AN INVESTIGATION OF CERTAIN COMPLEX IONS OF TRIVALENT CHROMIUM BY SPECTROPHOTOMETRIC AND OTHER PHYSICAL METHODS

by

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NOTE

The nomenclature used for the chromium complexes discussed in this work is that of Werner, with certain minor modifications recently recommended (1). The suffix -iate indicating a complex anion of a trivalent metal has been retained.

SUMMARY

Although chromium coordination compounds are of considerable technological importance, they have been subjected to few thorough investigations since Werner's original experiments, in spite of the fact that we now possess a number of accurate physical methods, not available in Werner's time, for the study of coordination complexes.

The object of the work described in this thesis was to obtain further information on the chemistry of complex chromium(III) ions, with special reference to the dioxalato-diaquochromiate system, $\left[Cr(C_2O_4)_2(H_2O)_2\right]$. For this purpose, spectrophotometric and potentiometric measurements were combined to yield information on a number of topics.

The spectrophotometric investigations consisted in measuring the absorption spectra of the potassium salts of the complexes under consideration, and in observing the changes in light absorption which occur during their formation and decomposition. The instrument used was a Beckmann Quartz Spectrophotometer model du.

More than twelve new absorption spectra were measured in this work and, in conjunction with the spectra of other chromium and cobalt complexes reported by earlier workers, these are used to review the position of spectrophotometry as a method of investigating chromium complexes. The reasons for the shapes of the absorption spectra are discussed

and it is concluded that spectrophotometry is useful for observing the progress of reactions involving complex ions and for analysing solutions, but that more fundamental data cannot be expected from the absorption curves.

The potentiometric investigations consisted in plotting the acid and alkali pH titration curves for solutions of the complexes. These were then used to detect the presence of acidic or basic groups and to estimate, approximately, the quantities titrating. Changes in pH during reactions involving complex ions were also recorded.

Investigations on the Dioxalatochromiate System

Investigations into the mechanism of complex formation with chromium(III) are complicated by the fact that there are six coordination positions available for substitution. Dioxalatodiaquochromiate, however, has only two positions available, since the oxalate groups which occupy four of the six positions are fairly strongly coordinated and remain firmly attached under most conditions. Accordingly, the dioxalatochromiate system was chosen for study, since it was hoped that this relatively simple case would throw some light on the mechanism of coordination, especially with dibasic acids.

Before commencing these studies, it was necessary to investigate fully the properties of the dioxalatodiaquochromiate ion $\left[Cr(C_2O_4)_2(H_2O)_2\right]^-$ itself, as reflected in spectrophtometric and potentiometric data, since very little information on this ion could be found in the literature. As this complex may exist in either the trans or the cis configuration, preliminary investigations were undertaken in order to elucidate the conditions under which either form could be isolated for study. It was found that Werner's method was suitable for the preparation of the trans potassium salt in a pure form but the isolation of the cis isomer presented difficulties. However, it was established that in solution the trans isomer converts to the cis form quantitatively - in about 3 hours at room temperature for a .01M solution - so that it was not necessary to isolate the salt. The discovery of this conversion depended on the fact that the two isomers have different absorption spectra in solution. Kinetic studies, based on the change in light absorption during the trans - cis conversion, showed that this reaction is of the first order. A tentative value for the activation energy of the conversion was calculated.

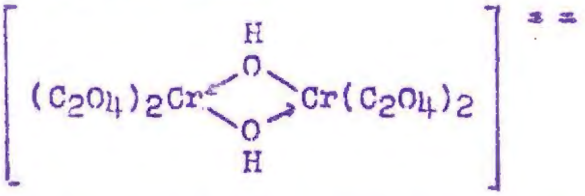
In subsequent experiments, solutions of the cis isomer were used. The acid and alkali potentiometric titrations were measured and, from the curves, values for the acid constants of the two aquo groups were calculated.

The neutralisation of the two aquo groups by alkali results in the production of the mono and dihydroxo derivatives. The cis forms of these complexes, namely

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

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

were studied in dilute solution. It was found that the dihydroxo ion decomposes in solution at room temperature with the liberation of oxalate. On boiling solutions of the cis mono hydroxo derivative, condensation occurs with the formation of the dimer:

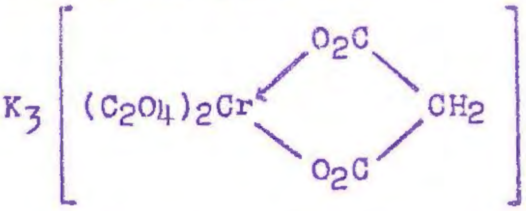


This process, known as "olation", was studied semi-quantitatively by measuring the alkali pH titration curves of solutions which had olated to different extents. It was concluded that on boiling a solution of the cis dioxalatchydroxoaquochromiate ion, olation proceeds to about 80% of theoretical.

The reactions of the cis dioxalatodiaquochromiate ion with a number of dibasic acid groups were then investigated. The trioxalatochromiate ion $\left[Cr(C_2O_4)_3\right]^{\equiv}$ is known and its properties have been established by previous investigators. In this thesis, the conditions of formation of this ion were studied and it was found that correct conditions of pH are essential for its formation. In addition, it was found that the ion is decomposed to some extent in acid solution.

Using this knowledge of the conditions of formation of the trioxalatochromiate ion, the kinetics of the reaction between potassium oxalate and potassium cis dioxalatodiaquochromiate in dilute solution were investigated by measuring the change in light absorption, and it was proved that the reaction is of the second order. The primary salt effect was also studied and from the application of the Brønsted-Bjerrum equation it was deduced that the rate determining step in the reaction involves the cis dioxalatodiaquochromiate ion and either the oxalate $(COO)_2^{=}$ or the binoxalate ion $(COO)_2H^{-}$. The Arrhenius equation was applied and tentative values for the activation energy at various ionic strengths calculated. These kinetics experiments were regarded as preliminary in view of the experimental difficulties encountered.

The reactions between cis dioxalatodiaquochromiate and the dibasic acid groups - malonate, succinate, adipate, fumarate, maleate and phthalate - were investigated next. It was found that reaction occurred in all cases, but the interpretation of the spectrophotometric and potentiometric data proved very difficult and there are indications that more than one complex was formed in many cases. The malonate group showed the greatest tendency to coordinate and a malonato derivative was isolated as a non-crystalline compound, probably having the structure:



Since the results from the reactions between certain dibasic organic acids and cis dioxalatodiaquochromiate, in dilute solution, were difficult to interpret, an attempt was made to study the reactions of an inorganic dibasic group, namely, the sulphate group. The reaction was studied by evaporating an equimolar mixture of the potassium salts to dryness. A peculiar, green solid was obtained which had the properties of the compound

$$K_3\left[(C_2O_4)_2(SO_4)(H_2O)\right]$$

An approximately .01M solution of this solid was found to decompose at room temperature (20°C) in about 15 hours with the liberation of SO_4 from the complex. The effect of adding benzidine hydrochloride to this solution at intervals during the decomposition, was observed. When freshly prepared, a large precipitate formed which was found to contain chromium. After the solution had aged for 7 hours, almost no precipitation occurred on adding benzidine in spite of the fact that, according to the spectrophotometric and potentiometric data, free $SO_4^{=}$ was present in solution. These anomalies throw considerable doubt on the benzidine method for estimating non-coordinated sulphate in the presence of anionic chrome complexes.

In conclusion, the question of the relative stability of the chromium complexes has been discussed and the possibility of Resonance contributing to their stability mentioned.

CONTENTS

Chapter 1

INTRODUCTION AND DISCUSSION OF PHYSICAL METHODS

1. The Chemistry of Trivalent Chromium Coordination Compounds

In the past sixty years, two great advances have been made in our knowledge of the chemistry of the transition elements. The first was the postulation of the Coordination Theory by A. Werner, and the second the concept of bond hybridisation developed by L. Pauling and others using the methods of wave mechanics.

The neutral chromium atom is considered to have the electronic configuration:

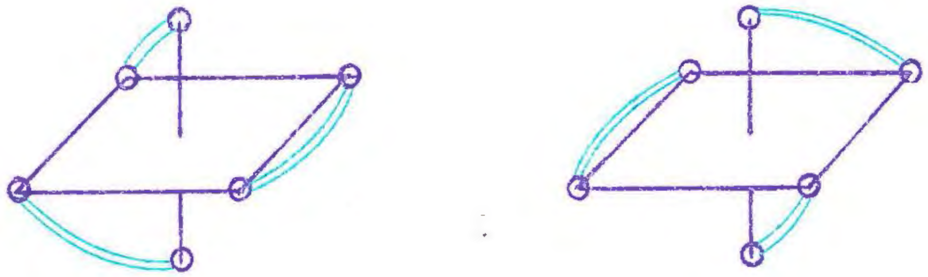
4p	OOO
3d	⊙⊙⊙⊙⊙
4s	⊙

while that of the chromic ion is:

4p	OOO
3d	OO⊙⊙⊙
4s	O

in which there are six empty orbitals. According to Pauling, these orbitals can be filled by electrons from other ions or molecules, the result being a complex or coordination compound. The six new bonds formed in this way are the so-called sp^3d^2 bonds which are directed towards the corners of a regular octahedron.

In the case of cobalt and other elements which are considered to form sp^3d^2 bonds, it has been shown by X-ray diffraction methods that six octahedral bonds are formed as predicted. However, X-ray diffraction has not been used in the same manner for chromium, since complex chromium compounds suitable for X-ray studies are not obtained as unmixed crystals; this has been discussed by Theis (2). For this reason, the evidence in favour of sp^3d^2 bond formation by chromium(III) is indirect, and the most significant is the discovery by Werner that certain coordination compounds can be resolved into optical isomers. One of the compounds studied by Werner (3) was potassium trioxalatochromiate $K_3\left[Cr(C_2O_4)_3\right]$. If the octahedral configuration theory is correct, then it is possible for the trioxalatochromiate ion to have the structures:



In this figure the double lines represent the oxalate groups and the circles the positions of attachment to the chromium atom. It is seen that these structures are mirror images so that they are enantiomorphs. This interpretation was criticised by Britton (4) and others who favoured the theory that the trioxalate solid was really a mixed crystal of potassium and chromium oxalates exhibiting colloidal properties in solution. However, Werner's experiment has been confirmed and the rate of racemisation of the trioxalatochromiate ion determined (5, 6). Pauling has accepted these results (7) and they are probably the best evidence we have in support of sp^3d^2 hybridisation in the case of trivalent chromium. No recent evidence has been adduced which is in contradiction to the hybridisation theory and so its acceptance appears to be fully justified.

At an early stage in his work on coordination, Werner showed that the properties of ions and molecules which enter a complex undergo considerable modification. The best known example is probably that of the cobalt chlorides in which the coordinated chloro groups are no longer immediately precipitated by silver nitrate in solution; in general it may be stated that all groups lose their identity on being included in a complex. Stiasny and coworkers in the period from 1920 to 1935 (8, 9, 10) extended Werner's investigations by studying those chromium complexes which are of interest to the theory of chrome tanning. From the results of these and other investigators, for example Weinland (11), it is now known that a large number of groups, both organic and inorganic, are capable of coordinating with trivalent chromium. Amongst the most important complex forming groups are: chloride, sulphate, acetate, formate, oxalate, tartrate (12). The nitrate and perchlorate ions have very little coordinative power.

Trivalent chromium complexes are all highly coloured and most of them are soluble in water. However, their other properties differ widely; for example, the trioxalatochromiate ion is perfectly stable in dilute solution, while the acetatodioxalatochromiates are unstable even as the solid potassium salts (13).

Much of the recent work on coordination (14, 15) has involved the complexes formed by copper and other metals which, unlike chromium and cobalt, do not form octahedral bonds. The results obtained for these complexes are not necessarily applicable to the study of chromium and cobalt complexes.

2. Methods of Investigating Chromium Complexes.

Coordination compounds combine the features of both organic and inorganic chemistry; for example, typically organic characteristics such as hybrid bonds and carboxyl groups occur in conjunction with highly charged ions which are found more commonly in inorganic chemistry. For this reason, neither the methods of organic nor the methods of inorganic chemistry are entirely applicable in an investigation of chromium complexes. Special techniques have, therefore, been evolved to study these substances. Some of these methods are outlined below:

(a) The change in the density of a solution containing complex ions has been used to measure the extent to which coordinated water molecules have been displaced by other groups. This method has been used by Plant for the phthalato complexes (16). An advantage of the method is that it can be applied without interfering with the state of the system.

(b) Dialysis and electrodialysis of solutions containing complex ions have been used extensively, especially by Brintzinger (17), to investigate changes in the particle size of complexes.

These methods are considered unreliable when applied to complicated solutions.

(c) A method of studying complex ions developed by Gustavson (18, 19) and others makes use of the ion exchange properties of zeolites and certain resins. Gustavson has obtained results in agreement with those from other methods, but the method is open to the objection that the substance used to extract the complexes may alter the state of the system.

(d) Conductometric measurements have been used by a number of workers including Densham (20) and more recently by Shuttleworth (21, 22). In this manner the changes in the conductivity of a solution containing complex ions are readily detected. Attempts are then made to correlate the changes in conductivity with changes in the structures of the complexes.

(e) A method recently applied to investigate the coordination of organic acids involves the extraction of the uncoordinated acid with solvents. In this way is obtained a measure of the extent to which complex formation has occurred (16). This method is difficult to apply to mixtures containing more than one acid, and it is also open to the objection that the removal of the acid may upset the equilibrium of the system.

(f) In recent years, spectrophotometry has been applied to investigate chromium complexes (23, 24), especially by Theis and coworkers (2). Chromium compounds have long been favourite subjects for colorimetric investigations but it is only comparatively recently that instruments have been available for measuring light absorption accurately at definite wavelengths. A review of some of the earlier work is given by Theis (2). Spectrophotometry has an advantage over most of the methods listed above since the equilibrium of the system is not affected during the measurements, and also, measurements can be made almost instantaneously.

(g) Another method which has been applied fairly extensively to investigate complex ions makes use of potentiometric measurements. Stiasny (9) performed numerous experiments in which the hydrolysis of chlorides, sulphates and other complexes was studied by observing the changes in electrode potentials and pH. A more advanced form of potentiometry, involving the examination of the pH curves of solutions containing complex ions, has been used by Britton (4), and by Atkin and Chollet (25). Potentiometric measurements provide evidence, which cannot be obtained by any other method, concerning the existence of acidic and basic groups in a complex.

The two chief physical methods used throughout this work are Spectrophotometry and Potentiometry.

Spectrophotometry

Spectrophotometry is that branch of photometry or "light measurement" which deals with the measurement of light absorption by solutions or liquids. Light of known wavelength is used and the range of wavelengths usually employed extends from 200 $m\mu$ to more than 2000 $m\mu$; that is, from the ultra-violet to the infra-red.

Light absorption measurements on solutions or liquids have two objects. The first is to obtain the Absorption Spectrum, which is the curve showing the relation between the amount of light absorbed and the wavelength or frequency and the second is to determine the concentration of substances which are capable of absorbing light.

It is well known that, whereas the spectra of gaseous atoms and their ions consist of a large number of lines, each of which shows fine structure owing to the multiplicity of the electronic energy levels, the absorption spectra of gaseous molecules in the visible and near ultra-violet region consist of a number of groups of bands. Sometimes the individual bands can be resolved into lines.

The band groups correspond to the transitions of electrons between electronic energy levels in the molecule. Each electronic energy level (A) - see figure - may be split up into a number of subsidiary levels (B), since quantised vibration is possible to a certain extent amongst the atoms of the molecule or ion. This splitting up of the electronic energy levels is responsible for the appearance of more than one band in each band group. The fine structure of the bands is due to changes in the rotational energy (C) of the system as a whole, although these rotational

changes are much smaller than the vibrational or electronic changes. Thus the absorption spectra of gaseous molecules are extremely complicated.

The absorption spectra of molecules and ions in solution do not usually show a fine structure although in some cases a few single broad lines have been observed (26). More commonly, a number of ill-defined bands of varying intensity are observed, and the absorption spectra generally have the form of a more or less smooth curve. The absence of fine structure is, according to Sidgwick (27), due to the strong magnetic field which exists in solutions, especially in the presence of polar solvents like water. The field splits up each of the spectral lines into a large number of other lines which coalesce and form a broad band. This phenomenon, known as the Stark Effect, is observed for the spectra of gases in a magnetic field.

It is probable that solvent molecules contribute to the absence of fine structure in other ways. For example, the solvation of solute molecules and ions may be expected to influence the vibrational or rotational energy levels, although no information on this aspect is available. Because of the absence of fine structure, the interpretation of the spectra of solutions is not nearly so exact as that for gases.

In the case of the absorption spectra of organic molecules in solution, it has been possible in some cases to associate light absorption in a certain region of the spectrum with the presence of particular atomic arrangements, such as double bonds or carboxyl groups, and in many cases the constitution of unknown molecules has been indicated by a resemblance of the absorption curve to those of known compounds.

Unfortunately, the spectra of solutions of coordination compounds cannot be treated in this way. Most of the known complexes of trivalent chromium and cobalt exhibit absorption maxima in the visible and ultra-violet which are now thought to be due to transitions of the hybridised 4s, 4p and 3d electrons. A discussion of these spectra is deferred until Chapter 10 after some of the absorption curves have been examined.

The second application of spectrophotometry is concerned with the analysis of coloured solutions. In this respect it is really an accurate form of colorimetry. The method is based on two elementary laws: that of Lambert, which deals with the variation in the light absorption of a solution as the thickness is varied; and that of Beer, which gives the relation between the absorbing power of a solution and the concentration. These laws both assume monochromatic light and are best summarised by the equation:

$$I = I_o\, 10^{-kcl} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.1)$$

where I_o is the intensity of the incident monochromatic light and I is its intensity after passing through a solution of thickness 'l' containing an absorbing substance at concentration c. The term k is known as the Extinction Coefficient and is a constant for a given substance at a given wavelength. It is referred to as the "Molar Extinction Coefficient" if the concentration c is in moles per litre, and the "Specific Extinction Coefficient" if c is in grams per litre.

The quantity I/I_0 is known as the Transmission of the solution and can be used directly as a measure of the amount of light absorbed. It is more convenient, however, to use the Optical Density (D) for this purpose. The optical density is defined as:

$$D = \log_{10}I_0/I \qquad \text{.........................} \quad (1.2)$$

It follows from (1.1) that:

$$D = klc \qquad \text{..............................} \quad (1.3)$$

which is another way of expressing the Beer-Lambert law.

From equation (1.3) the concentration in solution of a substance which obeys Beer's law can be obtained, the extinction coefficient being calculated from measurements on solutions of known concentration. A more important application of this equation is to obtain the concentrations of two or more absorbing substances in solution. This procedure was used on several occasions during this work.

It is found experimentally that Lambert's law is obeyed in most cases but deviations from Beer's law are common. The significance of these deviations is apparent from the following considerations:

If a solution contain a solute which is capable of absorbing light of a particular wavelength then, since light is absorbed in quanta, it is clear that the amount of light absorbed by the solution will be proportional to the number of molecules of solute, that is, to the concentration, provided that no change which alters the absorbing power of the solute molecules occurs on dilution. This indicates that Beer's law should be obeyed strictly only when neither dissociation nor association nor any other such change occurs in solution. It must be remembered that Beer's law assumes light of only one wavelength. The fact that this is not easy to obtain in practice is probably one reason why better agreement with Beer's law has not been reported. The effect of solvation is another possible reason. It was found in the present work that the chromium compounds tested obeyed the law with remarkable precision, and so a detailed study of the reasons for the Beer's law discrepancies was not undertaken. This subject has been discussed in detail recently (28, 29).

Unfortunately, there is no uniformity of nomenclature in spectrophotometry, either in connection with the quantities plotted on the absorption spectra or in connection with the symbols used to represent these quantities. For example, the abscissa of an absorption spectrum may represent the wavelength in Ångstrom Units or in millimicrons or the frequency in sec.$^{-1}$, etc., while the ordinate may be expressed as percentage transmission, optical density, extinction coefficient and so on. Throughout this thesis the abscissa of the absorption curves represent the wavelength expressed in millimicrons (mμ). The ordinates give the optical density (D) defined as above. All of the curves in this work were measured on solutions having the same chromium concentration so that these curves are strictly comparable. The concentration found suitable for the particular instrument used was .00921M, i.e. .07% Cr_2O_3. An important review of the methods of spectrophotometry has recently been given by Mellon (30).

Potentiometry

In this work, use is made of the pH curves of solutions containing chromium complexes together with the ions of dibasic acids. From these data the amount of free acid in solution was calculated. It must be emphasised that only approximate values were obtained from these curves and, wherever possible, additional evidence was sought in order to confirm the potentiometric calculations.

The theory of the pH curves of weak and strong monobasic acids is well known but it is convenient at this stage to outline the theory of the neutralisation of a dibasic acid, excluding theoretical refinements which are considered unnecessary in view of the use to which the titrations have been put. The following treatment, originally due to Atkin (80), will be used:

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

$$H_2A \rightleftharpoons H^+ + HA^- \quad \ldots\ldots\ldots\ldots\ldots\ldots (1.4)$$

$$HA^- \rightleftharpoons H^+ + A^= \quad \ldots\ldots\ldots\ldots\ldots\ldots (1.5)$$

From these, the constants K_1 and K_2 are given by

$$K_1[H_2A] = ha_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1.6)$$

$$K_2a_1 = ha_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1.7)$$

where, for convenience:

$$h = [H^+]$$

$$a_1 = [HA^-]$$

and $$a_2 = [A^=]$$

the square brackets signifying concentrations in gram ions per litre. Now, for all solutions, the total concentration C of acid H_2A is given by

$$C = [H_2A] + a_1 + a_2 \qquad \text{.......................(1.8)}$$

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

$$Na + h = oh + a_1 + 2a_2 \qquad \text{..................(1.9)}$$

where $Na = [Na^+]$ and $oh = [OH^-]$

Also, for an aqueous solution

$$h \times oh = Kw \qquad \text{..........................(1.10)}$$

where Kw is the ionic product of water.

Now, using equations (6) to (10), an equation can be derived showing how the hydrogen ion concentration h varies with the addition of alkali. For this derivation, the term (Na + h − oh) is replaced by Na_1, for convenience.

Thus from (8) and (9)

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

and from (6) and (7)

$$\frac{Na_1}{C} = \frac{hK_1 + 2K_1K_2}{h^2 + hK_1 + K_1K_2} \qquad \text{................(1.11)}$$

or $Na_1h^2 = K_1h(C-Na_1) + K_1K_2(2C - Na_1)$ ....(1.12)

In the above derivation it has been assumed, for simplicity, that no large change in volume occurs during the titration with alkali.

In Chapter 4 the constants K_1 and K_2 for a very weak dibasic acid are obtained from the potentiometric titration curve. The method used depends on the above equation, 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 (1.11)

$$\alpha = \frac{hK_1 + 2K_1K_2}{h^2 + hK_1 + K_1K_2} \qquad \text{..................(1.13)}$$

In order to obtain K_1, two points are selected on the titration curve equidistant from the midpoint of neutralisation (i.e. $\alpha = 1$). This point corresponds to the neutralisation of the first stage of the acid. Let the hydrogen ion concentrations at the two points selected be h_1 and h_2, and let the degree of neutralisation at h_1 be α. Then that at h_2 will be $(2 - \alpha)$. Then from (1.13)

$$\alpha = \frac{K_1h_1 + 2K_1K_2}{h_1^2 + K_1h_1 + K_1K_2} \qquad \text{..............................(1.14)}$$

$$\text{and } (2-\alpha) = \frac{K_1h_2 + 2K_1K_2}{h_2^2 + K_1h_2 + K_1K_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.15)$$

These can be solved for K_1 giving

$$K_1 = \frac{\alpha h_1 - (2-\alpha)h_2}{(1-\alpha)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.16)$$

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

Thus, to find K_1 and K_2, the quantities Na, C, h_1, h_2 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 can be taken as the average of many values.

In order to illustrate the effectiveness of this method, the values for the constants of succinic acid obtained in this way are compared, in the table below, with those given in the literature.

Succinic Acid

pK_1	pK_2	Source
4.19	5.47	Experimental
4.18	5.55	Handbook of Chemistry and Physics, 1944
4.2	5.5	Atkin and Thompson (31)

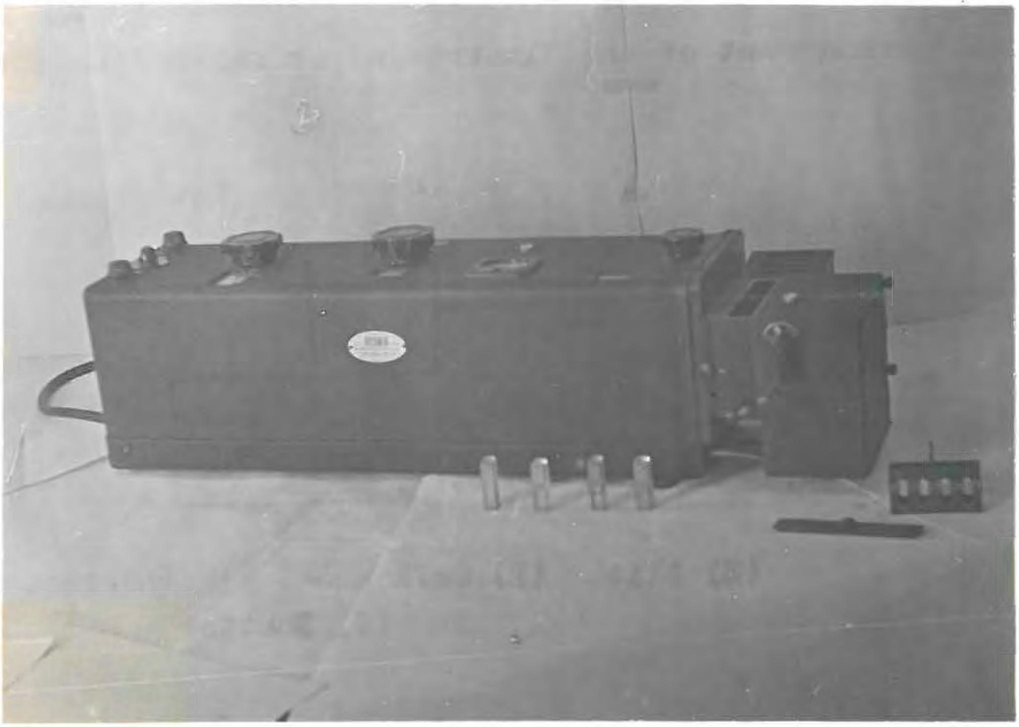


FIG 1

The Beckmann Quartz
Spectrophotometer.

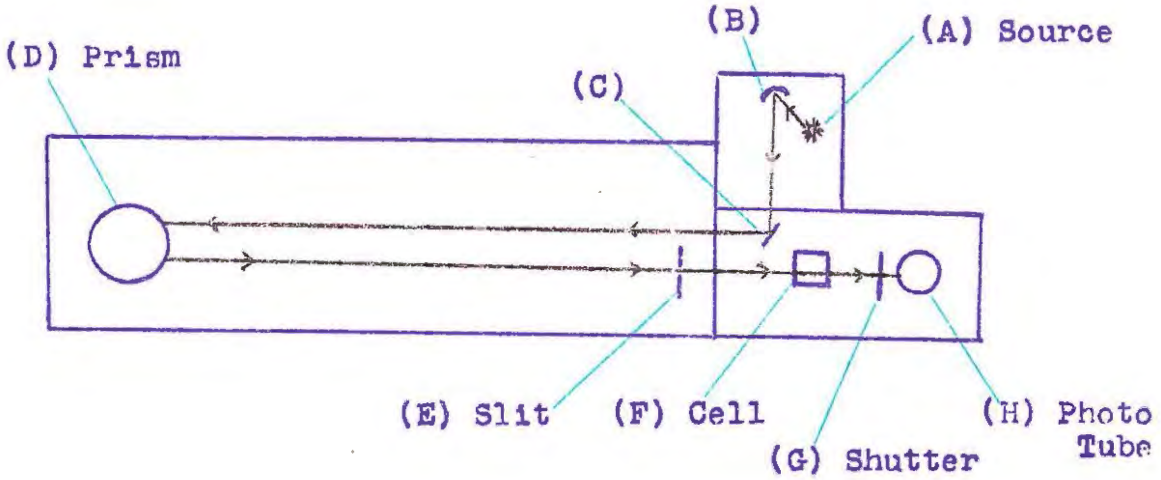
Chapter 2

EXPERIMENTAL TECHNIQUES

1. Spectrophotometry

(a) Apparatus

The instrument employed was a Beckmann Quartz Spectrophotometer Model du, a photograph of which is shown in Fig. 1. The optical arrangement of this instrument is represented below:



Light from the source (A), which is either a hydrogen discharge lamp for wavelengths from 220 to 350 mμ or a tungsten filament lamp for from 350 to 1000 mμ, is reflected by the aluminised mirrors (B) and (C) so that it falls upon the quartz prism (D) where it is refracted. The prism can be rotated by means of one of the large knobs which are visible on the top of the instrument in Fig. 1, and a calibrated scale is provided for selecting the desired wavelength. After leaving the prism, the beam of light passes through a narrow slit (E) whose width can be varied from 0 to 2 millimeters. The solution or liquid under test is placed in an absorption cell (F) in the path of the beam and the light not absorbed by this reaches the photoelectric cell (H). Two such cells, which can be interchanged by moving a lever, are provided in the instrument, one for observations below and the other above 625 mμ. The light beam can be excluded from the photoelectric cell by operating the shutter (G).

The electrical changes produced by the impingement of light on a photoelectric cell are balanced by a potentiometer circuit employing a rugged, null-point galvanometer which is incorporated in the instrument. The potentiometer scale is graduated to give directly both the transmission of the solution and the optical density.

The electrical circuit, which is supplied by four 6-volt dry cells and a 6-volt accumulator, includes variable resistances for standardising the galvanometer circuit and for the fine adjustment of the sensitivity of the instrument.

Two types of absorption cell are supplied: of fused silica for use over the whole spectral range from 230 to over 1000 mμ, and of optical "corex" glass which cannot be used for observations in the ultraviolet region. Incorporated in the instrument is a cell holder in which four absorption cells may be placed. Each of these can be brought into the path of the light beam in turn by operating a sliding bar attached to the cell holder. One cell is always kept filled with pure solvent during measurements on solutions. The optical density reading of the cells of each set of four should be the same, otherwise corrections are necessary. This is easily checked by matching the cells against each other when filled with pure solvent.

The "light path length" of each 1 cm absorption cell is recorded to .001 cm by the manufacturer, and the individual cells of the sets used in this work did not differ by more than .002 cm.

By adjusting the slit width (E), the width of the spectral band which passes through the absorption cell can be controlled. This band width varies for different parts of the spectrum owing to diffraction effects. For example, a slit width of 1 mm transmits a spectral band of width 2 mμ at wavelength 250 mμ, but transmits a band of width 35 mμ at wavelength 600 mμ. A calibration chart is provided by the manufacturer. The slit width also controls the sensitivity of the instrument, although fine adjustment is made by altering the balance of the electrical circuit. In general, the larger the slit width the greater the sensitivity but, since a larger section of the spectrum is allowed to pass through the solution, a smoothing-out of the minor characteristics of the absorption curve is to be expected. The slit widths employed throughout this work were fairly wide since for most experiments great sensitivity was desirable and, in view of the nature of the absorption spectra measured, it is considered that no loss in detail occurred.

In connection with the accuracy of the instrument, the wavelength scale could be read to 0.1% over all regions and the optical density scale to within .001 or .002 units, the most accurate part of this scale being between 0.4 and 0.8.

A number of reports on the Beckmann spectrophotometer have been published (32, 33) 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.

The Beckmann instrument used in the present work was standardised by using the 656.3 mμ line of the hydrogen spectrum and by measurements on potassium trioxalatochromiate solutions. (Vide Chapter 3).

(b) Procedure

In order to measure the light absorption of a solution the following operations are performed:

The potentiometer circuit is standardised with shutter (G) closed—the so-called "dark current" adjustment. The desired wavelength is selected by rotating the prism; the absorption cell containing pure solvent is placed in the path of the light beam and the shutter (G) opened.

The slit width is then adjusted to centre the galvanometer needle approximately; the sensitivity control resistance is set to give maximum sensitivity and, if necessary, the slit width is increased to centre the needle again. Finally, the needle is brought exactly to the centre of the scale by adjusting the sensitivity control resistance.

The solution under examination is placed in an absorption cell in the path of the light beam and the galvanometer needle centred once again, this time by rotating the potentiometer resistance. The optical density or transmission is then read on the potentiometer scale.

A systematic procedure was adopted for all measurements. The absorption cells were kept in distilled water when not in use and were rinsed twice with each solution to be measured. They were always orientated in the same manner in the cell holder and one cell of each set of four was always kept for the solvent blank. The solvent used was distilled water which had been redistilled.

In general, several readings were taken at each wavelength and these were averaged if variations occurred.

2. Potentiometry

(a) Apparatus

A Cambridge "Bench Type" pH meter, having dipping calomel and glass electrodes, was used. It was standardised against a benzoate buffer of pH 4.16 (34) and, as a check on the higher pH values, a borate buffer of pH 9.20 was employed.

(b) Procedure

A 250 ml beaker was used as titration vessel for all the potentiometric titrations discussed in this work. The solutions under examination contained about 0.1% Cr_2O_3, the volume being 100 ml. Stirring was effected by an air bubbler having a soda-lime trap to remove carbon dioxide.

The standard solutions used were:

0.3590N potassium hydroxide (CO_2 free)

and

0.4297N nitric acid.

NPL Grade A burettes and microburettes were used for additions.

3. Analytical Methods

Throughout this work, the purity and composition of a number of chromium complex salts were determined by analysis for chromium, potassium and oxalate. The methods employed are as follows:

(a) Chromium (35).

About 0.2 gm of the chromium compound was accurately weighed into a 150 ml Erlenmeyer flask and approximately 5 ml of water added. Then 3 ml of an oxidising mixture was added. This mixture consisted of 60% perchloric acid and 80% sulphuric acid in the volume ratio 2 : 1. For compounds containing reactive organic groups, 10 ml of a 10% nitric acid solution was added as well.

The mixture was heated gently until oxidation had occurred (i.e. until the solution became the colour of dichromate), and then for a further 3 minutes. When bubbling ceased 10 ml of water was added cautiously and the mixture boiled for five minutes to expel chlorine. The solution was finally titrated against a standard ferrous solution using n phenylanthranilic acid as indicator.

(b) Potassium

About 3 ml of A. R. 60% perchloric acid was added to about 0.3 gms of the compound, which had been accurately weighed into a 150 ml Erlenmeyer flask. Then 5 ml of water was added and the mixture evaporated gently to dense fumes and allowed to cool. Next 10 ml of absolute alcohol was added and, after standing for an hour or two, the mixture was filtered through a sintered glass crucible. The precipitate of potassium perchlorate was weighed after drying for one hour at 140°C. It was found that if the evaporation were allowed to proceed until the chromium had become oxidised to dichromate, erratic results were obtained.

The method could not be used in the presence of sulphate.

(c) Oxalate

A known quantity of the salt (about 0.3 gms) was dissolved in about 100 ml of water and an excess of 40% sodium hydroxide solution added. The solution was boiled until a precipitate of chromium hydroxide appeared after which it was set aside to allow the precipitate to coagulate. The mixture was filtered and the precipitate washed thoroughly. The filtrate was acidified with SO_2-free 50% sulphuric acid; excess was added and the solution titrated against standard permanganate in the usual manner.

For compounds containing other organic groups besides oxalate, it was found more accurate to precipitate the oxalate as the calcium salt after the removal of chromium. In any case, the oxalate determination was less accurate and precise than the methods for chromium and potassium.

The results obtained by analysing a sample of purified potassium trioxalatochromiate for chromium, potassium and oxalate are given in the next chapter.

