,133 cals/mole.

If on the other hand the data for the highest temperature is excluded, on the grounds that this point introduces a non linear relationship into the Arrhenius plot, the value of E_A would be 26,571 cals/mole and the corresponding value of P about 1.4×10^4.

In either case it would appear that more molecules are activated than can be accounted for by collisions, an observation which is not uncommon in the case of ionic reactions in solution (77, 78).

If the energy may be distributed among s harmonic oscillators, application of the Maxwell-Boltzmann law shows that the bimolecular velocity constant with concentrations expressed in terms of moles/litre is given by : (82)

$$k_o = Z_o . e^{-E/RT} \left[\frac{E}{RT}\right]^{s-1} \frac{1}{(s-1)!}$$

where Z_o, the collision number is given by equation (6.18) and s represents the total number of degrees of freedom (translational, rotational and vibrational) among which the energy in the activated molecule may be distributed. Since one translational degree of freedom may be identified with vibration along the axis of the bond between the reactants, (s-1) may be replaced by F, the "internal" degrees of freedom. Thus :

$$k_o = Z_o e^{-E/RT} \left[\frac{E}{RT}\right]^F \frac{1}{F!} \quad .... (6.19)$$

$$= \bar{Z}_o \sqrt{T}\, e^{-E/RT} \left[\frac{E}{RT}\right]^F \frac{1}{F!} \quad ...... (6.20)$$

By taking logarithms and differentiating with respect to T, assuming E to be independent of temperature :

$$\frac{d \ln k_o}{dT} \doteq \frac{E}{RT^2} - \frac{(F-\frac{1}{2})}{T}$$

whence it follows that :

$$E = E_A + (F - \tfrac{1}{2})\, RT \quad .... (6.21)$$

Here it must be pointed out that equation (6.19) is an approximation; it can be shown that the full expression for the value of E as given by (6.21) may be expressed by :

$$E = E_A - \tfrac{1}{2} RT + \frac{\sum_o^F \left[\frac{E}{RT}\right]^i}{\sum_o^F \frac{1}{i!}\left[\frac{E}{RT}\right]^i} \cdot RT$$

Taking the simpler relation (6.21) in order to obtain the value of E for substitution in equation (6.20), F corresponding to $P = 73$ is calculated to be 1 and for $P = 1.4 \times 10^4$, $F = 3$ (at 50°C).

In view of the evident curvature of the graph in Fig. 47, these values must be regarded as very approximate and it would be unwise at this stage to attempt an interpretation in physical terms. It would be more satisfactory if such a course is intended, to find an expression based on theoretical considerations, which would permit the data to be fitted more accurately than can be done on the assumption that Fig. 47 represents a linear relationship between E_A and $1/T$. This is attempted in the following section.

Quasi Thermodynamic Method Applied to the Kinetic Data

An alternative approach to the data represented in Fig. 47 is to assume that the Arrhenius plot is not necessarily linear. For reversible reactions in equilibrium the Van't Hoff isochore

$$\frac{d \ln K}{dT} = \frac{\Delta H^o}{RT^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6.22)$$

may be applied, and which on integration is of the same form as that given by Arrhenius, (6.14). In equation (6.22) K is an equilibrium constant and ΔH^o corresponds to the critical increment E_A as given by the slope of the Arrhenius plot. This relationship follows from the definition of the thermodynamic quantities, namely the change in the Gibbs free energy of the system ΔF^o, the corresponding change in entropy ΔS^o, and the change in heat content ΔH^o, all these quantities referring to some arbitrary standard state. The constant K is an equilibrium constant and not a velocity constant, although as will be shown later, it is possible to relate the rate constant of a kinetic reaction to an "equilibrium" constant representing a hypothetical equilibrium between activated and normal molecules, the so-called "stationary state".

Now in deriving the Arrhenius equation from the Van't Hoff isochore by integration with respect to T, the implicit assumption is made that ΔH^o is a constant and does not vary with T. Since for a solution at constant pressure $d\Delta H^o/dT$ is in fact the change in specific heat of the system (Kirchoff's Equation), the implication is that $\Delta C_p = 0$. In other words, the heat capacity of the reactants does not differ from that of the products. If ΔC_p is a constant, it is easy to show that :

$$\frac{d \ln K}{dT} = \frac{A}{T^2} + \frac{C}{T}$$

where A and C are constants.

The integrated form of the Van't Hoff isochore therefore is :

$$\ln K = \frac{-A}{RT} + \frac{C}{R} \ln T + \frac{B}{R} \quad \ldots\ldots\ldots\ldots (6.23)$$

Accordingly we should expect some curvature to be introduced by the term $^C/_R \ln T$. For computational purposes, i.e. in order to derive an equation of this form from the data, it is more convenient to express (6.23) in the form :

$$-RT \ln K = A - BT - CT \ln T \quad \ldots\ldots (6.24)$$

Before these equations can be applied to the present case with any theoretical justification, it is necessary to relate the equilibrium constant K, which refers to a reversible system, to the specific reaction rate k_o, which

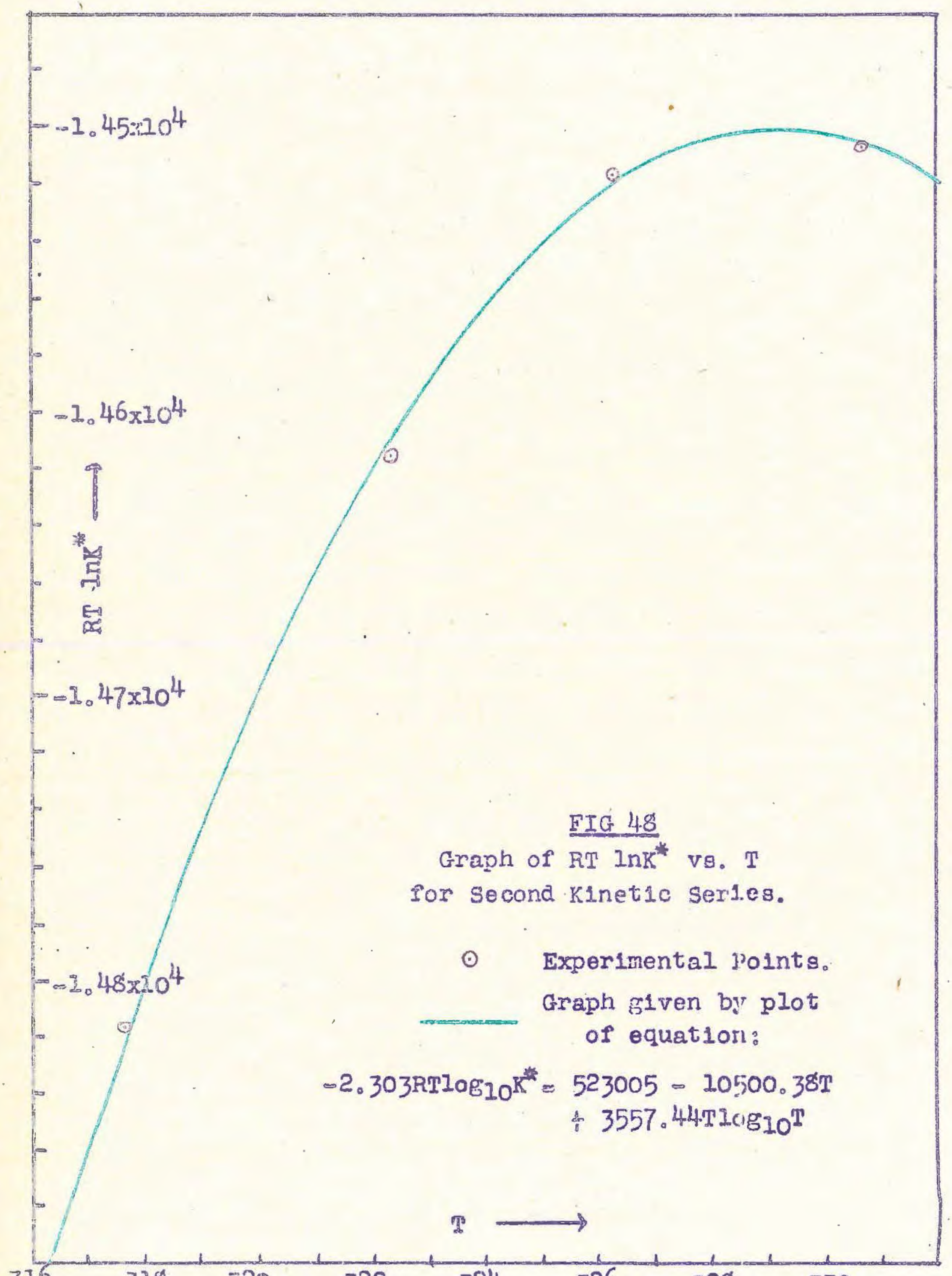


FIG 48

Graph of RT $\ln K^*$ vs. T for Second Kinetic Series.

applies to a non-reversible system. Fortunately on the stationary state hypothesis as developed in the theory of Absolute Reaction Rates based on Statistical Mechanics, it has been shown (79) that :

$$K^{*} = \frac{1}{\kappa} \cdot \frac{k_0 h}{\bar{k}\ T} \quad \ldots\ldots\ldots\ldots\ldots (6.25)$$

where K^{*} is the hypothetical equilibrium constant previously referred to, κ is the transmission coefficient (normally considered to be unity) and $\bar{k}$ and h are Boltzmann's and Planck's constants respectively.

Using this theoretical relationship, the equilibrium constant K^{*} was calculated from the extrapolated k_0 values for each temperature at $\mu = 0$ and the corresponding values of $-RT \ln K^{*}$ thus obtained. These values are recorded in Table A 31 of the Appendix and plotted in Fig. 48.

The author is indebted to Dr. G. E. Cunningham for fitting an equation of the form given by (6.24) to the data in Table A 31 by the method of least squares. This empirical equation (6.26) was employed to calculate the data shown in Table A 32 of the Appendix, represented by the full line in Fig. 48. The equation in full is :

$$-2.3026\ RT\log_{10}K^{*} = 523004.7 - 10500.3805T + 3557.4421T\log_{10}T \quad ..(6.26)$$

It is seen that the slope of the line decreases with temperature until at a value of about 329°K, the curve reaches a maximum.

The entropy of activation ΔS^* is a function of temperature and its value at any temperature is given by the slope of the curve in Fig. 48. It is of interest at this stage to calculate the values of the free energy of activation ΔF^*, change in heat content ΔH^*, and entropy of activation ΔS^* for the reaction at various temperatures using the quasi-thermodynamic method. Now from Kirchoff's equation :

$$\frac{\partial \Delta H}{\partial T} = \Delta C_P$$

$$\Delta H = \Delta H_o^o + \Delta C_P T$$

From the Van't Hoff isochore, which follows directly from the definitions of the thermodynamic quantities and the Gibbs-Helmholtz relationship between them :

$$R \frac{d \ln K}{dT} = \frac{\Delta H}{T^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6.27)$$

$$= \frac{\Delta H_o^o}{T^2} + \frac{\Delta C_P}{T}$$

$$\therefore R \ln K = \frac{-\Delta H_o^o}{T} + \Delta C_P \ln T + B$$

$$\therefore -RT \ln K = \Delta H_o^o - BT - \Delta C_P T \ln T \ldots.(6.28)$$

The above equation may be compared to equation (6.26) and the values of the thermodynamic quantities obtained as shown below.

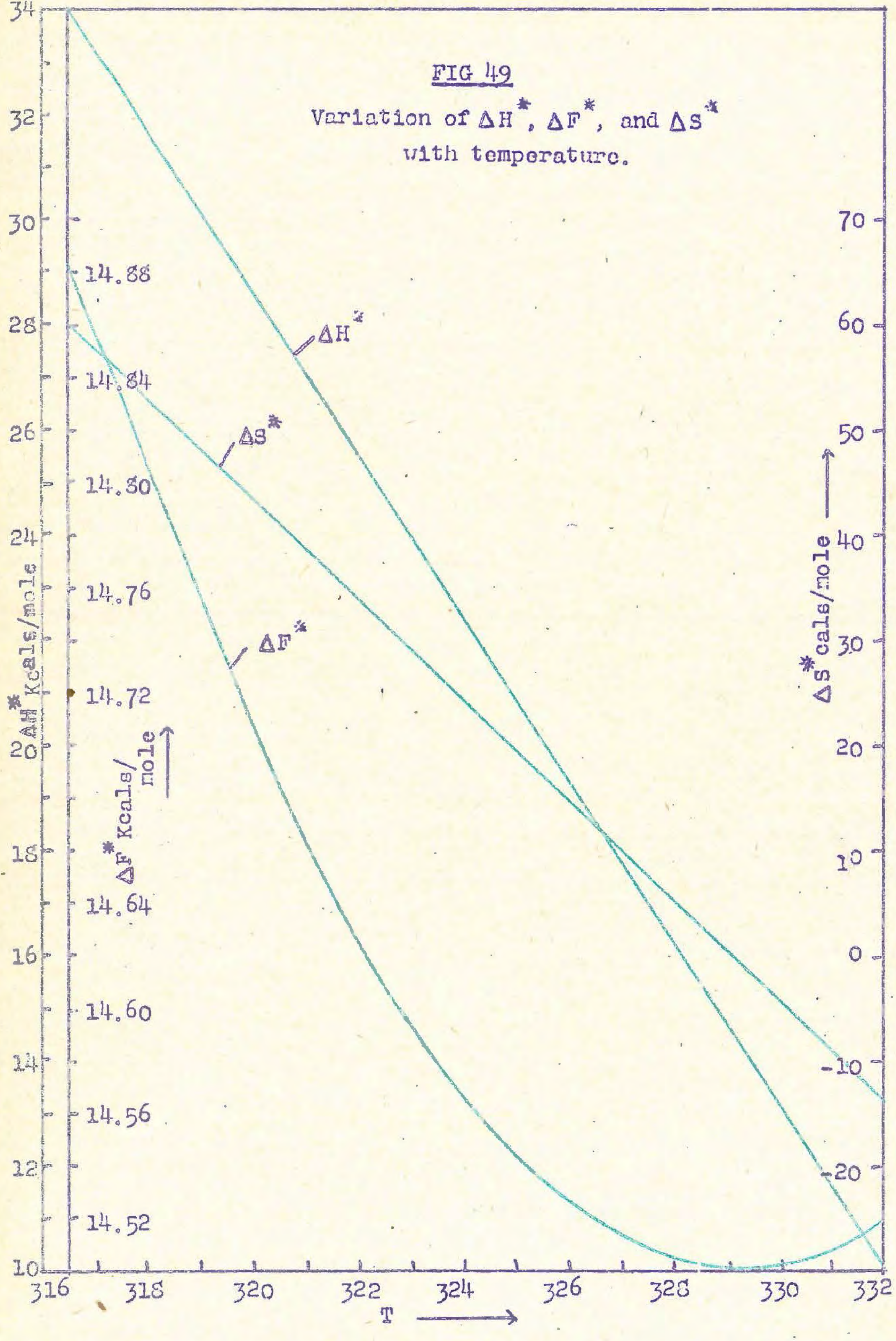


FIG 49

Variation of ΔH^*, ΔF^*, and ΔS^* with temperature.

Equation (6.26) may be written as :

$$-RT \ln K = A - BT + CT \log_{10} T$$

$$= A - BT + C'T \ln T \qquad C' = \frac{C}{2.30259}$$

$$\therefore A = \Delta H_0^o \ ; \ C' = -\Delta C_p$$

$$\Delta H^* = A - C'T \quad \ldots\ldots\ldots\ldots (6.29)$$

Now

$$\Delta F^* = \Delta H^* - T\Delta S^* \quad \ldots\ldots\ldots\ldots (6.30)$$

$$= (\Delta H_0^o + \Delta C_p T) - T\Delta S^*$$

$$= (A - C'T) - T\Delta S^*$$

Whence $-BT + C'T + C'T \ln T + T\Delta S^* = 0$

$$\therefore \Delta S^* = B - C'(1 + \ln T)$$

$$= (B - C') - C \log_{10} T \quad \ldots\ldots\ldots (6.31)$$

Values of ΔF^*, ΔH^* and ΔS^*, calculated from equations (6.29 - 6.31) for various values of T are given in Table A 33 of the Appendix and Fig. 49 shows the variation of these quantities with temperature.

It is seen that at the temperature where K^* is a maximum (Fig. 48), the value of ΔS^* is zero and ΔF^* is at a minimum (Fig. 49). This temperature was calculated from (6.31) and was found to be 329.13°K or 55.97°C. It is at this temperature then (56°C) that the correct values of E_A are obtained for the application of the simple form of the Arrhenius equation :

$$k = Z_o e^{-E_A/RT}$$

to the kinetic data, where Z_o is the collision number in moles/litre/second.

It must be remembered that ΔS^* is the change in entropy for the reactants in a standard state, defined such that when the concentration is expressed in moles/litre, the activities are unity. The positive values of ΔS^* obtained at the lower temperatures show that under these conditions the thermodynamic probability favours the formation of activated molecules. It should be noted that the value of ΔS^* will also include the dielectric contribution to the entropy of activation, and since the formation of activated molecules involves reaction between two singly charged negative ions to form one with two negative charges, this contribution must be negative. This follows from the fact that the dielectric contribution at any temperature may be calculated from the relation (80) :

$$\Delta S_1 = \frac{\varepsilon^2 Z_A Z_B}{r\, D^2}\left(\frac{\partial D}{\partial T}\right)_p \cdot \frac{N_o}{8.3144 \times 10^7} \text{ cals/mole} \quad \ldots\ldots(6.32)$$

Where ε is the electronic charge = 4.774×10^{-10}

$Z_A Z_B$ is the product of the charges on the ions = + 1

r is the molecular diameter of the reacting molecules = 3.6×10^{-8} cm.

D is the dielectric constant for water = 69.94 at 50°C. (73).

$\frac{\partial D}{\partial T}$ = -0.3268 at 50°C. (73).

N_o is Avegadro's number = 6.023×10^{23}.

S_1 was found to be -3.07 cals/mole at 50°C, and over the temperature range considered (44 - 57°C) does not depart significantly from this value. Accordingly the entropy of activation, excluding the effect of charge, is approximately 3 cals/mole greater than shown by Fig. 49.

Physical Interpretation of Reaction Mechanism in Terms of the Collision Theory and the Thermodynamic Method of Absolute Reaction Rates

According to the theory of absolute reaction rates (81), the bimolecular velocity constant k_o is related to the hypothetical equilibrium constant relating the concentration of activated to inactivated molecules by the expression equation (6.25) or

$$k_o = \frac{\bar{k}T}{h} K^{*} \quad \ldots\ldots\ldots\ldots\ldots (6.33)$$

whence $$k_o = \frac{\bar{k}T}{h} e.^{\Delta S^{*}/R} e.^{-\Delta H^{*}/RT} \ldots (6.34)$$

It follows from (6.33) that

$$\frac{d \ln k_o}{dT} = \frac{d \ln K^{*}}{dT} + \frac{1}{T}$$

and from equation (6.27) that :

$$E_A = \Delta H^{*} + RT$$

If we re-write equation (6.34) and (6.19) in the form of the Arrhenius Equatión, we have :

$$k_o = \left[e \, \frac{\bar{k}T}{h} \, e^{\Delta S/R} \right] e^{-E_A/RT} \quad \ldots\ldots (6.35)$$

and

$$k_o = \left[\frac{e^{-(F-\frac{1}{2})}}{F!} \left(\frac{E_A}{RT} \right)^F \cdot Z_o \right] e^{-E_A/RT} \quad \ldots (6.36)$$

where $E_A = \Delta H^{*} + RT$.

It follows that the terms in square brackets correspond to the A term (= PZ_o) of the Arrhenius equation applied to the kinetic data.

Equating these and taking logarithms, we have after rearranging :

$$\ln \bar{Z}_o - (F+\tfrac{1}{2}) - \ln F! - \ln \frac{\bar{k}}{h} = \frac{\Delta S}{R} - F \ln \frac{E_A}{R} - (F-\tfrac{1}{2}) \ln T$$

where $\bar{Z}_o = Z_o/\sqrt{T}$ as given by (6.20). .... (6.37)

It is seen that the left hand side of the above equation remains constant for a given value of F, while the right hand side varies with F and with T. Values of the left hand side were calculated over a range of F from zero to 5, and to evaluate the right hand side of the equation, four temperatures were chosen, one of them ($T = 329^{\circ}K$) corresponding to the maximum in Fig. 48 where $\Delta S^{*} = 0$. For each temperature the corresponding values of ΔS^{*} and ΔH^{*} were read off from Fig. 49, and E_A was then obtained from the relationship $E_A = \Delta H^{*} + RT$. The values of the right hand side of the equation were then calculated for $F = 0$ to 5 for each of the four temperatures.