All the results recorded in this work are the averages of values which did not differ by more than 0.2% for the chromium and potassium estimations and by more than 0.4% for the estimation of oxalate.

(d) Sulphate

The usual method for finding the amount of uncoordinated sulphate in a solution containing sulphato complexes consists in precipitating the uncoordinated sulphate as benzidine monosulphate (36).

A benzidine hydrochloride solution was prepared by heating 15 gms of pure benzidine with 50 ml of concentrated hydrochloric acid and making up to one litre with distilled water.

To 20 ml of the chrome solution under test, containing about .1% Cr_2O_3, 20 ml of the benzidine hydrochloride solution was added and the mixture left to stand for exactly 1 minute, after which it was filtered by suction using a 1½ inch diameter Buchner funnel and a Whatmann 42 paper. After washing the precipitate with 10 ml portions of distilled water, the filter paper and precipitate were placed in a conical flask and water added. The benzidine sulphate precipitate was hydrolysed by boiling and the liberated sulphuric acid titrated with standard decinormal sodium hydroxide solution, using phenolphthalein indicator.

The method was standardised on known potassium sulphate solutions with the following results:

	Found	Theoretical
% SO_4	54.5% 54.6 54.9	55.1%
Average:	54.7%	

These results were considered sufficiently accurate and precise for the purpose to which the determination was put. (Vide Chapter 9)

4. The Preparation of Chromium Complex Salts

In this work, frequent reference is made to a number of complex chromium salts which had already been prepared by previous investigators. For convenience, the preparation and purification of these compounds is given in this section.

(a) Potassium Trioxalatochromiate (37)

To a solution of 19 gms of $K_2Cr_2O_7$ dissolved in about 50 ml of water were added 23 gms of $(COOK)_2$ and 55 gms of $(COOH)_2 2H_2O$ in about 100 ml of water. Effervescence occurred, and when this subsided the solution was boiled down to a small volume and allowed to crystallise.

The reaction proceeds according to the following equation:

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

The blue-green crystalline mass was filtered off, recrystallised from hot water and dried over fused calcium chloride.

(b) Potassium trans Dioxalatodiaquochromiate

The method of preparation used was similar to that given by Werner (13):

450 gms of oxalic acid hydrate were added to about 2000 ml of water and heated to boiling. Then 150 gms of powdered potassium dichromate were added cautiously in small portions. Violent effervescence occurred and when this had subsided, the solution was boiled gently for 30 minutes 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 minute crystals floating on the surface of the solution were visible. The solid which formed was filtered off each day and washed with small quantities of water. The separate portions of solid were combined and the salt was purified by dissolving in water containing about 1% of strong nitric acid, boiling for 30 minutes and allowing to crystallise as before. The recrystallisation was repeated 3 times and the final product allowed to dry in a vacuum desiccator over concentrated sulphuric acid.

(c) Potassium cis Dioxalatodiaquochromiate

Although Werner's directions were followed, this salt could not be obtained in a pure condition. Consequently, it was used merely for preliminary preparations of other complexes. Werner's method (13) is as follows:

450 gms of oxalic acid hydrate and 150 gms of potassium dichromate were pulverised and mixed well in a large mortar. The mixture was moistened with about 50 ml of water and stirred thoroughly to form a brown paste. After a short time reaction started; the mixture became dark brown and blue-green bubbles appeared at the surface. This was followed by violent evolution of carbon dioxide and steam after which a violet liquid remained in the mortar. On being left overnight, this liquid set to a solid mass of brown crystals which were moistened with a minimum quantity of water and filtered off.

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.

5. Miscellaneous

Thermostatic Control

In experiments to be described later, thermostatic control over periods of up to 20 hours was necessary. This was ensured by using a water bath of 90 litre capacity heated by two 1000 watt elements. A "sunvic" model E.A. 2 electronic relay and proportioning head, including a mercury-toluene regulator, was installed. This apparatus maintained constant temperature to within .02°C for temperatures below 35°C and to within

.05° for up to 60°C. For temperatures above 45°C a heat-lamp of 300 watts was fitted in the water bath and kept on.

Chapter 3

STANDARDISATION OF METHODS ON THE TRIOXALATOCHROMIATE ION

1. Introductory

A review of the literature showed that complex ions of chromium containing oxalate groups are amongst the most stable that are formed and that of these, the trioxalatochromiate ion has been subjected to the most thorough study. For this reason it was decided to commence this work with an investigation of the spectrophotometric and potentiometric properties of potassium trioxalatochromiate solutions. Although the structure of this compound is known, very little literature could be found dealing with the conditions of its formation and so this aspect has also been investigated and is described in a later chapter.

Potassium trioxalatochromiate has been known for more than a century. In 1842 Croft (38) described a method of preparation from oxalic acid, potassium oxalate and potassium dichromate. This method has been named after him although he was not the only investigator.

As already mentioned in Chapter 1, A. Werner succeeded in resolving the compound into optical isomers. His work has been confirmed by Johnson and others (5, 6).

Rideal and Thomas (39) appear to have been the first to publish an absorption curve of a solution of the compound and they found that addition of acetone increased the height of the maxima.

A thorough investigation of the light absorption curves of certain oxalatochromiates was made by Mead in 1934 (40) using extremely accurate Hilger instruments. An absorption curve of the trioxlatochromiate ion was published and is referred to later in this chapter.

In 1924 Long (41) 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. No measureable interchange was detected at a temperature of 35°C at a concentration of .06M and he concluded that the trioxalatochromiate ion racemises in solution by intramolecular rearrangement of the oxalate groups. This investigation is of great importance since it shows that the trioxalatochromiate ion is completely stable in solution under the conditions described.

From a dialysis experiment, Brinztinger and Eckardt (17) found that, unlike the oxalates of certain other metals, the trioxalatochromiate ion does not condense to form dimers in solution.

Recently, Ueberbacher and Dröscher (24) proposed a colorimetric method for estimating chromium in tanning salts in solution by conversion to the trioxalatochromiate ion. Their work was repeated, more accurately, by Theis and co-workers (2) using a Beckmann quartz spectrophotometer. These workers have published absorption spectra of a number of chromium complexes including that of the trioxalatochromiate.

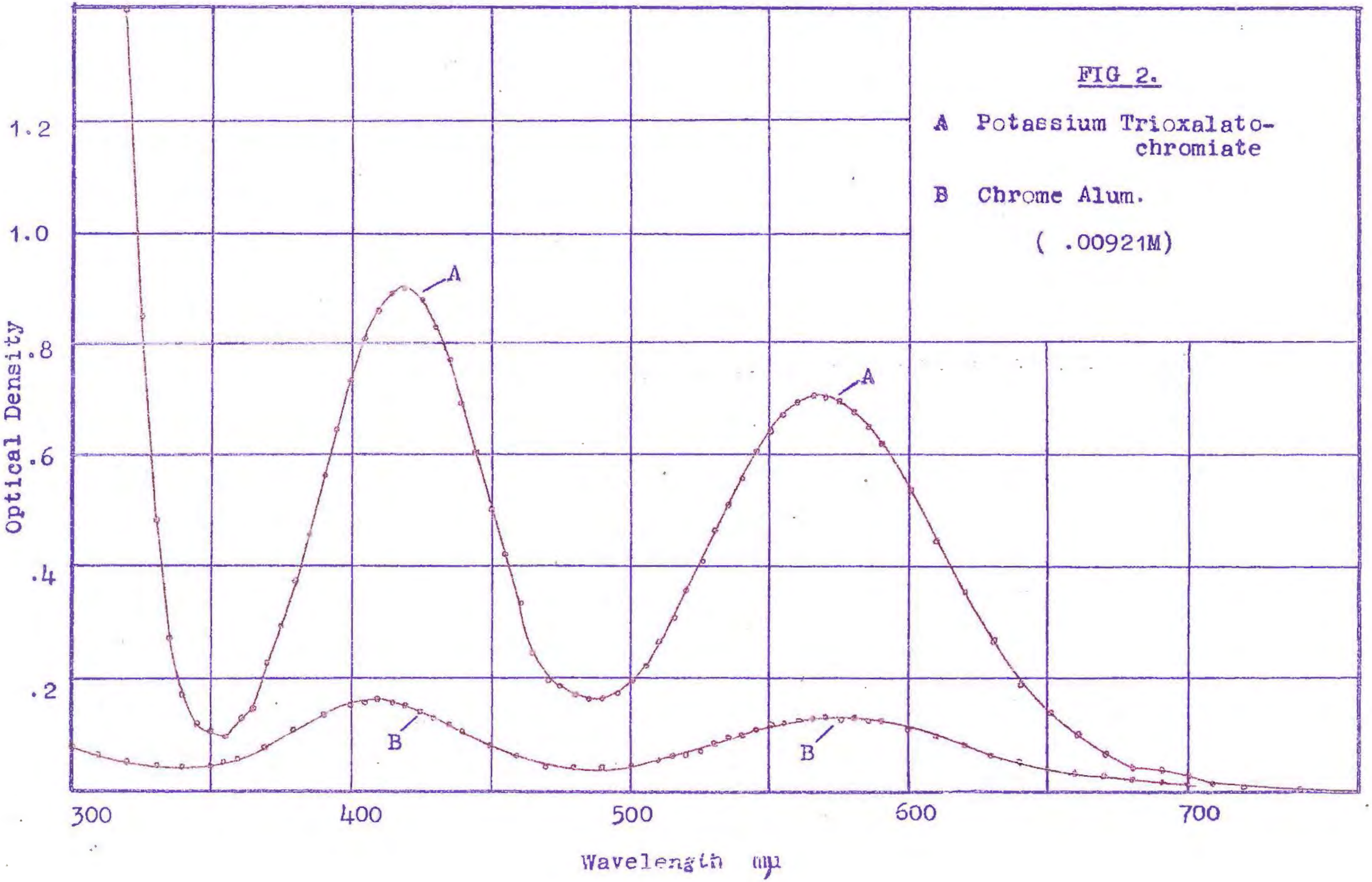


FIG 2.

A Potassium Trioxalato-chromiate
B Chrome Alum.
(.00921M)
A
A
B
B
1.2
1.0
.8
.6
.4
.2
Optical Density
300
400
500
600
700
Wavelength mμ

2. Spectrophotometric Investigation

As a comparison with the results of previous investigators, the absorption spectrum of a .00921M solution of pure potassium trioxalatochromiate was measured between the wavelengths 300 and 800 mμ (Fig. 2, Curve A). The actual readings are recorded in the Appendix, Table A1.

The shape of this curve agrees almost exactly with those obtained by Mead (40) and by Theis (2) and in the table below the wavelengths at which the absorption maxima occur are compared:

Investigator	Instrument	First Max	Second Max
Mead (40)	Hilger	417.5 mμ	575.0 mμ
Theis (2)	Beckmann	418	568
Author	Beckmann	419	569

It is believed that the solutions of trioxalatochromiate used by Theis contained small quantities of other chromium complex ions (See Chapter 6); nevertheless it is considered that the positions of the maxima on the wavelength scale were not altered measureably even if this were the case.

The purity of the compound used in the present work was checked by analysis:

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

	Found	Theoretical
Cr	10.66%	10.68%
K	23.99	24.07
$(COO)_2$	54.2	54.18

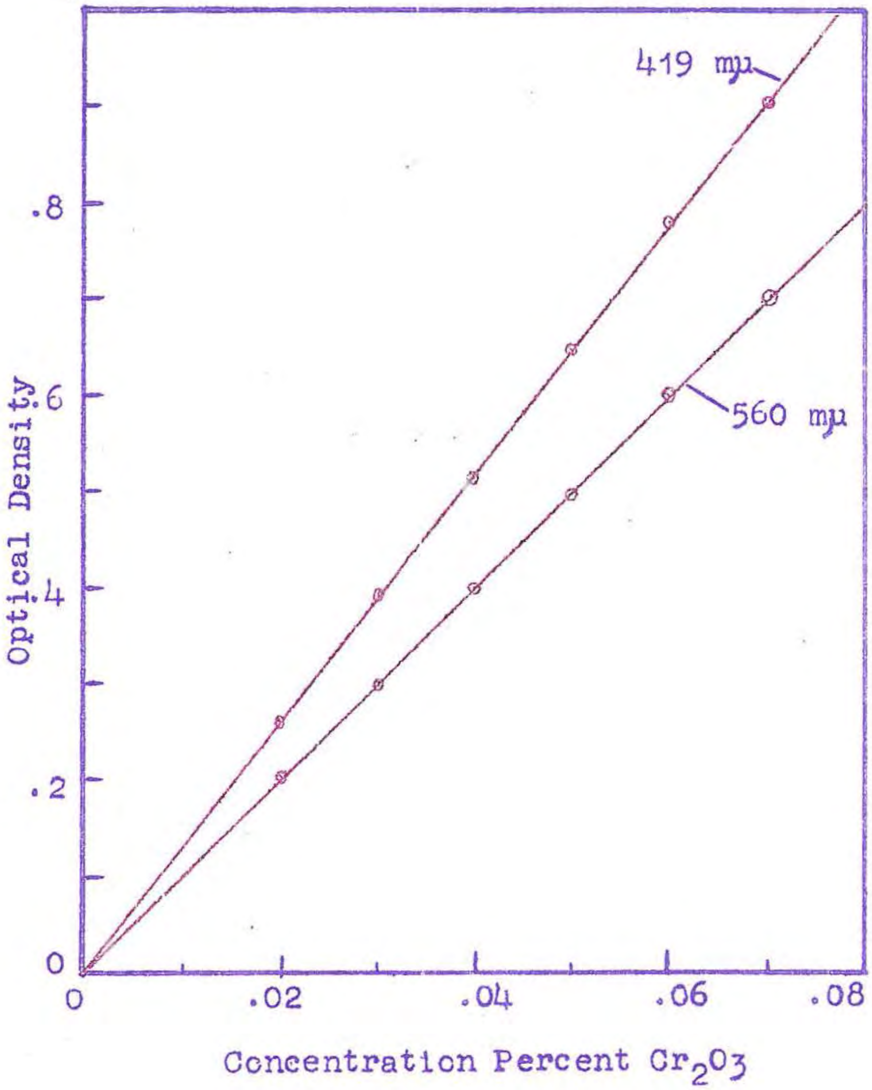


FIG 3

Beer's Law for
Trioxalatochromiate.

In spite of the slight differences in the wavelengths of the second maximum, it is considered that the wavelength values recorded above indicate that there was no serious source of error in the spectrophotometer used.

It is known that the trioxalatochromiate ion is perfectly stable in solution, and so, as a further check on the reliability of the spectrophotometer, the agreement with Beer's law was investigated for this ion.

A number of solutions of potassium trioxalatochromiate, having concentrations from .02 to .07% Cr_2O_3 (i.e. from .00263 to .00921M) were prepared and their optical densities measured at wavelengths 419 and 560 mμ, that is, in the vicinity of the maxima. In Fig. 3 these values have been plotted against the concentrations.

The fact that straight lines are obtained shows that Beer's law is obeyed, although a better idea of the agreement is obtained from the constancy of the molar extinction coefficients at the two wavelengths. These are recorded below:

TABLE 1

Concentration		419 mμ		560 mμ	
% Cr_2O_3	Moles/litre	Opt Dens	Ext Coeff	Opt Dens	Ext Coeff
.07%	.00921M	.903	98.0	.700	76.0
.06	.00789	.779	98.7	.600	76.0
.05	.00658	.648	98.5	.500	76.0
.04	.00526	.516	98.1	.400	76.0
.03	.00395	.388	98.2	.300	75.9
.02	.00263	.259	98.5	.202	76.8
Averages used:			98.3		76.0

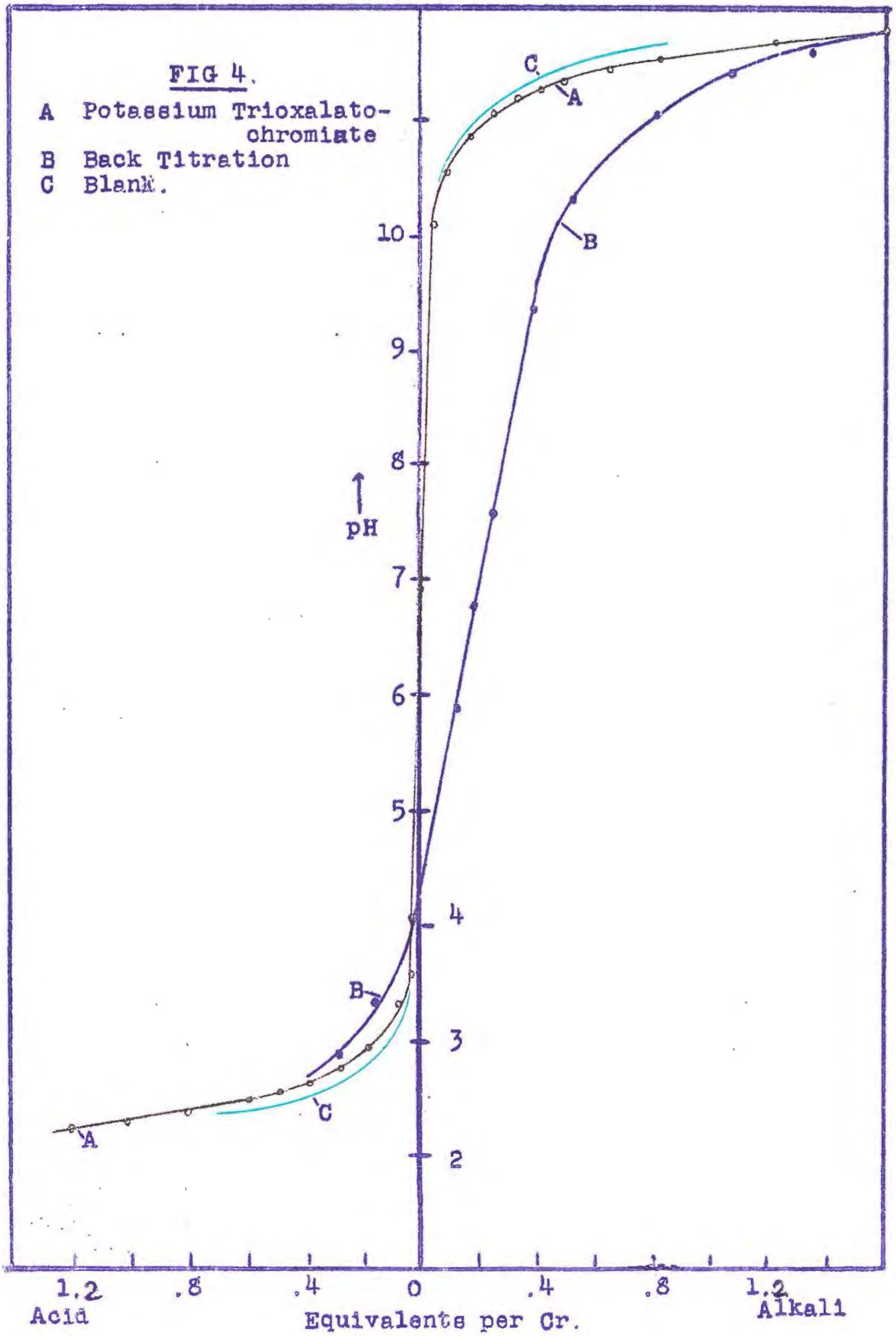


FIG 4.

A Potassium Trioxalato-chromiate
B Back Titration
C Blank.
pH
10
9
8
7
6
5
4
3
2
C
A
B
B
C
A
1.2
.8
.4
0
.4
.8
1.2
Acid
Alkali
Equivalents per Cr.

In Fig. 2 the absorption spectrum of a freshly prepared chrome alum solution, also at a concentration of .00921M is shown (Curve B). Now it may be assumed that in a freshly prepared chrome alum solution most of the chromium is in the form of $Cr(H_2O)_6^{+++}$, with small amounts of the hydroxo complexes $Cr(H_2O)_5(OH)^{++}$ and $Cr(H_2O)_4(OH)_2^{+}$. Thus the fact that the absorption curve of the trioxalatochromiate ion $Cr(C_2O_4)_3^{\equiv}$ is considerably higher than that of an equimolar solution of chrome alum must be due, in some way, to the replacement of the six coordinated water molecules by oxalate groups.

3. Potentiometric Investigation

No reference to previous potentiometric studies on the pure trioxalatochromiate ion could be found, and so the object of this investigation was to determine whether the properties of this ion already known could be confirmed by potentiometric measurements.

Two solutions, containing approximately equal quantities of pure potassium trioxalatochromiate were titrated potentiometrically against standard acid and standard alkali, respectively. The pH curves are illustrated in Fig. 4 (Curve A). In this figure, the right hand side represents titration with alkali and the left, titration with acid. The volumes added during titration have been converted to equivalents of alkali or acid per Cr and the same procedure is adopted throughout this work.

For comparison, titrations were performed on solutions of a neutral salt (potassium nitrate) having an ionic strength approximately equal to that of the potassium trioxalatochromiate solutions. The results are shown as Curve C, Fig. 4. The fact that the curve for the trioxalatochromiate solution (Curve A) is very close to that of the potassium nitrate blank (Curve C), shows that potassium trioxalatochromiate is also a neutral salt with no weak acidic or basic groups. This is in conformity with the accepted formula $Cr(C_2O_4)_3^{\equiv}$ for the trioxalatochromiate ion.

The solution used for titration against alkali was back-titrated with standard acid (Fig. 4, Curve B). It is clear that the back titration did not coincide with the initial titration and, although the reason for this hysteresis is not immediately obvious, it must be connected with the action of excess alkali on the trioxalatochromiate ion. It was noticed that if the solution were left overnight after adding six equivalents of KOH per Cr, a green precipitate formed which resembled $Cr(OH)_3$. When this had settled, the supernatent liquid was clear and colourless and free oxalate could be detected by neutralising and testing with Ca^{++}. A similar green precipitate was observed after boiling the solution with six or more equivalents of alkali. This proves that excess alkali is capable of decomposing the complex by displacement of oxalate and it seems likely that the hysteresis observed on back titration is caused by the fact that a certain amount of oxalate has been displaced from the complex.

4. Summary

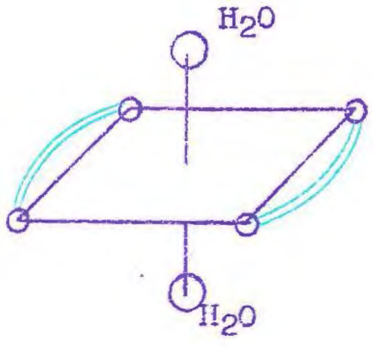
From the spectrophotometric investigation of pure potassium trioxalatochromiate solutions, it is evident that the apparatus and techniques employed were capable of yielding results which agreed with those of other workers, while the potentiometric data are consistent with the results obtained by other methods.

Chapter 4

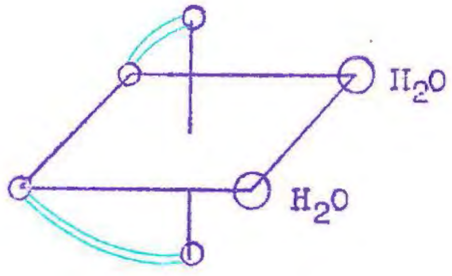
THE POTASSIUM DIOXALATODIAQUOCHROMIATES

1. Introductory

Compounds of chromium containing two oxalate groups per Cr were first prepared in 1842 (42) but for many years there was considerable doubt about their constitution. The position was clarified in 1901 by Werner (43) and others (44) in terms of the newly postulated Coordination Theory. These workers showed that the six coordination positions of chromium can be filled by two oxalate groups and two water molecules, giving the formula $Cr\left[(C_2O_4)_2\ (H_2O)_2\right]^-$ for the dioxalatodiaquochromiate ion. In 1914 Werner and co-workers described the results of an extensive series of experiments designed to elucidate the properties of the dioxalato compounds (13). During this work two geometrically isomeric forms of the dioxalatodiaquochromiate ion were prepared, the cis and trans forms. These, Werner showed, have the following configurations:



trans



cis

In addition, numerous crystalline salts of both the cis and the trans form were prepared and properties like solubility and stability were investigated qualitatively. Werner found that addition of alkali to a solution of either isomer caused a colour change from pink to green. This was shown to be due to the formation of the hydroxo complexes:

$Cr[(C_2O_4)_2(H_2O)(OH)]^=$ Dioxalato hydroxoaquochromiate

$Cr[(C_2O_4)_2(OH)_2]^≡$ Dioxalato dihydroxochromiate

The properties of the potassium dioxalatodiaquochromiates, according to Werner (13), 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 also pink but very much more soluble in cold water than the trans isomer, so that it cannot be purified satisfactorily by recrystallisation and can only be prepared using a minimum quantity of water.

No other references to the dioxalatodiaquochromiates could be found, apart from some tanning experiments by Gustavson (45) whence it appeared that no investigation of the physical properties of these compounds had been undertaken.

2. Purification of the Dioxalatodiaquochromiates

Since numerous attempts to prepare the cis salt by Werner's method (See p. 26) all gave products which did not quite agree with Werner's analytical figures, this salt was not used for physical measurements.

The trans salt was obtained in a much purer state but the analytical figures suggested that the first preparations were contaminated with potassium trioxalatochromiate. This impurity was removed by boiling the solution with about 1% of nitric acid which, it is shown later, decomposes the trioxalatochromiate ion. The figures for the final preparation were:

Formula $K[Cr(C_2O_4)_2(H_2O)_2].3H_2O$. Mol. Wt. 357.2

	Found	Theoretical
Cr	14.50%	14.56%
K	10.92	10.95
(C_2O_4)	49.2	49.27

(The details of preparation have been given on p. 26)
These crystals were used for a number of investigations.

3. Potentiometric Investigation

Chromium complex ions which possess coordinated water molecules, or aquo groups as they are termed, are acidic. It is not certain whether this acidity is due to the ionisation of the aquo groups to give hydrogen ions:

$$Cr-OH_2 \longrightarrow Cr-OH + H$$

or to the replacement of the aquo groups by hydroxyl ions from

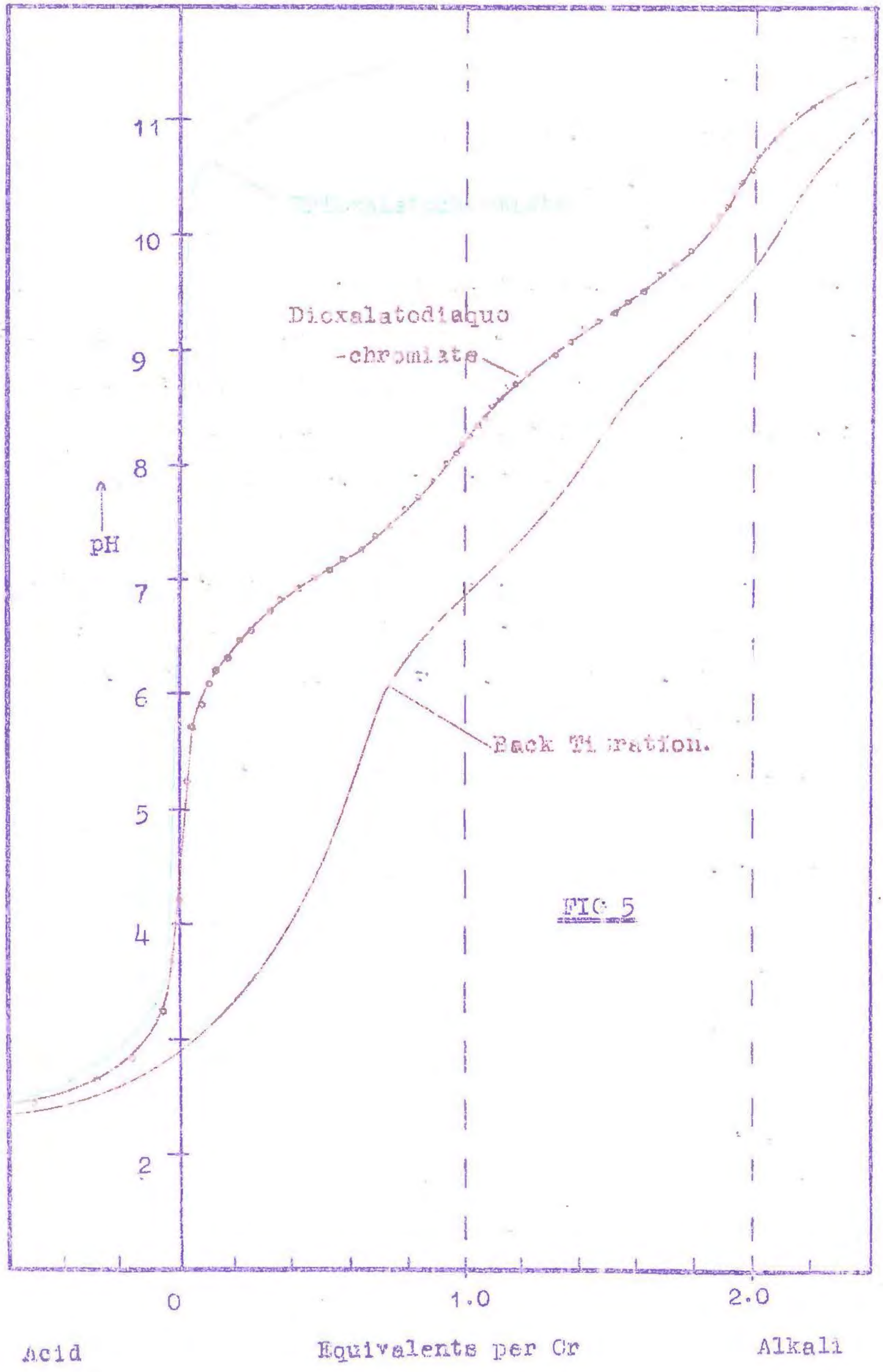

Trioxalatochromate
Dioxalatodiaquo
-chromiate
Back Titration.
pH
11
10
9
8
7
6
5
4
2
0
1.0
2.0
Acid
Equivalents per Cr
Alkali

FIG 5

from the solution·

$$Cr{-}OH_2 + OH \rightarrow Cr{-}OH + H_2O$$

The result is the same in either case: the solution is acid and a corresponding amount of hydroxo complex is present. It is more convenient to consider that the aquo groups ionise in solution.

The dioxalatodiaquochromiate complex is no exception to this rule and a .01M solution of the potassium salt has a pH of about 4.2. In Fig. 5 the results of acid and alkali potentiometric titrations on solutions of the pure trans salt are illustrated, and for comparison the curve for pure potassium trioxalatochromiate is shown.

It is apparent from the shape of the curve above pH 6 that the dioxalatodiaquochromiate ion is weakly acidic. Two shallow end points are just discernable corresponding approximately to 1.0 and 2.0 equivalents of alkali per Cr.

It is assumed that 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:

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

$$Cr\left[(C_2O_4)_2(HO)_2\right]^{\equiv}$$

The formation of these ions is responsible for the change in colour from pink to green which occurs during alkali titration.

The dioxalatodiaquochromiate ion is thus a weak dibasic acid and from the titration curve the following approximate values for the acid constants were derived, using the method outlined in Chapter 1:

pK_1 7.09

pK_2 9.45

In Fig. 5 the curve obtained by back titrating a dioxalatodiaquochromiate solution, to which about 3.0 equivalents of alkali per Cr had been added, is shown. Although the reasons for the considerable hysteresis were not investigated in detail, further work, to be discussed in the next chapter, has established that the dihydroxo ion is unstable in solution and rapidly liberates oxalate ion, the titration of which probably accounts for most of the hysteresis observed.

4. The Conversion from trans to cis Dioxalatodiaquochromiate

Anomalous results obtained during some initial kinetics experiments involving potassium trans dioxalatodiaquochromiate, to be described later, necessitated an investigation of the stability of this compound in aqueous solution. It was found that, for an approximately .01M solution of the trans salt, the optical density at a number of wavelengths underwent a slow increase until a limiting value was reached; this took about three hours at room temperature (20°C). The kinetics of this process was investigated as follows:

> Exactly 0.6580 gms of the finely pulverised trans salt were weighed into a dry beaker, and distilled water at the temperature to be used for the experiment was added. The salt was dissolved as quickly as possible by vigorous stirring. The solution was made to 200 ml (to give a .00921M solution), shaken, and rapidly

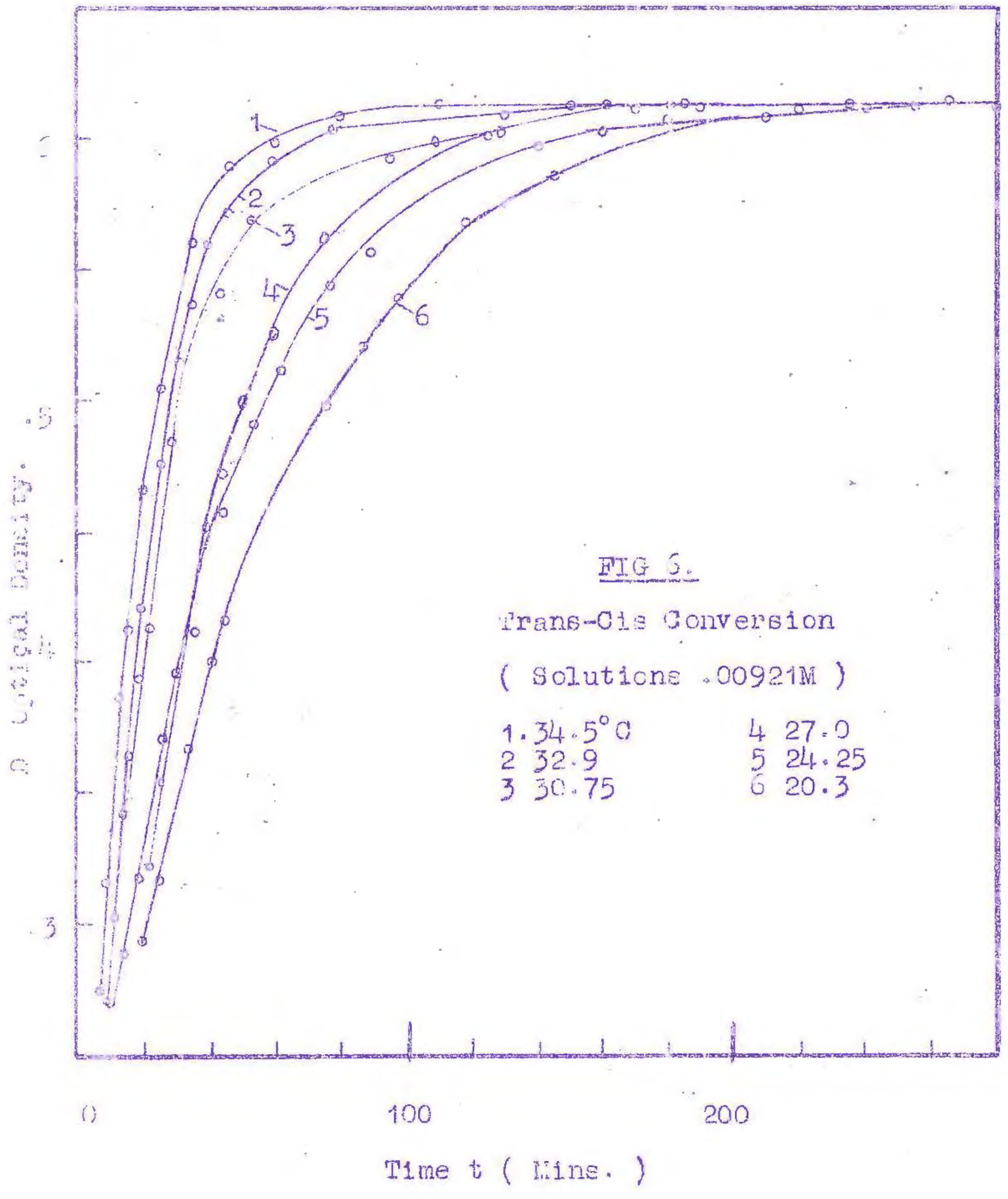


FIG 6.

Trans-Cis Conversion

(Solutions .00921M)

transferred to a dry 300 ml conical flask which had been allowed to attain the desired temperature. This flask was immersed in the constant temperature water bath (See p. 27) and small portions of the reaction solution were withdrawn at intervals of time during the experiment by means of a pipette. An absorption cell of the spectrophotometer was rinsed and filled with this solution and the optical density at 420 mµ was determined. Less than 30 seconds elapsed from the removal of the sample from the flask to the reading of the spectrophotometer. The time was noted from the moment the instrument was read. Readings were taken until constant and then for a further period, about three hours in all. The same procedure was repeated for the temperatures 34.5, 32.9, 30.75, 27.0, 24.25, 20.3 °C and for the much higher temperature of 56.7°C. At this temperature the solution had to be cooled to room temperature by passing through a spiral condenser before measurements.

The actual readings obtained during this experiment have been recorded in the Appendix, Table 3, and in Fig. 6 the curves showing the increase in the optical density, of the first six solutions, with time are shown. The exact zero time could not be determined in this experiment and so the positions of the curves on the time scale have been fixed arbitrarily for the purpose of clarity. For one of the above series of measurements, that at 30.75°C, the pH was measured at intervals during the change. It remained practically constant at 4.2 throughout the period of investigation.

In the table below, the limiting values of the optical density reached when the above solutions had come to equilibrium are given:

TABLE 2

Concentration .00921M

No.	Temp.	Optical Density Dc
(1)	34.5°C	.609
(2)	32.9	.610
(3)	30.75	.611
(4)	27.0	.610
(5)	24.25	.611
(6)	20.3	.612
(7)	56.7	.611

From the appearance of the curves in Fig. 6 it is obvious that a definite change had occurred, resulting in a product with a higher extinction coefficient (at 420 mμ) than the pure <u>trans</u> isomer; while from the above table, it is apparent that the final value was independent of temperature within the range from 20°C to nearly 60°C. This constancy of the limiting value may be regarded , either as evidence that the reaction had gone to completion, or as evidence that the system contained an equilibrium mixture, the equilibrium constant being independent of temperature within the range considered. The latter type of reaction does not appear to be very common, so it was assumed that the reaction had gone practically to completion. The data obtained throughout the rest of this work are consistent with this view. It is possible that a very small amount of the trans form might still be present in equilibrium even when the reaction had apparently gone to completion, and this case is discussed later.

There are a number of changes which might be undergone by potassium trans dioxalatodiaquochromiate in solution which could lead to an increase in optical density:

(i) The compound might decompose giving free oxalate ions and other chromium complexes.

(ii) Two or more dioxalatodiaquochromiate ions might combine , with elimination of water, to form "olated" polymers of the type (46):

$$-\mathrm{Cr}-\underset{\mathrm{H}}{\mathrm{O}}-\mathrm{Cr}-\underset{\mathrm{H}}{\mathrm{O}}-\mathrm{Cr}-$$

(iii) The trans form might convert to the cis form.

The first explanation is untenable since no free oxalate could be detected in solution at any stage during the transformation.

All types of olation involve a decrease in the pH of the solution. This invalidates explanation (ii), since it has been shown above that no change in the pH of the solution occurred during reaction.

Explanation (iii) was then considered. On the assumption that the cis form has a higher extinction coefficient at 420 mμ than the *trans* form, it would appear that the phenomenon is due to a conversion of the *trans* to the *cis* isomer. If this were true, then it would be expected that the reaction would be of the first order.

The first order equation is:

$$dx/dt = k(a - x) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.1)$$

where k is the velocity constant,

a is the concentration of the reactant at time 0,

x is the concentration of the resultant at time t.

Integration yields the familiar equation:

$$t = \left(\frac{2.303}{k}\right) \log_{10}\left(\frac{a}{a - x}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.2)$$

In the postulated *trans-cis* conversion, (a - x) is the concentration of the *trans* form at time t. This quantity is obtained from the optical density (D) of the solution by assuming Beer's law holds at 420 mμ. It is shown later that the law holds very well for the *cis* form, and it is reasonable to assume that it also holds for the *trans* isomer.

Then for a solution containing both *trans* and *cis* dioxalatodiaquochromiate ions, at time t during the reaction,

$$D = k_t . C_t . 1. + k_c . C_c . 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.3)$$

where D is the optical density of the solution at time t, "1" is the thickness of the solution, k_t and k_c are the molar extinction coefficients of the *trans* and *cis* isomers respectively, and C_t and C_c are the concentrations of these isomers (in moles per litre).

Now the total concentration of dioxalatodiaquochromiate, C moles per litre, is known so that:

$$C = C_t + C_c \quad \ldots\ldots(4.4)$$

C_t, the concentration of the trans form at time t, may be found by solving (4.3) and (4.4) simultaneously, giving:

$$C_t = \frac{k_c . C.1 - D}{1(k_c - k_t)} \quad \ldots\ldots(4.5)$$

$$= (a - x) \text{ as mentioned earlier.}$$

This equation can be put in a more convenient form by noting that, if Dc and Dt are the optical densities of solutions of the pure cis and pure trans potassium salts respectively, each at a concentration equal to C, then:

$$Dc = k_c . C.1 \text{ or } k_c = Dc/C.1$$

and $$Dt = k_t . C.1 \text{ or } k_t = Dt/C.1$$

Substitution in (4.5) gives:

$$C_t = C\left(\frac{Dc - D}{Dc - Dt}\right) = (a - x) \quad \ldots\ldots(4.6)$$

The thickness of the solution "1" cancels out only if the same spectrophotometer absorption cell is used for all measurements. This was always the case during these experiments.

Substituting the above value for (a - x) in equation (4.2) and remembering that C = a, gives:

$$t = \left(\frac{2.303}{k}\right) \log_{10} \left(\frac{Dc - Dt}{Dc - D}\right)$$

i.e. $$t = \left(\frac{2.303}{k}\right) \log_{10} (Dc - Dt) - \left(\frac{2.303}{k}\right) \log_{10} (Dc - D) \ldots \quad \ldots(4.7)$$

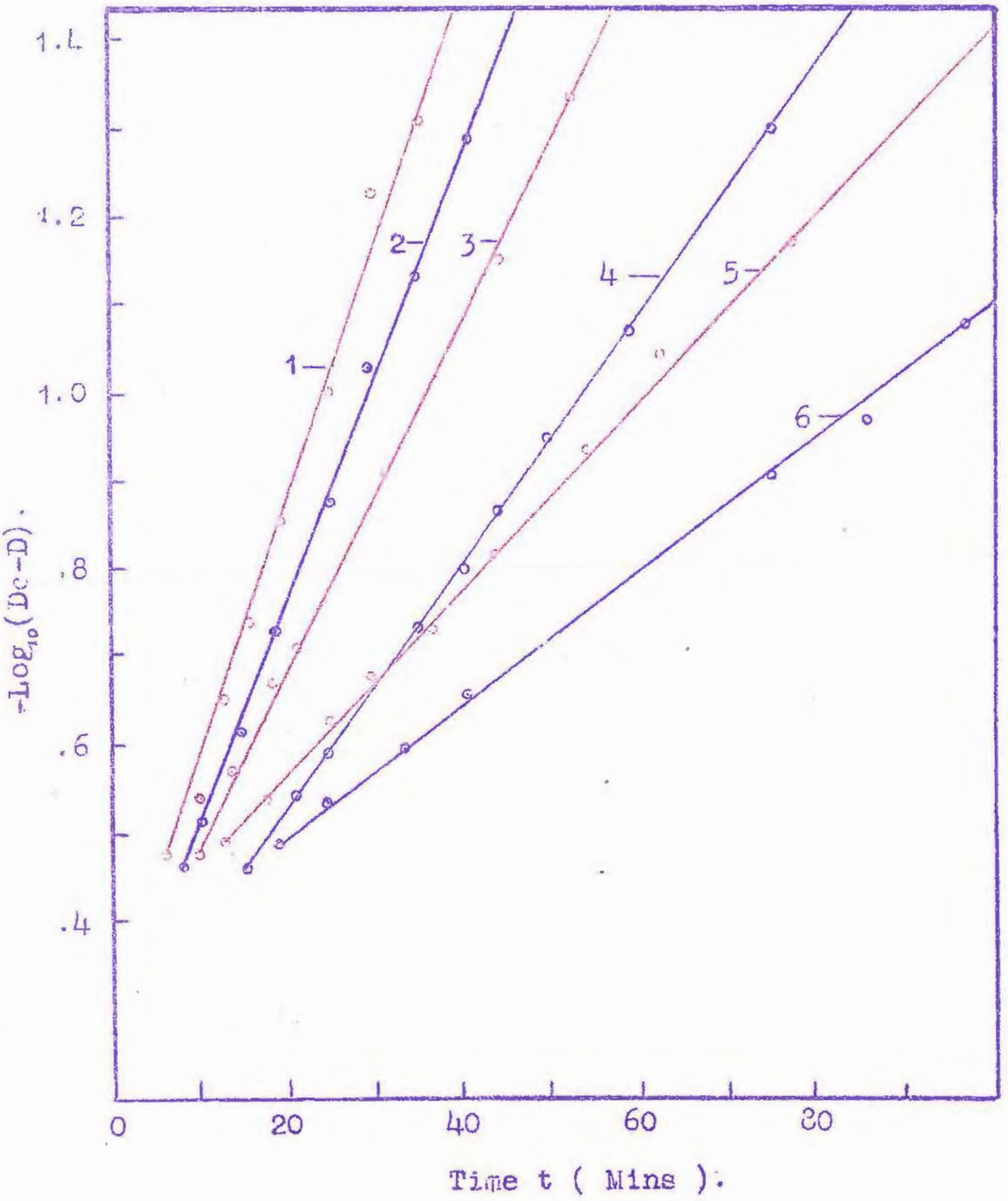


FIG 7

1. 34.5°C
2 32.9
3 30.75

4 27.0
5 24.25
6 20.3

The quantities in the first term of the right hand side of this equation are constant so that if the reaction is of the first order, then the graph of t against $-\log_{10}$ (Dc - D) should be linear.

Thus it was necessary to obtain Dc, the limiting value of the optical density when the reaction had gone to completion. A number of methods are available for finding the most accurate value of this quantity for similar first order reactions (47, 48) and the method of taking readings of the final value over a period at least as long as that required for the reaction to attain approximate completion was adopted. In this way, a value of Dc was obtained which was known with greater accuracy than any of the individual values of D. In Fig. 7, $-\log_{10}$ (Dc - D) has been plotted against the time t for the reaction at the six temperatures corresponding to the exponential curves in Fig. 6. Evidently the graphs are linear, indicating the reaction to be of the first order.

It should be noted that the lines in Fig. 7 are independent and that their relative positions have no significance, apart of course, from their slopes. They have been arranged, merely for convenience, by arbitrarily fixing the position of the initial readings on the time scale. This procedure was necessary because the zero time could not be determined with certainty.

From the slopes of the lines in Fig. 7 the velocity constants, or better, the apparent velocity constants, were obtained by using the equation:

$$k = -2.303(\text{slope}) \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (4.8)$$

The values are given below:

TABLE 3

No.	Temp.	1/T ($^{\circ}$A)	Slope (sec^{-1})	k (sec^{-1})	$\log_{10}$ k
(1)	34.5°C	.003250	-5.17×10^{-4}	11.91×10^{-4}	-2.92
(2)	32.9	.003267	-4.14	9.53	-3.02
(3)	30.75	.003290	-3.28	7.55	-3.12
(4)	27.0	.003331	-2.311	5.322	-3.27
(5)	24.25	.003362	-1.813	4.175	-3.38
(6)	20.3	.003407	-1.280	2.948	-3.53

In view of the kinetic data, the explanation involving a conversion from trans to cis dioxalatodiaquochromiate seems most probable.

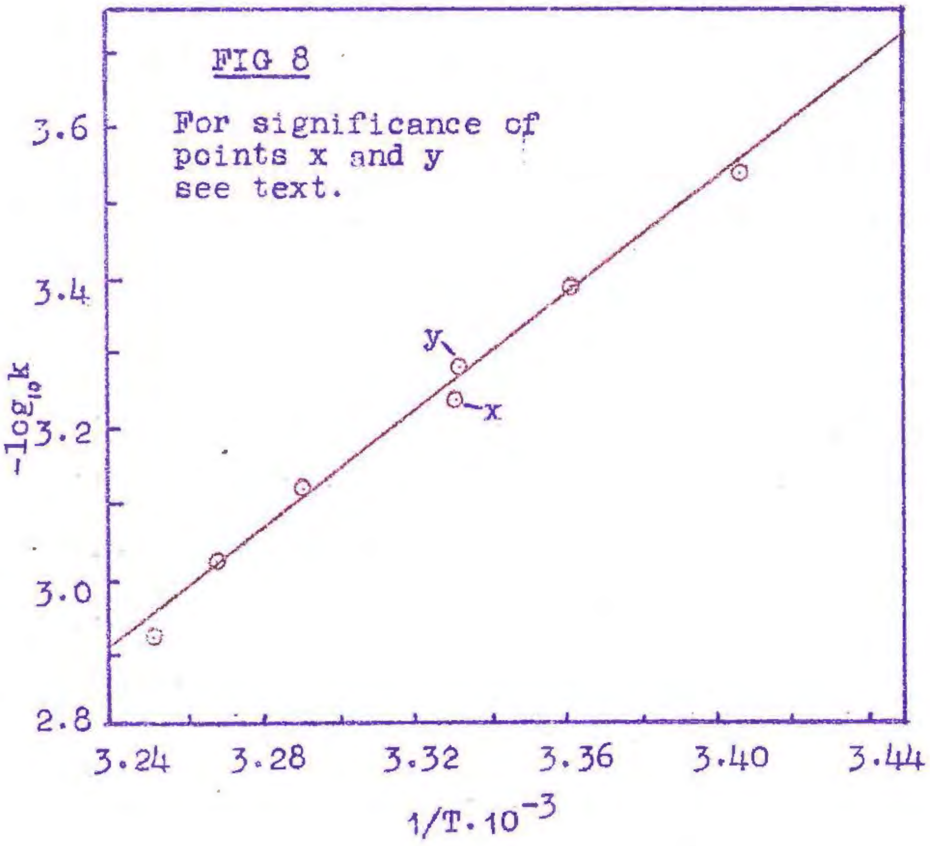
There is still the difficulty that the trans salt crystallises out from a strong solution of what is now known to be the cis isomer, if left for several days. This can be explained on the assumption that solutions of the cis salt always contain a small amount of the trans isomer in equilibrium. Even if this amount is negligible at low concentrations it may be sufficient to exceed the solubility product of the trans potassium salt at high concentrations. It is known that the potassium salt of the trans ion is very much less soluble than the corresponding cis salt. When some of the trans salt has crystallised out, the equilibrium is disturbed and more of the trans form is produced. Evidently this process should ultimately lead to fairly high yields of the trans salt and it is not inconceivable that it should take place slowly.

In order to ascertain whether the kinetic data were consistent with the Arrhenius Equation:

$$k = Ae^{-\frac{E}{RT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.9)$$

i.e. $$\log_{10}k = \log_{10} A - E/(2.303RT) \quad \ldots\ldots\ldots\ldots (4.10)$$

where E is the activation energy or the "experimental activation energy" of the reaction, T is the absolute temperature and A is a factor depending on steric and other considerations, a graph of $-\log_{10}k$ against 1/T was plotted (Fig. 8).



The fact that a reasonable straight line is obtained indicates that the equation is obeyed within the temperature range used. From this graph values for E and A, per mole, were calculated as:

$$k = 3x10^9 \; e^{-\frac{17.6 \text{ K cals}}{RT}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.11)$$

Before attempting an assessment of the value of these figures, it is important to consider the effects of the ionisation of the dioxalatodiaquochromiate ion on the rate of conversion to the cis isomer.

One effect to be considered is that the hydroxoaquo ions might have extinction coefficients different from those of the corresponding diaquo ions. If this were the case then the simple Beer's law relations employed earlier would not give valid results. However, it will be shown in the next chapter that at the wavelength used for the kinetics experiments (420 mμ) the cis monohydroxoaquo ion has almost the same extinction coefficient as the cis diaquo complex and it is probable that a similar relation holds for the trans derivatives. The effects of the dihydroxo ions need not be considered since a negligible amount will be present below pH 8.

Another, more important, consideration is that the trans form of the dioxalatohydroxoaquochromiate ion might change to the cis form in solution and that the conversion might not proceed at the same rate as that for the diaquo ion. Consequently, the rate of conversion from trans to cis was determined using solutions of different concentrations of potassium dioxalatodiaquochromiate at a fixed temperature (27.0°C). Different concentrations were used in order to observe any variations in the rate of conversion due to the different relative proportions of diaquo and hydroxo ions. The graphs of $\log_{10}(Dc - D)$ against t were linear in all cases and were similar to those in Fig. 7 so they have not been given here. The actual optical density and time readings are recorded in the Appendix, Table A 3. From these data, the slopes and values for k and $\log_{10}k$ were obtained and these are given in Table 4 below. The pH values of each of these solutions are recorded and, in addition, the pH values of three other dioxalatodiaquochromiate solutions are given.

TABLE 4

(Temperature 27.0°C)

No.	Concentration	Slope of $-\log_{10}(Dc-D)$ vs t graph	k	$\log_{10}k$	pH
(4)	.00921M	$-2.311\times10^{-4}\text{sec}^{-1}$	$5.32\times10^{-4}\text{sec}^{-1}$	-3.274	4.71
(8)	.00549	-2.569	5.92	-3.228	5.08
(9)	.00702	-2.439	5.62	-3.250	5.01
(10)	.00785	-2.370	5.46	-3.263	4.90
(11)	.01570	-2.306	5.31	-3.275	4.62
	.00856				4.77
	.01135				4.67
	.01463				4.64

The numbers in column 1 refer to Table A 3 in the Appendix where the actual readings may be found.

It is apparent from Table 4 that the experimental velocity constant k is not altogether constant in this case. In Fig. 9

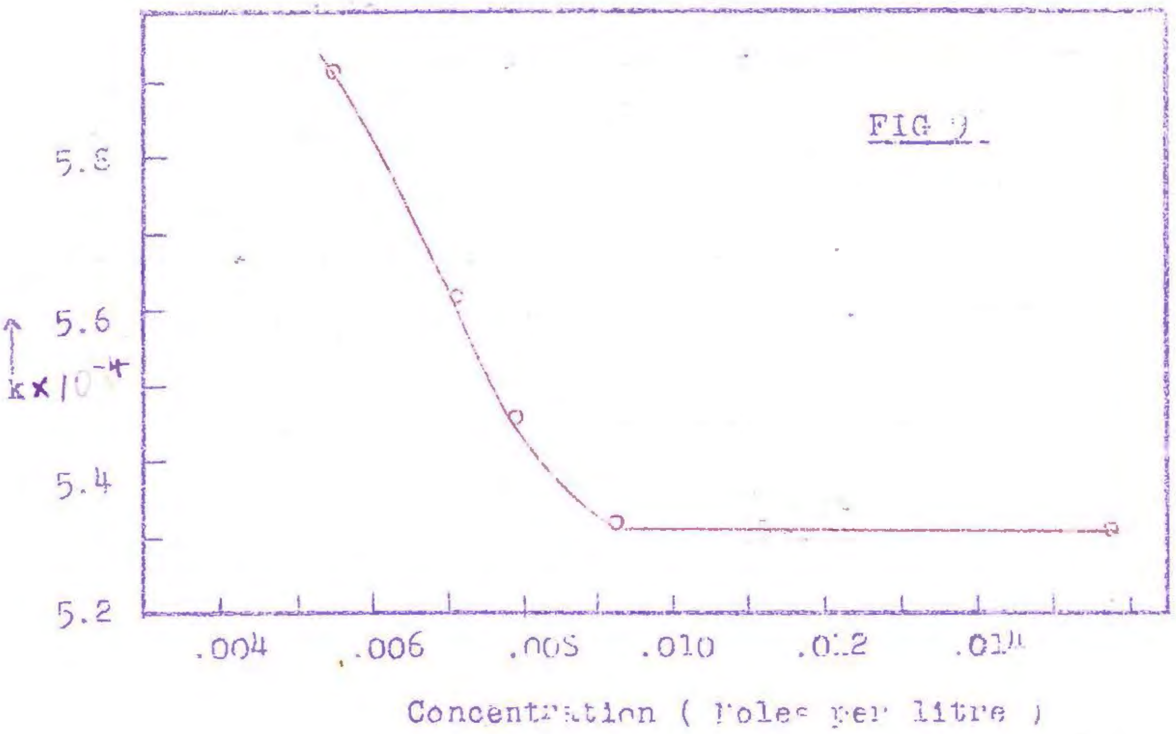


FIG 9
5.8
5.6
k x 10^-4
5.4
5.2
.004
.006
.008
.010
.012
.014
Concentration (Moles per litre)

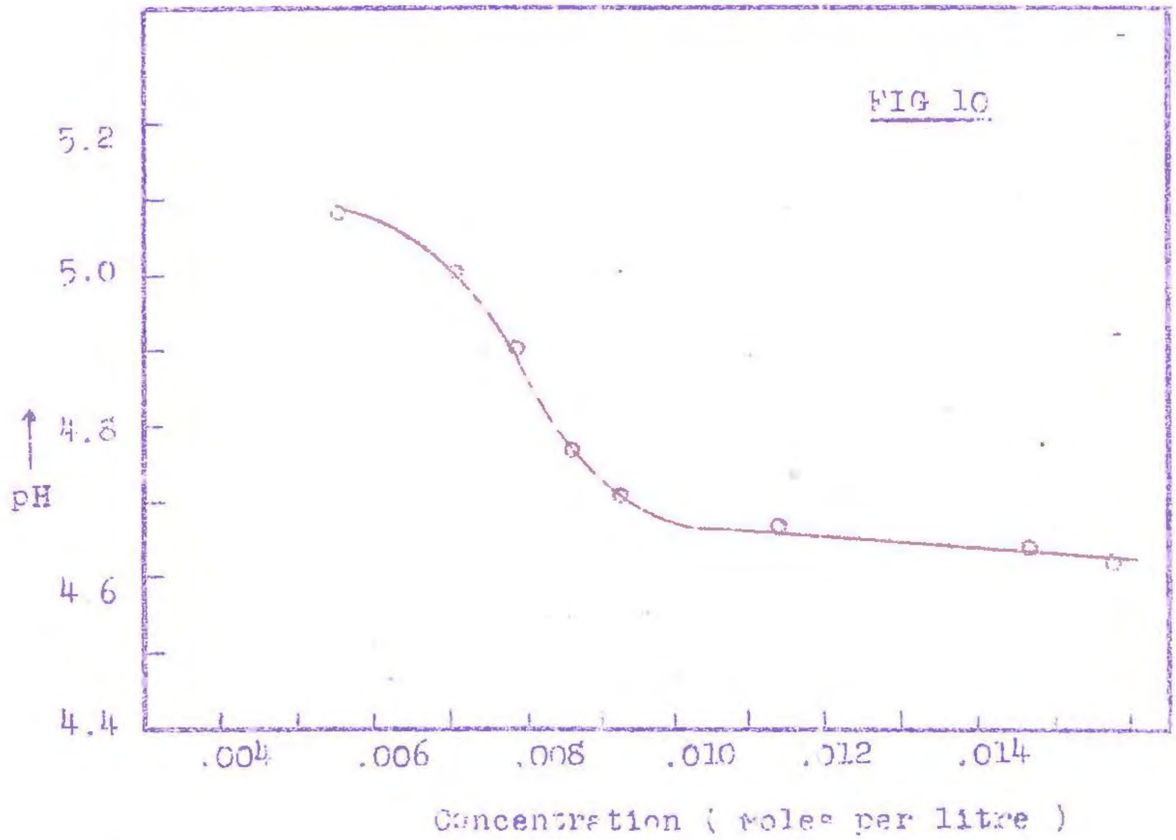
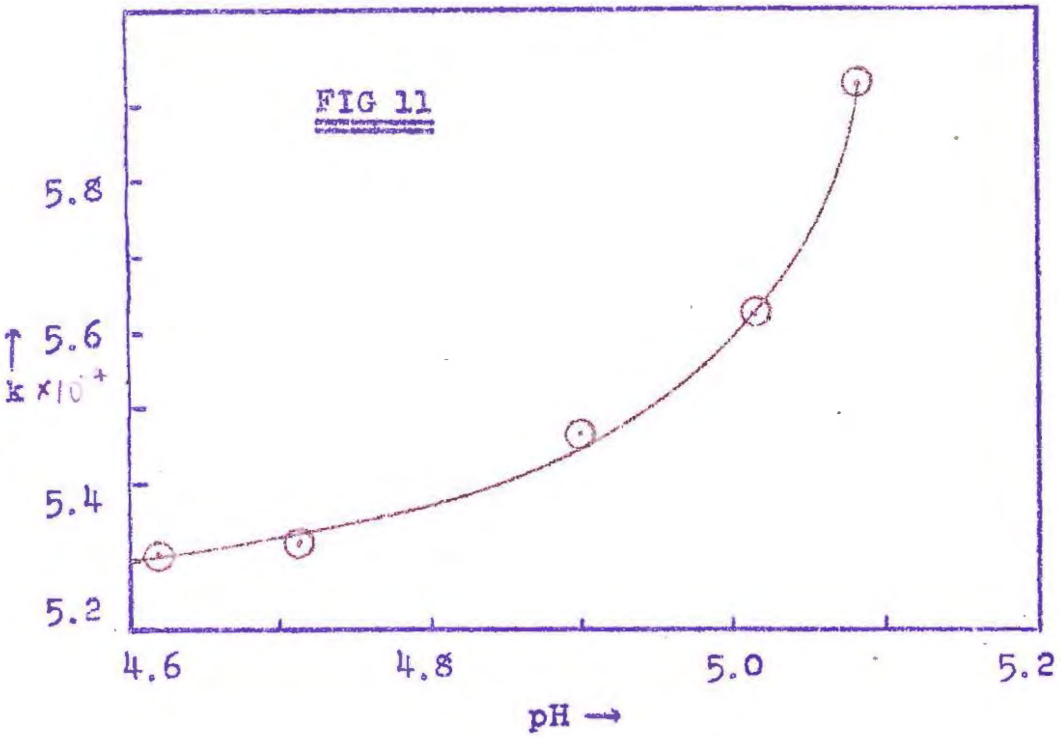


FIG 10
5.2
5.0
4.8
pH
4.6
4.4
.004
.006
.008
.010
.012
.014
Concentration (moles per litre)

the relation between the experimental velocity constant k and the concentration of dioxalatodiaquochromiate in solution is shown, while Fig. 10 shows the relation between pH and concentration. It will be noted that these curves have roughly the same shape. A better idea of the relation between the experimental velocity constant and the pH of the solution is obtained from Fig, 11:



These graphs show clearly that the experimental velocity constant for the trans-cis conversion depends on the pH of the solution. The rate of reaction is fastest when the solution is most dilute; that is, when most hydrolysis occurs. It appears, therefore, that the increase in the reaction rate at higher dilutions depends on the relatively higher proportion of hydroxo complex ions. This in turn suggests that the trans hydroxoaquo complex changes to the cis isomer at a more rapid rate than the corresponding diaquo complex.

In order to ascertain whether the changes in the apparent velocity constant k were not merely due to an effect of dilution, one of the reaction series (that at 27.0°C and concentration .00702M) was repeated with the addition of nitric acid in order to decrease the concentration of hydroxo derivative by suppressing the ionisation of the aquo groups. The results obtained are:

	pH	k
Before adding acid	5.01	5.62×10^{-4}
After adding acid	3.01	5.52×10^{-4}

The chromium concentration of these two systems was identical, but the ionic strength of the solution containing added nitric acid must have been different. In a further experiment, however, it was determined that increasing the ionic strength by a factor of more than two by the addition of potassium nitrate had no appreciable effect on the value of k. The fall in the value of k in the presence of acid is, therefore, most probably accounted for by the corresponding decrease in the concentration of hydroxoaquo ions, which indicates that these ions have a faster rate of conversion than the diaquo ions.

Theoretical

The above discussion shows that the velocity constant k obtained from spectrophotometric data is probably the resultant velocity constant of the two first order equations:

$$\text{trans}\ [Cr(C_2O_4)_2(H_2O)_2] \longrightarrow \text{cis}\ [Cr(C_2O_4)_2(H_2O)_2]$$

$$\text{trans}\ [Cr(C_2O_4)_2(H_2O)(OH)] \longrightarrow \text{cis}\ [Cr(C_2O_4)_2(H_2O)(OH)]$$

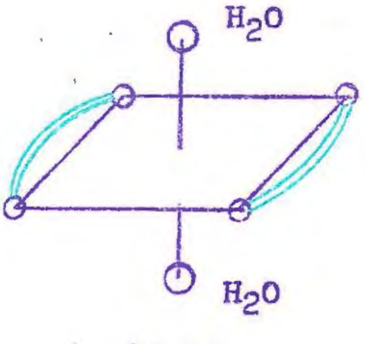
The fact that k does not only refer to the conversion of the dioxalatodiaquochromiate ions, but also to the conversion of the hydroxo complexes indicates that the values obtained above for the Arrhenius constants A and E must be in error.

In order to obtain some idea of the magnitude of the errors involved, the maximum and minimum values of $\log_{10} k$ at 27.0°C, as obtained from Table 4, are recapitulated below:

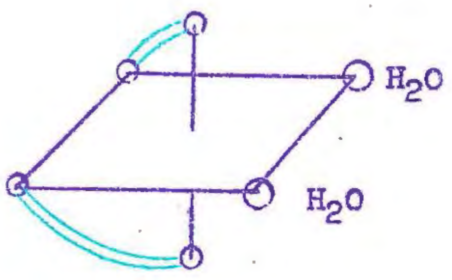
Maximum	-3.228
Minimum	-3.275

These values are plotted as points x and y respectively, in Fig. 8. From this graph it is apparent that, although the values of E and A obtained from the straight line are probably of the right order of magnitude, they must be regarded as approximations.

In considering possible mechanisms for the <u>trans-cis</u> conversion, it will be recalled that the two forms of the dioxalatodiaquochromiate ion are:



trans



cis

It is probable that transformation occurs by the intramolecular rearrangement of the oxalate groups since no free oxalate was detected in solution during the change. Thus, if this is true, conversion must involve the following steps;

(i) One end of an oxalate group detaches itself from the chromium.

(ii) A water molecule fills the position vacated by the oxalate.

(iii) One of the coordinated water molecules leaves the complex.

(iv) The free end of the oxalate group attaches itself to the position left vacant by the water molecule.

It is possible that step (iii) occurs before (i) or (ii).

In 1939 Bushra and Johnson (6) investigated the rates of racemisation of the complex ions, trioxalatochromiate and trioxalatocobaltiate which are known to proceed by intramolecular rearrangement of the oxalate groups. From their kinetic data they calculated that, for the racemisation of the trioxalatochromiate ion;

$$k = 10^{8} . e^{-\frac{15.8 \text{ Kcals}}{RT}}$$

while for the trioxalatocobaltiate ion;

$$k = 10^{14.5} . e^{-\frac{26.0 \text{ Kcals}}{RT}}$$

Now from the investigations described earlier in this section, the conversion from <u>trans</u> to <u>cis</u> dioxalatodiaquochromiate gave the following values;

$$k = 3\times10^{9}.e^{-\frac{17.6\ \text{Kcals}}{RT}}$$

(The activation energies refer to molar quantities)

It is apparent that the values for the conversion from trans to cis dioxalatodiaquochromiate are of approximately the same order of magnitude as those for the racemisation of the trioxalatochromiate ion, although it must be remembered that the former are open to doubt in view of the interference of the hydroxo derivatives. Nevertheless, this agreement strongly suggests that the rate determining step is the same in both reactions. In other words the rate determining step in the conversion from trans to cis dioxalatodiaquochromiate is either the detachment of one end of an oxalate group (step(i)) or its reattachment to the chromium atom (step(iv)). This is not inconsistent with the fact that the trans hydroxoaquo complex appears to convert to the cis isomer at a more rapid rate, since it is difficult to predict how the mechanism given above will be affected by the replacement of an aquo group by hydroxo.

5. Spectrophotometric Investigation

To obtain the absorption spectrum of potassium cis dioxalatodiaquochromiate, a solution of the pure trans salt was prepared having a concentration of .00921M. This solution was allowed to age for several hours to convert the complex to the cis isomer, the progress of the conversion being checked by measuring the optical density at 420 mµ. The absorption spectrum, between wavelengths 300 mµ and 740 mµ was then measured on a sample of

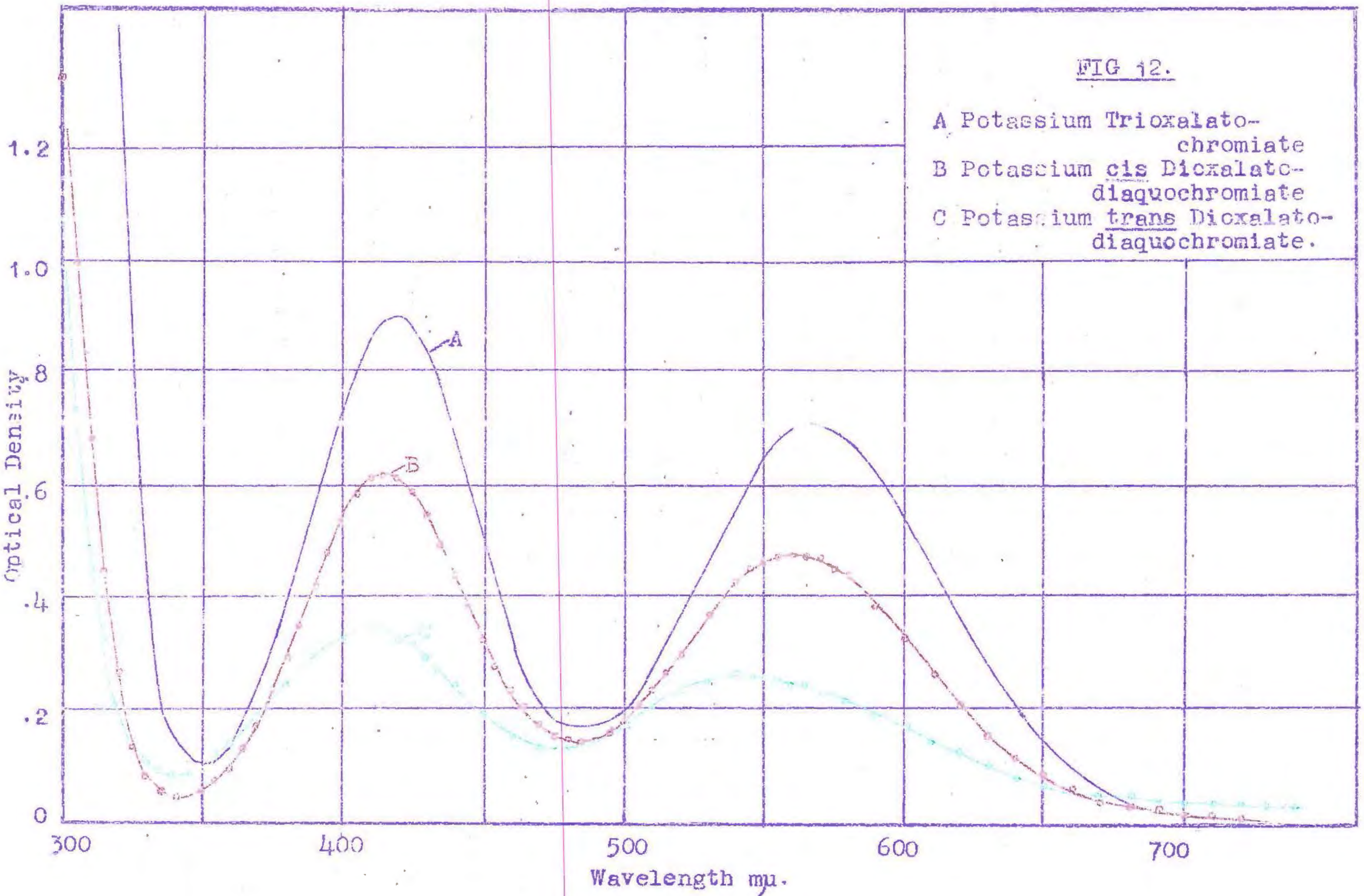


FIG 12.