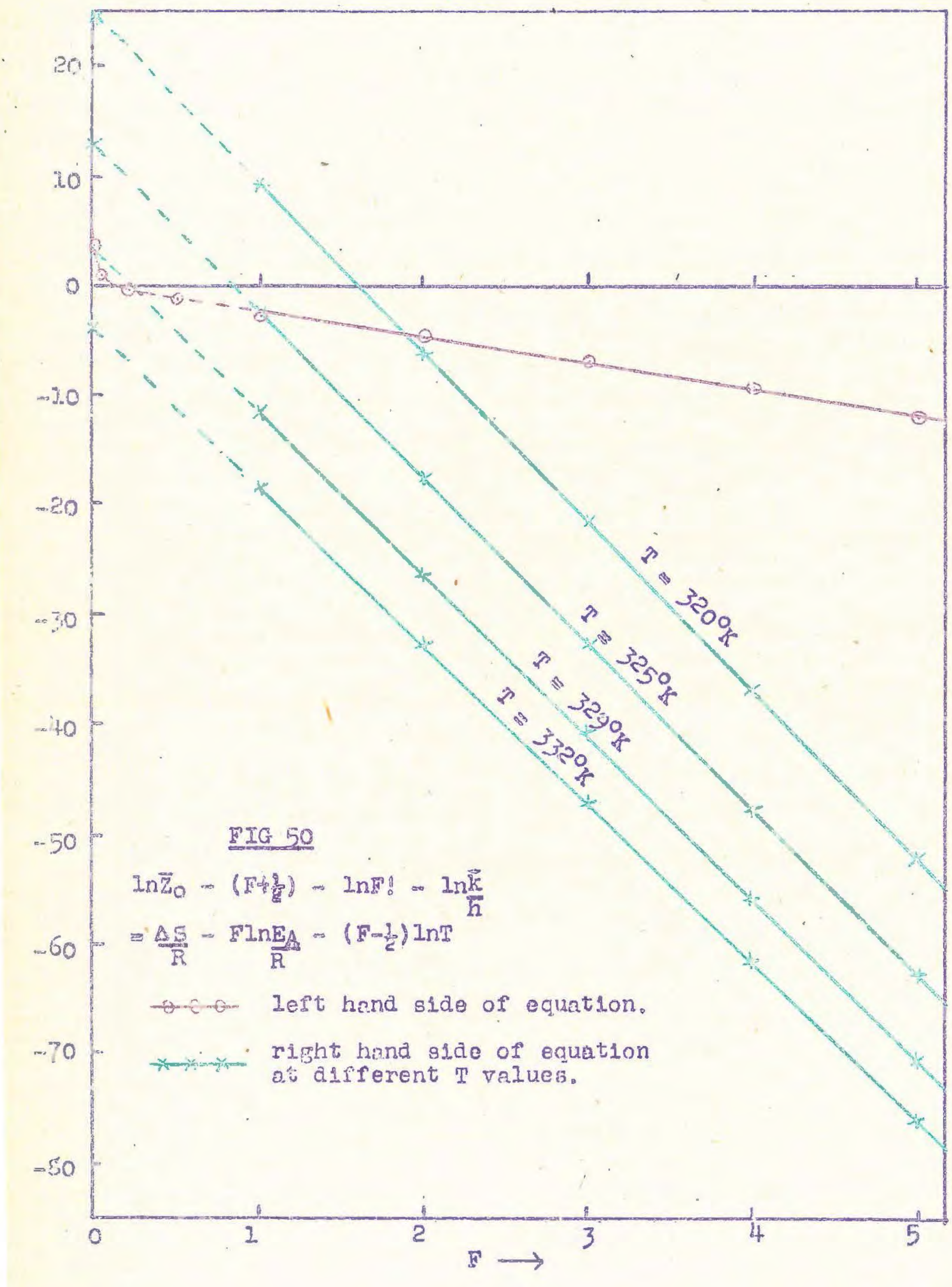


FIG 50

$$\ln\bar{Z}_0 - (F+\tfrac{1}{2}) - \ln F! - \ln\frac{\vec{k}}{h}$$
$$= \frac{\Delta S}{R} - F\ln\frac{E_A}{R} - (F-\tfrac{1}{2})\ln T$$

The results have been shown graphically in Fig. 50 where the values of the left hand and right hand sides of the equation have been plotted against F. The value of F at which the two lines intersect gives the number of internal degrees of freedom at that temperature.

It is seen that F is not fixed for the reaction but varies with temperature; thus at $T = 320^{\circ}K$ the number of degrees of freedom is about 2, while at $T = 325^{\circ}K$, $F = 1$, and when $\Delta S^{*} = 0$ at $T = 329^{\circ}K$, $F = 0$.

This shows that as the temperature is increased, the number of internal degrees of freedom is diminished until at $329^{\circ}K$ there are no internal degrees of freedom, and at this point the velocity constant of the reaction corresponds with that given by the kinetic theory; equation (6.17).

It is seen then that in this reaction involving the formation of trioxalatochromiate ions by the reaction between cis dioxalatodiaquochromiate and oxalate ions, the increase in reaction rate with increasing temperature is not as great as that given by the collision theory. The rate of reaction does of course increase with temperature, but not as rapidly as would be expected from the increase in the collision number.

The previous discussion has shown that as the temperature is increased, the value of E_A decreases, the entropy of activation decreases, the change in free energy approaches a minimum, the number of internal degrees of freedom is diminished, and the change in heat capacity is negative. These facts are all in agreement with the observation that the ~~relativ~~e increase in reaction rate diminishes with temperature.

A possible explanation of the relative decrease in reaction rate and thermodynamic constants with temperature is attempted below in a qualitative manner.

The complex ions under consideration possess oxalate groups, each of which occupies two coordination positions, the positions being linked by the ring formation of the oxalate group. These rings must not be regarded as being rigidly fixed, but that there is a constant opening and closing and molecular rearrangement of the rings under normal conditions. However, in most cases when oxalate and other ring-forming groups such as ethylenediamine are coordinated to chromium, substitution and ring closure are aided by heating. The rate of combination and reaction is of course increased by heating, but there seems to be a definite tendency towards ring closure and stabilisation at higher temperatures.

Considering for the moment the lower temperatures, a certain amount of ring opening and closing is occurring, and therefore at these temperatures there are a greater number of degrees of freedom amongst which the energy of the molecule may be distributed, and it is possible that this energy may be considerable.

As the temperature is increased, ring closure and stabilisation are favoured and the number of degrees of freedom is thereby diminished. The total energy might therefore be expected to be smaller as there are less degrees of freedom among which it can be distributed. The entropy of activation is a measure of the randomness of the distribution of the energy and this would also decrease as the number of degrees of freedom grow smaller. The relative decrease in reaction rate would thus be diminished and this is consistent with the observations made.

For temperatures over and above 329°K, the increase of reaction rate may be expected to be given by the collision theory and is due solely to the increased energy of the reacting molecules and not to any additional positions at which activation can occur.

5. SUMMARY

The kinetics of the formation of the trioxalatochromiate ion by the reaction between cis dioxalatodiaquochromiate and oxalate ions in aqueous solution were studied using the Evelyn Colorimeter. Two series of kinetics were studied; one on equimolar mixtures of potassium cis dioxalatodiaquochromiate and potassium oxalate at various concentrations, and the other on a fixed equimolar concentration of the reactants, the ionic strength being varied by the addition of increasing quantities of potassium nitrate.

Results showed that the reaction is of the second order but the first series of kinetics do not obey

the Brønsted-Bjerrum relationship at the lowest ionic strengths. The second kinetic series indicates that the product of the ionic charges is unity and that the rate-determining step in the reaction is the reaction between the binoxalate ion $\left[(COO)_2H\right]^-$ and the cis dioxalatodiaquochromiate ion $\left[Cr(C_2O_4)_2(H_2O)_2\right]^-$. The possibilities that the ionic strength changes during reaction and that the reaction might be one of the third order involving hydrogen ions are discussed.

The Arrhenius equation has been applied to the data and values of the energy of activation and frequency factor determined and limitations set on these values due to the non-linearity of the Arrhenius plot. The collision number and probability factor have been derived from the collision theory.

On thermodynamic considerations, values of the entropy of activation, change in free energy and heat content have been obtained at different temperatures and a physical interpretation of the reaction mechanism in terms of the collision theory and the thermodynamic method of absolute reaction rates has been attempted.

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APPENDIX

Spectrophotometric Data

In this Appendix, the following symbols are used :

λ = wavelength in millimicrons

D = Optical Density.

TABLE A 1.

Absorption Curve of Potassium Trioxalatochromiate .009208 M.

16°C. Fig. 1.

λ	D	λ	D	λ	D	λ	D
300	-	410	.846	525	.390	635	.227
305	-	415	.880	530	.445	640	.192
310	-	420	.886	535	.495	645	.161
315	1.86	425	.867	540	.545	650	.135
320	1.25	430	.825	545	.593	655	.120
325	.78	435	.770	550	.628	660	.102
330	.440	440	.682	555	.657	665	.084
335	.249	445	.595	560	.685	670	.667
340	.148	450	.490	565	.695	675	.057
345	.098	455	.407	570	.698	680	.044
350	.082	460	.328	575	.694	655	.037
355	.090	465	.262	580	.676	690	.033
360	.115	470	.208	585	.647	695	.045
365	.155	475	.178	590	.617	700	.028
370	.212	480	.164	595	.580	705	.018
375	.297	485	.157	600	.540	710	.015
380	.358	490	.157	605	.500	720	.008
385	.445	495	.165	610	.450	730	.006
390	.540	500	.187	615	.406		
395	.628	505	.215	620	.375		
400	.725	510	.253	625	.297		
405	.795	515	.296	630	.260		
		520	.342				

TABLE A 2

Absorption curves of a) Pot. cis dioxalatodiaquechromiate

b) Pot. trans dioxalatodiaquochromiate

at 0.009208 M. 5 - 8°C. Fig. 2.

λ	D a)	D b)	λ	D a)	D b)	λ	D a)	D b)
300	1.05	.800	430	.555	.255	565	.467	.292
305	.840	.600	435	.505	.263	570	.460	.287
310	.595	.402	440	.455	.233	575	.448	.280
315	.387	.250	445	.390	.206	580	.430	.272
320	.235	.137	450	.332	.179	585	.410	.260
325	.147	.671	455	.283	.155	590	.382	.247
330	.102	.040	460	.240	.137	595	.355	.231
335	.090	.027	465	.205	.122	600	.328	.217
340	.091	.025	470	.177	.112	605	.294	.198
345	.100	.030	475	.153	.107	610	.270	.185
350	.112	.040	480	.138	.110	620	.212	.152
355	.128	.055	485	.138	.117	630	.150	.101
360	.153	.076	490	.142	.128	645	.097	.067
365	.187	.100	495	.153	.140	650	.083	.060
370	.225	.127	500	.173	.156	660	.057	.045
375	.272	.160	505	.195	.173	670	.037	.035
380	.327	.193	510	.222	.192	675	.033	.036
385	.387	.220	515	.255	.211	680	.027	.033
390	.448	.246	520	.288	.230	690	.029	.033
395	.500	.218	525	.320	.247	700	.012	.023
400	.560	.285	530	.355	.265	710	.007	.020
405	.600	.302	535	.385	.278	720	.004	.018
410	.623	.314	540	.414	.291	730	.003	.016
415	.632	.317	545	.436	.300			
420	.622	.315	550	.452	.307			
425	.598	.305	555	.464	.295			
			560	.469	.296			

TABLE A 3

Absorption curve of Potassium cis dioxalato diaquochromiate. Prepared by Werner's method i) and unwashed with alcohol.
0.009208 M. 18°C. Fig. 4.

λ	D	λ	D	λ	D	λ	D
300	-	404	.645	490	.160	564	.466
310	.660	408	.663	492	.163	566	.464
320	.350	410	.671	494	.166	568	.462
325	.297	412	.674	496	.170	570	.458
328	.290	414	.674	498	.177	574	.450
332	.298	416	.672	500	.183	578	.440
336	.321	418	.668	504	.200	582	.422
340	.342	420	.660	510	.228	588	.394
345	.368	424	.641	516	.265	594	.360
350	.388	428	.612	522	.304	600	.334
355	.403	432	.578	528	.340	610	.271
360	.415	436	.532	534	.375	620	.217
365	.425	440	.488	540	.410	630	.162
370	.443	446	.422	544	.430	640	.121
375	.464	452	.354	548	.445	650	.090
380	.490	458	.294	552	.454	660	.064
385	.530	464	.247	554	.458	680	.031
390	.558	470	.207	556	.463	690	.031
395	.594	476	.178	558	.465	700	.015
400	.623	482	.165	560	.468	710	.008
		488	.160	562	.467		

TABLE A 4.

Absorption curve of Potassium *cis* dioxalatodiaquochromiate
Trans salt aged to *cis* isomer.

0.009208 M. 18°C. Fig. 5.

λ	D	λ	D	λ	D
300	.840	440	.435	580	.431
305	.687	445	.382	585	.411
310	.477	450	.323	590	.384
315	.330	455	.275	595	.356
320	.190	460	.233	600	.331
325	.101	465	.200	605	.305
330	.053	470	.172	610	.271
335	.032	475	.150	615	.246
340	.027	480	.138	20	.214
345	.030	485	.137	625	.184
350	.043	490	.139	630	.164
355	.061	495	.152	635	.140
360	.086	500	.172	640	.122
365	.122	505	.193	645	.105
370	.166	510	.220	650	.085
375	.241	515	.253	655	.074
380	.280	520	.286	660	.061
385	.347	525	.320	665	.052
390	.411	530	.353	670	.037
395	.472	535	.382	675	.033
400	.529	540	.411	680	.029
405	.577	545	.437	685	.030
410	.605	550	.451	690	.029
415	.617	555	.463	695	.020
420	.618	560	.469	700	.014
425	.585	565	.469	710	.008
430	.540	570	.461	720	.006
435	.491	575	.449	730	.005

TABLE A 5

Absorption Curve of Potassium cis dioxalatodiaquochromiate. Prepared by Werner's method i) and washed with alcohol.
0.009208 M. 17°C. Fig. 6.

λ	D	λ	D	λ	D
300	1.05	440	.443	590	.389
305	.804	445	.357	595	.359
310	.568	450	.329	600	.332
315	.347	455	.282	605	.306
320	.207	460	.237	610	.274
325	.111	465	.201	615	.246
330	.059	470	.172	620	.212
335	.037	475	.151	625	.185
340	.031	480	.139	630	.160
345	.035	485	.137	635	.136
350	.045	490	.141	640	.119
355	.061	495	.152	645	.102
360	.089	500	.173	650	.087
365	.124	505	.194	655	.077
370	.169	510	.224	660	.061
375	.222	515	.256	665	.051
380	.283	520	.259	670	.039
385	.352	525	.322	675	.034
390	.420	530	.358	680	.029
395	.482	535	.389	685	.031
400	.545	540	.418	690	.029
405	.590	545	.443	695	.021
410	.616	550	.459	700	.015
415	.630	555	.470	705	.012
420	.622	560	.476	710	.009
425	.600	565	.476	720	.004
430	.554	570	.467	730	.004
435	.504	575	.454		
		580	.436		
		585	.415		

TABLE A 6

Absorption curve of a) Potassium trans dioxalato aquohydroxochromiate

b) Potassium cis dioxalato aquohydroxochromiate.

0.009208 M. 5 - 8°C. Fig. 7.

λ	D a)	D b)	λ	D a)	D b)	λ	D a)	D b)
300	-	-	440	.422	.538	585	.309	.413
305	1.90	1.90	445	.421	.524	590	.301	.408
310	1.68	1.62	450	.420	.505	595	.293	.400
315	1.30	1.25	455	.410	.483	600	.278	.385
320	.923	.920	460	.390	.457	605	.270	.372
325	.623	.650	465	.366	.430	610	.257	.356
330	.420	.443	470	.344	.397	615	.246	.342
335	.277	.304	475	.314	.365	620	.230	.322
340	.132	.215	480	.277	.330	625	.208	.300
345	.132	.158	485	.248	.298	630	.195	.275
350	.110	.140	490	.221	.267	635	.181	.255
355	.112	.147	495	.200	.242	640	.167	-
360	.129	.177	500	.182	.217	645	.152	.212
365	.161	.221	505	.177	.210	650	.132	.192
370	.190	.277	510	.176	.211	655	.122	-
375	.232	.338	515	.183	.217	660	.110	.160
380	.275	.400	520	.193	.227	665	.097	.140
385	.317	.453	525	.207	.243	670	.055	-
390	.355	.500	530	.223	.263	675	.072	.107
395	.377	.532	535	.241	.284	680	.063	.095
400	.400	.558	540	.257	.307	685	-	.085
405	.420	.570	545	.272	.330	690	.054	.078
410	.430	.575	550	.287	.351	695	.050	.072
415	.428	.578	555	.301	.367	700	.043	.063
420	.427	.576	560	.310	.386	710	.030	.045
425	.426	.570	565	.315	.393	720	.022	.036
430	.425	.562	570	.318	.407	730	.016	.022
435	.423	.553	575	.320	.413			
			580	.313	.415			

TABLE A 7

Absorption curves of A) .009208 M Potassium dioxalatosulphatoaquochromiate.
B) .009208 M Potassium dioxalatosulphatoaquochromiate in saturated KNO_3
C) Saturated potassium nitrate.

5°C. Fig. 16.

λ	D A)	D B)	λ	D A)	D B)	λ	D C)
300	1.15	–	480	.174	.167	325	1.65
305	1.15	–	490	.135	.134	327	1.30
310	.870	–	500	.128	.130	330	.905
315	.580	–	510	.153	.155	332	.720
320	.355	–	520	.204	.204	334	.560
325	.200	–	530	.265	.263	336	.425
330	.110	1.25	540	.333	.327	338	.325
335	.057	.560	550	.402	.390	340	.240
340	.037	.270	560	.430	.425	342	.140
345	.030	.135	564	.445	.435	344	.087
350	.032	.087	568	.457	.445	346	.054
360	.055	.087	572	.465	.452	348	.027
370	.100	.137	576	.471	.453	350	.010
380	.187	.223	580	.472	.452	352	0
390	.305	.340	584	.470	.449		
400	.445	.472	588	.462	.441		
408	.550	.560	592	.454	.430		
410	.570	.590	596	.438	.414		
414	.602	.605	600	.425	.400		
420	.630	.642	610	.390	.358		
424	.639	.628	620	.338	.303		
428	.630	.615	630	.260	.240		
430	.622	.623	640	.208	.193		
436	.585	.562	650	.163	.152		
440	.560	.528	660	.120	.112		
450	.447	.420	670	.080	.077		
460	.327	.314	680	.055	.054		
470	.243	.230	690	.053	.052		
			700	.030	.032		

Potentiometric Data

TABLE A 8

Titration of 0.009208 M Potassium Nitrate against 0.5N KOH and 0.5N HNO_3. 20°C. Fig. 9.

Glass Electrode		"Alki" Electrode		Glass Electrode	
ml. Alkali	pH	ml. Alkali	pH	ml. Acid	pH
0.0	5.94	-	-	0.0	6.04
.044	9.17	-	-	.050	3.83
.087	10.28	.087	10.28	.101	3.50
.132	10.69	.132	10.77	.151	3.17
.175	10.90	.175	10.87	.202	3.07
.220	11.02	.220	10.98	.252	2.97
.263	11.12	.263	11.10	.303	2.88
.350	11.20	.350	11.23	.404	2.72
.439	11.37	.439	11.28	.504	2.66
.614	11.48	.614	11.44	.706	2.52
.877	11.62	.877	11.62	1.01	2.38
1.32	11.77	1.32	11.74	1.51	2.21
1.75	11.94	1.75	11.90	2.02	2.09
2.20	12.03	2.20	11.98	2.52	1.98
2.63	12.10	2.63	12.08	3.03	1.92
3.50	12.19	3.50	12.17	4.04	1.80
4.39	12.25	4.39	12.24	5.04	1.70
5.26	12.32	5.26	12.32	6.05	1.62
6.14	12.38	6.14	12.37	7.06	1.56
7.02	12.44	7.02	12.42	8.07	1.52
7.89	12.47	7.89	12.47	9.08	1.46
8.77	12.50	8.77	12.52	10.09	1.42

TABLE A 9.