A Potassium Trioxalato-chromiate
B Potassium cis Dioxalato-diaquochromiate
C Potassium trans Dioxalato-diaquochromiate.
A
B
Optical Density
1.2
1.0
.8
.6
.4
.2
0
300
400
500
600
700
Wavelength mμ.

this solution and is illustrated in Fig. 12, Curve B. The optical density readings are recorded in Table A 4 in the Appendix.

The absorption curve for the trans isomer could not be measured at room temperature (20°) because of the conversion to the cis form, but it was found that at 8°C the rate of conversion was sufficiently slow to enable a curve to be measured rapidly. (Curve C, Fig. 12). It was estimated that this curve is not more than one or two percent too high in spite of conversion during measurements.

The fact that the absorption curve of the trans salt in solution is different from that of the cis isomer is important from the point of view of the interpretation of the absorption data of complex ions and is discussed in Chapter 10. At first it seemed unlikely that such a small change in structure could have such a relatively large effect on the spectrum. However, in 1931 Matsuno (49) found qualitatively that the relative positions of coordinated water molecules in certain aminoaquo complexes of cobalt(III) had a considerable effect on the light absorption. He found that complexes having water molecules in the trans position had less absorbing power than equimolar solutions of the corresponding cis isomers.

Conformity of the cis dioxalatodiaquochromiate ion with Beer's law was tested by preparing solutions of the pure trans salt of different concentrations, ageing to convert to the cis isomer and measuring the limiting values of the optical density at wavelengths 419 mμ and 560 mμ in the vicinity of the maxima. The relation between the optical density and the concentration, in moles per litre, is illustrated below:

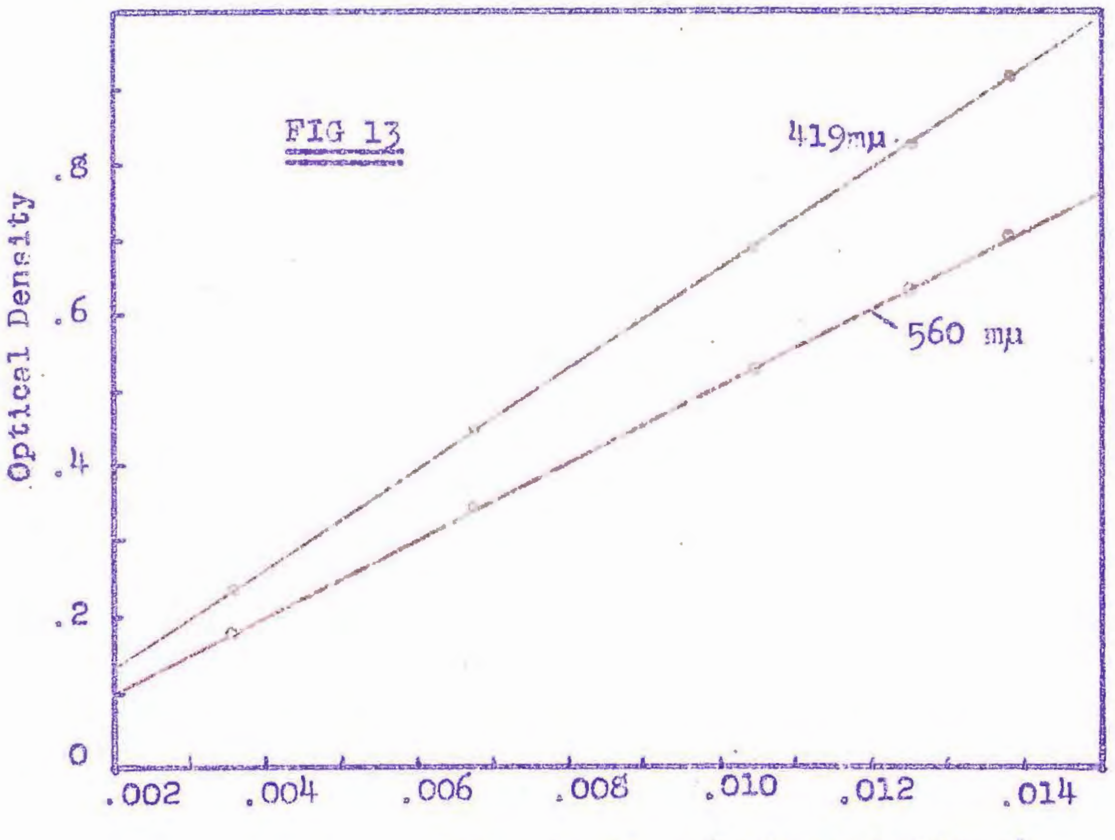


FIG 13

Concentration (Moles per litre)

The straight lines in this figure indicate that the law is obeyed reasonably well at 419 and 560 mµ and a better idea of the agreement is obtained from the constancy of the extinction coefficients recorded in Table 5 on page 58. It may appear somewhat supprising that Beer's law is obeyed by solutions of dioxalatodiaquochromiate in view of the fact that hydrolysis is known to occur in solution involving the formation of hydroxo derivatives. However, this merely implies that the extinction coefficients for the dioxalatohydroxoaquochromiate ion at 419 mµ and 560 mµ are close to those of the dioxalatodiaquochromiate ion. This deduction is confirmed by the absorption curve of the hydroxoaquo derivative, given in the next chapter.

TABLE 5

Concentration moles per litre	419 mμ		560 mμ	
	Opt. Dens.	Ext. Coeff.	Opt. Dens.	Ext. Coeff.
.00358	.237	66.2	.179	50.0
.00675	.444	65.8	.341	50.5
.01047	.690	65.9	.529	50.5
.01250	.826	66.0	.631	50.5
.01383	.917	65.8	.701	50.7
Averages used:		65.9		50.5

6. Summary

The pH curve of potassium dioxalatodiaquochromiate, in aqueous solution, has been drawn and evidence for the titration of the two aquo groups presented. From this curve, values for the acid constants of the dioxalatodiaquochromiate ion have been calculated.

It has been established that potassium trans dioxalatodiaquochromiate is unstable in solution and the data obtained is consistent with the view that it changes to the cis form in a about three hours at 20°C for a .01M solution. This conversion, which is probably intramolecular, has been shown to occur by a first order mechanism. The rate determining step is probably connected with the rate of detachment or attachment of one end of an oxalate.

It has been found that the experimentally determined rate constant is larger when, owing to hydrolysis, relatively more of the dioxalatohydroxoaquochromiate ions are present. This is probably because these ions have a faster rate of conversion from trans to cis.

By applying the Arrhenius equation, a tentative value for the activation energy of the conversion from trans to cis dioxalatodiaquochromiate ion has been calculated.

The absorption spectra of both the trans and the cis isomers, in aqueous solution, have been measured and it has been established that the cis isomer obeys Beer's law at 419 mμ and 560 mμ.

Chapter 5

THE PROPERTIES OF THE DIOXALATOHYDROXOCHROMIATE IONS WITH SPECIAL REFERENCE TO OLATION

1. Introductory

The dioxalatohydroxochromiate ions are formed by adding alkali to solutions of the dioxalatodiaquo salts. The compounds discussed in this chapter are:

Potassium cis dioxalatohydroxoaquochromiate $K_2[Cr(C_2O_4)_2(H_2O)(OH)]$
Potassium cis dioxalatodihydroxochromiate $K_3[Cr(C_2O_4)_2(OH)_2]$

These salts are both readily soluble in water to give green, alkaline solutions. It has already been mentioned that they were discovered by Werner and collaborators (13) who performed a qualitative investigation of their properties and those of the corresponding salts of other kations. The trans isomers were also studied by Werner but these have not been dealt with in this work because of their instability in solution.

As Werner experienced difficulty in obtaining the hydroxo salts in a pure condition, no attempt was made to isolate them. Instead, standard solutions of pure potassium cis dioxalatodiaquochromiate were used and to these were added the calculated amount of alkali, to form the monohydroxo and dihydroxo ions respectively.

2. Potassium cis Dioxalatohydroxoaquochromiate

A known weight of pure potassium trans dioxalatodiaquochromiate was dissolved in water and warmed to convert to the

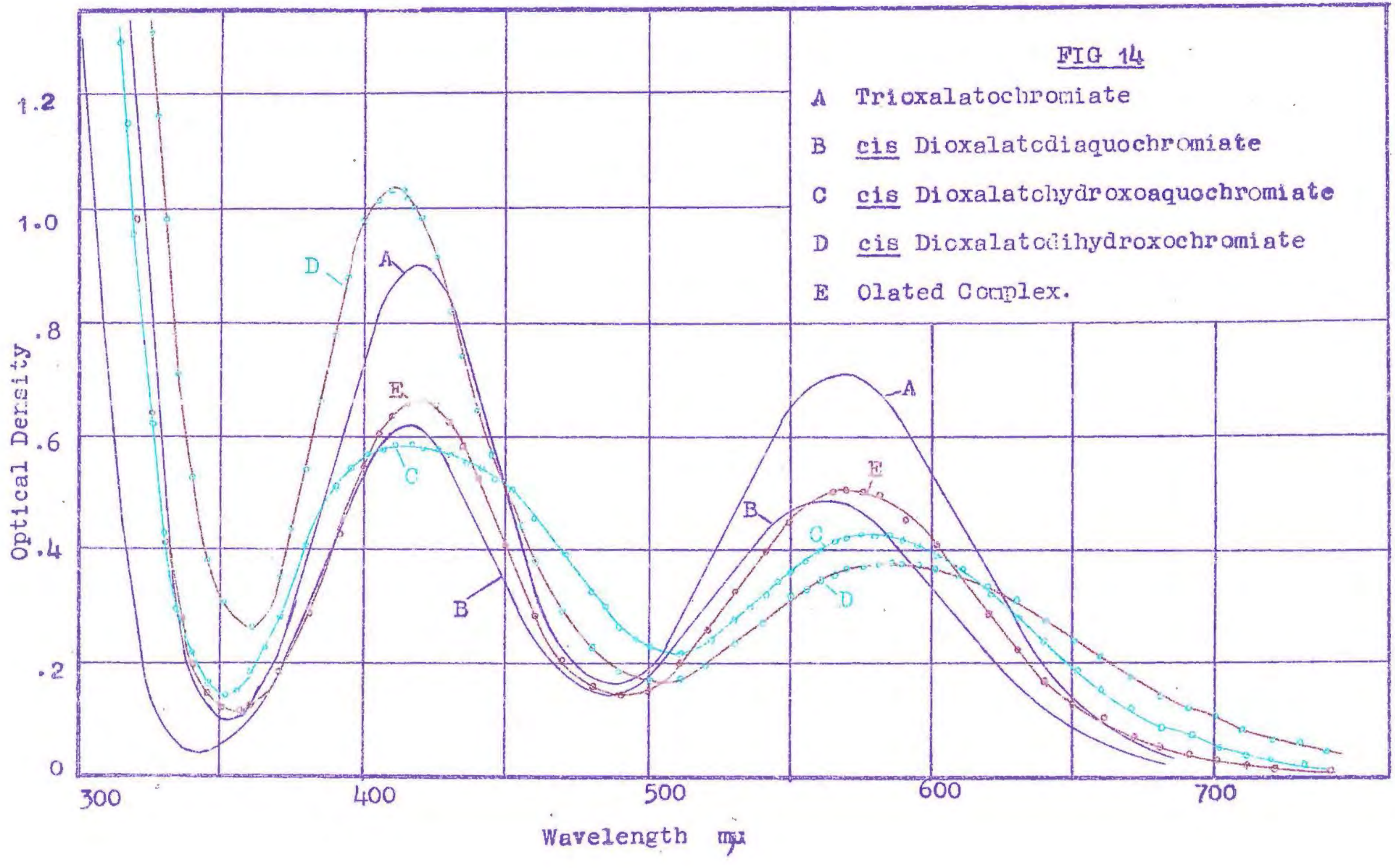


FIG 14

A Trioxalatochromiate
B cis Dioxalatodiaquochromiate
C cis Dioxalatohydroxoaquochromiate
D cis Dioxalatodihydroxochromiate
E Olated Complex.
Optical Density
0
.2
.4
.6
.8
1.0
1.2
Wavelength mμ
300
400
500
600
700
A
B
C
D
E

cis isomer. Then the exact amount of standard alkali solution required to form the monohydroxo complex, was added, after which the solution was cooled and made up to a concentration of .00921M (i.e. .07% Cr_2O_3).

The stability of the solution was investigated by measuring both the optical density at several wavelengths, and the pH, at frequent time intervals. It was found that these remained constant for at least six hours at room temperature (20°C), indicating that the solution was stable during this time.

The absorption spectrum of this solution was measured and is shown if Fig. 14, Curve C, where the curves for the cis dioxalatodiaquochromiate and the trioxalatochromiate at the same concentration are also given (Curves B and A). The optical density readings are recorded in the Appendix as usual.

It is apparent that, in the region of the maxima, the curve for the hydroxoaquo derivative (C) is close to that of the dioxalatodiaquochromiate ion (B), and this is the reason why solutions of the latter obey Beer's law even though, owing to hydrolysis, varying amounts of the hydroxo ion are present at different concentrations.

It should be mentioned that it was found that boiling a solution of potassium cis dioxalatohydroxoaquochromiate caused a change in the absorption spectrum and a decrease in pH. The latter phenomenon, usually ascribed to "olation", is a characteristic of hydroxoaquo ions and is discussed later, in Section 4.

3. Potassium cis Dioxalatodihydroxochromiate

A solution of this compound was prepared by adding to a solution of cis dioxalatodiaquochromiate sufficient alkali to titrate both of the coordinated water molecules completely, the final concentration being .00921M as in previous experiments. The stability of this solution at room temperature (20°C) was then investigated by reading the optical density at 420 mμ and 560 mμ and also the pH, over a period of time. The results are tabulated below.

TABLE 6

Time	Optical Density		pH
	420 mμ	560 mμ	
0 min	-	-	-
5	.965	.335	
15	.940	.335	10.0
50	.910	.335	
57	.900	.335	10.0
1hr 25 min	.872	.333	9.95
2 2	.837	.334	9.82
2 52	.807	.333	9.74
3 35	.782	.333	9.55
5 45	.715	.333	9.35
8 45	.668	.333	9.28
24 hrs	.608	.325	

The fact that over a period of about 24 hours the optical density at 420 mμ dropped considerably while the pH decreased indicates that the dihydroxo ion is unstable in solution. Free oxalate ion was detected in the solution after 24 hours and so it is evident that the dioxalatodihydroxochromiate ion decomposes under these conditions with liberation of oxalate.

In order to obtain the absorption spectrum of the dihydroxo complex, a .00921M solution was prepared using ice cold water and the curve measured at about 8°C. Measurements had to be taken as rapidly as possible, but at this temperature it was found that only a very small decrease in the optical density occurred during the period of observation. The spectrum is illustrated as Curve D Fig. 14. Attention is drawn to the extraordinarily high optical density at about 412 mμ.

A study of the disintegration products of the dihydroxo ion is undoubtedly of importance, but unfortunately it could not be pursued further.

4. Olation

When solutions of certain chromium complex ions, possessing coordinated water molecules and hydroxo groups are boiled, the pH of the solutions drops and the chemical properties of the complex ions undergo slight modifications. This process was first observed by Bjerrum (50) for certain chloro complexes and it has been explained in terms of "Olation" by Stiasny (9) who performed an extensive series of experiments to investigate the olation of the sulphato complexes.

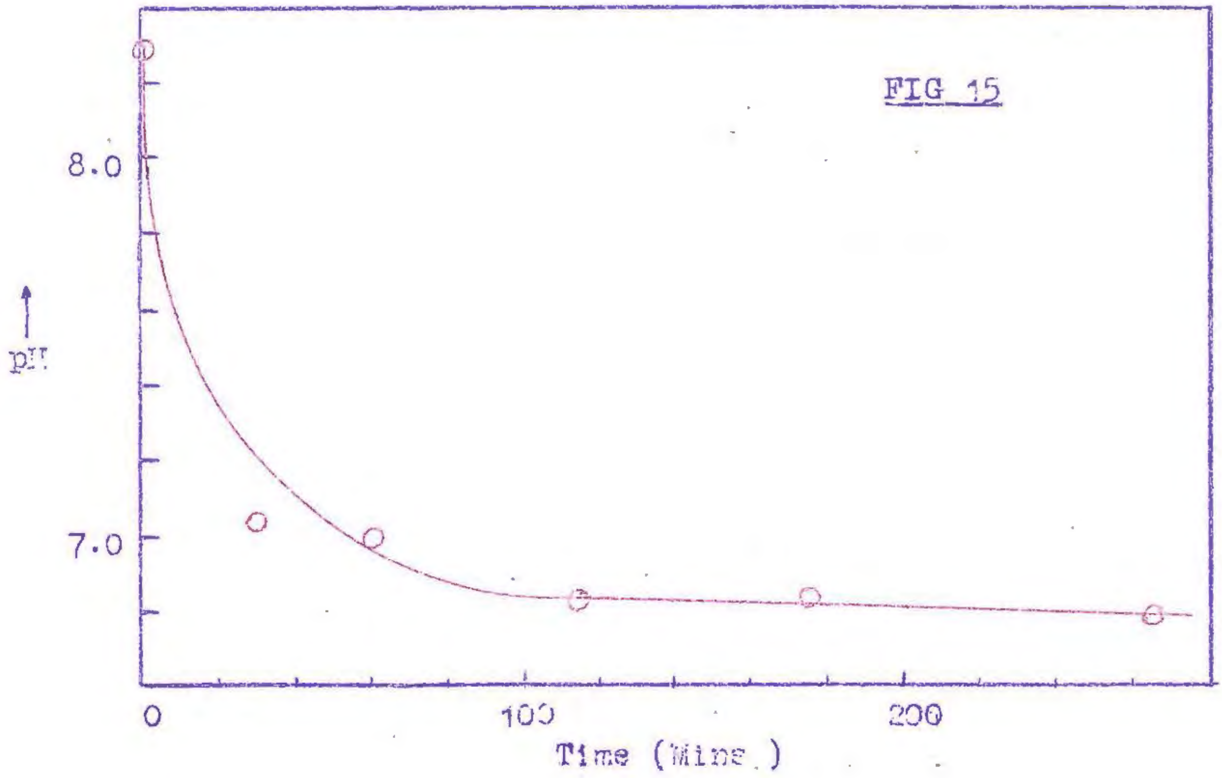

8.0
7.0
pH
0
100
200
Time (Mins.)

FIG 15

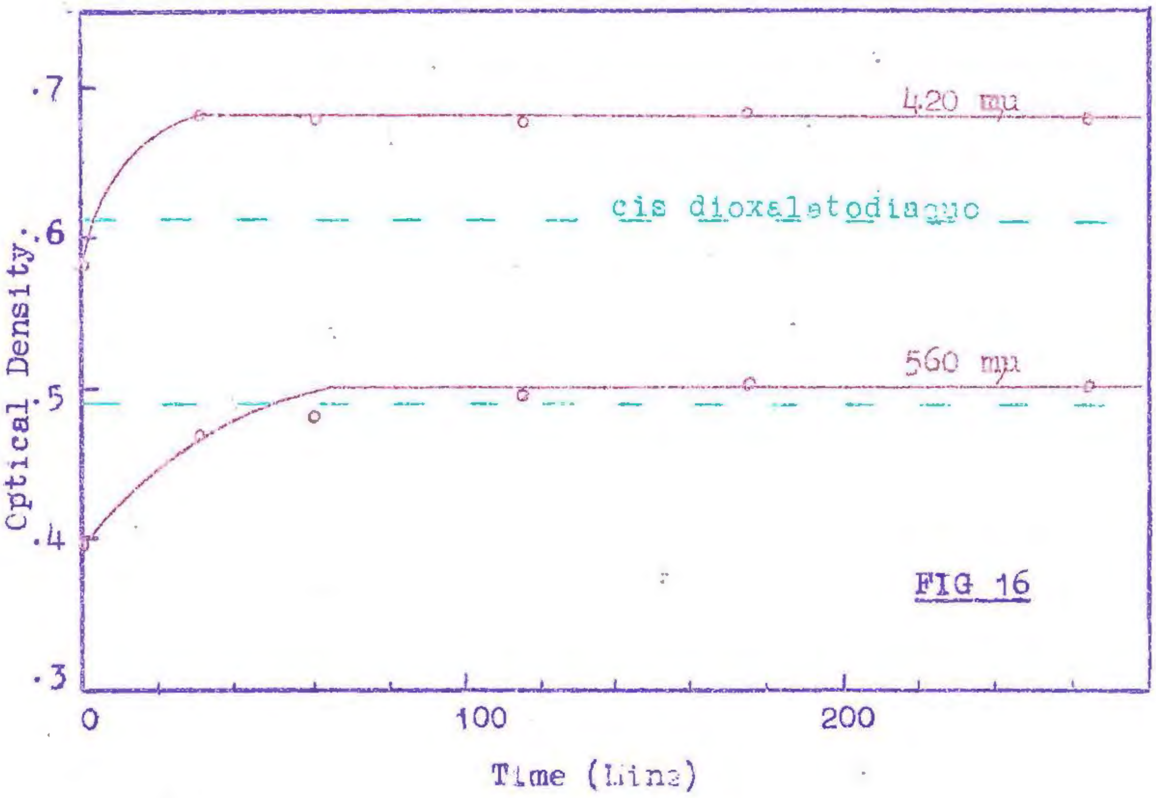
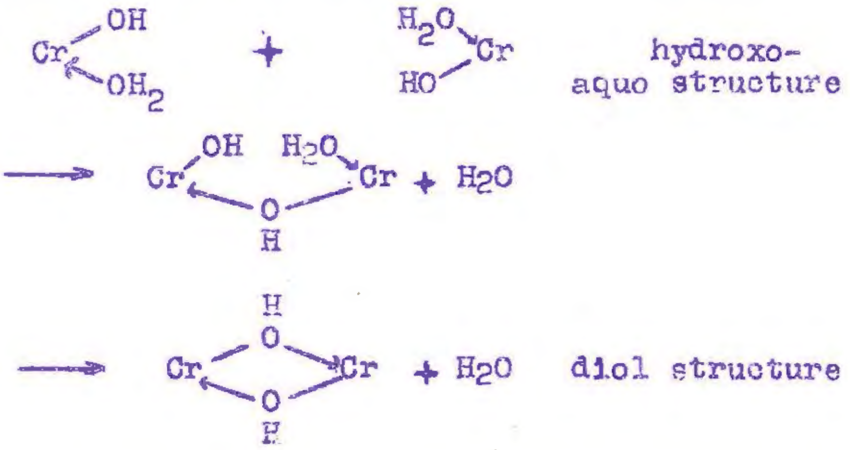

.7
.6
.5
.4
.3
Optical Density.
420 mμ
cis dioxalatodiaquo
560 mμ
0
100
200
Time (Mins)

FIG 16

Although the exact mechanism by which olation occurs is not well understood, it is generally accepted that it involves condensation to form a dimer or polymer:



The olation of the cis dioxalatohydroxoaquochromiate ion was first observed by Werner in 1914 (13) although an extensive investigation was not attempted. In 1947, Gustavson (51) used a solution containing the olated complex prepared by Werner's methods, to perform some tanning experiments.

During attempts to investigate a number of less readily formed complexes, to be described later, the effects of olation were encountered frequently and, since no further information could be obtained from the literature, it was decided to carry out a more thorough study of the olation of the dioxalatochromiate complexes.

A .00921^{M} solution of potassium cis dioxalatohydroxoaquochromiate, prepared as in Section 2 above, was boiled under reflux and portions were removed at intervals of time, for a period of about five hours. These portions were cooled, and the pH and optical density at 420 mμ and 560 mμ measured. In Figs

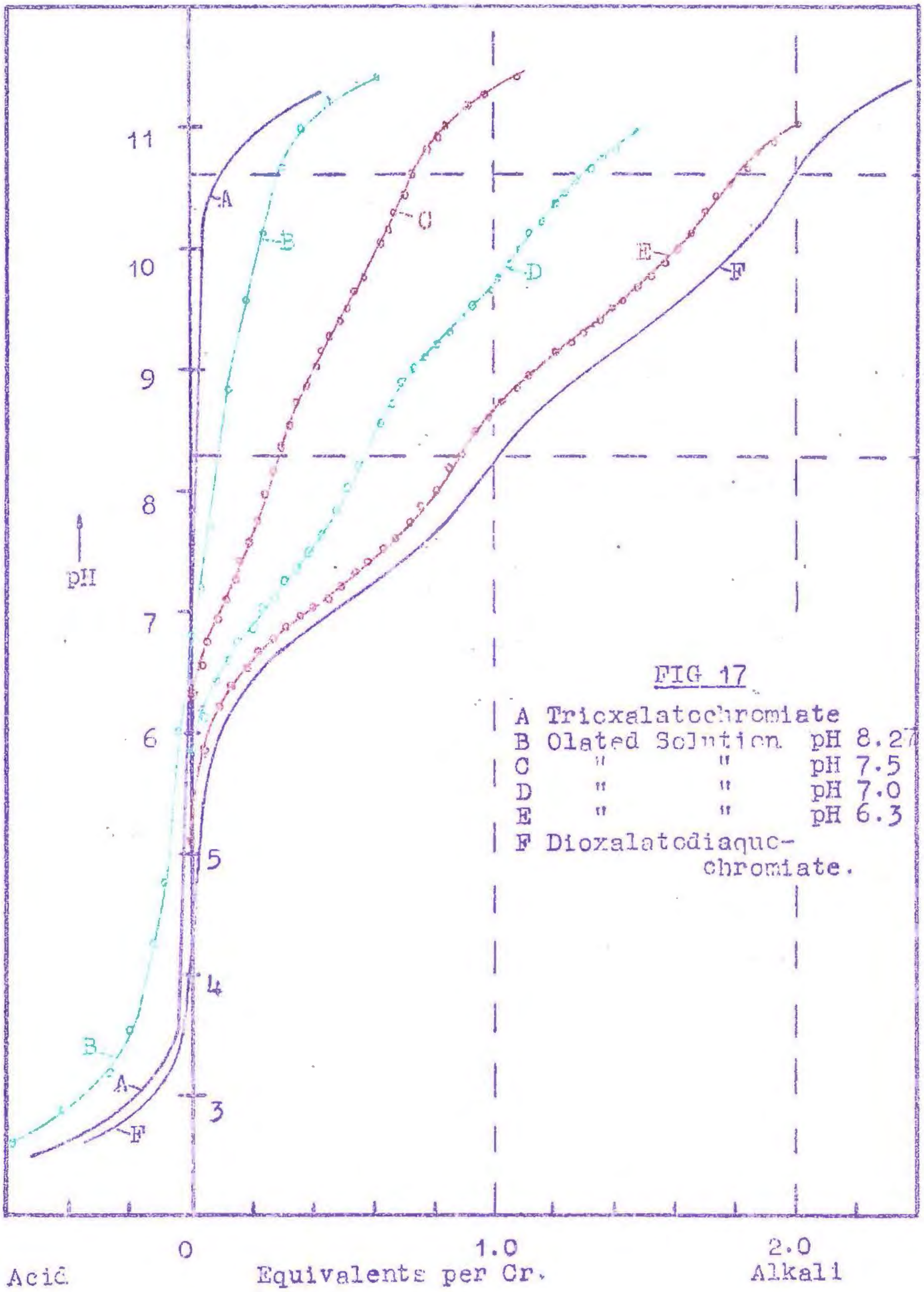

11
10
9
8
pH
7
6
5
4
3
A
B
C
D
E
F
0
1.0
2.0
Acid
Equivalents per Cr.
Alkali
A Trioxalatochromiate
B Olated Solution pH 8.27
C " " pH 7.5
D " " pH 7.0
E " " pH 6.3
F Dioxalatodiaquo-chromiate.

FIG 17

15 and 16 these values have been plotted against the time. This experiment was not intended to be very accurate, but it is apparent that during boiling a decrease in pH and an increase in optical density of the cis dioxalatohydroxoaquochromiate solution occurred.

The absorption spectrum between 300 mμ and 740 mμ was measured on a sample of the boiled solution (Fig. 14, Curve E) and it is seen to differ from that of the cis dioxalatodiaquochromiate (Curve B) and that of the cis dioxalatohydroxoaquochromiate (Curve C).

Acid and alkali potentiometric titrations were performed on aliquots of the boiled solution of dioxalatohydroxoaquochromiate and the curves have been combined and plotted in Fig. 17 Curve B. It was observed that during the acid titration a faint turbidity appeared at about pH 3, although no explanation for this could be found.

In Fig. 17 the curves for pure dioxalatodiaquochromiate (Curve F) and trioxalatochromiate (Curve A) are illustrated and it is apparent that the curve for the boiled solution (Curve B) appears to represent the titration of very little weak acid. Thus both the potentiometric and spectrophotometric evidence indicates that boiling a solution of potassium cis dioxalatohydroxoaquochromiate causes a change in the complex and that the product has properties different from the original complex.

In order to investigate the mechanism of this change, three solutions of potassium dioxalatodiaquochromiate were prepared and different amounts of alkali were added to each to bring them to the pH values 7.5, 7.0 and 6.3 respectivley. These solutions were then boiled for more than two hours and, when cool, they were titrated potentiometrically against standard alkali. The curves have been recorded in Fig. 17, Curves C,D and E. It is seen that, for these solutions, the reaction had proceeded to different extents depending on the quantity of alkali added initially. The curves have the same shape as that of the pure dioxalatodiaquochromiate ion, so probably they contained successively less of this ion.

In attempting to determine the extent to which the reaction had proceeded in these solutions, it may be noted that for the pH curve of potassium dioxalatodiaquochromiate, (Fig. 17 Curve F) the pH values corresponding to 1.0 and 2.0 equivalents of alkali per Cr may be considered to represent the end points in the titration of the first and second aquo groups respectively. These occur at pH 8.27 and 10.6. Thus an estimate of the amount of dioxalatodiaquochromiate ion in an unknown solution may be made by measuring the amount of alkali required to raise the pH from 8.27 to 10.6.

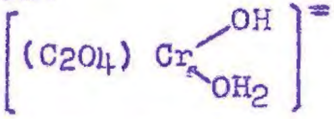
The solutions B, C, D and E above contained unknown amounts of diaquo and hydroxoaquochromiate ions. These both titrate above pH 8.27 and so the quantity of alkali required to raise the pH from 8.27 to 10.6 gives the sum of the amounts of these ions in solution. This sum has been recorded in Table 7 below (Column 5) as the percentage of dioxalatochromiate titrating above pH 8.27 It was determined that boiling a solution of pure potassium dioxalatodiaquochromiate for two hours, produced only a very small decrease in pH and no noticeable change in the titration curve.

TABLE 7

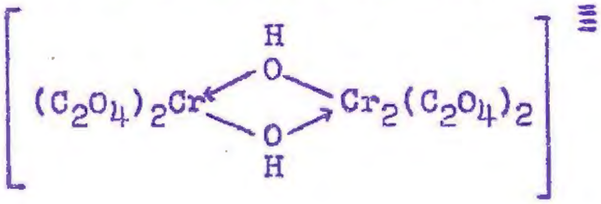
1	2	3	4	5
Curve	pH		Alkali added initially (Equivs per Cr)	Percentage Dioxalate titrating
	before boiling	After boiling		
B	8.27	6.8	1.0	20%
C	7.5	6.3	0.73	43
D	7.0	5.6	0.47	72
E	6.3	5.1	0.17	90
F	4.5	4.3	0	100

Evidently for solutions B, C, D and E a decrease in pH occurred and, more important, the amount of dioxalatochromiate ion titrating between pH 8.27 and 10.6 decreased as the amount of alkali added initially was increased.

It is considered that these results are consistent with the view that, on boiling a solution containing <u>cis</u> dioxalatohydroxoaquochromiate ion:



condensation occurs to form the olated complex:



It has recently been recommended (1) that this complex be known as the Tetraoxalato μ dihydroxodichromate(III) ion, in place of Werner's original Tetraoxalatodiolodichromiate (13).

This ion possesses no weak acidic or basic groups and, therefore, does not titrate in the region from pH 3.27 to 10.6. For each hydroxoaquochromiate ion which olates, the solution gains potentially one hydrogen ion, because of the removal of the basic hydroxo group. When successively more alkali is added to solutions of dioxalatodiaquochromiate, as in the above experiment, more hydroxoaquo ions are formed which olate on boiling, thereby reducing the pH of the solution owing to the removal of hydroxo groups. If the olation of a solution containing only hydroxoaquochromiate ions and kations went to completion, the pH should be 7.0 since no weak acid or basic groups should be present. It is apparent from Table 7 that Solution B did not olate quite to completion since, after boiling, about 20% of dioxalatochromiate still titrated. Solutions such as C, D, and E above, which contained fractional amounts of hydroxoaquochromiate before boiling, would still contain some of the diaquo ion after boiling, even if all of the hydroxoaquo ions initially available had olated. For this reason, the pH of these solutions is less than 7 after boiling.

As a measure of the extent to which olation has occurred in a given solution, the " degree of olation" may be defined as that fraction of the initial number of chromiate ions which has olated. This obviously is that fraction of the initial number of chromiate ions which does not titrate in the region from pH 8.27 to 10.6 and, for the solutions discussed above, is readily obtained from Column 5 in Table 7. The values calculated in this way are recorded below in Table 8 column 3.

Theoretically a check on these values is available by considering the quantities of alkali added to the solution, before and after boiling. Thus, for any solution containing dioxalatodiaquochromiate ions the amount of alkali added before boiling <u>plus</u> that required to titrate to pH 10.6 after boiling should be 2.0 equivalents per Cr, provided that no olation has occurred. To the extent that hydroxoaquo ions are removed by olation, the solution gains one (potential) hydrogen ion for each hydroxo group removed in this way. However, one acidic aquo group is also lost to the solution at the same time. This means that for a solution which had olated completely the <u>total</u> alkali required in order to raise the pH to 8.27 would be one equivalent per Cr and a solution which had not olated to completion would require a <u>total</u> amount of alkali intermediate between 1.0 and 2.0 equivalents, depending on the extent to which olation had proceeded.

In other words, the degree of olation is given by the difference between 2.0 and the <u>total</u> amount of alkali required to raise the pH to 10.6. By "total amount of alkali" is meant that added to the dioxalatodiaquochromiate solution before boiling *plus* that required during the titration to pH 10.6 after boiling, expressed as equivalents per Cr. The values for the degree of olation calculated by this and by the previous method are compared below:

TABLE 8

1	2	3	4
Curve	Alkali added before boiling	Degree of Olation	
		1st method	2nd method
B	1.0	.80	.78
C	.73	.57	.55
D	.47	.28	.27
E	.17	.10	.15
F	0	0	0

The values obtained by the two methods are not really independent since both depend on the alkali reading at pH 10.6. There are a number of reasons why these values for the degree of olation must be regarded as approximate:

(i) The glass electrode is less reliable at the pH of the second end point, 10.6, although errors due to this were minimised by working with dilute solutions (about .01M). The question of the reliability of the glass electrode is discussed in the next chapter and it is concluded that no very serious errors may be expected under the conditions used.

(ii) The decomposition of the dihydroxochromiate ion above pH 8,27, necessitated rapid measurements above this value.

(iii) The difficulty in obtaining very accurate values from the graphical methods which had to be used.