Titration of 0.009208 M. Potassium Nitrate against
0.5 N KOH at
a) 20°C using glass electrode
b) 5°C Fig. **10.**

a) 20°C			b) 5°C		
ml Alkali	Equiv. Alkali/Cr	pH	ml Alkali	Equiv. Alkali/Cr	pH
0.00	0.00	5.94	0.0	0.0	5.86
0.044	0.024	9.17	0.049	0.026	10.10
0.087	0.047	10.28	0.098	0.053	10.95
0.132	0.072	10.69	0.147	0.080	11.23
0.175	0.095	10.90	0.197	0.107	11.36
0.220	0.120	11.02	0.295	0.160	11.54
0.263	0.143	11.12	0.394	0.214	11.71
0.350	0.190	11.20	0.492	0.267	11.80
0.439	0.239	11.37	0.591	0.321	11.90
0.614	0.334	11.48	0.788	0.428	12.04
0.877	0.476	11.62	0.985	0.535	12.12
1.32	0.718	11.77	1.18	0.641	12.20
1.75	0.950	11.94	1.38	0.750	12.28
2.20	1.19	12.03	1.57	0.856	12.34
2.63	1.43	12.10	1.77	0.962	12.38
3.50	1.90	12.19	1.97	1.07	12.43
4.39	2.39	12.25	2.36	1.28	12.48
5.26	2.85	12.32	2.76	1.50	12.54
6.14	3.34	12.38	3.15	1.71	12.59
7.02	3.81	12.44	3.54	1.93	12.63
7.89	4.28	12.47	3.94	2.14	12.66
8.77	4.76	12.50	4.33	2.35	12.70
			4.72	2.56	12.74
			5.12	2.78	12.76
			5.15	3.00	12.79
			5.90	3.20	12.81

TABLE A 10

Titration of 0.009208M Potassium cis dioxalatodiaquochromiate against .5N KOH and .5N HNO_3. Prepared by Werner's method ii) 20°C. Fig. 11.

Equiv. of Alkali/Cr	pH	Equiv. of Acid/Cr	pH
0	4.80	0	4.88
.024	5.66	.027	3.78
.047	5.98	.054	3.30
.072	6.17	.109	3.02
.095	6.32	.164	2.84
.142	6.49	.218	2.71
.190	6.62	.328	2.54
.237	6.72	.434	2.44
.285	6.85	.546	2.33
.380	7.02	.658	2.26
.475	7.15	.765	2.19
.570	7.25	.875	2.14
.679	7.51	.984	2.09
.760	7.67	1.09	2.04
.853	7.92	1.31	1.98
.950	8.12	1.53	1.91
1.06	8.42	1.75	1.85
1.14	8.73	1.96	1.80
1.23	8.97		
1.33	9.15		
1.42	9.30		
1.52	9.48		
1.61	9.63		
1.71	9.80		
1.80	10.03		
1.90	10.21		
1.99	10.55		
2.09	10.91		
2.18	11.20		
2.28	11.39		
2.38	11.50		
2.47	11.61		
2.56	11.68		
2.66	11.75		
2.75	11.80		
2.85	11.84		

TABLE A 11

Titration of 0.009208M Potassium cis dioxalatodiaquochromiate against .5N KOH. Prepared by ageing the trans salt to the cis 18°C. Corrections for blank from Fig. 9(a).

Equiv. of Alkali/Cr	pH	Equiv. of Alkali/Cr	pH	Corrected Equiv. Alkali/Cr	pH
0.0	4.32	1.60	9.57	1.28	99.01
.026	5.10	1.70	9.77	1.77	10.00
.053	5.74	1.78	9.90	1.89	10.30
.809	5.91	1.81	10.00	1.94	10.54
.107	6.13	1.88	10.12	1.97	10.61
.161	6.39	1.91	10.22	2.02	10.84
.215	6.58	1.94	10.30	2.04	11.01
.269	6.69	1.96	10.35	2.04	11.29
.377	6.92	1.99	10.38	2.03	11.46
.484	7.12	2.00	10.54	2.04	11.63
.592	7.29	2.04	10.61	2.08	11.79
.700	7.49	2.10	10.84	2.08	11.90
.753	7.59	2.15	11.01	2.05	11.99
.807	7.71	2.19	11.18	2.06	12.08
.861	7.83	2.26	11.29		
.915	7.99	2.30	11.39		
.941	8.04	2.35	11.46		
.967	8.13	2.40	11.52		
.988	8.23	2.51	11.63		
1.02	8.28	2.61	11.71		
1.05	8.35	2.77	11.79		
1.07	8.44	2.88	11.85		
1.13	8.60	2.94	11.90		
1.18	8.74	3.04	11.94		
1.24	8.90	3.15	11.99		
1.28	9.01	3.47	12.08		
1.37	9.20	4.00	12.20		
1.49	9.40				

TABLE A 12

Titration of 0.009208M cis dioxalatodiaquochromiate against .5N KOH and 0.009208M trans dioxalatodiaquochromiate against .5N KOH.
cis salt prepared by Werner's method ii).
Corrections from Fig. 9(b).
8°C. Fig. 12.

Equiv. of Alkali/Cr	pH cis	pH trans	Equiv. of Alkali/Cr	pH cis	pH trans
0	4.85	4.95	1.24	9.24	9.97
.026	5.91	5.97	1.34	9.45	10.22
.053	6.30	6.21	1.45	9.62	10.41
.089	6.46	6.37	1.56	9.86	10.56
.107	6.57	6.59	1.67	10.06	10.75
.161	6.78	6.79	1.78	10.24	10.94
.215	6.98	6.96	1.83	10.40	11.03
.269	7.08	7.12	1.88	10.59	11.12
.377	7.31	7.32	1.91	10.70	11.16
.484	7.49	7.49	1.94	10.79	11.24
.592	7.68	7.65	1.96	10.88	11.27
.700	7.84	7.87	1.99	10.99	11.29
.753	7.94	7.99	2.04	11.19	11.36
.807	8.07	8.14	2.10	11.41	11.52
.861	8.17	8.30	2.15	11.63	11.61
.888	8.25	8.38	2.26	11.89	11.81
.915	8.33	8.50	2.42	12.10	11.98
.941	8.40	8.69	2.58	12.24	12.11
.967	8.52	8.81	2.80	12.37	12.25
.988	8.57	8.91	3.03	12.46	
1.02	8.67	9.15			
1.05	8.75	9.33			
1.07	8.85	9.50			
1.10	8.93	9.57			
1.13	8.97	9.67			
1.18	9.10	9.83			

Corrections cis Salt

Equiv. of Alkali/Cr	pH
1.65	10.06
1.76	10.24
1.81	10.40
1.85	10.59
1.88	10.70
1.90	10.79
1.91	10.88
1.93	10.99
1.96	11.19
1.98	11.41
1.96	11.63
1.95	11.89
1.92	12.10

Corrections trans Salt

Equiv. of Alkali/Cr	pH
1.43	10.41
1.63	10.75
1.77	11.03
1.83	11.16
1.85	11.27
1.89	11.29
1.95	11.52
1.98	11.81
2.04	11.98
2.09	12.11

TABLE A 13

Titrations of 0.009208M trans dioxalatodiaquochromiate against .5N KOH and .5N HNO_3. 8°C. Fig. 13.

Equiv. of Alkali/Cr	pH	Equiv. of Alkali/Cr	pH	Equiv. of Acid/Cr.	pH
0	4.95	1.78	10.94	0	5.07
.026	5.97	1.83	11.03	.054	3.55
.053	6.21	1.88	11.12	.109	3.28
.081	6.37	1.91	11.16	.217	3.02
.107	6.59	1.94	11.24	.326	2.85
.161	6.79	1.96	11.27	.435	2.73
.215	6.96	1.99	11.29	.544	2.66
.269	7.12	2.04	11.36	.760	2.53
.377	7.32	2.10	11.52	.977	2.43
.484	7.49	2.15	11.61	1.19	2.36
.592	7.65	2.26	11.81	1.41	2.29
.700	7.87	2.42	11.98	1.63	2.25
.753	7.99	2.58	12.11	1.84	2.20
.807	8.14	2.80	12.25	2.06	2.16
.861	8.30				
.888	8.38				
.915	8.50				
.941	8.69				
.967	8.81				
.988	8.91				
1.02	9.15				
1.05	9.33				
1.07	9.50				
1.10	9.57				
1.13	9.67				
1.18	9.83				
1.24	9.97				
1.34	10.22				
1.45	10.41				
1.56	10.56				
1.67	10.75				

TABLE A 14

Titration of 0.009208M Potassium dioxalatosulphatoaquochromiate against .5N KOH and .5N HNO_3. 5°C. Fig. 15.

Equiv. of Alkali/Cr	pH	Equiv. of Acid/Cr	pH	Corrections	
				Equiv. of Alkali/Cr	pH
0	3.68	0	3.97	.680	10.11
.026	4.08	.055	2.64	.708	10.23
.053	6.41	.109	3.32	.733	10.41
.081	6.85	.164	3.19	.750	10.72
.107	7.34	.274	3.00	.757	10.87
.161	7.72	.382	2.87	.773	11.04
.215	8.12	.546	2.73	.781	11.18
.269	8.42	.656	2.67	.778	11.36
.326	8.62	.765	2.60	.795	11.43
.377	8.75	.875	2.56	.781	11.55
.430	8.97	.982	2.51	.787	11.60
.484	9.16	1.09	2.47	.778	11.68
.533	9.30	1.20	2.43	.780	11.73
.592	9.51	1.31	2.40	.790	11.79
.619	9.63	1.42	2.37	.780	11.83
.646	9.80	1.53	2.34	.820	11.88
.674	9.95	1.63	2.32	.820	11.96
.700	10.11	1.91	2.26	.830	12.06
.728	10.23	2.07	2.23	.810	12.17
.753	10.41	2.29	2.19		
.780	10.72	2.45	2.16		
.807	10.87				
.833	11.04				
.861	11.18				
.888	11.36				
.915	11.43				
.941	11.55				
.967	11.60				
.988	11.68				
1.02	11.73				
1.05	11.79				
1.07	11.83				
1.13	11.88				
1.18	11.96				
1.28	12.06				
1.37	12.17				
1.49	12.21				
1.60	12.28				
1.70	12.33				
1.81	12.37				
1.92	12.40				

TABLE A 15

pH values with 0.5 and 1.5 equivalents of alkali/Cr added to 0.009208M cis and trans dioxalatodiaquochromiates at various ionic strengths. 8°C. Fig. 14.