Nevertheless, it is considered that the results in Table 8 can be taken as a useful measure of the degree of olation.

Evidently the solution to which one equivalent of alkali had been added prior to boiling (Solution B Table 8) did not olate to completion. This indicates that the absorption spectrum of this solution (Fig. 14, Curve E) is only an approximation to that of the pure olated complex. In order to obtain more information on the properties of the olated complex, several attempts were made to isolate the potassium salt.

5. Attempts to Prepare Potassium Tetraoxalato μ dihydroxo-dichromiate.

Werner (13) prepared the ammonium salt of this complex from ammonium cis dioxalatodiaquochromiate and ammonia but a method for the potassium salt does not appear to have been reported. Since only potassium salts are considered in this work, a number of attempts were made to prepare the potassium salt of the olated complex. These may be summarised as follows:

(i) To a 50% (w/v) solution of potassium cis dioxalato-diaquochromiate prepared by warming a corresponding solution of the pure trans isomer, the calculated amount of standard alkali solution was added and the solution boiled for more than an hour. A small quantity of a light-green almost colloidal precipitate appeared (Precipitate B) which was filtered off with great difficulty. Unsuccessful attempts were made by stirring and cooling to induce the filtrate to crystallise. The addition of 50% of absolute alcohol separated a grey-green powder (Precipitate A) while the alcoholic solution remained blue-green. The powder was filtered, dried and analysed.

Precipitate A.

	Found	Molar Ratio
Cr	18.06%	1.00
K	18.4%	1.36
(C_2O_4)	42.7%	1.40

These figures did not correspond to any known complex and the molar ratios indicated that the solid was probably a mixture. Reprecipitation with alcohol did not effect a separation and the solid was not investigated further.

When the alcoholic filtrate was allowed to evaporate, a mixture of a greyish powder interspersed with blue-green needle shaped crystals was obtained. The crystals were very like those of potassium trioxalatochromiate but the two solids could not be separated sufficiently to be tested.

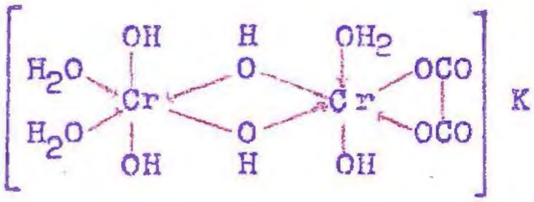
(ii) The light green colloidal precipitate (Precipitate B) was then investigated. By adding excess alkali to the boiling hydroxoaquochromiate solution, more of this precipitate formed. This was filtered off and dried — a process which took nearly a week in a vacuum desiccator over concentrated sulphuric acid, since it clung to water tenaciously. When dry, Precipitate B was dark-green, and very hard. The analytical figures for this solid are:

Precipitate B

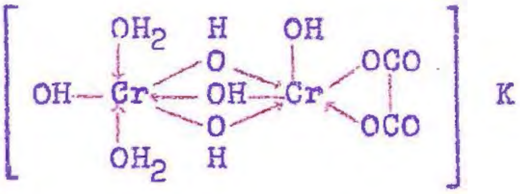
	Found	Molar Ratio	Theoretical	
			I	II
Cr	29.7%	1.0	28.1%	29.5%
K	8.7%	0.4	10.6%	11.1%
(C_2O_4)	28.6%	0.6	23.8%	25.0%

The experimental results did not correspond with any known chromium complex. A number of hypothetical structures were considered, the two most likely being as follows:

(I)



(II)



The empirical formulae for these are:

(I) $K[Cr_2(C_2O_4)(OH)_5(H_2O)_3]$ Mol. Wt 370

(II) $K[Cr_2(C_2O_4)(OH)_5(H_2O)_2]$ Mol. Wt 352

The theoretical figures for these structures are tabulated above. It is interesting to note that these complexes both contain one oxalate group per two chromium atoms. However, neither is in complete agreement with the analytical figures and it is not surprising that the precipitate was found to be a mixture. When Precipitate B was shaken with water, a green solution formed but a small amount of a dark-green residue remained which would not dissolve on boiling with strong sodium hydroxide solution, although it was soluble in strong sulphuric acid.

(iii) It was found that if alkali were added to the <u>cis</u> dioxalatodiaquochromiate solution in small portions, boiling between additions, then the appearance of the light-green Precipitate B could be avoided. The solution formed by this means was dark-green and a grey-green solid separated out on adding alcohol. Unfortunately, the results were not reproducible. Figures for two of these alcohol separations, labelled (1) and (2), are given below together with the theoretical figures for the olated complex:

Olated Complex $K_4\left[Cr_2(C_2O_4)_4(HO)_2\right]$ Mol. Wt. 646.4

	(1)		(2)		Theoretical
	Found	Molar Ratio	Found	Molar Ratio	
Cr	12.26%	1.00	13.3%	1.00	16.1%
K	23.4	2.52	23.3	2.30	24.2
(C_2O_4)	53.2	2.55	52.9	2.30	54.4

From these figures it is apparent that the solids contained impurity and so no physical measurements were undertaken. Attempts to obtain purer products were unsuccessful.

6. Summary.

The absorption spectra of the cis dioxalatohydroxoaquochromiate and cis dioxalatodihydroxochromiate ions have been measured and it has been shown that the latter ion decomposes rapidly in aqueous solution.

Evidence has been presented indicating that the cis dioxalatohydroxoaquochromiate ion olates on boiling in dilute solution and the process has been studied semi-quantitively. The "degree of olation" has been defined and has been found to increase with addition of alkali, as would be expected from theory. The maximum degree of olation observed was approximately 80% of theoretical.

Attempts to isolate the olated complex from concentrated solutions have been unsucessful although the analytical figures indicate that some of the solids obtained probably contained a large proportion of this complex, contaminated with other salts.

Chapter 6

AN INVESTIGATION INTO THE CONDITIONS OF FORMATION AND STABILITY OF THE TRIOXALATOCHROMIATE ION

1. Introductory

In recent years a number of investigations have been carried out with a view to utilising the strong colour of the trioxalatochromiate ion as a rapid colorimetric method for estimating chromium.

In 1939, Ueberbacher and Dröscher (24) found that by boiling solutions of a number of chromium salts, including chromic salts, chromates and dichromates, with an excess of oxalic acid, blue-green solutions were obtained. They measured the absorption curves of these solutions using a Zeiss step photometer and determined that Beer's law was obeyed approximately. They assumed that the reaction between the chromium ions and oxalic acid had gone to completion, with the production of trioxalatochromiate. Oxalic acid was used because in some earlier work, it had been shown that under alkaline conditions oxalate did not enter the complex completely. As a result of these tests, a method of determining chromium in tanning salts was proposed in which solutions were boiled with about ten moles of oxalic acid per Cr_2O_3, the light absorption being measured in the usual colorimetric manner.

This work was repeated in 1946 by Theis and co-workers on a more accurate scale, using a Beckmann spectrophotometer (2). An aged chrome sulphate solution was used and increasing amounts of oxalic acid were added to equal aliquots which were then boiled. The light absorption of these solutions was found to increase on adding oxalic acid until 20 moles per Cr_2O_3 had been added, when a limiting value appeared to have been reached. On ageing this solution a slight rise in the absorption was observed and it was concluded that boiling with 20 moles of oxalic acid converted about 96% of the Cr into trioxalatochromiate, complete penetration being obtained on subsequent ageing. Agreement with Beer's law was tested for solutions of different chromium salts which had been boiled with about 20 moles of oxalic acid and it was found that the law was obeyed, although the precision was not high.

From an examination of the reports of these investigators, it appeared that the evidence purporting to prove that most chromium salts could be converted into the trioxalatochromiate ion quantitatively, by boiling with a large excess of oxalic acid in solution, was not conclusive. Consequently, as a check on this work, a solution of pure potassium trioxalatochromiate was boiled with 20 moles of oxalic acid per Cr_2O_3 for 30 minutes, cooled and then made to standard volume such that the concentration was .07% Cr_2O_3. The optical density of this solution was read at 419 and 560 mμ. In the table below, these readings are compared with those for the pure trioxalatochromiate at the same concentration.

Wavelength	Optical Density	
	Trioxalatochromiate unboiled	After boiling with oxalic acid
419 mμ	.903	.793
560 mμ	.700	.611

The drop in the optical density on boiling with oxalic acid may be assumed to be due to the decomposition of some of the trioxalatochromiate. It was determined that boiling a solution of the pure trioxalatochromiate alone for 30 minutes produced a negligible change in the optical density readings.

This preliminary test indicated that the formation of the trioxalatochromiate ion from chromium salts and oxalic acid might be influenced by factors other than the oxalate concentration in solution. In view of the importance of this reaction, it was decided to carry out a more thorough investigation and, as a result, it has been shown that the pH of the solution is the most important factor which determines the stability of the trioxalatochromiate complex in solution.

2. Conditions of Formation of the Trioxalatochromiate Ion

The conditions of formation were investigated starting from oxalic acid and potassium dichromate in order to avoid any complications due to the presence of sulphate and other ions which were usually prevalent in the solutions employed by previous workers (2). The pure salts were used in the stoichiometric amounts demanded by the equation:

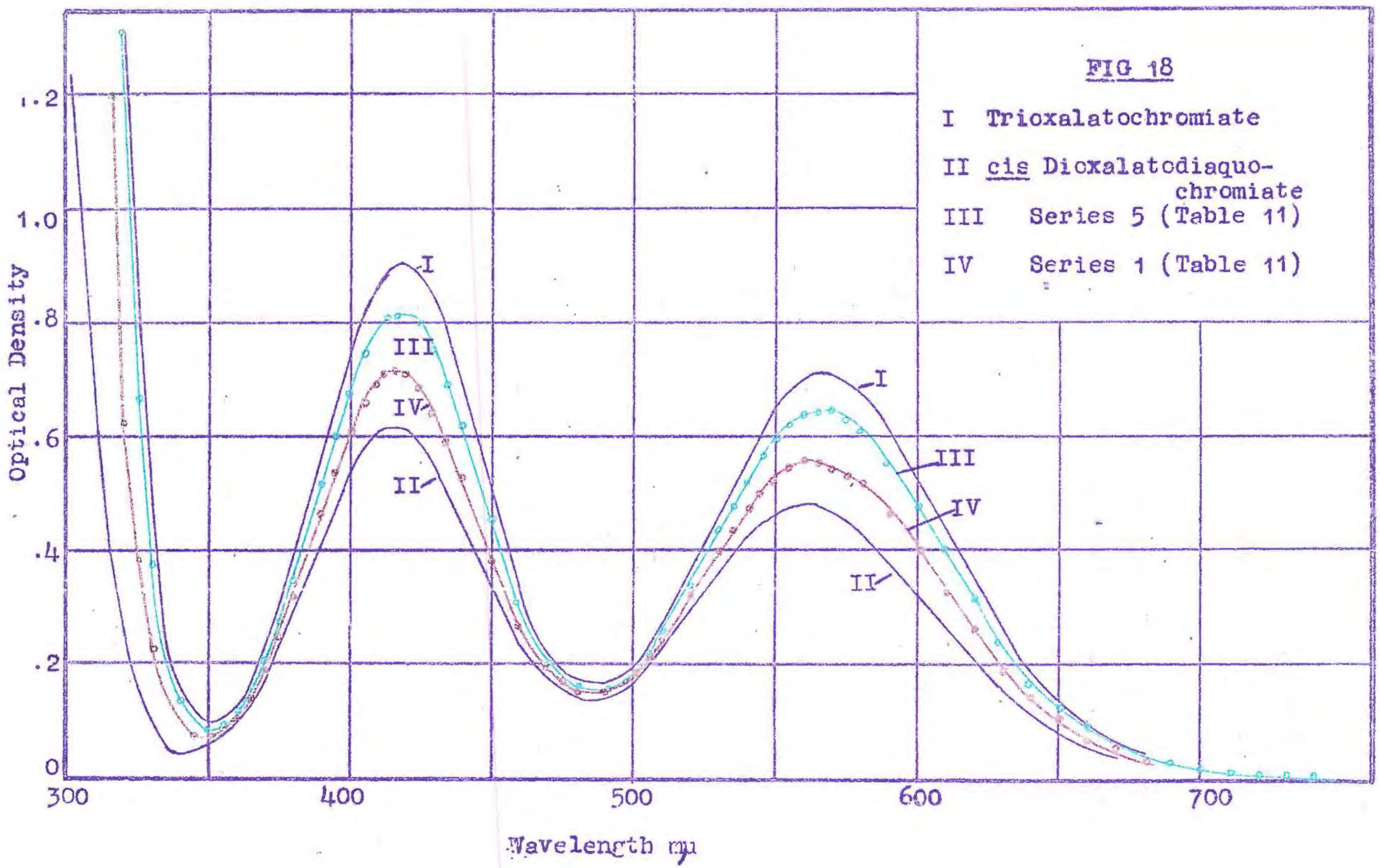


FIG 18

I Trioxalatochromiate
II cis Dioxalatodiaquo-chromiate
III Series 5 (Table 11)
IV Series 1 (Table 11)
Optical Density
1.2
1.0
.8
.6
.4
.2
0
300
400
500
600
700
Wavelength mμ
I
III
IV
II
I
III
IV
II

$K_2Cr_2O_7 + 9\ H_2C_2O_4 \longrightarrow 2\ KH_2\ Cr(C_2O_4)_3 + 6\ CO_2 + 7\ H_2O$ ...(6.1)

Exactly 22.066 gms of A.R. $K_2Cr_2O_7$ and 85.097 gms of A.R. $(COOH)_2.2H_2O$ were dissolved in about 300 ml of distilled water with heating. The solution was boiled for more than an hour under reflux, cooled and made to 500 ml. This was tested for dichromate with diphenyl carbazide solution, but none was detected, proving that reduction was complete. Aliquots of Solution A, suitably diluted, were used for physical measurements.

First, an aliquot of Solution A was boiled (under reflux) for a further hour to ensure that equilibrium had been attained; then it was diluted to a concentration corresponding to .07% Cr_2O_3 and this solution was used for optical density measurements. The absorption curve of this solution is shown in Fig. 18 (Curve IV) and the readings are recorded in the Appendix, Table A9. The curves for pure trioxalatochromiate and pure cis dioxalatodiaquochromiate at the same concentration of Cr_2O_3 are also shown n Fig. 18, Curves I and II.

The fact that Curve IV does not coincide with that of the trioxalatochromiate indicates that the reaction given in equation (6.1) above could not have gone to completion even though reduction was complete. In other words, the solution contained a mixture of several types of chromium ion. It has been shown already that no dichromate ions were present , so that possible constituents of this mixture were; trioxalatochromiate, cis

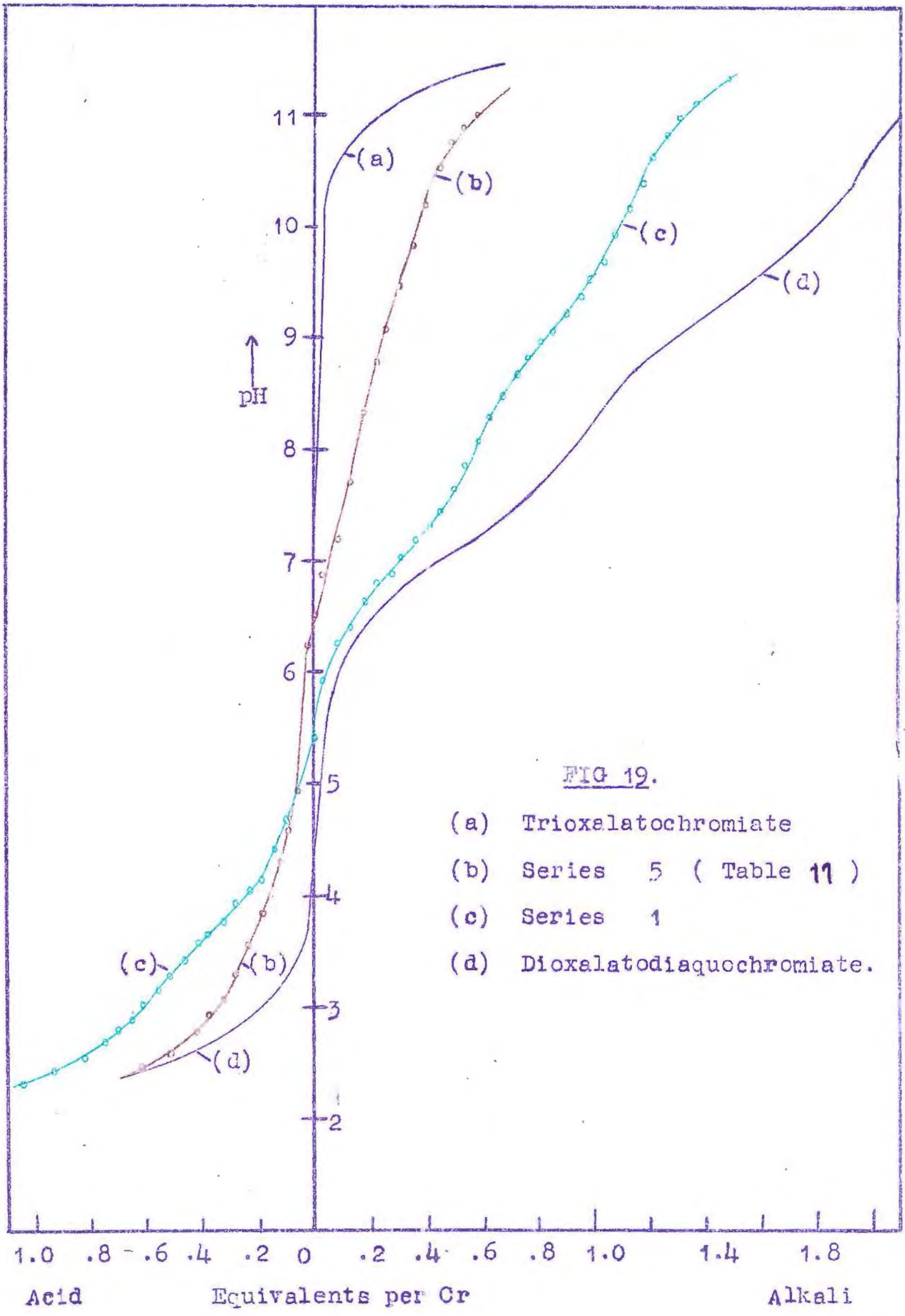


FIG 19.

(a) Trioxalatochromiate

(b) Series 5 (Table 11)

(c) Series 1

(d) Dioxalatodiaquochromiate.

dioxalatodiaquochromiate, mono-oxalatochromiate and chromic ions. Now in 1925 Gustavson (45) boiled a solution of dichromate and oxalic acid in amounts sufficient to form the dioxalatodiaquochromiate. After reaction, an electrophoresis experiment was performed on the solution, which established that the chromium was completely anionic, i.e. no chromic or mono-oxalatochromiate ions were present. For this reason, it was assumed that Solution A contained chromium as the trioxalato and <u>cis</u> dioxalatodiaquochromiate ions only. This was consistent with the spectrophotometric data since from the shape of Curve IV in Fig. 18 it is apparent that the solution could well be a mixture of these ions.

In Fig. 19 Curve (c) the acid and alkali potentiometric titrations of aliquots of Solution A are illustrated and similar curves for the trioxalato and dioxalatodiaquochromiates are also shown (Curves (a) and (d)). Below pH 5 the shape of Curve (c) is consistent with the titration of oxalic acid while above pH 7, the shallow end points due to the titration of dioxalatodiaquochromiate ions are visible. Thus the potentiometric data confirms that Solution A contained dioxalatodiaquochromiate and free oxalate ions.

Since boiling stoichiometric amounts of oxalic acid and chromic ions did not form the trioxalatochromiate ion completely, efforts were made to obtain maximum yields of this ion by varying the physical conditions of the solution before boiling. Increasing the pH of the solution was found to be most effective.

To six 50 ml portions of Solution A, increasing amounts of potassium hydroxide solution (.3590N) were added and the solutions boiled for an hour. This period was found to be long enough to ensure that the system attained equilibrium. The solutions were then cooled and made to standard volume (Solutions B). Aliquots of Solutions B were diluted for spectrophotometric and potentiometric measurements.

The relevent data for this series of solutions are recorded in Table 11 later, (p 87). In Column 2 of this table the total amount of potassium ion present in solution after the addition of potassium hydroxide is given as equivalents per Cr. Each of these figures represents the amount of potassium initially present, in Solution A (one equivalent per Cr) plus that added as potassium hydroxide. The data for Solution A, without the addition of alkali, are recorded as "Series 1".

In order to determine the percentages of trioxalato and dioxalatodiaquochromiate in these solutions, several methods based on the spectrophotometric and potentiometric measurements were employed. These methods are discussed in some detail since they are used in other sections of this work:

(a) Spectrophotometric Calculations

Aliquots of each of the Solutions B, containing dioxalatodiaquochromiate and trioxalatochromiate ions, were diluted to a concentration corresponding to .07% Cr_2O_3 and the optical densities were measured at 419 and 560 mμ. These have been recorded in Table 11 Columns 4 and 5.

Theoretically it is possible to obtain the concentrations of any number of components of a solution which obey Beer's law, provided that the optical density of the solution is known at a number of different wavelengths — equal to the number of components — and provided that the extinction coefficients of the components are known at these wavelengths. In practice, however, it is not always possible to apply this method to solutions of more than two components, and even for two components, it can only be applied if the extinction coefficients at the two wavelengths differ by a sufficiently large amount. In the case of the solutions containing trioxalato and cis dioxalatodiaquochromiate ions, which are known to obey Beer's law, the optical densities were measured near the two maxima (419 and 560 mμ) but even at these wavelengths the extinction coefficients were not sufficiently different to enable the concentrations to be determined by the use of Beer's law alone. Fortunately, the total chromium concentration of the mixtures was known and this fact was used used to derive an additional equation:

Let

k_t^1 be the molar extinction coefficient of trioxalatochromiate at 419 mμ

k'_d be the molar extinction coefficient of cis dioxalatodiaquochromiate at 419 mµ

k''_t be the molar extinction coefficient of trioxalatochromiate at 560 mµ

k''_d be the molar extinction coefficient of cis dioxalatodiaquochromiate at 560 mµ.

Now for a solution containing trioxalato and cis dioxalatodiaquochromiate ions at molar concentrations Ct and Cd respectively, if D' is the optical density of this solution at 419 mµ and D" that at 560 mµ, then since it has been established that both of these ions obey Beer's law at these wavelengths,

$$D' = Ct.k'_t.1 + Cd.k'_d.1 \quad \ldots\ldots\ldots\ldots (6.2)$$

$$D'' = Ct.k''_t.1 + Cd.k''_d.1 \quad \ldots\ldots\ldots\ldots (6.3)$$

where "1" is the thickness of the solution.

Also, if C is the total molar concentration of chromiate in the mixture;

$$C = Ct + Cd \quad \ldots\ldots\ldots\ldots (6.4)$$

Ct or if necessary Cd, can be obtained in two ways, from the 419 mµ maximum by solving (6.4) and (6.2) simultaneously, and from the 560 mµ reading by solving (6.4) with (6.3):

$$Ct = \frac{D' - C.k'_d.1}{1(k'_t - k'_d)} \quad \text{at 419 m}\mu \quad \ldots\ldots \quad (6.5)$$

$$Ct = \frac{D'' - C.k''_d.1}{1(k''_t - k''_d)} \quad \text{at 560 m}\mu \quad \ldots\ldots \quad (6.6)$$

To obtain the concentration of trioxalatochromiate ion in solution, expressed as a percentage of the theoretically

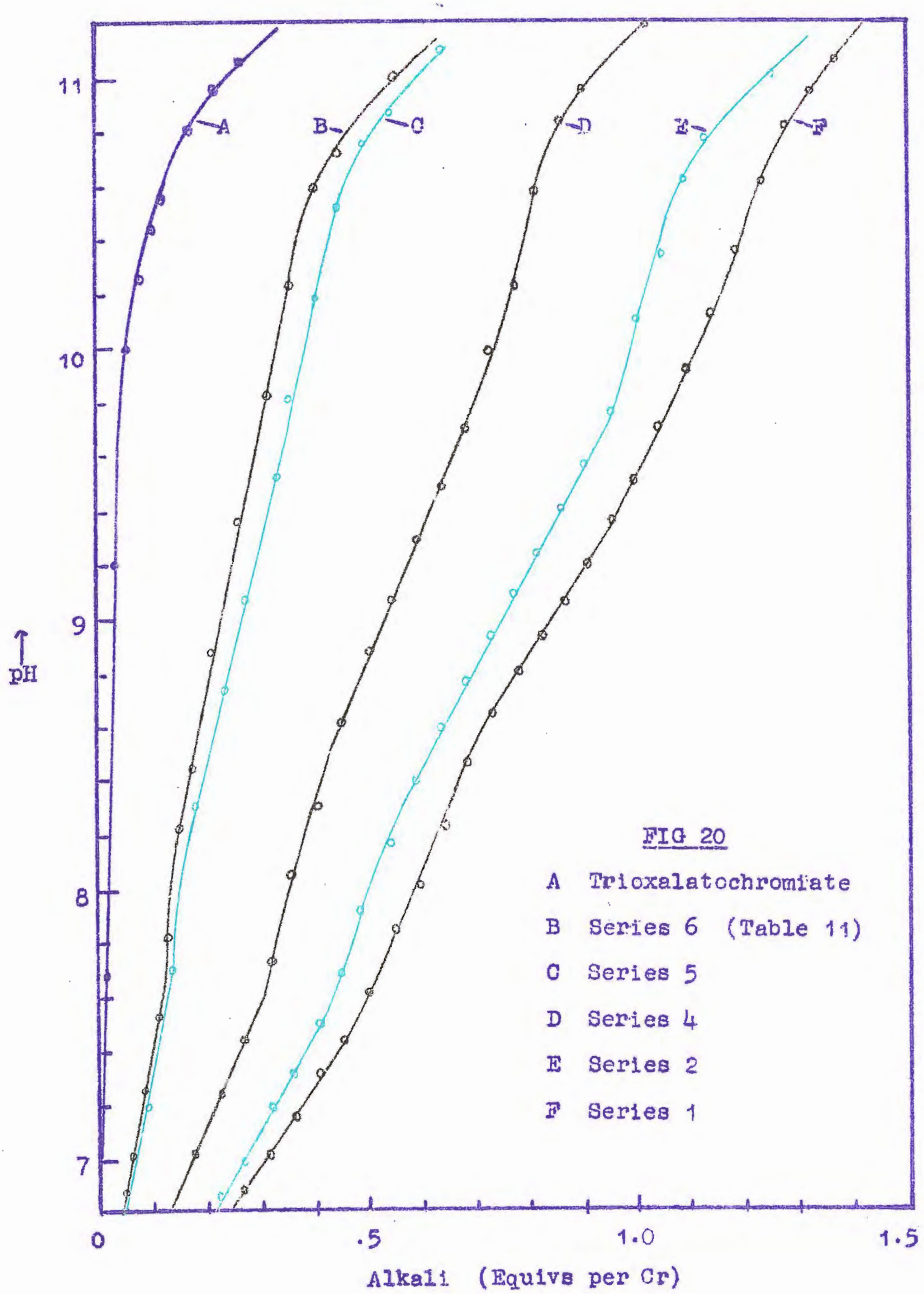


FIG 20

A Trioxalatochromiate
B Series 6 (Table 11)
C Series 5
D Series 4
E Series 2
F Series 1

possible maximum:

$$Ct = \frac{100}{.00921} \cdot \frac{D' - C.k'_d.1}{(k'_t - k'_d)1} \quad \% \text{ at } 419 \text{ m}\mu$$

$$Ct = \frac{100}{.00921} \cdot \frac{D'' - C.k''_d.1}{(k''_t - k''_d)1} \quad \% \text{ at } 560 \text{ m}\mu$$

In the evaluation of these equations, the molar extinction coefficients k were taken as the average values given earlier in Tables 1 and 5; C the concentration of chromiate was always .00921 gram ions per litre for these solutions and the light path length "1" of the absorption cell used was 1.00 cm.

Using these values:

$$Ct = \frac{D' - .607}{.002984} \quad \% \text{ at } 419 \text{ m}\mu \quad \ldots\ldots\ldots\ldots\ldots\ldots (6.7)$$

$$Ct = \frac{D'' - .465}{.002349} \quad \% \text{ at } 560 \text{ m}\mu \quad \ldots\ldots\ldots\ldots\ldots\ldots (6.8)$$

The values for the percentage of trioxalatochromiate obtained from these equations are independent estimates and are recorded in Table 11 Columns 6 and 7.

(b) Potentiometric Calculations

Two independent potentiometric methods were available; the first utilising the titration curves above pH 7 (Fig. 20) and the second those below pH 5 (Fig. 21).

In Fig. 20 the sections of the pH curves of the Series 1, 2, 4, 5 and 6 are plotted on an enlarged scale. Now from the titration curve of a solution containing an unknown amount of a weak acid, the concentration of this acid can be determined from the volume of alkali required to reach a given pH value, provided that the degree of neutralisation of the acid at this pH is known and provided that there is no other substance in solution which titrates in the same region. The degree of neutralisation can be found from the pH curve of a standard solution of the acid.

From the titration curve of pure potassium dioxalatodiaquochromiate (Fig. 19 Curve (d)), the degree of neutralisation was calculated at a number of pH values between 7.48 and 9.09 using the equation;

$$\alpha = V/T$$

where α is the degree of neutralisation at a given pH value,

V is the alkali required to reach this value, measured from the origin,

T is the alkali required for complete neutralisation of both aquo groups, i.e. to pH 10.6.

The values of α obtained in this way are recorded in Table 9 below. From these values the percentages of dioxalatodiaquochromiate ion were obtained for the curves in Fig. 20, the theoretical maximum being taken as 100%. These percentages have been converted to percentages of trioxalatochromiate (by subtraction from 100%) and recorded in Table 9.

The mean values are recorded again later in Table 11 Column 8 for comparison with the other methods.

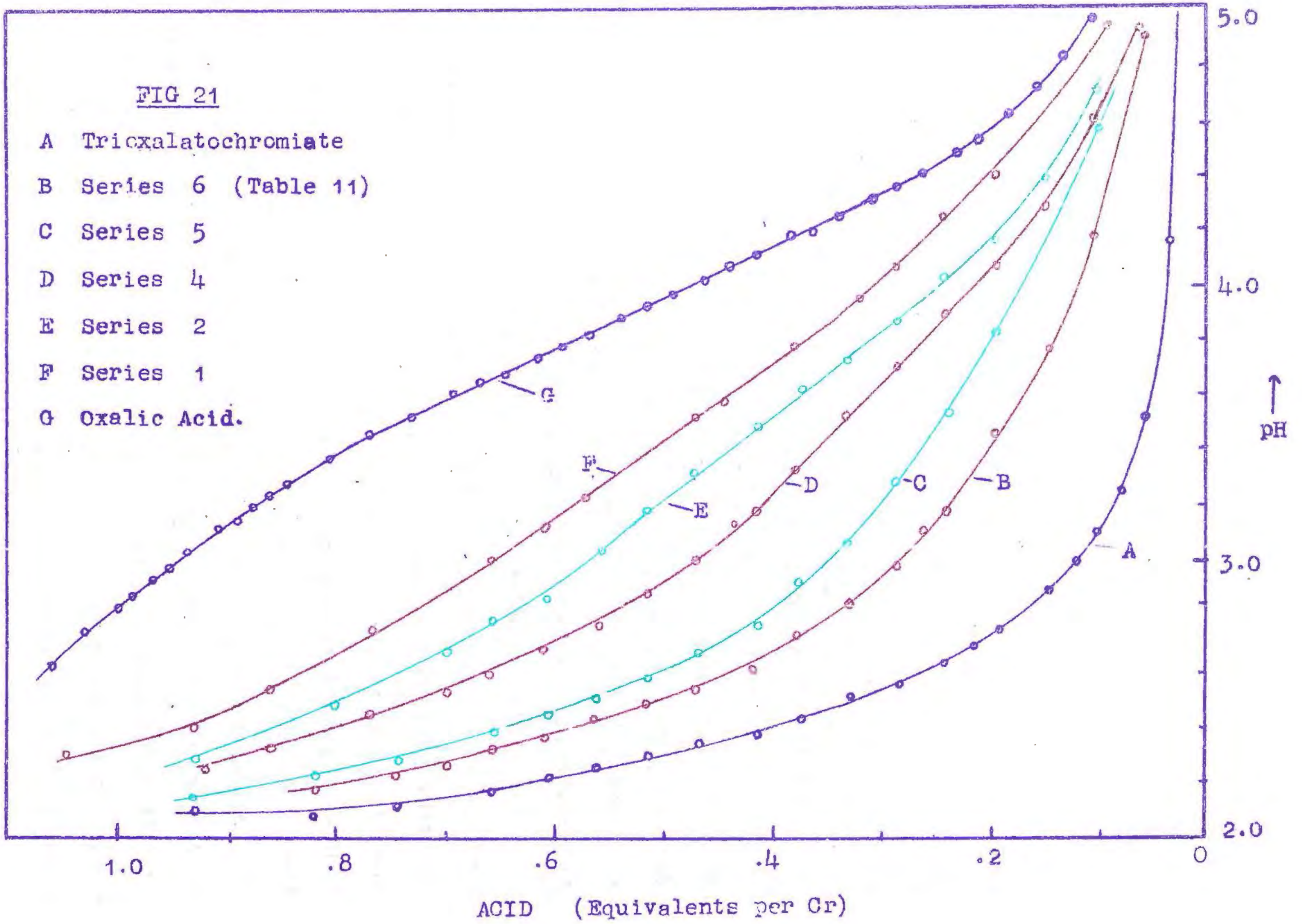


FIG 21

A Tricxalatochromiate
B Series 6 (Table 11)
C Series 5
D Series 4
E Series 2
F Series 1
G Oxalic Acid.
G
F
E
D
C
B
A
5.0
4.0
3.0
2.0
pH
1.0
.8
.6
.4
.2
0
ACID (Equivalents per Cr)

TABLE 9

pH	α	Trioxalatochromiate				
		Series 1	Series 2	Series 4	Series 5	Series 6
7.48	.363	37.1%	46.3%	63.1%	85.7%	-
7.70	.419	38.5	47.7	64.0	84.8	87.0%
8.03	.470	39.4	48.0	63.6	85.1	87.2
8.82	.615	38.5	45.1	61.9	82.3	85.3
9.09	.680	37.7	45.0	61.8	82.1	85.1
Mean:		38.2%	46.4%	62.9%	84.0%	86.2%

The second potentiometric method uses the titration curves below pH 5. In Fig. 21 the sections of these curves below this value are plotted on an enlarged scale for the Series 1, 2, 4, 5 and 6. The curve for pure oxalic acid is also given (Curve G), but for this curve the volume units are equivalents of KOH per equivalent of oxalic acid.

From this curve of oxalic acid, the amount of free oxalate titrating in the unknown solutions was estimated by the same procedure as that used above. That is, by finding the degree of neutralisation (α) of pure oxalic acid at a number of pH values and using these quantities to calculate the percentage of free oxalate for the other curves in Fig. 21. Since the molar ratio of oxalate to Cr, in all these solutions, was 3:1 after reduction, the amount of uncoordinated oxalate determined in this way must be equal to the amount of dioxalatodiaquochromiate in solution and from this, the percentage of trioxalatochromiate is obtained. Three pH values

TABLE 11

1	2	3	4	5	6	7	8	9	10	11
Series	Potassium (equivs per Cr)	pH .01M after boiling	Opt. Dens.		PERCENTAGE TRIOXALATOCHROMIATE					
			419mμ	560mμ	419mμ	560mμ	above pH 7	below pH 5	MEAN	(check) 8.27-10.6
1	1.0	5.4	.722	.559	39.6	40.0	38.2	43.4	40.3	40.8
2	1.5	5.6	.748	.579	47.3	48.5	46.4	52.8	48.8	47.0
3	1.75	5.7	.761	.591	51.6	53.6	-	-	52.6	-
4	2.0	5.9	.785	.602	59.7	58.3	62.9	62.8	60.9	63.5
5	2.5	6.4	.802	.623	65.3	67.3	84.0	75.4	73.0	71.0
6	2.65	6.6	-	-	-	-	86.2	82.6	84.4	74.5
7	3.0	7.0	.903	.698	99.3	99.1	(100)	(100)	99.2	-

were selected, and the results are:

TABLE 10

pH	α	Trioxalatochromiate				
		Series 1	Series 2	Series 4	Series 5	Series 6
2.84	.500	43.3%	52.6%	63.4%	76.5%	83.0%
3.20	.562	44.1	52.3	62.9	75.3	82.7
3.82	.716	42.9	53.6	62.0	74.5	82.1
Mean:		43.4%	52.8%	62.8%	75.4%	82.6%

The mean values are recorded again in Table 11 Column 9.