0.5 equivalents of alkali/Cr		
$\sqrt{\mu}$	Trans salt	Cis salt
.1175	7.50	7.42
.1962	7.40	7.34
.2516	7.37	7.30
.2996	7.34	7.28
.3360	7.27	7.23

1.5 equivalents of alkali/Cr		
$\sqrt{\mu}$	Trans salt	Cis salt
.1517	10.46	9.75
.2184	10.37	9.68
.2693	10.27	9.62
.3118	10.20	9.60
.3494	10.07	9.53

TABLE A 16

Determination of the value of R

S = value of shunt resistance in parallel with R

S_o = value of decade resistance at balance with S out of circuit.

S_i = value of decade resistance at balance with S in parallel with R.

$$R = \frac{S_i - S_o}{S_o} . S$$

Temperature = 18°C.

Dial Setting p	Shunt Resistance S ohms	Decade Resistance		R ohms	Dial Setting p	Shunt Resistance S ohms	Decade Resistance		R ohms
		S_o ohms	S_i ohms				S_o ohms	S_i ohms	
2	2.001	262	9630	71.1	140	140.01	806.5	1876.5	185.8
5	5.002	574.7	21790	183.5	160	160.02	921.6	1990.8	185.7
8	8.004	734.0	15700	163.2	180	180.02	1045.6	2123.7	185.5
10	10.003	65.1	935.7	133.7	200	200.00	1151.1	2219.7	185.6
14	14.005	96.5	1372.1	184.9	220	220.00	1267.2	2336.4	185.6
20	20.000	1184.2	12442	190.6	240	240.00	1380.3	2447.7	185.6
23	23.002	144.9	866.3	114.3	260	260.01	1496.1	2563.8	185.5
28	28.004	173.3	1317.3	185.3	280	280.01	1609.7	2672.6	184.9
30	30.003	1751.8	12030	175.7	300	300.02	1715.8	2776.4	185.5
34	34.005	211.7	1433.5	196.4	320	320.02	1820.4	2875.3	185.6
37	37.006	230.6	1296.5	170.6	340	340.02	1935.8	2991.4	185.4
40	40.000	223.5	1270.1	187.7	360	360.02	2058.9	3119.5	185.5
44	44.002	268.1	1388.5	184.0	380	380.02	2167.1	3222.3	185.3
50	50.004	289.9	1375.4	187.3	400	400.02	2279.2	3335.2	185.5
60	60.007	338.3	1391.8	186.8	420	420.02	2394.1	3450.7	185.2
70	70.004	396.7	1448.7	185.6	440	440.02	2509.8	3567.0	185.5
80	80.007	462.6	1537.6	185.9	460	460.02	2623.5	3680.4	185.5
90	90.004	511.0	1566.9	186.0	480	480.02	2729.3	3783.2	185.5
100	100.01	586.9	1678.6	186.1	500	500.02	2789.9	3823.0	185.2
120	120.01	691.9	1763.5	185.9					

TABLE A 17

Values of P giving balance for varying settings of dial (p).
Fig. 24 (b).

Dial p	P ohms	Dial p	P ohms
5	63.68	0	27.4
10	81.24	1	31.8
15	96.61	2	34.6
20	134.9	3	48.0
25	154.5	4	63.2
30	191.7	5	63.7
35	221.1	7	73.4
40	240.4	9	81.5
45	268.7	10	81.6
50	306.9	12	82.2
60	355.2	15	97.0
70	431.5	17	110.7
80	479.1	20	135.1
90	527.7	22	144.5
100	604.0	25	163.6
150	880.9	27	173.2
200	1167.7	30	192.4
250	1454.5		
300	1741.2		
350	2008.7		
400	2305.7		
450	2583.2		
500	2807.8		

TABLE A 18

Beer's Law Relationship for potassium trioxalatochromiate and potassium *cis* dioxalatodiaquochromiate using Evelyn Colorimeter. Fig. 34. $\lambda = 565$ mμ

TRIOXALATE			DIOXALATE		
Molarity	% T	D	Molarity	% T	D
.0004	90.15	0.0451	.001	80.00	0.0969
.0005	86.45	0.0632	.002	63.80	0.1952
.0008	81.05	0.0912	.003	50.50	0.2967
.001	75.15	0.1241	.004	40.00	0.3979
.002	52.70	0.2782	.005	31.90	0.4962
.003	36.95	0.4324	.006	25.30	0.5969
.004	25.30	0.5969			
.005	18.30	0.7375			

TABLE A 19

Standardisation Graphs on the Evelyn Colorimeter. $\lambda = 565$ mμ 18°C.

Fig. 35(a) 0.005M. Fig. 35(b) 0.003M.

Triox/ Diox	A		B		Triox/ Diox	a		b	
	% T	D	% T	D		% T	D	% T	D
0/100	100.0	0	100.0	0	0/100	100.0	0	100.0	0
10/90	92.5	.0339	92.4	.0343	10/90	94.4	.0250	95.8	.0186
20/80	86.7	.0620	86.3	.0635	20/80	88.8	.0516	91.9	.0367
30/70	80.7	.0937	80.1	.0964	30/70	84.0	.0757	88.2	.0545
40/60	75.3	.1226	74.2	.1269	40/60	79.8	.0980	84.9	.0711
50/50	70.0	.1549	68.6	.1643	50/50	75.0	.1249	81.0	.0915
60/40	64.9	.1878	63.1	.2000	60/40	71.4	.1463	78.6	.1046
70/30	60.1	.2211	58.3	.2343	70/30	66.1	.1798	74.7	.1267
80/20	57.1	.2434	54.9	.2604	80/20	62.1	.2069	71.5	.1457
90/10	52.3	.2815	50.0	.3010	90/10	58.4	.2336	69.0	.1612
100/0	48.0	.3188	45.2	.3443	100/0	54.0	.2676	66.0	.1805

KINETICS. Evelyn Colorimeter

Wavelength used : $\lambda = 565$ mμ.

Meaning of Symbols

μ = ionic strength of reacting solution.

t = time of reaction in minutes.

T_R = % transmission of reaction solution.

T_T = % transmission of standard Trioxalate solution.

D_R = optical density of reaction solution = 2-log T_R

D_T = optical density of standard Trioxalate solution = 2-log T_T

x' = percentage conversion to Trioxalate = $D_R \times 100/D_T$

No Potassium Nitrate Added

TABLE A 20

I. Reaction Temperature 44.42°C.

(A) 0.005M. Solutions. $\sqrt{\mu} = 0.1414$. Fig. 36 I

t	T_R	D_R	T_T	D_T	x'	$\frac{1}{100-x'}$
480	94.9	.0227	57.0	.2441	9.30	.01103
720	92.4	.0343	57.0	.2441	14.05	.01163
960	89.3	.0491	57.2	.2426	20.24	.01254
1200	88.0	.0555	57.2	.2426	22.88	.01297
1440	86.9	.0610	57.3	.2418	25.23	.01338
1680	83.9	.0762	57.2	.2426	31.42	.01458
1880	83.9	.0762	57.2	.2426	31.42	.01458
2160	82.3	.0846	57.5	.2403	35.22	.01544
2400	82.0	.0862	57.2	.2426	35.53	.01551

(B) 0.004M. Solutions.
$\sqrt{\mu}$ = 0.1265
Fig. 37 I

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0141	.2111	.01072
470	.0250	.2111	.01134
720	.0315	.2104	.01176
960	.0395	.2083	.01234
1200	.0443	.2083	.01270
1440	.0521	.2090	.01332
1680	.0521	.2083	.01333
1915	.0560	.2076	.01370
2175	.0610	.2055	.01422
2400	.0716	.2055	.01534

(C) 0.003M. Solutions.
$\sqrt{\mu}$ = 0.1095
Fig. 38 I

t	D_R	D_T	$\frac{1}{100-x'}$
480	.0106	.1451	.01079
690	.0177	.1427	.01142
945	.0205	.1457	.01164
1170	.0250	.1427	.01213
1410	.0232	.1427	.01194
1665	.0278	.1457	.01236
1920	.0311	.1457	.01271
2160	.0320	.1451	.01283
2400	.0429	.1487	.01405

(D) 0.002M. Solutions.
$\sqrt{\mu}$ = 0.0894
Fig. 39 I

t	D_R	D_T	$\frac{1}{100-x'}$
225	.0017	.0894	.01019
480	.0070	.0888	.01086
720	.0097	.0862	.01126
945	.0088	.0894	.01110
1425	.0137	.0888	.01184
1665	.0132	.0894	.01164
2160	.0150	.0878	.01206
2385	.0192	.0894	.01274

(E) 0.001M. Solutions.
$\sqrt{\mu}$ = .0633
Fig. 40 I

t	D_R	D_T	$\frac{1}{100-x'}$
480	.0022	.0315	.01075
1260	.0022	.0315	.01075
1680	.0061	.0315	.01240
1920	.0057	.0315	.01221
2160	.0052	.0315	.01198
2400	.0052	.0292	.01217

TABLE A 21

II. Reaction Temperature 48.34°C.

(A) 0.005M Solutions.
$\sqrt{\mu}$ = 0.1414
Fig. 36 II

t	D_R	D_T	$\frac{1}{100-x'}$
95	.0180	.3010	.01064
363	.0419	.3143	.01154
453	.0475	.3188	.01175
535	.0535	.3251	.01197
621	.0630	.3307	.01235
717	.0691	.3316	.01263
801	.0747	.3316	.01291
935	.0830	.3288	.01338
1080	.0752	.2652	.01396
1309	.0888	.2144	.01506

(B) 0.004M. Solutions.
$\sqrt{\mu}$ = 0.1265
Fig. 37 II

t	D_R	D_T	$\frac{1}{100-x'}$
180	.0200	.2284	.01096
369	.0283	.2284	.01142
727	.0419	.2291	.01224
1061	.0555	.2284	.01321
1258	.0610	.2284	.01364
1500	.0731	.2284	.01471
1740	.0726	.2291	.01464
1983	.0883	.2291	.01628