The titration curves for Series 7 (Table 11) were very close to those of pure trioxalatochromiate and, therefore, they have not been recorded. It is clear that this series could not be used to obtain a quantitative potentiometric estimate of the amount of trioxalatochromiate formed, but it may be stated, qualitatively, that the reaction had proceeded to completion in this case.

(c) Assessment of Results

In Table 11 the results for the percentage of trioxalatochromiate in different solutions, obtained by four independent methods described above, are compared. All of these methods are liable to fairly large errors.

The errors involved in the spectrophotometric methods arise because of the closeness of the extinction coefficients of trioxalato and cis dioxalatodiaquochromiate, even at their maxima, and from the fact that the optical densities could not be read to more than about .2% in the range from

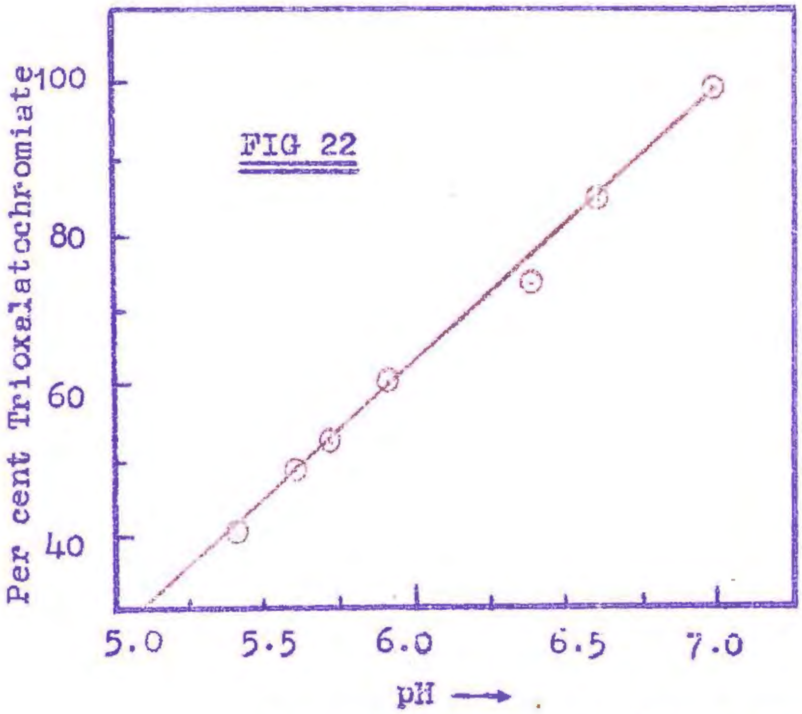
.4 to .9 units. As a measure of the error in the percentages of trioxalatochromiate, the calculation for Series 7 at 560 mμ may be considered:

The optical density was .698, and the percentage of trioxalatochromiate, obtained from equation (6.8), was 99.1%. If it is assumed that the error in the optical density readings is .002 units, then the value for the percentage of trioxalatochromiate may be from 98.3% to 100.1%. By similar calculation, the values obtained from the 419 mμ measurement for Series 7 may vary from 98.5% to 99.9%. In other words, the reaction had probably proceeded to completion for Series 7 within the experimental error of the spectrophotometric measurements. The values obtained are probably less unreliable than the above calculation of errors would indicate, since each reading was the mean of a number of readings on the same solution at the same wavelength.

In general the two values found from the spectrophotometric data agree with each other better than do the potentiometric values. The figures for the 560 mμ readings are probably more reliable since Beer's law is obeyed with greater exactitude at this wavelength by both the trioxalatochromiate and the dioxalatodiaquochromiate ions.

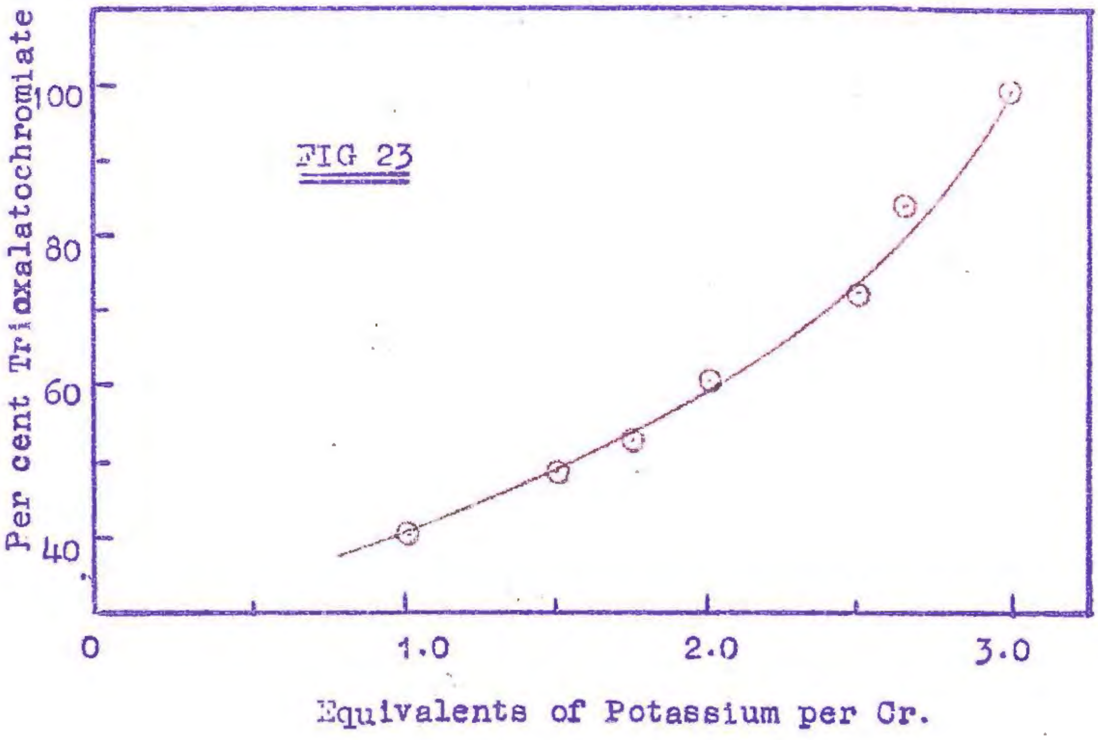
The two potentiometric methods are liable to the usual errors involved in reading values from graphs and the figures for the series containing smaller amounts of dioxalatodiaquochromiate and oxalic acid may be expected to be less reliable

FIG 22



(a ·01M solution after boiling)

FIG 23



in view of the small distances to be measured. Nevertheless the potentiometric values (Table 11 Columns 8 and 9) evidently gave results of the right order of magnitude. This is important since similar methods were used in the present work under conditions which did not permit of comparison with independent methods.

The percentage of dioxalatodiaquochromiate in solution could have been obtained by the same method which had to be employed in Chapter 5 for the elucidation of the olated solutions; namely, by measuring the amount of alkali required to raise the pH from the end point at 8.27 to that at 10.6. This method is theoretically less accurate than that actually used because of the uncertainty of the measurements of the glass electrode at high pH values. As a check on this method, the percentages of dioxalatodiaquochromiate and hence of trioxalatochromiate were calculated using the data plotted in Fig. 20. The results are recorded in Table 11 Column 11, for comparison with the mean values for the other four methods. The fact that fair agreement is obtained, especially for the Series 1, 2, and 5, indicates that the use of the glass electrode does not entirely invalidate the results of this method.

(d) Discussion of Results.

The results of the above calculations are best expressed graphically. In Fig. 22 is shown the relation between the percentage of trioxalatochromiate formed and the pH of the solution after boiling; while Fig. 23 shows the relation between the concentration of potassium ion in solution and the amount of trioxalatochromiate formed. In both cases the percentages of trioxalatochromiate given are the average values recorded in Table 11 Column 10.

These graphs are obviously interdependent and they prove that, if the pH of a solution containing oxalic acid and ions of chromium, in the stoichiometric quantities necessary to form the trioxalatochromiate ion, is increased so that after boiling the solution approaches neutrality, then the reaction to form the trioxalatochromiate ion approaches completion.

It was found that if alkali were added so that more than three equivalents of potassium were present per Cr, then a precipitate was obtained on boiling. This precipitate resembled Precipitate B , discussed in Chapter 5, and was evidently the result of the action of excess of alkali on the oxalatochromiate ions. Previous workers (24) have mentioned that trioxalatochromiate could not be obtained satisfactorily under alkaline conditions.

Thus the conditions of formation of the trioxalatochromiate ion are rather critical. The solution containing chromium ions and oxalic ions must not be too alkaline initially or else, as soon as the dioxalatodiaquochromiate is formed, mono and di hydroxo derivatives appear, with the subsequent decomposition of the latter and the danger of precipitation. If the solution be too acidic initially, then an equilibrium mixture of dioxalatodiaquo and trioxalatochromiate ions is formed, the position of equilibrium depending on the pH.

So far the conditions of formation of the trioxalatochromiate ion have been investigated above pH 5 only. Further work on the properties of the oxalatochromiates at lower pH values seemed desirable.

3. The Stability of Oxalatochromiate Ions under Acid Conditions

The stability of potassium trioxalatochromiate solutions at low pH values was studied spectrophotometrically:

> To each of four 50 ml aliquots of a .01570M solution of pure potassium trioxalatochromiate, different amounts of standard nitric acid (.3450N) were added. The solutions were boiled under reflux for more than two hours by which time they had attained equilibrium. The solutions, when cool, were made to a standard volume such that if no decomposition occurred, the solutions would have been .00785M with respect to trioxalatochromiate, i.e. .05% Cr_2O_3. The optical densities at 420 and 560 mμ were then measured. The pH of these solutions was measured, before and after boiling.

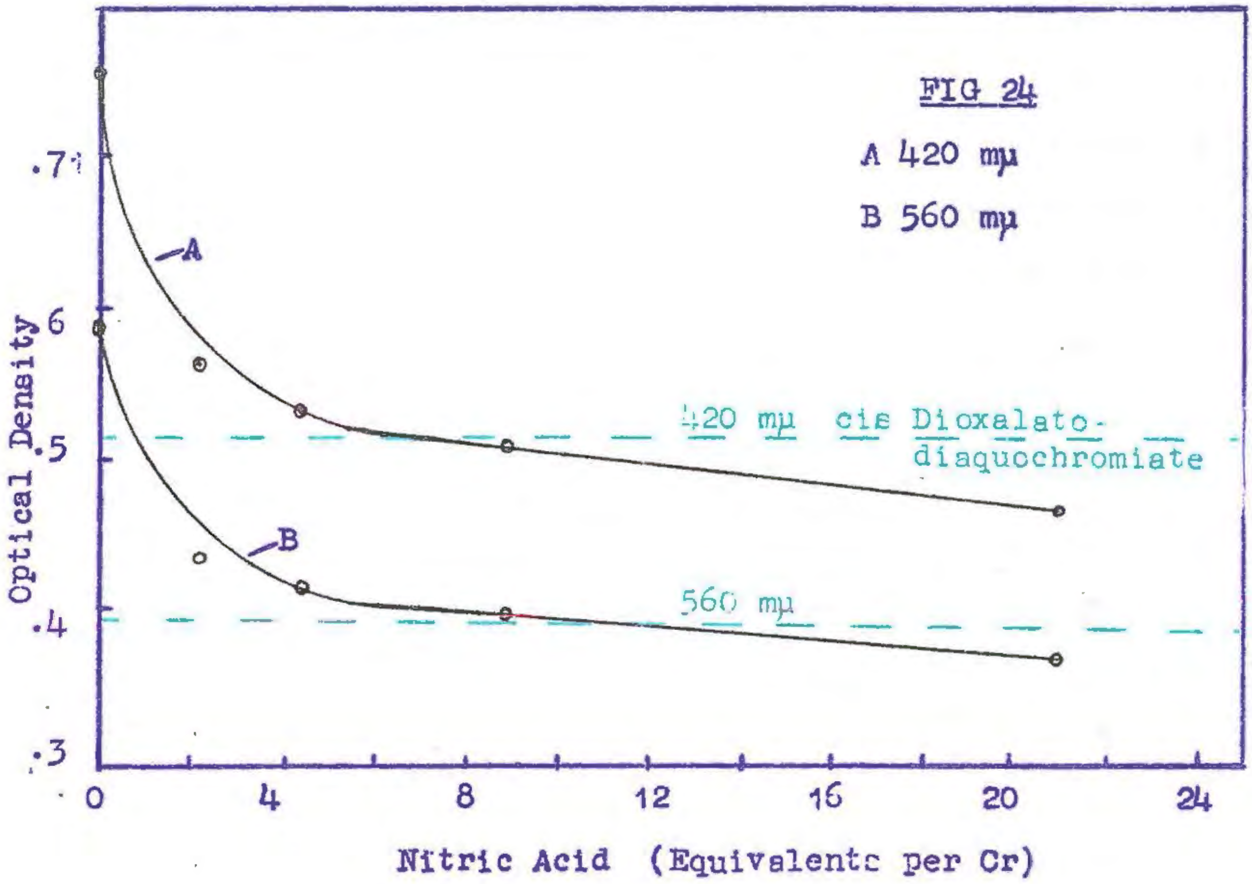


FIG 24

A 420 mμ
B 560 mμ
A
B
420 mμ cis Dioxalato-diaquochromiate
560 mμ
Optical Density
.7
.6
.5
.4
.3
0
4
8
12
16
20
24
Nitric Acid (Equivalents per Cr)

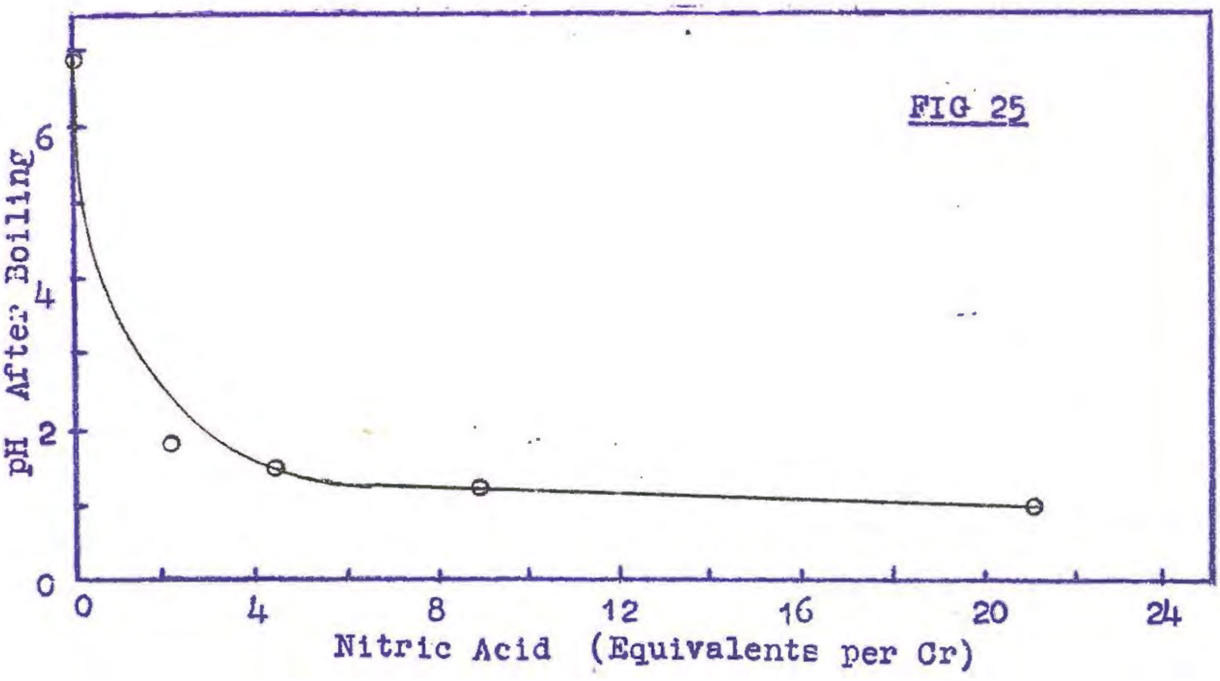


FIG 25

pH After Boiling
6
4
2
0
0
4
8
12
16
20
24
Nitric Acid (Equivalents per Cr)

The results of this experiment are tabulated below. The amounts of nitric acid added to each solution are recorded as equivalents per Cr and the optical density and pH values for .00785M solutions of pure trioxalato and cis dioxalatodiaquochromiate are also given.

TABLE 12

HNO_3 added (equivs/ Cr)	Optical Density 420 mµ	560 mµ	pH before boiling	pH after boiling
2.20	.561	.433	1.68	1.88
4.40	.532	.415	1.45	1.41
8.79	.507	.397	1.05	1.20
21.97	.465	.368	.78	.90
Trioxalato	.758	.587	7.0	-
cis Dioxalato	.514	.396	4.5	-

These results are illustrated graphically in Figs 24 and 25. In Fig. 24 the relation between the amount of acid added to the solution initially and the final optical densities at 420 mµ and 560 mµ is shown. The shape of the curves shows that the optical density decreased at both wavelengths as the amount of acid was increased. This proves that the trioxalatochromiate ion is decomposed by acid and from the results discussed in the previous section, it may be assumed that cis dioxalatodiaquochromiate and oxalic ions are the first products of decomposition. When more than about eight equivalents per Cr of nitric acid had been added, the optical density readings decreased below those of pure cis dioxalatodiaquochromiate at the same Cr_2O_3 concentration. This shows that even the cis dioxalatodiaquochromiate ion is decomposed at this stage, although the pH had to drop as low as pH 1 before the effects of this decomposition were measurable. The decomposition products were not investigated but probably the hexa-aquo chromic ion was formed with the mono-oxalatochromiate as a possible intermediate, although the existence of this complex has not been confirmed.

It should be noted that the optical density readings recorded in Table 12 and plotted in Fig, 24 are really the resultant values of the optical densities of all the complexes in solution which are capable of absorbing light of the specified wavelengths. Consequently they cannot be used to estimate the quantities present in solution without further knowledge of the nature of these complexes.

Thus it may be stated, qualitatively, that the trioxalatochromiate ion is decomposed to some extent in acid solution, while the cis dioxalatodiaquochromiate ion appears to be stable down to fairly low pH values.

4. Discussion of Previous Investigations

An explanation of some of the results of earlier workers can now be given in view of the experiments discussed above.

Even after the general acceptance of the Werner Coordination Theory, some workers have maintained that in systems similar to those considered here, the titration characteristics and other properties of the solutions are to be regarded as evidence for the colloidal nature of the compounds in solution. For example, Britton (4) boiled a solution containing a mixture of oxalic acid and chromic ions in the molar ratio 3:1 and obtained a "claret-red" solution. The pH curve of this solution against standard alkali was similar to Curve (c) Fig. 19. It is evident,. therefore, that under the conditions used, Britton had not succeeded in obtaining the pure trioxalatochromiate and that his solution contained free oxalate, together with dioxalatodiaquochromiate. Thus the deductions made by Britton on the basis of the pH titration curves are untenable. In other words, colloidal phenomena need not be invoked to explain these data.

In passing, another aspect of Britton's paper may be mentioned. On page 279 of this paper (4) is the statement: "Although no precipitate is formed, it is significant that the claret-red solution began to turn green just when the hydrion concentration had become that at which chromium hydroxide is normally precipitated. This suggests that the colour is in some way related to the hydroxide itself". By "claret-red solution" is meant the boiled solution of oxalate and chromic ions. From the work discussed in this chapter it is apparent that this solution was red because of the presence of a large amount of dioxalatodiaquochromiate. It was shown in Chapter 5 that the green colour is due to the formation of the hydroxo complexes and has nothing to do with chromium hydroxide.

Britton (4) mentioned the anomalous results obtained by previous experimenters using solutions of chromium salts and oxalic acid and there is no doubt that these anomalies are due to the fact that the reaction between chromic ions and oxalate ions does not go to completion to form the trioxalatochromiate at a low pH.

The results of Theis and co-workers (2), already mentioned, can be discussed in the same way. These workers found that increasing the ratio of oxalic acid to chromium in solution, with subsequent boiling, caused an increase in the light absorption, evidently due to the formation of more trioxalatochromiate. They found that when 20 moles of oxalic acid per Cr_2O_3 were present, in solution, further addition of oxalic acid produced very little increase in light absorption.

These workers also showed that a number of chrome solutions obey Beer's law, approximately, after boiling with 20 moles of oxalic acid per Cr_2O_3. A colorimetric method for the determination of chromium was, therefore, proposed in which the chrome solution under examination is boiled with about 20 moles of oxalic acid per Cr_2O_3, made to standard volume and the light absorption measured, (51,53).

Now it has been shown in Section 1 of this chapter that when a solution of pure trioxalatochromiate is boiled with 20 moles of oxalic acid per Cr_2O_3, decomposition occurs to some extent. In other words, it appears that for the solutions used by Theis, reaction had not gone to completion to form the trioxalatochromiate ion. These solutions must, therefore, have contained trioxalatochromiate together with other complexes, the most probable complex being the cis dioxalatodiaquochromiate. Such solutions will obviously obey Beer's law since it is obeyed by both trioxalatochromiate and cis dioxalatodiaquochromiate ions.

Nevertheless, the Theis method may be recommended when only approximate values for the chromium content are required, provided that the colorimeter used is calibrated on standard chrome solutions which have been boiled with 20 moles of oxalic acid per Cr_2O_3. The large excess of oxalic acid ensures that approximately the same state of equilibrium between trioxalatochromiate, cis dioxalatodiaquochromiate and oxalic acid is reached in all cases. It is suggested that a more accurate, and scarcely more difficult, method would be to add a slight excess of oxalic acid and then to control the pH so that, after boiling, the solution is about neutral. The light absorption would then be measured in the usual colorimetric or spectrophotometric manner.

Recently, Shuttleworth (54) has investigated the reaction of oxalic acid and sodium oxalate with chrome alum in dilute solution using a conductometric method. His conclusions may be summarised as follows:

The addition of oxalic acid or sodium oxalate to solutions of chrome alum results in displacement of coordinated sulphate groups. In the case of oxalic acid, the reaction proceeds stoichiometrically until four SO_4 groups per Cr_2O_3 have been displaced, that is, until dioxalatochromiate has been formed. Large excess of oxalic acid has to be added before further penetration occurs. With sodium oxalate, however, a large excess is not required for complete penetration to the trioxalatochromiate.

It is thus apparent that the results obtained by this conductometric method have been substantiated quantitatively by the combined spectrophotometric and potentiometric methods discussed in this chapter.

These discussions of the work of other investigators emphasise the importance of using the correct conditions of formation when studying the trioxalatochromiate system and it may be concluded that the stability of the trioxalatochromiate ion in solution depends on, firstly the pH of the solution and ,secondly the concentration of oxalate in solution.

5. Summary

The experiments described in this chapter indicate the important part played by pH in the formation and stability of the trioxalatochromiate ion in dilute solution.

In view of this work, the conclusions reached by earlier investigators have been discussed.

It has been shown that in solutions of mixtures of dioxalatodiaquochromiate and trioxalatochromiate of given total chromium content, the proportion of either ion may be determined by spectrophotometric or potentiometric means, the agreement between the two methods being fairly good.

Chapter 7

A PRELIMINARY INVESTIGATION INTO THE KINETICS OF THE REACTION BETWEEN POTASSIUM cis DIOXALATODIAQUOCHROMIATE AND POTASSIUM OXALATE IN AQUEOUS SOLUTION

1. Introductory

In the previous chapter it was shown that the reaction between stoichiometric amounts of chromium ions and oxalate ions went practically to completion when the solution contained three equivalents of potassium ion per Cr. An attempt was then made to learn more about the mechanism of this reaction by a kinetic study. The simplest reaction possible was chosen for this preliminary investigation, namely, that between equimolar quantities of potassium cis dioxalatodiaquochromiate and potassium oxalate. This mixture fulfils the conditions of formation of the trioxalatochromiate ion already established. By boiling a dilute solution of the equimolar mixture, it was determined from the optical density of the resultant solution, that reaction had really gone to completion as expected.

Of the methods available for following the course of the reaction in aqueous solution, the spectrophotometric measurement of the change in light absorption was by far the most rapid and convenient, although, as shown in Chapter 6, a high degree of accuracy could not be expected. However, the decision to use this method was supported by the work of B.Adel (55) who in 1941, investigated the kinetics of the coordination reaction:

$$[Co(NH_3)_5Cl]^{++} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{+++} + Cl^-$$

He employed three methods ;

(i) Spectrophotometric determination of the amounts of complex ions from optical density readings.

(ii) Electrometric determination of chloride ion concentration using a silver-silver chloride half cell.

(iii) Potentiometric determination of chloride ion concentration by titration.

From the results of these methods he concluded that spectrophotometry was the most satisfactory method.

The kinetics of reactions involving complex ions is of considerable theoretical importance, since they include some of the few ionic reactions which proceed at a measurable rate. However, the number of investigations which have been performed is not large (56) and no reference to an investigation involving dioxalatodiaquochromiate could be found in the literature.

2. Discussion of Procedure

It was assumed that the reaction between potassium cis dioxalatodiaquochromiate $K[Cr(C_2O_4)_2(H_2O)_2]$ and potassium oxalate $(COOK)_2$ in solution proceeds by a second order mechanism as follows:

cis Dioxalatodiaquochromiate ion + oxalic ion ⟶

Trioxalatochromiate ion + water. (7.1)

No assumptions concerning the charges on the ions can be made at this stage.

Now the differential and integrated forms of the second order equation, when both reactants have the same intial concentration, are:

$dx/dt = k(a - x)^2$ ....(7.2)

$1/(a - x) = 1/a + kt$ ....(7.3)

where a is the concentration of reactants at time $t = 0$.

x is the concentration of resultants at time t.

k is the velocity constant.

In reaction (7.1) above, $(a - x)$ is the concentration of the dioxalatodiaquochromiate, at time t. This concentration was determined from spectrophotometric measurements of the optical density during the course of the reaction.

Let Dd and k_d be the optical density and molar extinction coefficient, respectively, at a given wavelength (420 mµ) for a solution of pure cis dioxalatodiaquochromiate at molar concentration C. Let Dt and k_t be the corresponding quantities for a trioxalatochromiate solution at the same wavelenght and concentration.

Then from Beer's law;

$Dd = k_d.C.1$ ....(7.4)

$Dt = k_t.C.1$ ....(7.5)

where "1" is the thickness of the solution whose light absorption is measured.

Let D be the optical density (at 420 mµ) of a solution containing cis dioxalatodiaquochromiate and trioxalatochromiate ions at time t during the reaction.

Then from Beer's law;

$$D = l(\,Ct.k_t + Cd.k_d\,) \quad \ldots\ldots (7.6)$$

Let Ct be the molar concentration of trioxalatochromiate in this solution at time t and let Cd be that of dioxalatodiaquochromiate i.e. Cd = (a-x).

$$\text{Then } C = Cd + Ct \quad \ldots\ldots (7.7)$$

From the last four equations;

$$Cd = (a - x) = C\left(\frac{Dt - D}{Dt - Dd}\right) \quad \ldots\ldots (7.8)$$

In the derivation of this equation it is assumed that the same absorption cell is used for all measurements, so that the term "l" cancels out. This was always the case during this experiment.

Subsituting in (7.3) and remembering that a = C;

$$\frac{(\,Dt - Dd\,)}{C(\,Dt - D\,)} = \frac{1}{C} + kt \quad \ldots\ldots (7.9)$$

The quantities C, k, Dd and Dt may be taken as constant and so the graph of 1/(Dt - D) against t should be linear for a second order equation. The velocity constant is calculable from the slope;

$$k = (1/C).(Dt - Dd).(\text{slope}) \quad \ldots\ldots (7.10)$$

The reaction velocity was studied using solutions containing equimolar quantities of potassium oxalate and <u>cis</u> dioxalatodiaquochromiate by measuring the optical density D of portions of these solutions at known time intervals. In this experiment a compromise had to be reached between two important factors.

The first was that the solution used should be very dilute since it was hoped that, by performing the experiment at a number of different ionic strengths, the Brønsted-Bjerrum equation could be applied. Secondly, if the solution were too dilute, then optical density measurements would not be possible on the spectrophotometer available. In practice, the reaction solution used had an ionic strength of .031 initially and the optical density increased from .5 to .7 in the course of the reaction. In order that the reaction should proceed at a reasonable rate a temperature range of from 48 to 56°C had to be used, with the attendant difficulties of working at high temperatures. The reaction was measured over a period of from 6 to 8 hours during which time about two thirds of the reactants had undergone change. Practical details will now be given.

3. Experimental

(a) Preparation of materials

The potassium cis dioxalatodiaquochromiate used was obtained by dissolving the pure trans salt in water and warming to convert to the cis isomer.

"Analar" potassium oxalate was used which was found to be at least 99.8% pure as indicated by titration against a potassium permanganate solution which had been standardised directly with "Analar" sodium oxalate and indirectly against "Analar" potassium dichromate.

The ionic strength of the solutions was adjusted by addition of A.R. potassium nitrate.

It was determined spectrophotometrically that neither the potassium oxalate nor the potassium nitrate had a measurable optical density at 420 mμ in solutions of the concentrations used during the experiment.

(b) Procedure

Exactly 175 ml of a .00897M potassium oxalate solution was added to a 300 ml conical flask at room temperature. Then 25 ml of a .0628M cis dioxalatodiaquochromiate solution was buretted into a thin-walled glass bulb which was immediately sealed and placed inside the conical flask. The flask was stoppered tightly and clamped inside a thermostatically controlled water bath (See page 27) and then left to reach temperature equilibrium -- about an hour was found sufficient. At zero time the stopper was removed cautiously and the glass bulb broken with a glass rod.

This method ensured the thorough mixing of the reaction solutions at high temperatures, to give a mixture of concentration .00785M with respect to both reactants. Other methods for mixing these solutions at high temperatures, such as pipetting the hot solutions, were found to be unsatisfactory.

At each temperature, six reaction flasks were prepared and to five of these, increasing amounts of potassium nitrate were added with the potassium oxalate solution to increase the ionic strength as required.

Portions of the reaction solutions were removed at frequent intervals during the course of the reaction. The technique employed was as follows;

A 10 ml pipette was used to draw off samples from the reaction flasks and the liquid was allowed to trickle down a spiral, vertically fixed, water-jacketted condenser and collected in a test-tube. The solution took a few seconds to pass down the condenser and it emerged at room temperature (20 to 25°C). It was determined that negligible reaction occurred at this temperature for a period of up to 30 minutes. Two portions were pipetted. The first was used to rinse out the condenser, the test-tube and a spectrophotometer absorption cell, and the optical density at 420 mμ was measured on the second portion. The same absorption cell was used for all measurements. The time was noted from when half of the second portion had entered the condenser.

The readings for the six series of measurements at five different temperatures have been recorded in the Appendix (Table A10). The ionic strengths given were calculated from the familiar equation;

$$\mu = \tfrac{1}{2}\sum c_i . z_i^2$$

where c_i is the concentration (i.e. molality) of an ion of charge z_i.

If the reaction flasks were not almost completely immersed in the water bath, errors due to condensation on the cooler parts of the flask were observed. It was also found

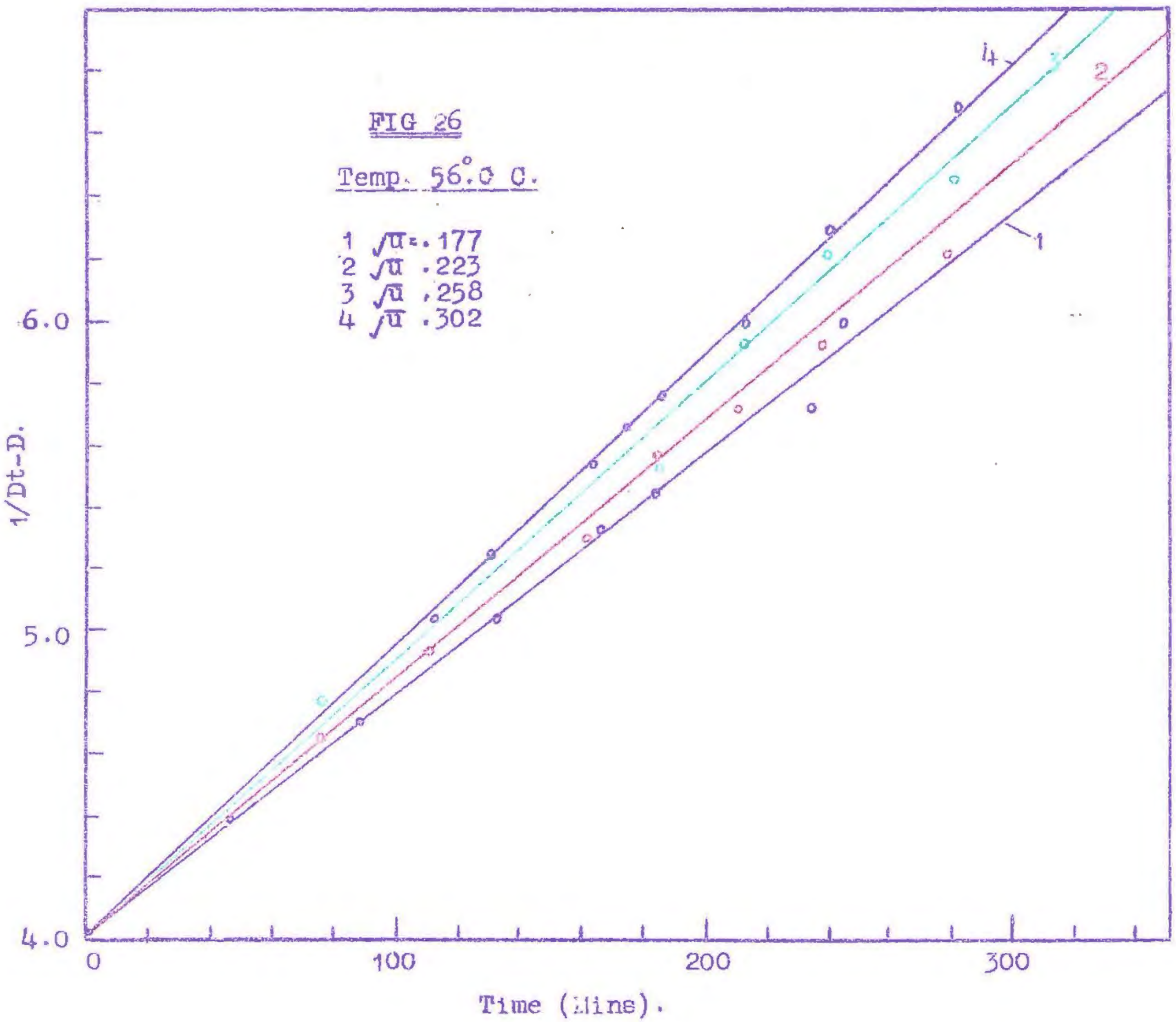


FIG 26

Temp. 56.0° C.