(C) 0.003M. Solutions.
$\sqrt{\mu}$ = 0.1095
Fig. 38 II

t	D_R	D_T	$\frac{1}{100-x'}$
100	.0106	.1752	.01064
185	.0137	.1752	.01085
255	.0168	.1759	.01105
370	.0195	.1752	.01125
458	.0232	.1752	.01154
644	.0269	.1752	.01181
911	.0339	.1752	.01240
1065	.0343	.1624	.01268
1309	.0391	.1618	.01318
1543	.0424	.1612	.01357
1860	.0506	.1618	.01455

(D) 0.002M. Solutions.
$\sqrt{\mu}$ = 0.1084
Fig. 39 II

t	D_R	D_T	$\frac{1}{100-x'}$
180	.0031	.1085	.01030
360	.0083	.1085	.01082
720	.0155	.1090	.01166
905	.0173	.1107	.01185
1071	.0186	.1085	.01207
1500	.0255	.1085	.01307
1732	.0283	.1055	.01353
1960	.0320	.1085	.01418

(E) 0.001M. Solutions. $\sqrt{\mu} = 0.0633$

Fig. 40 II

t	D_R	D_T	$\frac{1}{100-x'}$
89	.0013	.0545	.01025
276	.0031	.0545	.01060
424	.0044	.0550	.01087
548	.0048	.0545	.01097
930	.0066	.0545	.01138
1087	.0079	.0545	.01170
1215	.0092	.0550	.01201
1428	.0097	.0545	.01217
1560	.0088	.0506	.01211
1817	.0106	.0506	.01265
2136	.0128	.0506	.01339

TABLE A 22

III. Reaction Temperature 51.49°C.

(A) 0.005M. Solutions.
$\sqrt{\mu} = 0.1414$
Fig. 36 III

t	D_R	D_T	$\frac{1}{100-x'}$
235	.0301	.2620	.01130
490	.0521	.2628	.01247
732	.0680	.2676	.01340
1218	.1057	.2676	.01653
1450	.1146	.2627	.01749
1674	.1244	.2676	.01868
1925	.1314	.2676	.01965
2283	.1451	.2692	.02170
2394	.1512	.2716	.02268

(B) 0.004M. Solutions.
$\sqrt{\mu} = 0.1265$
Fig. 37 III

t	D_R	D_T	$\frac{1}{100-x'}$
248	.0311	.2284	.01158
492	.0419	.2284	.01226
729	.0580	.2284	.01340
956	.0670	.2284	.01415
1193	.0731	.2284	.01471
1422	.0835	.2284	.01576
1677	.0899	.2328	.01629
1921	.0993	.2328	.01744
2158	.1057	.2328	.01832
2390	.1152	.2328	.01979

(C) 0.003M. Solutions.

$\sqrt{\mu}$ = 0.1095

Fig. 38 III

t	D_R	D_T	$\frac{1}{100-x'}$
235	.0114	.1561	.01079
488	.0246	.1561	.01187
730	.0311	.1561	.01249
962	.0334	.1561	.01272
1214	.0386	.1561	.01329
1437	.0448	.1549	.01406
1680	.0555	.1561	.01552
1925	.0610	.1580	.01629
2147	.0635	.1549	.01695
2400	.0650	.1561	.01713

(D) 0.002M. Solutions.

$\sqrt{\mu}$ = 0.0894

Fig. 39 III

t	D_R	D_T	$\frac{1}{100-x'}$
230	.0132	.1024	.01148
468	.0137	.1024	.01155
712	.0177	.1024	.01209
1200	.0278	.1024	.01373
1440	.0264	.1024	.01348
1683	.0329	.1024	.10473
1924	.0357	.1046	.01516
2152	.0410	.1046	.01645
2391	.0434	.1040	.01716

(E) 0.001M. Solutions.

$\sqrt{\mu}$ = 0.0633

Fig. 40 III

t	D_R	D_T	$\frac{1}{100-x'}$
235	.0044	.0448	.01109
825	.0110	.0443	.01331
958	.0137	.0453	.01434
1191	.0141	.0443	.01466
1417	.0128	.0453	.01394
1779	.0137	.0443	.01447
1895	.0168	.0453	.01590
2160	.0205	.0453	.01827
2425	.0223	.0453	.01969

TABLE A 23

IV. Reaction Temperature 54.84° C.

(A) 0.005M. Solutions

$\sqrt{\mu} = 0.1414$

Fig. 36 IV

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0434	.2557	.01205
480	.0721	.2573	.01389
720	.0888	.2573	.01527
1200	.1169	.2573	.01833
1440	.1325	.2573	.02062
1680	.1397	.2541	.02221
1920	.1494	.2557	.02406
2400	.1593	.2557	.02653

(B) 0.004M. Solutions

$\sqrt{\mu} = 0.1265$

Fig. 37 IV

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0311	.2161	.01168
480	.0555	,2182	.01341
720	.0706	.2182	.01478
960	.0814	.2182	.01595
1200	.0953	.2182	.01775
1440	.1024	.2182	.01884
1680	.1062	.2147	.01978
1920	.1129	.2147	.02110
2160	.1192	.2168	.02220
2400	.1278	.2182	.02413

(C) 0.003M. Solutions

$\sqrt{\mu} = 0.1095$

Fig. 38 IV

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0164	.1457	.01126
480	.0237	.1457	.01195
735	.0362	.1481	.01324
960	.0395	.1457	.01372
1200	.0506	.1457	.01532
1440	.0580	.1457	.01661
1670	.0605	.1463	.01705
2385	.0742	.1481	.02004

(D) 0.002M. Solutions

$\sqrt{\mu} = 0.0894$

Fig. 39 IV

t	D_R	D_T	$\frac{1}{100-x'}$
230	.0083	.0872	.01105
480	.0150	.0872	.01208
705	.0164	.0872	.01232
960	.0218	.0872	.01333
1440	.0301	.0872	.01527
1950	.0386	.0899	.01756
2145	.0410	.0888	.01858
2400	.0424	.0888	.01914

(E) 0.001M. Solutions.

$\sqrt{\mu} = 0.0633$

Fig. 40 IV

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0026	.0334	.01085
450	.0039	.0329	.01134
1080	.0070	.0329	.01271
1920	.0119	.0334	.01553
2400	.0132	.0343	.01626

TABLE A 24

V. Reaction Temperature 57.83°C.

(A) 0.005M. Solutions

$\sqrt{\mu} = 0.1414$

Fig. 36 V

t	D_R	D_T	$\frac{1}{100-x'}$
227	.0501	.2366	.01269
480	.0825	.2373	.01533
715	.1013	.2366	.01749
962	.1169	.2366	.01976
1219	.1290	.2366	.02200
1413	.1349	.2373	.02317
1793	.1421	.2321	.02589

(B) 0.004M. Solutions

$\sqrt{\mu} = 0.1265$

Fig. 37 V

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0362	.1959	.01227
456	.0491	.1945	.01338
731	.0757	.1945	.01637
958	.0825	.1972	.01719
1384	.0904	.1938	.01874
1694	.1018	.1858	.02212
1893	.1118	.1972	.02308
2172	.1135	.1904	.02476

(C) 0.003M. Solutions

$\sqrt{\mu}$ = 0.1095

Fig. 38 V

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0177	.1439	.01140
480	.0278	.1439	.01240
720	.0410	.1439	.01399
960	.0477	.1427	.01502
1230	.0550	.1439	.01619
1695	.0655	.1445	.01829
1920	.0701	.1439	.01950
2400	.0794	.1427	.02253

(D) 0.002M. Solutions

$\sqrt{\mu}$ = 0.0894

Fig. 39 V

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0092	.0883	.01116
480	.0186	.0904	.01259
720	.0209	.0825	.01339
1230	.0315	.0878	.01560
1425	.0357	.0904	.01653
1680	.0482	.0915	.02113
1920	.0462	.0915	.02020

(E) 0.001M. Solutions

$\sqrt{\mu}$ = 0.0633

Fig. 40 V

t	D_R	D_T	$\frac{1}{100-x'}$
480	.0061	.0348	.01213
960	.0101	.0339	.01425
1230	.0132	.0348	.01611
1680	.0155	.0362	.01749
2385	.0177	.0362	.01959

Varying Amounts of Potassium Nitrate Added to 0.003M. Solutions

TABLE A 25

I. Reaction Temperature 44.42°C.

(A) $\sqrt{\mu}$ =- 0.1095
Fig. 41(a)

t	D_R	D_T	$\frac{1}{100-x'}$
480	.0106	.1451	.01079
690	.0177	.1427	.01142
945	.0205	.1457	.01164
1170	.0250	.1427	.01213
1410	.0232	.1427	.01194
1665	.0278	.1457	.01236
1920	.0311	.1457	.01271
2160	.0320	.1451	.01283
2400	.0429	.1487	.01405

(B) $\sqrt{\mu} = 0.1916$
Fig. 41(b)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0048	.1494	.01033
480	.0132	.1387	.01104
765	.0177	.1397	.01145
960	.0246	.1391	.01215
1200	.0241	.1373	.01213
1440	.0315	.1391	.01293
1680	.0357	.1373	.01351
1920	.0381	.1355	.01391
2160	.0376	.1355	.01384

(C) $\sqrt{\mu} = 0.2480$
Fig. 41(c)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0044	.1373	.01033
480	.0110	.1355	.01088
720	.0223	.1355	.01197
960	.0283	.1308	.01276
1200	.0292	.1302	.01289
1440	.0362	.1308	.01383
1680	.0395	.1362	.01436
1920	.0434	.1385	.01456
2160	.0491	.1439	.01518
2400	.0496	.1427	.01533

(D) $\sqrt{\mu} = 0.2936$
Fig. 41(d)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0070	.1302	.01057
480	.0150	.1385	.01121
720	.0246	.1439	.01266
960	.0292	.1427	.01257
1200	.0362	.1415	.01344
1440	.0410	.1427	.01403
1680	.0429	.1415	.01435
1910	.0477	.1409	.01512
2190	.0516	.1409	.01578
2385	.0555	.1397	.01659

TABLE A 26

II. Reaction Temperature 49.17°C.

(A) $\sqrt{\mu}$ = 0.1095

Fig. 42(a)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0097	.1385	.01075
480	.0141	.1391	.01113
720	.0259	.1385	.01230
1440	.0419	.1391	.01431
1680	.0477	.1397	.01519
1905	.0496	.1391	.01554
2160	.0516	.1385	.01601

(B) $\sqrt{\mu}$ = 0.1916

Fig. 42(b)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0128	.1494	.01094
470	.0264	.1494	.01215
720	.0362	.1494	.01320
960	.0453	.1494	.01435
1440	.0580	.1494	.01635
1680	.0560	.1494	.01599
1910	.0620	.1494	.01709
2250	.0655	.1494	.01781
2390	.0706	.1494	.01896

(C) $\sqrt{\mu}$ = 0.2480

Fig. 42(c)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0177	.1494	.01134
470	.0283	.1494	.01234
810	.0362	.1494	.01320
950	.0434	.1494	.01409
1200	.0487	.1494	.01484
1430	.0555	.1494	.01591
1680	.0630	.1494	.01729
1860	.0615	.1494	.01700
2390	.0721	.1494	.01932

(D) $\sqrt{\mu}$ = 0.2936

Fig. 42(d)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0164	.1487	.01124
470	.0292	.1487	.01244
765	.0434	.1481	.01414
950	.0482	.1481	.01483
1200	.0521	.1481	.01543
1440	.0550	.1481	.01594
1680	.0675	.1481	.01837
1915	.0650	.1487	.01776
2160	.0716	.1481	.01936
2390	.0716	.1463	.01959

(E) $\sqrt{\mu}$ = 0.3333

Fig. 42(e)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0200	.1481	.01156
475	.0315	.1481	.01270
720	.0419	.1481	.01395
950	.0462	.1463	.01461
1430	.0605	.1463	.01705
1680	.0685	.1481	.01860
1920	.0701	.1481	.01898
2130	.0757	.1481	.02045
2400	.0794	.1463	.02186

TABLE A 27

III. Reaction Temperature 53.07°C.

(A) $\sqrt{\mu}$ = 0.1095

Fig. 43(a)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0164	.1415	.01131
510	.0278	.1427	.01242
680	.0334	.1427	.01305
950	.0462	.1427	.01478
1170	.0491	.1439	.01518
1410	.0526	.1439	.01576
1665	.0595	.1439	.01704
1980	.0670	.1439	.01872

(B) $\sqrt{\mu}$ = 0.1916

Fig. 43(b)

t	D_R	D_T	$\frac{1}{100-x'}$
230	.0182	.1403	.01149
540	.0287	.1403	.01257
720	.0414	.1427	.01408
950	.0467	.1415	.01493
1200	.0605	.1427	.01736
1440	.0645	.1427	.01825
1740	.0675	.1415	.01913
1910	.0731	.1415	.02068
2160	.0794	.1427	.02260
2395	.0788	.1397	.02294

(C) $\sqrt{\mu}$ = 0.2480

Fig. 43(c)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0205	.1403	.01171
470	.0311	.1403	.01285
710	.0424	.1403	.01433
960	.0531	.1403	.01609
1190	.0570	.1403	.01684
1500	.0670	.1403	.01915
1680	.0731	.1427	.02056
1980	.0737	.1415	.02088
2150	.0825	.1415	.02399
2400	.0835	.1427	.02420

(D) $\sqrt{\mu}$ = 0.2936

Fig. 43(d)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0200	.1427	.01163
540	.0400	.1415	.01395
710	.0477	.1415	.01509
895	.0550	.1397	.01649
1200	.0625	.1421	.01785
1500	.0716	.1427	.02011
1600	.0809	.1427	.02307
1910	.0814	.1415	.02354
2200	.0872	.1403	.02643
2330	.0931	.1427	.02875

(E) $\sqrt{\mu}$ = 0.3333.

Fig. 43(e)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0241	.1427	.01203
470	.0381	.1415	.01369
760	.0506	.1403	.01565
950	.0605	.1427	.01736
1200	.0620	.1397	.01798
1430	.0814	.1427	.02327
1680	.0742	.1397	.02133
1905	.0835	.1415	.02440
2160	.0915	.1415	.02831
2370	.0915	.1397	.02898

TABLE A 28

IV. Reaction Temperature 57.42°C.

(A) $\sqrt{\mu}$ = 0.1095
Fig. 44 (a)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0195	.1397	.01162
470	.0264	.1349	.01244
720	.0434	.1385	.01456
960	.0521	.1397	.01595
1190	.0560	.1349	.01710
1480	.0670	.1391	.01930
1680	.0701	.1355	.02072
1920	.0716	.1355	.02121
2150	.0737	.1385	.02137
2400	.0804	.1355	.02459

(B) $\sqrt{\mu}$ = 0.1916
Fig. 44 (b)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0209	.1397	.01175
470	.0376	.1349	.01386
760	.0605	.1391	.01770
960	.0605	.1385	.01775
1190	.0726	.1355	.02154
1430	.0778	.1385	.02281
1680	.0778	.1355	.02349
1860	.0825	.1355	.02557
2400	.0888	.1343	.02952

(C) $\sqrt{\mu}$ = 0.2480
Fig. 44 (c)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0283	.1373	.01260
480	.0472	.1397	.01510
710	.0526	.1343	.01644
960	.0706	.1373	.02058
1190	.0731	.1343	.02195
1950	.0835	.1319	.02725
2150	.0878	.1325	.02964
2400	.0888	.1325	.03031

(D) $\sqrt{\mu}$ = 0.2936
Fig. 44 (d)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0297	.1373	.01276
470	.0429	.1349	.01466
750	.0531	.1319	.01674
950	.0620	.1325	.01880
1200	.0680	.1325	.02055
1430	.0788	.1325	.02467
1680	.0814	.1325	.02593
1910	.0894	.1357	.02890

(E) $\sqrt{\mu} = 0.3333$

Fig. 44 (e)

t	D_R	D_T	$\frac{1}{100-x'}$
240	.0278	.1325	.01266
470	.0472	.1367	.01527
720	.0555	.1331	.01715
960	.0731	.1379	.02128
1200	.0788	.1397	.02294
1440	.0872	.1379	.02720
1680	.0883	.1397	.02719
1910	.0942	.1385	.03126
2130	.0969	.1385	.03328
2400	.0980	.1343	.03700

TABLE A 29

Values of Velocity Constants

1. No Potassium Nitrate Added

Fig. 45.

$\sqrt{\mu}$	44.42°C.		48.34°C.		51.49°C.	
	$k \times 10^{-3}$	log k	$k \times 10^{-3}$	log k	$k \times 10^{-3}$	log k
.1414	0.8193	-3.0865	1.176	-2.9296	1.681	-2.7744
.1265	0.7899	-3.1024	1.172	-2.9311	1.510	-2.8210
.1095	0.6385	-3.1949	1.155	-2.9375	1.615	-2.7918
.0894	0.8854	-3.0529	1.701	-2.7693	2.344	-2.6301
.0633	0.1458	-3.8363	2.430	-2.6144	4.026	-2.3952

$\sqrt{\mu}$	54.84°C.		57.83°C.	
	k × 10^{-3}	log k	k × 10^{-3}	log k
.1414	2.357	-2.6276	3 0513	-2.5156
.1265	2.229	-2.6519	2.760	-2.5591
.1095	2.290	-2.6402	2.696	-2.5692
.0894	3.055	-2.4150	3.733	-2.4280
.0633	4.479	-2.3488	7.01	-2.1543

2. Potassium Nitrate Added

Fig. 46

$\sqrt{\mu}$	44.42°C.		49.17°C.	
	k × 10^{-3}	log k	k × 10^{-3}	log k
.1095	0.764	-3.1169	1.6158	-2.7916
.1916	1.110	-2.9547	1.8865	-2.7244
.2480	1.125	-2.9488	2.060	-2.6861
.2936	1.500	-2.8239	2.305	-2.6374
.3333	-	-	2.592	-2.5864

$\sqrt{\mu}$	53.07°C.		57.42°C.	
	k × 10^{-3}	log k	k × 10^{-3}	log k
.1095	2.383	-2.6228	3.330	-2.4776
.1916	2.940	-2.5317	4.258	-2.3708
.2480	3.263	-2.4864	4.700	-2.3279
.2936	3.838	-2.4159	5.255	-2.2794
.3333	4.258	-2.3708	5.902	-2.2290

TABLE A 30

Variation of velocity constant with temperature at zero ionic strength (extrapolated)

Fig 47 (a)

$\mu = 0$

t^{o}_{c}	$\frac{1}{T} \times 10^{-3}$	$-\log_{10} k^{o}$
44.42	3.1488	3.213
49.17	3.1024	2.920
53.07	3.0653	2.730
57.42	3.0250	2.590

TABLE A 31

$-RT \ln K^{*}$ calculated for values of T from corresponding k_o values.

$T^{o}K$	k_o (expt)	$-RT \ln K^{*}$
317.58	6.124×10^{-4}	14,817
322.33	1.202×10^{-3}	14,616
326.23	1.862×10^{-3}	14,516
330.58	2.570×10^{-3}	14,507

TABLE A 32

$-RT \ln K^*$ values at various temperatures (T) calculated from equation:-

$$-2.303RT \log_{10} K^* = 523005 - 10500.38T + 3557.44T \log_{10}T$$

FIG 48.

T	$-RT \ln K^*$	T	$-RT \ln K^*$
316.50	14,880	326.23	14,520
317.58	14,817	327.00	14,511
319.00	14,744	328.00	14,504
320.00	14,698	329.00	14,501
321.00	14,657	330.00	14,502
322.33	14,610	330.58	14,504
323.00	14,590	332.00	14,519
324.18	14,558		

TABLE A 33

Variation of ΔH^*, ΔF^* and ΔS^* with temperature. (see FIG 49).

$T^{o}K$	ΔH^* Kcals/mole	ΔF^* Kcals/mole	ΔS^* cals/mole
316.50	34.020	14.811	60.5
317.58	32.352	14.852	55.1
319.00	30.158	14.745	48.3
320.00	28.622	14.708	43.5
321.00	27.068	14.658	38.7
322.33	25.013	14.610	32.3
323.00	23.978	14.591	29.1
324.18	22.155	14.558	23.4
326.23	18.988	14.522	13.7
327.00	17.798	14.513	10.0
328.00	16.253	14.505	5.3
329.00	14.708	14.502	0.6
329.13	14.507	14.507	0.0
330.00	13.163	14.503	-4.1
330.58	12.267	14.505	-6.8
332.00	10.073	14.521	-13.4

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