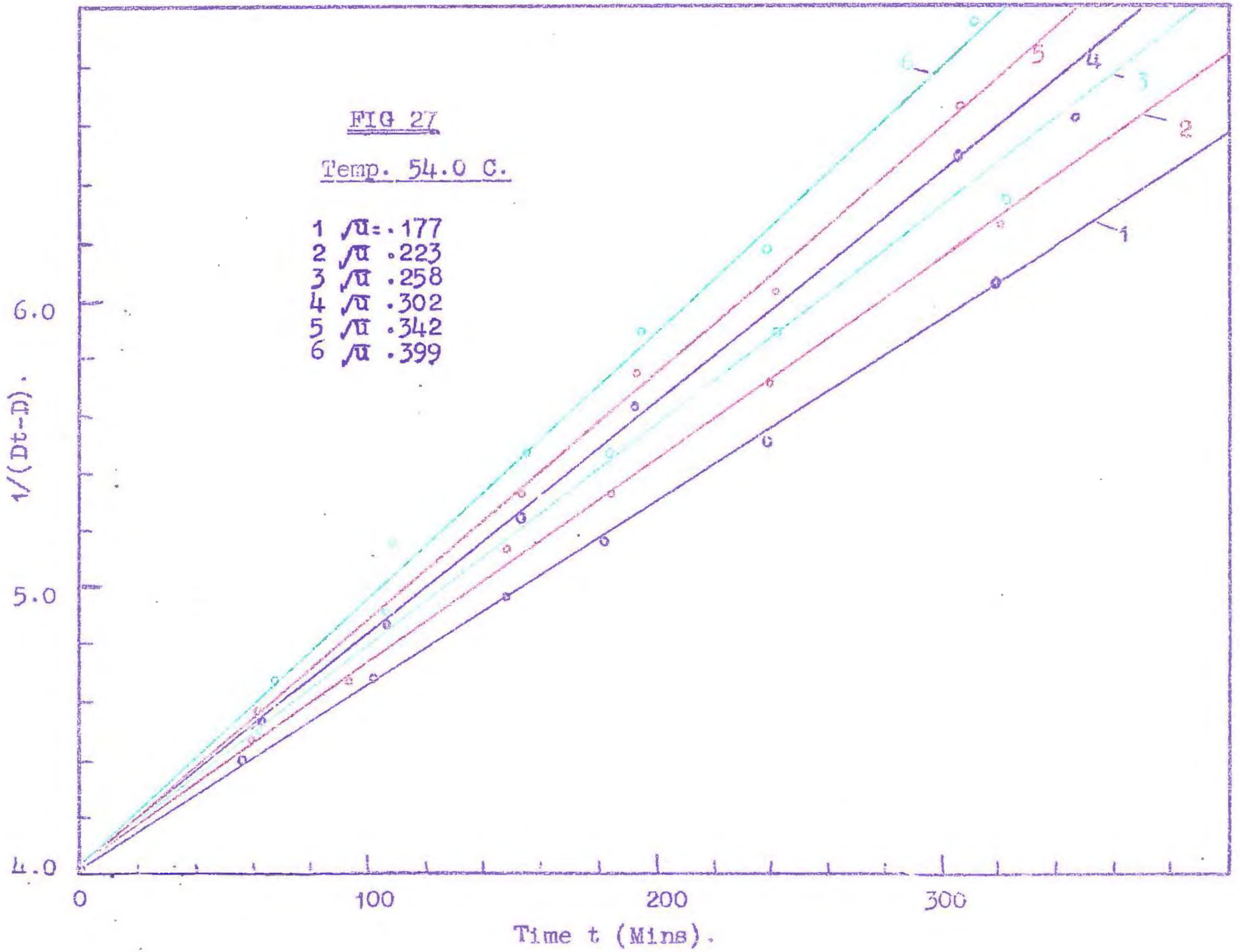


FIG 27

Temp. 54.0 C.

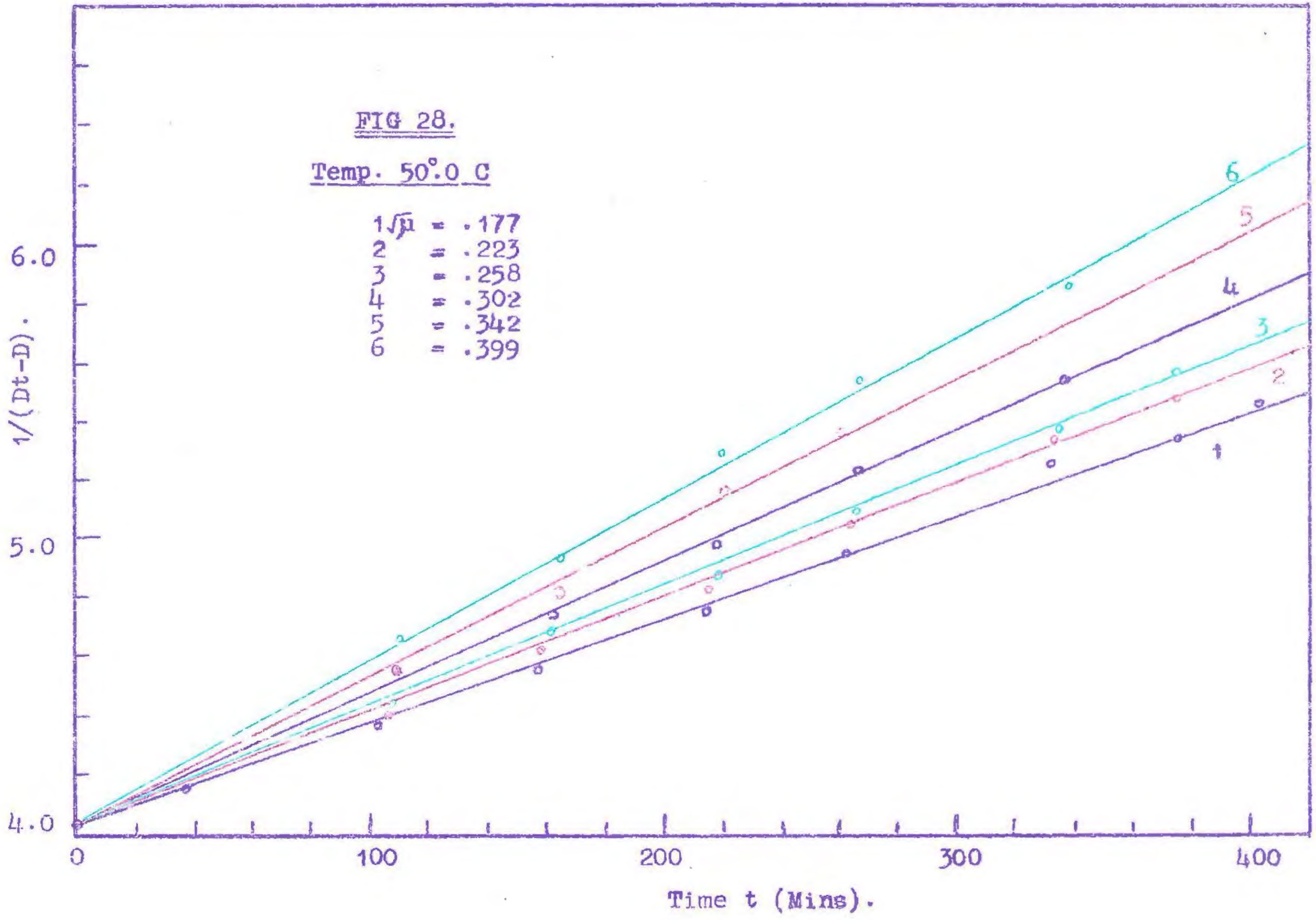


FIG 28.

Temp. 50°.0 C

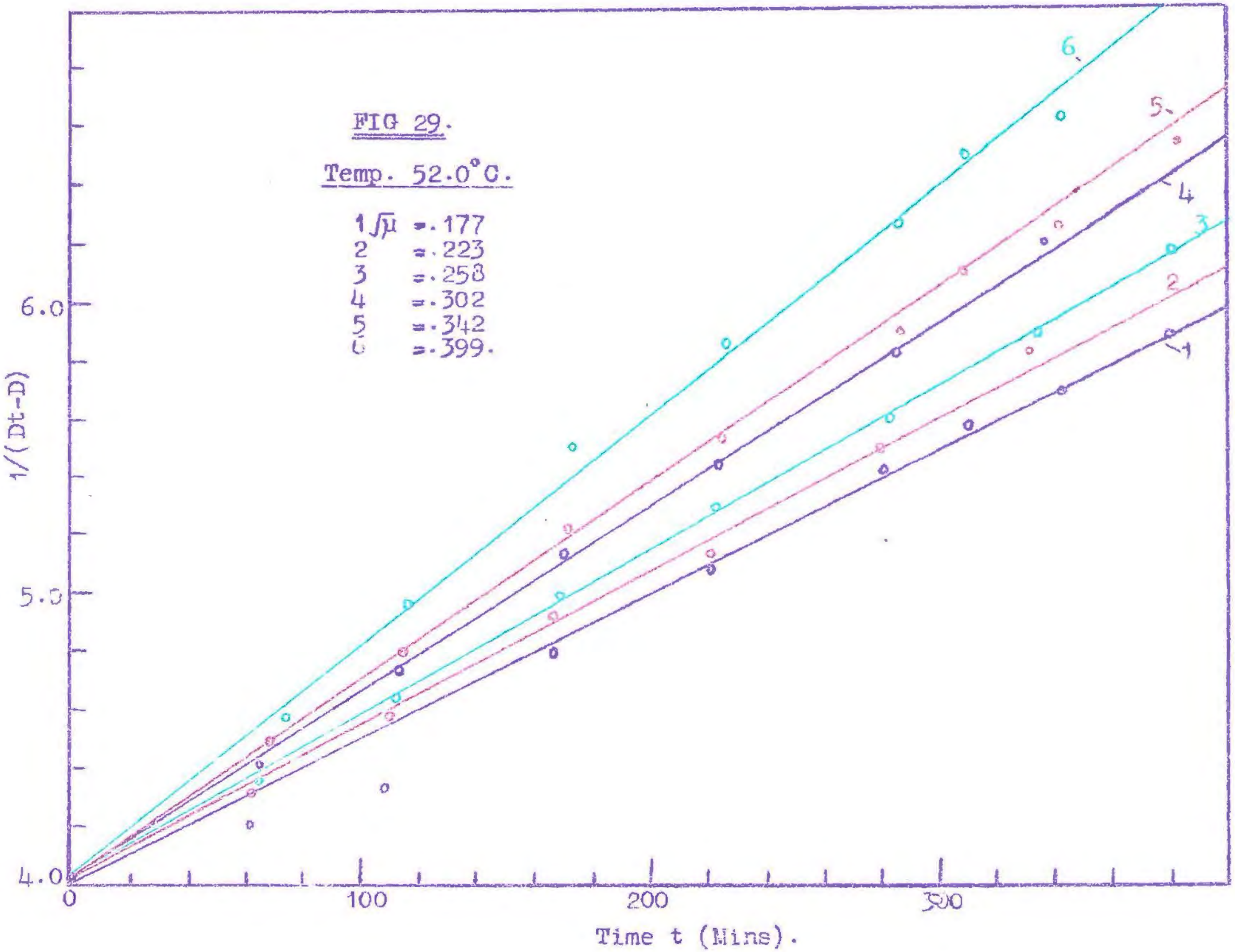


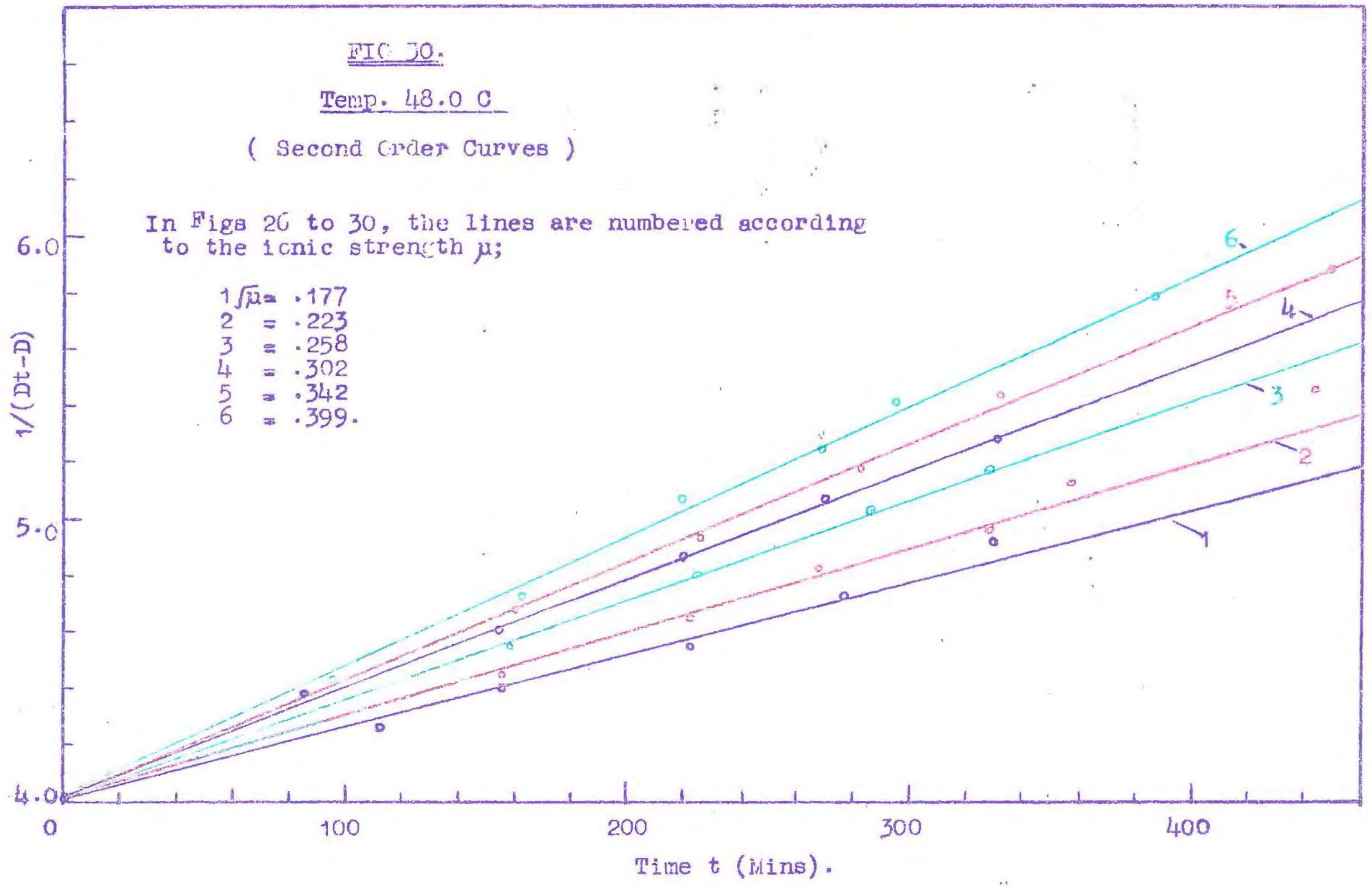
FIG 29.

Temp. 52.0°C.

FIG 30.

Temp. 48.0 C

(Second Order Curves)



In Figs 20 to 30, the lines are numbered according to the ionic strength μ;

$1 \ \sqrt{\mu} = .177$
$2 = .223$
$3 = .258$
$4 = .302$
$5 = .342$
$6 = .399.$

that evaporation losses occurred if the flasks were left unstoppered for too long a time during readings.

Values for Dt and Dd, the optical densities at 420 mμ of .00785M solutions of trioxalato and cis dioxalatodiaquochromiate respectively, were obtained from a large number of readings on solutions of the pure compounds, therefore, they were known with greater accuracy than the individual values for D.

The initial pH of the reaction solutions was 5.3.

4. Discussion

In Figs 27 to 30 the graphs showing the relation between 1/(Dt - D) and t at each of six different ionic strengths for four temperatures, are shown. In addition, Fig. 26 shows three series at a higher temperature (56°C).

Undoubtedly a linear relation exists, indicating that the reaction (7.1) above is of the second order. The points show considerable scatter, as is to be expected in view of the inaccuracies involved in the spectrophotometric method, especially as the reaction approaches completion, when the difference (Dt - D) becomes very small. The best straight lines through the points corresponding to each ionic strength have been obtained graphically, in preference to attempting a statistical derivation (47) which did not appear necessary in this preliminary experiment. All of the lines were drawn to pass through the initial point corresponding to $t = 0$, since this point is the same for all solutions and is known accurately.

It is apparent from these graphs that increasing the ionic strength causes an increase in the slopes of the lines due to an increase in the velocity constants. Values for the velocity constants (k) were calculated for each of these lines using the equation;

$$k = \left(\frac{Dt - Dd}{C.60}\right)(\text{slope})$$

(See equation (7.10))

The factor 60 is necessary since k is recorded in $(\text{secs})^{-1}(\text{moles/litre})^{-1}$ while on the graphs t is plotted in minutes.

Whence $k = 0.5287$ (slope)

All the slopes and values for k calculated by this means are recorded in Table All in the Appendix.

Now the variations in the velocity constant of a reaction in solution due to physical changes in the solution conform to the Brønsted-Bjerrum equation in simple cases.

Consider a reaction in solution between ionic or molecular species A and B to give resultants C and D. This reaction may be considered to proceed by way of an activated complex M:

$$A + B \rightarrow M \rightarrow C + D \quad ,\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7.11)$$

Then for this reaction, the general form of the Brønsted-Bjerrum equation is:

$$k = k_o\ (f_A f_B/f_M) \quad \ldots\ldots\ldots\ldots\ldots(7.12)$$

where k is the velocity constant of the reaction and k_o the value of this constant at infinite dilution. The terms "f" are the activity coefficients with reference to the solution at infinite dilution as standard state (57).

For a reaction involving ions, the activity coefficients "f" can be obtained by the Debye-Hückel treatment in terms of the ionic strength and other physical properties of the solution and its constituents. The Brønsted-Bjerrum equation thus becomes:

$$\log_{10}k = \log_{10}k_o + \frac{2A'Z_AZ_B}{2.303}\sqrt{\mu} \quad ..(7.13)$$

where Z_A and Z_B are the charges on the ions A and B respectively. The constant A' is given by:

$$A' = \frac{N^2\ e^3\ (2\pi)^{3/2}}{(DRT)^{3/2}\ (1000)^{\frac{1}{2}}}$$

where N is Avagadro's Number

e is the electronic charge

D is the dielectric constant of the medium

R is the Gas Constant

From equation (7.13) it is apparent that $\log_{10}k$ should vary linearly with $\sqrt{\mu}$ for a given reaction, provided that the solutions used obey the conditions for which the Debye-Hückel theory holds. Now although this theory can generally be used only for solutions having very low ionic strengths, it has been found that, for certain reactions, the graph of

$\log_{10}k$ against $\sqrt{\mu}$ is linear up to values of $\sqrt{\mu}$ equal to nearly 0.3 (56). For this reason, an attempt was made to apply equation (7.13) to the data recorded above, although it was recognised that the usual concentration limit for the Debye-Hückel approximations had been exceeded.

From equation (7.13) the product of the ionic charges Z_AZ_B can be obtained if the constant A' is known.

In Fig. 31 the graph of $-\log_{10}k$ against $\sqrt{\mu}$ is plotted for the data recorded in Table A 11 in the Appendix.

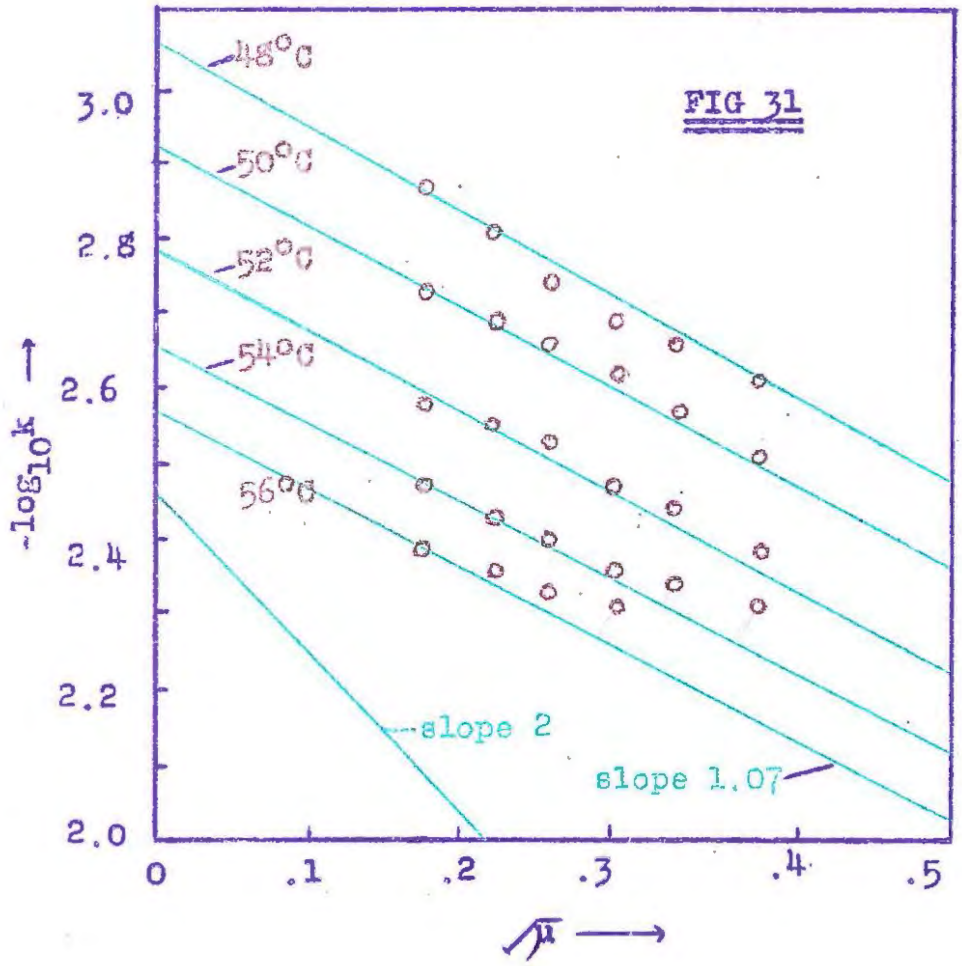


FIG 31

If it be assumed that the rate determining step of the reaction between <u>cis</u> dioxalatodiaquochromiate and oxalate is the combination of the two singly charged <u>negative</u> ions $[Cr(C_2O_4)_2(H_2O)_2]^-$ and $(COO)H^-$, then for this reaction;

$$Z_AZ_B = +1$$

The value for A/2.303 at 25°C is 0.509 for an infinitely dilute solution for which the dielectric constant D is 78.54 (57). By using the value 69.94 at 50°C, obtained from tables (58), the value for A/2.303 was calculated as 0.537; whence by substitution for A/2.303 and Z_AZ_B in equation (7.13) we have:

$$\log_{10}k = \log_{10}k_0 + 1.07\sqrt{\mu}$$

Using the value 1.07 for the slope, lines have been drawn through the first points of each series in Fig. 31. It was calculated that the change in dielectric constant D over the range from 48 to 56°C was too small to affect the slope appreciably, and in any case, the value for D is an approximation since it applies to infinite dilution.

It is apparent that, although departures are noticeable at the higher temperatures and for large values of $\sqrt{\mu}$, the points correspond roughly to the calculated lines.

If this is really the case, and if the Brønsted-Bjerrum equation is really applicable to these data, then it proves that the assumption made above, namely, that the rate determining step involves binoxalate ions $(COO)H^-$ and <u>cis</u> dioxalatodiaquochromiate ions, is correct.

However, it is very important to consider the limitations imposed on any interpretation of these results.

In view of the approximations in the derivation of equation (7.13), it may well be that the correspondence of the points in Fig. 31 with the theoretical slope is fortuitous, and that at values of $\sqrt{\mu}$ lower than those which had to be used , the points may lie on a line of slope 2. In other words, the reaction may actually involve the oxalate ion $(COO)^{=}$ and the cis dioxalatodiaquochromiate ion, for which $Z_A Z_B$ is + 2. A line with slope 2 has been drawn in the lower left corner of Fig. 31.

There is, however, no possibility that the reaction could involve a neutral molecule, for example $(COOH)_2$, since in this case $Z_A Z_B$ would be zero and the velocity constant would be independent of the ionic strength of the solution. Also, reactions involving positive ions do not seem possible in this case..

In Chapter 6 it was seen that reaction between oxalate and dioxalatodiaquochromiate goes to completion only when the solution approaches neutrality. From this it would appear that the reaction must involve oxalate ions $(COO)_2^{=}$ which are present in greater amount as the pH is increased However, it must be remembered that, even at pH 7, some binoxalate ions $(COO)H^{-}$ are present in equilibrium so that this fact cannot be used to determine which ion is involved in the rate determining step.

The correspondence of the above data with the Arrhenius equation was then investigated. The Arrhenius equation is;

$$k = A.e^{-\frac{E}{RT}}$$

$$\text{or} \quad \log_{10}k = \log_{10}A - E/(2.303RT) \quad \ldots\ldots\ldots\ldots(7.14)$$

E being the "experimental activation energy" of the reaction and A is a constant depending on steric and other factors; T is the absolute temperature and R the Gas Constant.

In order to test the applicability of this equation, the values of $-\log_{10}k$ were plotted against 1/T for the series at each of the three lowest ionic strengths at each temperature. (See Fig. 32).

Values for $-\log_{10}k_o$ were obtained by extrapolation from the calculated lines in Fig. 31. These are recorded in Table 13 below:

TABLE 13

Temperature	$\log_{10}k_o$
56°C	-2.57
54	-2.66
52	-2.78
50	-2.92
48	-3.05

These values have also been plotted in Fig. 32.

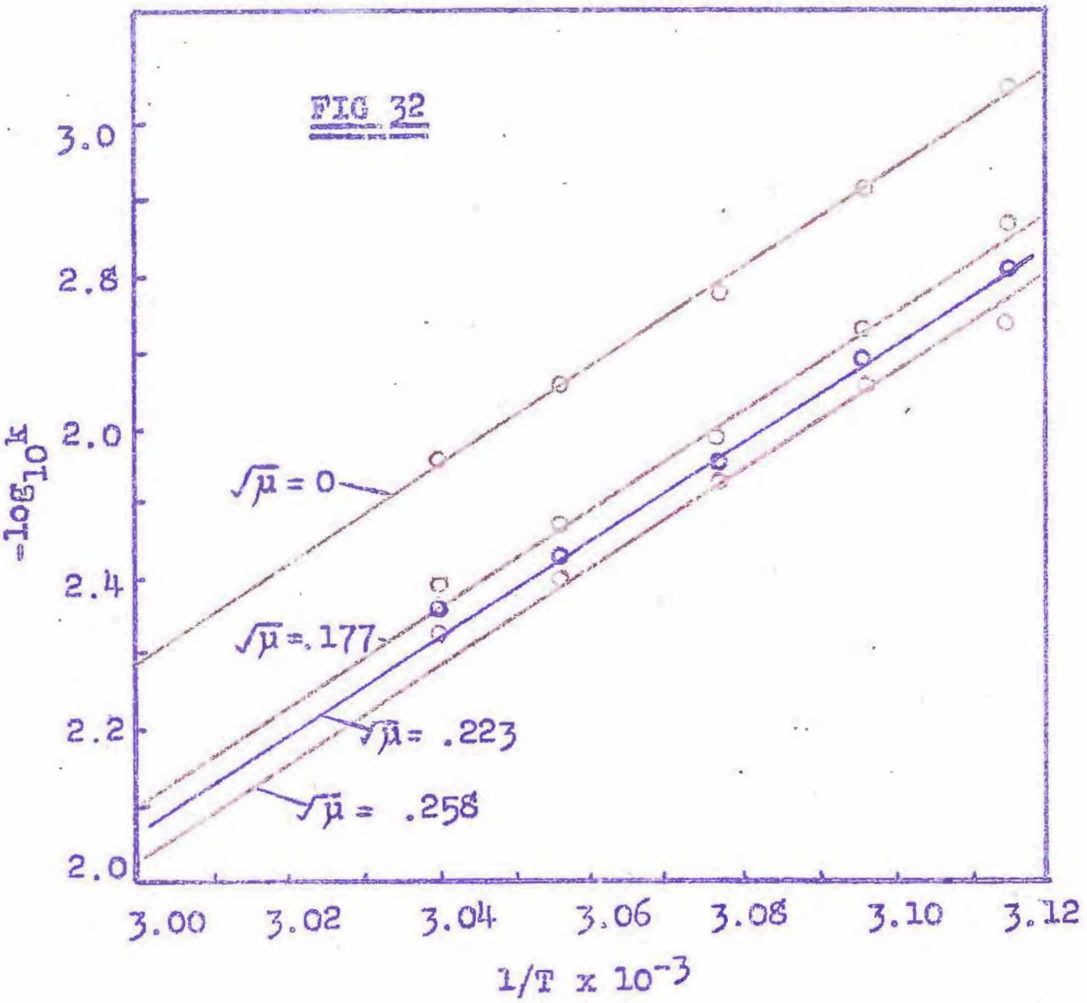


FIG 32

It is considered that the agreement with the Arrhenius equation is reasonable over the limited temperature range employed. From the lines, values for E and A were obtained in each case and are recorded in Table 14:

TABLE 14

$\sqrt{\mu}$	E (cals/mole)	$\log_{10}A$	A
0	3.03×10^4	22.8	6.3×10^{21}
.177	3.03×10^4	22.6	4.0×10^{21}
.283	2.99×10^4	22.2	1.6×10^{21}
.258	3.38×10^4	22.2	1.6×10^{21}

All these values must be regarded as approximate, especially those for infinite dilution. The values for E are open to less doubt than those for A since the former show less variation with ionic strength.

It is suggested that a more extended investigation of the kinetics of the reaction between oxalate and cis dioxalatodiaquochromiate would be of considerable interest.

5. Summary

It has been established that the reaction between oxalate and cis dioxalatodiaquochromiate proceeds by way of a second order mechanism to form the trioxalatochromiate.

The primary salt effect has been studied for this reaction and the application of the Brønsted-Bjerrum equation suggests that the rate determining step involves the cis dioxalatodiaquochromiate ion and either the binoxalate or the oxalate ion.

Values for the Arrhenius constants A and E have been obtained at a number of ionic strengths and tentative values for infinite dilution have been obtained by extrapolation as;

$$k_o = 6 \times 10^{21} . e^{-\frac{30\text{Kcals}}{RT}}$$

for molar quantities at 50°C.

Chapter 8

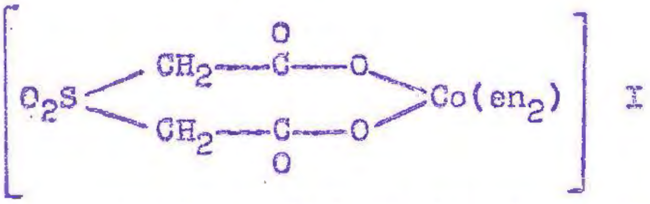
AN INVESTIGATION INTO THE REACTIONS BETWEEN THE cis DIOXALATODIAQUOCHROMIATE ION AND CERTAIN DIBASIC ORGANIC ACID GROUPS

1. Introductory

As a result of the experiments described in previous chapters, a considerable amount of information has been obtained on the properties of the dioxalatodiaquochromiate ion. It has been shown that the oxalate groups do not leave the complex easily in neutral or moderately acidic solutions, and that the two coordinated water molecules can be substituted by another oxalate under certain conditions.

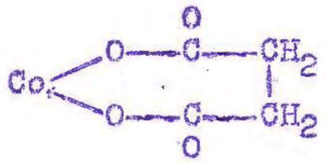
It was thought that the dioxalatodiaquochromiate ion provided an ideal system for studying the coordinative properties of other groups capable of replacing the water molecules.

The problem of the coordination of dibasic acids is of considerable importance. It is known for certain that the oxalate group coordinates with chromium(III) to form a five-membered ring (5) and that the malonate group forms a six-membered ring with cobalt(III) (59). The investigation of the complexes formed by higher dibasic acids has been extremely difficult. Werner tried unsuccessfully to isolate crystalline complexes containing succinate and other dibasic groups and in all cases he obtained only glassy solids or syrups. For this reason, he expressed the opinion in 191 (60) that dibasic acids with more carbon atoms than malonic acid were incapable of forming rings. Later, Price (61) prepared a cobalt complex which, it was proposed, contained an eight-membered ring with the structure;

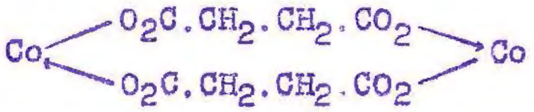


in which "en" represents the ethylene diamine group.

Following up this investigation, Price and Duff (62) isolated a series of succinato derivatives having the general formula; $[Co(en_2)(C_4H_4O_4)] X_3$, where X is a univalent anionic radicle. It was proposed that these compounds contained seven-membered rings i.e.



This structure has been accepted by Sidgwick (63) but it should be noted that it was obtained from the analytical figures alone. Since the molecular weights have not been determined, there is the possibility the these complexes might be dimers of the form;



In 1941, Holland (64) carried out a series of tanning experiments designed to investigate the effect of various dibasic organic acids on the tanning properties of chrome sulphate liquors. From the results of these experiments, Holland made certain postulates concerning the structures of the chromium complexes formed. Thus, he suggested that the malonate group formed a stable six-membered ring; that succinate, fumarate, adipate, suberate and phthalate were capable of forming dimers "in a manner rather similar to olation", but that maleate, owing to the cis position of the carboxyl groups, was incapable of forming a dimer. No evidence in favour of seven-membered or larger rings was obtained.

The coordinative properties of the phthalates have received attention by Plant (16). The methods used consisted in allowing phthalate solutions to react with solutions of 33% basic chrome sulphate, and various physical measurements were then performed on the resulting complicated mixtures. It was found that phthalate could displace coordinated sulphate groups, but a gelatinous precipitate was obtained when the molar ratio of phthalate to Cr_2O_3 exceeded unity.

Recently, Shuttleworth (65) has investigated the action of various dibasic acids and their salts on chrome alum in solution, using conductometric titrations. He found evidence that the malonate group formed a six-membered ring with chromium(III) and that maleate formed a ring with seven atoms. In experiments with succinates, fumarates and phthalates, he found no evidence for ring formation, and suggested that, in the case of these acids and also in the case of higher dibasic acids, the acid group links together series of chromium atoms to form less soluble complexes, which will obviously be dimers or polymers.

It was decided to attempt to obtain more information concerning the structures and properties of coordinated dibasic acid groups by the methods which had been used in the case of the oxalate group (Chapter 6), namely, by a spectrophotometric and potentiometric study of the reaction between the various dibasic acid groups and the cis dioxalatodiaquochromiate ion in dilute solution. Accordingly, the following dibasic acids were selected for study: malonic, succinic, adipic, fumaric, maleic and phthalic. On account of their different molecular formulae and stereo-configurations, it was hoped that different spectrophotometric and potentiometric curves would be obtained which would shed some light on the structures of the complex ions formed.

In Chapter 6 it was established that for the complete penetration of oxalate into the cis dioxalatodiaquochromiate complex, a final pH of nearly 7 was necessary. However, in Chapter 5 it was seen that at pH values above 6 the effects of olation are noticeable for dioxalatochromiate solutions. These were not observed during the reaction with oxalate to form the trioxalatochromiate, presumably because of the powerful coordinative properties of this ion, but preliminary studies on the coordination of other dibasic acids showed that conditions favouring olation would have to be avoided if possible if the changes due to the coordination of the acid groups were to be distinguishable from the effects of olation. For this reason the solutions of cis dioxalatodiaquochromiate and the organic acid were adjusted to a pH of about 6.3 before reaction. It has been shown (Chapter 5 Section 4) that at this pH the cis dioxalatochromiate solution olates on boiling to the extent of not more than 10%, and it was determined that no change in the light absorption occurs under these conditions.

2. The Reaction between the Malonate Group and cis Dioxalatodiaquochromiate

(a) Reactions in Dilute Solution

Malonic acid is the next homologue after oxalic in the dibasic acid series and so it was considered first.

A solution of potassium cis dioxalatodiaquochromiate was prepared by weighing out a known quantity of the pure trans salt, dissolving in water and ageing the solution to convert to the cis isomer. An equimolar quantity of pure malonic acid was added and the pH adjusted to 6.3 with potassium hydroxide. The solution was then boiled for more than an hour, by which time equilibrium was reached. When cool, it was made to standard volume such that the concentration of each constituent was .00921M.

The absorption spectrum was measured on a portion of this solution and the points near the maxima have been plotted in Fig. 33, Curve C. The data for the complete curve are recorded

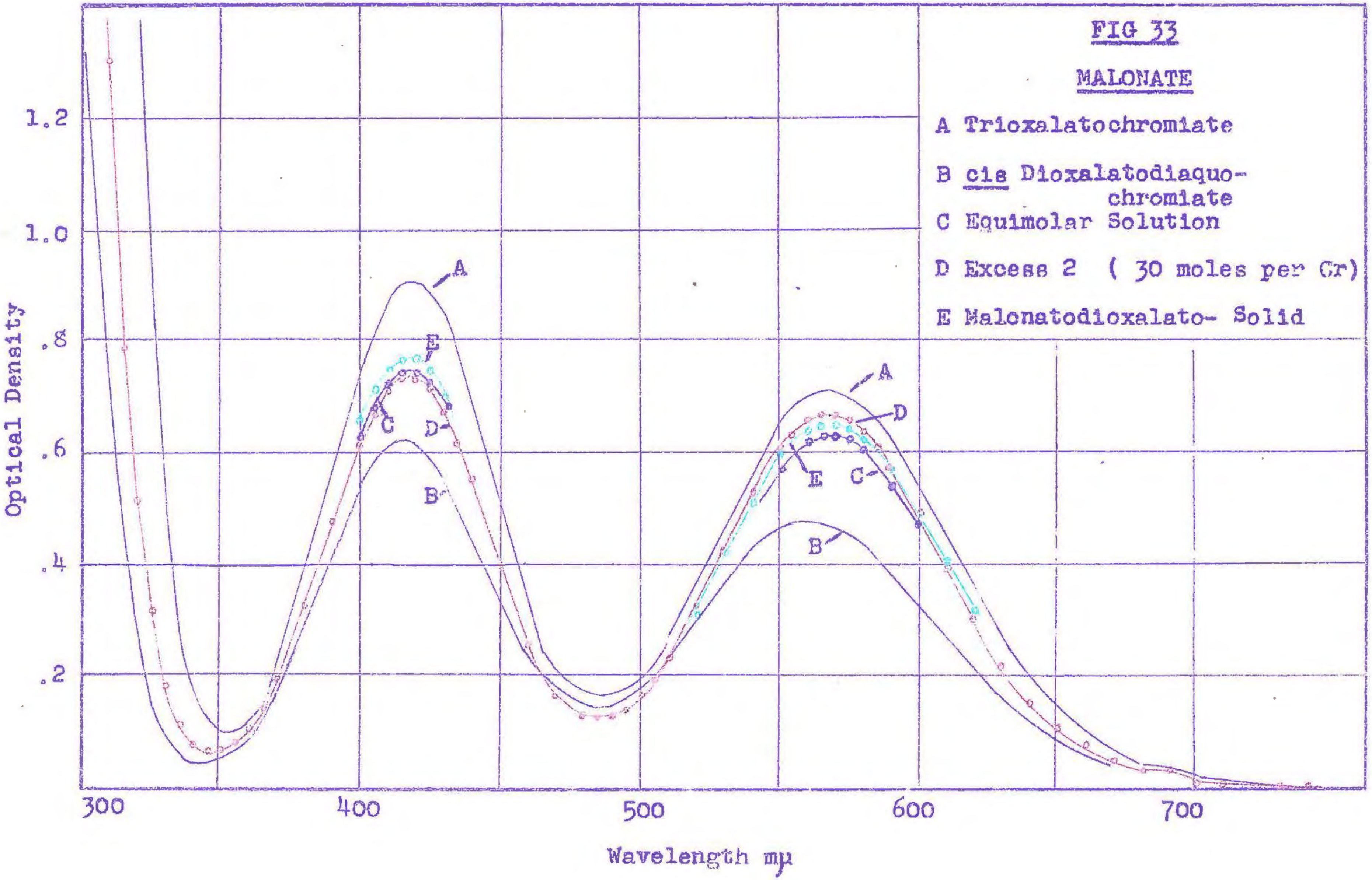


FIG 33

MALONATE

later in the Appendix Table A 12. The curves for trioxalato- and cis dioxalatodiaquochromiate at the same concentration are also shown in Fig. 33 (Curves A and B).

The considerable increase in absorption at the maxima over that of pure dioxalatodiaquochromiate must be due to the penetration of malonate into the chrome complex since the effects of olation have been largely excluded. It was determined that neither malonate nor any of the other groups discussed in this chapter absorbed light in the spectral region considered.

The results of acid and alkali potentiometric titrations on aliquots of the boiled solution are illustrated in Fig. 34 Curve (a). It is observed that most of the aquo groups are no longer titrating and that the pH after boiling was 6.7. The curve is rather like that in Fig. 19, Curve (b) (Chapter 6) showing the titration of a solution containing trioxalatochromiate with a small amount of unreacted dioxalatodiaquo complex and oxalic acid.

An approximate estimate of the percentage of dioxalatodiaquochromiate still titrating in Curve (a) was obtained by measuring the alkali required to raise the pH from the end point at 8.27 to that at 10.6. This method has already been discussed in Chapter 6. An estimate of the amount of free malonate titrating below pH 6 was obtained in a manner similar to that used for free oxalate, also described in detail previously. In brief, a titration curve for a standard

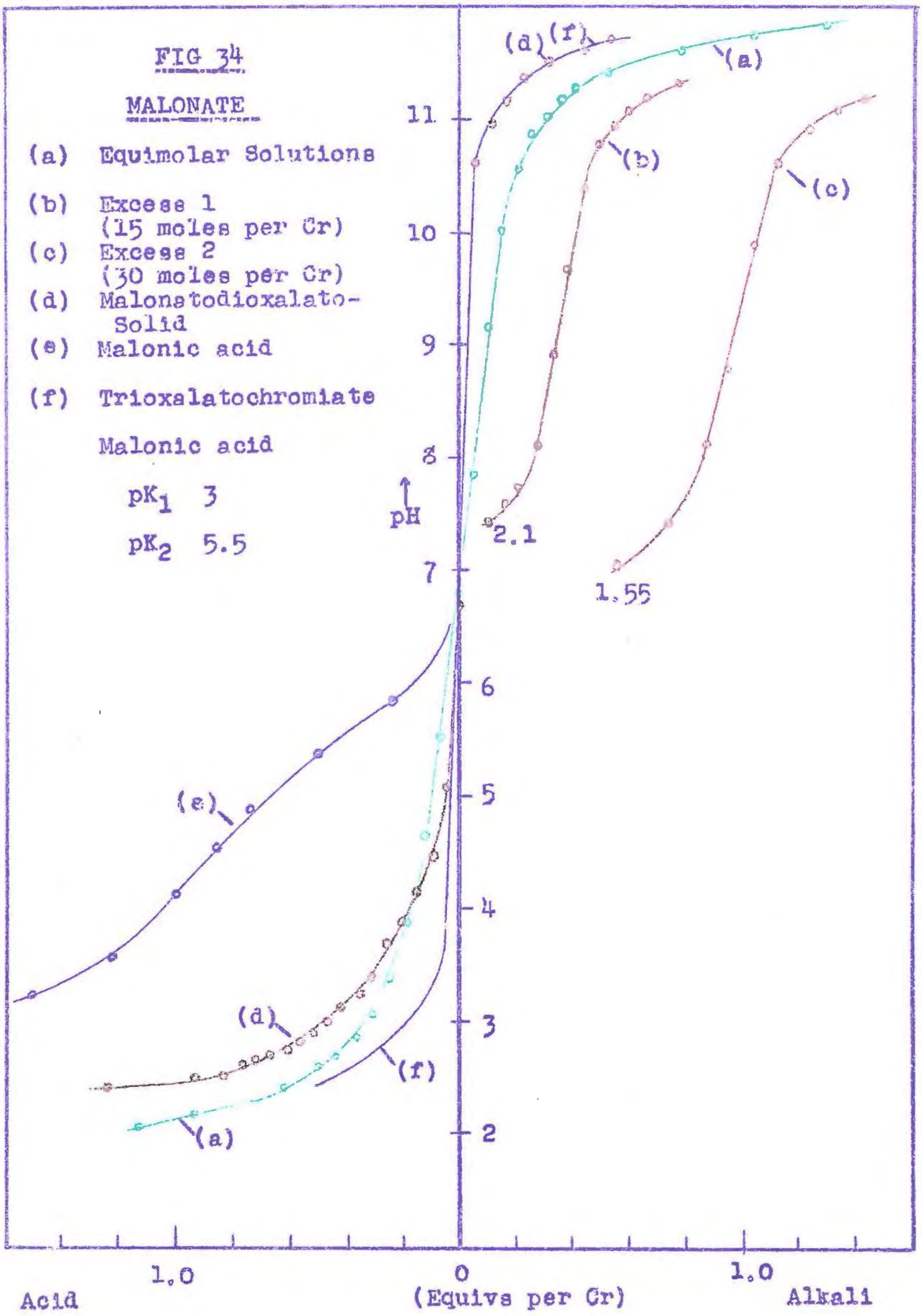


FIG 34

MALONATE

malonate solution, containing an amount of trioxalatochromiate equivalent to that used for the blank titration, was measured and is shown in Fig. 34, Curve (e). For this curve, the acid units must be read as equivalents per mole of malonate. From this curve the degree of neutralisation of malonic acid at a number of arbitrarily selected pH values was calculated and these were used to correct the quantities of alkali required to titrate the unknown solution to the same pH values, to give the amount of malonate present. The average results are recorded in Table 15 below. It should be noted that although malonic acid is decomposed by heat, the work of Fairclough (66) shows that neither the $(C_3H_2O_4)^=$ ion nor the $(C_3H_2O_4)H^-$ ion is decomposed appreciably in aqueous solution at 100°C. Thus it may be assumed that at the pH used (6.3) no decomposition occurred.

TABLE 15

Solution	Free Malonate	Unreacted Dioxalato-	pH		Opt. Dens.	
			before	after	420	560 mμ
Equimolar	14%	15%	6.3	6.7	.741	.621
Excess 1 (15 moles)	-	20%	6.3	6.3	.725	.648
Excess 2 (30 moles)	-	18%	6.3	6.3	.732	.657
Solid	?	0	6.3	6.3	.768	.638

The amounts of dioxalatodiaquochromiate and free malonate should be the same when equimolar quantities are used if these substances combine in a 1:1 ratio. This is evidently the case, approximately.

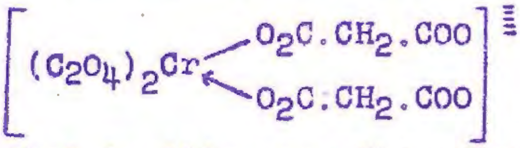
Since these results showed that the reaction had not gone to completion, an attempt was made to achieve this by using an excess of malonate.

Two solutions were prepared, the first containing 15 and the second 30 moles of malonate per mole of potassium cis dioxalatodiaquochromiate. After boiling for more than an hour, these solutions were cooled and made to standard volume such that the chromiate concentration was .00921M.

The absorption spectra of the solutions were measured and, since they were very similar, only one, that with 30 moles in excess is given, Fig. 33, Curve D. The readings for both series are recorded in the Appendix Tables A 13 and A 14.

From Curves C and D in Fig. 33, it is apparent that the absorption spectra for equimolar and excess quantities of malonate are slightly different. This is seen more clearly from the optical density readings at 420 mμ and 560 mμ recorded in Table 15 above. These readings are near the maxima, and it is seen that the equimolar curve is highest at the 420 mμ maximum, while the curves for the excess solutions are both above this at wavelength 560 mμ.

These differences in the shapes of the curves can be explained on the assumption that a different type of complex is formed when a large excess of malonate is used. For example, in the equimolar solution each malonate group might coordinate at each end while for the solutions with excess malonate, each malonate group might occupy only one coordination position leaving one carboxyl group free for each malonate coordinating. The latter possibility assumes a complex of the form:



$$\left[(C_2O_4)_2Cr\begin{array}{l}\diagup O_2C.CH_2.COO\\ \nwarrow O_2C.CH_2.COO\end{array}\right]^{\begin{smallmatrix}-\\-\\-\\-\\-\end{smallmatrix}}$$

It will be noted that in this case the molar ratio of malonate in the complex to chromium would be 2:1.

Alkaline potentiometric titrations were then performed on aliquots of the excess solutions. These are shown as Curves (b) and (c) in Fig. 34. These curves are only of interest above p^H 8 because of the titration of the large amount of malonate below this value. The alkali scale has been displaced for these titrations; (b) starts at 2.1 and (c) at 1.55 equivalents of alkali per Cr. Approximate values for the percentage of dioxalatodiaquochromiate remaining in solution are recorded in Table 15 above. These figures are probably not very reliable, but it is clear that some dioxalatodiaquochromiate still remained in solution in these cases.

Since no further information could be obtained from the reactions in dilute solution, attempts were made to isolate a malonato derivative.

(b) Attempts to Prepare Potassium Malonatodioxalatochromiate

To a 50% w/v solution of potassium cis dioxalatodiaquochromiate made as usual by dissolving the trans salt and warming, an equimolar quantity of potassium malonate was added. The solution was then boiled and evaporated to a small volume. On being left overnight, a crystalline mass settled to the bottom of the vessel. This was filtered off and analysed for chromium, potassium, oxalate, and non-coordinated water; the latter by heating at 100°C to constant weight. It was found that the analytical figures differed considerably from those expected for a complex containing one malonate and two oxalate groups per Cr, but they agreed remarkably well with those for potassium trioxalatochromiate trihydrate. The figures are:

TABLE 16

Found		Molar Ratio	Theoretical	
			(1)Trioxalato	(2)Malonato
Cr	10.63%	1.00	10.68%	11.58%
K	24.13%	3.02	24.07%	26.11%
(C_2O_4)	52.6%	2.92	54.18%	39.17%
H_2O	10.13%	2.42	11.08%	0

The theoretical figures have been calculated from the formulae:

(1) $K_3[Cr(C_2O_4)_3]\ 3H_2O$

(2) $K_3[Cr(C_2O_4)_2(C_3H_2O_4)]$

The absorption curve of the crystalline solid was measured from 300 to 700 mμ for a solution containing .07% Cr_2O_3 and it was almost identical with the curve for potassium trioxalatochromiate at the same concentration of Cr_2O_3. A microscopic examination of the crystals showed that they were of the same form as those of the trioxalatochromiate; that is, needle-shaped. In addition, the acid and alkali pH curves were the same as those recorded in Chapter 3 for the trioxalatochromiate. The potassium dioxalatodiaquochromiate used in the preparation was analysed carefully and found to contain no trioxalatochromiate and the malonic acid used was pure.

From the above data it was concluded that, during the preparation, a rearrangement occurred with the production of the trioxalatochromiate ion. The same phenomenon was observed with each of the other dibasic acids used in this chapter. In each case the yield of crystals obtained on allowing the concentrated solution to stand was about 20 to 30% on the weight of the reactants. The evaporation of the mother liquor produced a non-crystalline mass or syrup. In most cases the solutions were fairly acidic before boiling but it was found that for the succinate, adjusting the pH to nearly 7 still resulted in the production of a certain amount of trioxalatochromiate.

After a number of further unsuccessful attempts, a solid was prepared which contained a negligible amount of trioxalatochromiate. This was achieved by adding to an excess of a solution of almost neutral potassium malonate, a strong solution (50% w/v) of potassium cis dioxalatodiaquochromiate and then adjusting the pH to 6.3 with potassium hydroxide solution. The solution was boiled for about 30 minutes; cooled and an equal volume of absolute alcohol added. A viscid, dark-blue liquid separated out as globules and sank to the bottom of the vessel. The supernatant liquid was quickly decanted and the blue syrup washed several times with alcohol. The vessel was then placed in an oven at 90°C for two days, during which time the liquid dried to an amorphous solid which was easily pulverised. The powder was found to be extremely hygroscopic. The analytical figures for this solid were:

	Found		Theoretical
	Percentages	Molar Ratio	Percentages
Cr	10.40%	1.00	11.58%
K	27.19	3.48	26.11
$(COO)_2$	36.2	2.01	39.17

The theoretical figures were calculated from the empirical formula $K_3[Cr(C_2O_4)_2(C_3H_2O_4)]$

From this table, the molar ratio of Cr to oxalate indicated that about .01 moles per Cr of excess oxalate over that required for a dioxalato derivative were present, so that the solid contained only a small amount of trioxalatochromiate. Nevertheless, it appears that a certain amount of other impurity was present. In order to attempt to remove this, the solid was dissolved in water, reprecipitated with alcohol and separated as before. The analytical figures showed that after reprecipitation, the Cr and K content had increased, while an increase in the oxalate percentage indicated that more trioxalatochromiate had become concentrated in the precipitate. Consequently, this second product was discarded and tests were performed on the original solid to determine its properties and the nature of the impurity.

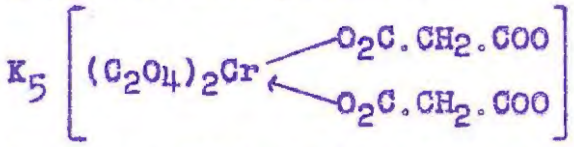
A solution of the solid was prepared containing .07% Cr_2O_3. The fact that the optical density at a number of wavelengths remained constant for at least two days indicated that the solution was stable over this period. The stability to boiling was then investigated by refluxing some of the solution until no change in optical density was observed. The final measurements at 420 mμ and 570 mμ were:

	Optical Density	
	420 mμ	570 mμ
Before boiling	.760	.643
After boiling	.751	.638

The small decrease in absorption is an indication that some decomposition had occurred on boiling, although it is not certain whether the malonato derivative or an impurity underwent decomposition. However, it appears that most of the malonato complex is reasonably stable.

Acid and alkali potentiometric titrations were next performed on solutions made by dissolving weighed amounts of the solid. The curve is shown in Fig. 34 Curve (d).

Above pH 7 this curve is identical with the trioxalatochromiate blank, Curve (f), indicating the absence of weak acid groups and hence of the dioxalatodiaquochromiate complex. Below pH 7 a certain amount of a moderately strong acid group was titrating. The curve in this region has a shape different from the curves showing the titration of relatively large quantities of free malonate (Curves (a) and (e)) and, particularly in view of the weak buffering at pH 5.5, it may be inferred that a negligible amount of free malonate was present in this case. Conversely, since there still appears to be a considerable amount of buffering between pH 3.0 to 4.5, it would appear that a titratable carboxyl group with a pK value of this order of magnitude was present in the solid. For example, the potassium salt of the dimalonato complex suggested earlier may have been present:

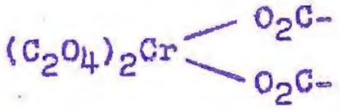


$$K_5\left[(C_2O_4)_2Cr\begin{matrix}\diagup O_2C.CH_2.COO\\ \diagdown O_2C.CH_2.COO\end{matrix}\right]$$

This is born out to some extent by the fact that the malonato solid contained an excess of potassium over that required for the tripotassium salt, as indicated by the analytical figures. However, this cannot be taken as conclusive since the analytical figures show that some other impurity was also present.

The absorption spectrum for a solution of the solid having a concentration of .07% Cr_2O_3 is shown in Fig. 33, Curve E.

In view of the heterogeneous nature of the products, no further deductions can be made at this stage, but it is interesting to speculate on the reasons for the appearance of the trioxalatochromiate when concentrated solutions are used. It is obvious that before oxalate can be liberated from a dioxalatodiaquochromiate ion, one or both of the water molecules must be replaced by malonate, since the dioxalatochromiate ion does not split up on boiling below pH 8 or not until about pH 1 (See Chapter 6). If both water molecules were replaced, a structure of the type:



$$(C_2O_4)_2Cr\begin{array}{l}\diagup O_2C-\\ \diagdown O_2C-\end{array}$$

would result. No assumptions need be made about the manner in which the carboxyls are attached since either a chelate ring or a linear dimer appears to be possible. In either case, the arrangement of carboxyl groups about the chromium atom is the same as in the trioxalatochromiate ion, the difference being that one of the carboxyl pairs is not joined directly. Now malonate combines with the dioxalatodiaquochromiate to form a complex which is of the same order of stability as, or only slightly less stable than, the trioxalatochromiate. This is shown by the fact that on boiling a dilute solution of the malonate derivative, very little decomposition occurred, which may, in fact, have been due to an impurity. Also, it should be noted that the reaction between equimolar quantities of malonate and dioxalatodiaquochromiate proceeds to almost the same extent as the reaction between oxalate and the dioxalatodiaquochromiate complex. Now since the trioxalatochromiate ion decomposes in acid solution at the boil, it may be assumed that the malonato ion will behave in a similar manner. Decomposition of the trioxalatochromiate ion involves the liberation of any one of the three oxalate groups, but for the malonatodioxalatochromiate ion, there is a choice between oxalate and malonate. The mathematical probability of an oxalate group being released is increased by the fact that the oxalates hold four of the six coordination positions. Thus the ratio of the amount of oxalate to malonate released under acid conditions will be $2(S_1/S_2)$, where S_1 and S_2 are functions of the stability of the malonato and oxalato groups respectively.

When an oxalate is released it is available for combination with a dioxalatodiaquochromiate ion to form the trioxalatochromiate and this may be assumed to be formed to a certain extent even under acid conditions.

Now when malonate and cis dioxalatodiaquochromiate are boiled together in dilute solution, the titration data, from Fig. 34, are inconsistent with the presence of a large amount of trioxalatochromiate in solution. This follows from the fact that the percentage of free malonate agrees with that of free dioxalatodiaquochromiate, after boiling. This does not, of course, exclude the possibility of there being a small amount of trioxalatochromiate under these conditions.

In order to explain why potassium trioxalatochromiate deposits from concentrated solutions while it does not appear to be formed to a large extent in dilute solution, it must be remembered that this salt exists as well-defined crystals which are much less soluble than the malonatodioxalato salt. The deposition of the trioxalatochromiate as crystals may be expected to displace the equilibrium in its favour.

Hence it is necessary to assume that some trioxalatochromiate is formed in all cases, even if in very small amount. The use of a large excess of malonate favours the formation of the malonato derivative, which explains why a solid containing very little trioxalato complex was obtained under these conditions.

It is convenient at this stage to summarise the main conclusions in connection with the reaction between malonate and dioxalatodiaquochromiate.

(i) When equimolar quantities of potassium malonate and potassium <u>cis</u> dioxalatodiaquochromiate are boiled together in dilute solution, at pH 6.3, about 80% of the malonate coordinates with about 80% of the chrome complex.

(ii) When a large excess of malonate is used, there is evidence that a dimalonatodioxalatochromiate ion forms. This evidence depends on the difference in the absorption spectra for solutions using equimolar and excess quantities of malonate respectively. It is supported by the fact that a solid was isolated which contained an excess of potassium over that required to form the tribasic monomalonato salt. This excess

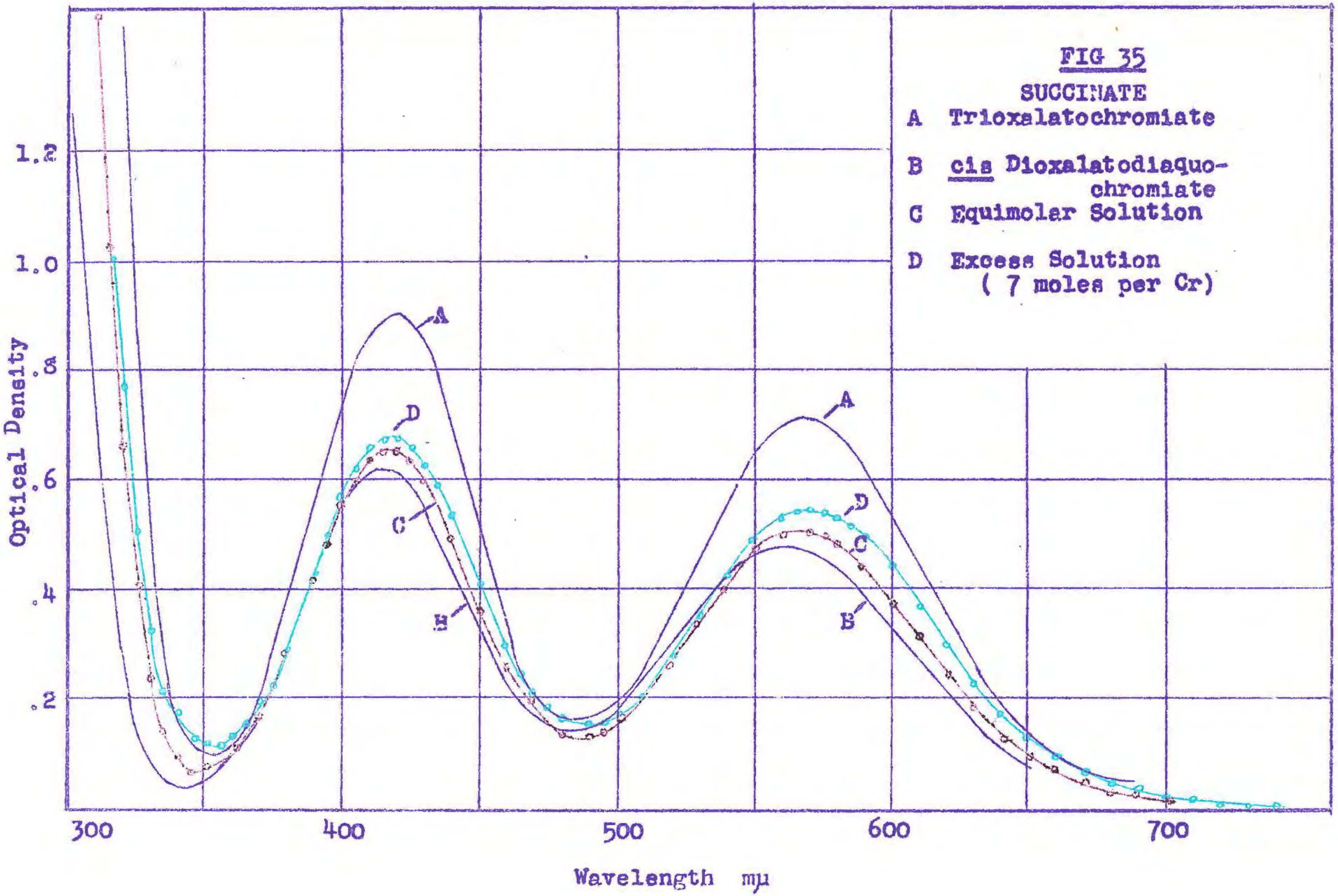


FIG 35
SUCCINATE
A Trioxalatochromiate
B cis Dioxalatodiaquochromiate
C Equimolar Solution
D Excess Solution (7 moles per Cr)
Optical Density
1.2
1.0
.8
.6
.4
.2
300
400
500
600
700
Wavelength mμ
A
A
D
D
C
C
B
B

could not be removed by reprecipitation and according to the pH curves, it did not exist solely as potassium malonate; nor could it be due to free potassium oxalate.

(iii) Reaction between equimolar quantities of malonate and dioxalatodiaquochromiate in concentrated solution tends to produce trioxalatochromiate which can be crystallised out as the potassium salt.

3. The Reaction between the Succinate Group and cis Dioxalatodiaquochromiate.

A solution containing equimolar quantities of succinic acid and potassium cis dioxalatodiaquochromiate was boiled for a period of one hour, then cooled and made to standard volume, the concentrations of each being .00921M. The pH, which had been adjusted to about 6.2 with potassium hydroxide before boiling, decreased to 5.37. The absorption curve of this solution is shown in Fig. 35, Curve C, and it is seen that a slight increase in absorption occurred, presumably due to the penetration of succinate into the complex.

Acid and alkali potentiometric titrations were performed on aliquots of this solution (Fig. 36, Curve (a)). From about pH 3 to pH 6, this curve shows the titration of one or more moderately strong acid groups. Any unreacted succinate will titrate in this region. If the curve below pH 3 be corrected for the blank titration, it is seen that the end-point of the acid titration occurs at about pH 3. The corrected curve is

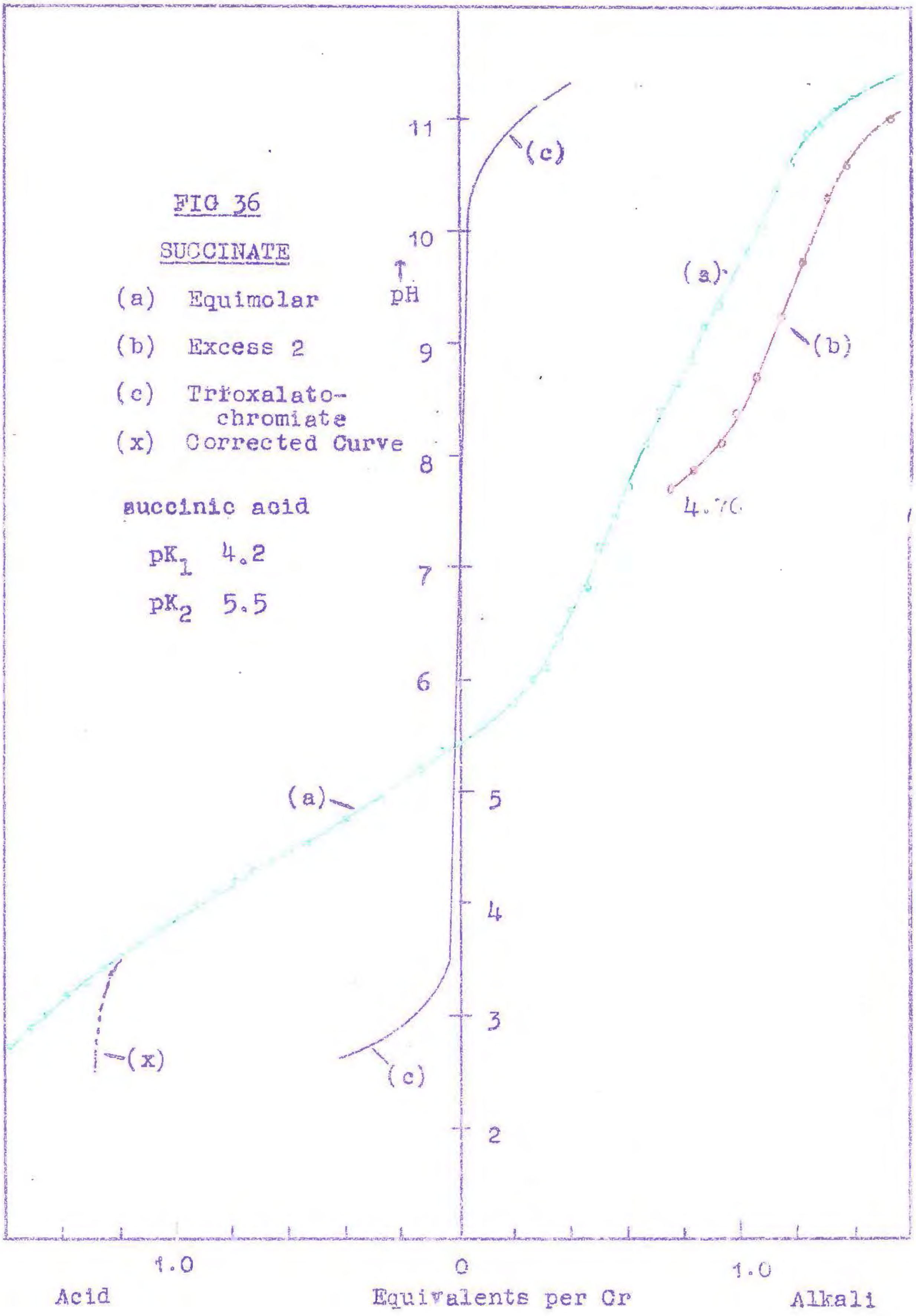
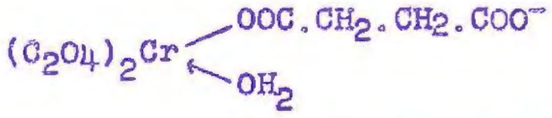


FIG 36

SUCCINATE

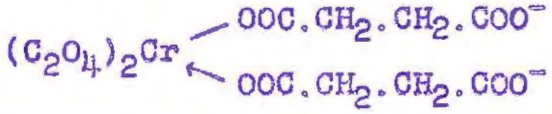
indicated as Curve (x). Now from pH 3 to 6, about 1.5 equivalents per Cr of acid is titrating. This does not necessarily represent free succinate, since one or more of the carboxyl groups of complexes of the type:

(I)



$$(C_2O_4)_2Cr \begin{array}{l} \diagup OOC.CH_2.CH_2.COO^- \\ \nwarrow OH_2 \end{array}$$

(II)



$$(C_2O_4)_2Cr \begin{array}{l} \diagup OOC.CH_2.CH_2.COO^- \\ \nwarrow OOC.CH_2.CH_2.COO^- \end{array}$$

if present, may be presumed to titrate over the same region.

Above pH 6, the curve is very similar to that of dioxalatodiaquochromiate and, if pH 8.27 and 10.6 are taken as end points, it may be calculated that about .96 equivalents per Cr of this ion remain unreacted. That is, about 52% of dioxalatodiaquochromiate had coordinated with succinate. This figure is probably a little high since about 10% of olation probably occurred. It must also be remembered that ions of the type (I) above may titrate in the region from pH 8.27 to 10.6 owing to the single aquo group, although from the general shape of the curve above pH 6 and from the fact that approximately equal quantities of alkali were required from pH 6 to 8.27 as from 8.27 to 10.6, it seems that a large amount of such ions could not have been present in solution.

As in the case of malonate, two solutions containing excess succinate were investigated. These contained 7 and 22 moles per Cr respectively, and the initial pH was adjusted to

6.2 before boiling. The absorption curve for the solution containing 7 moles excess is shown in Fig. 35, Curve D; the curve for the second excess solution is omitted since they were very similar. The actual figures are given in the Appendix Tables A 17 and A 18. The increase in light absorption over that of the equimolar solution shows that more penetration occurred when excess succinate was used.

The alkali potentiometric titration of the second excess solution is illustrated in Fig. 36, Curve (b) but the interference of the succinate up to pH 9 makes accurate quantitative deductions from this curve almost impossible. Nevertheless, it is evident that some of the dioxalatodiaquochromiate ion was still present.

An attempt was then made to isolate a succinate derivative. As in the case of the malonate, care was taken to prevent the formation of the trioxalatochromiate and in the final preparation, a strong solution (50% w/v) of potassium cis dioxalatodiaquochromiate was added to an excess of a concentrated solution of potassium succinate, the pH being adjusted to about 6.2. On the addition to this solution of 50% of its volume of alcohol, a black mass settled to the bottom. This was filtered off, dried and analysed. The analytical figures for this preparation, indicated below, were an improvement on those for previous attempts, but they indicate that a large amount of trioxalato complex was still present. The figures are;

	Found	Molar Ratio	Theoretical	
			Trioxalato	Succinato
Cr	10.83%	1.00	10.68%	11.27%
K	24.56	3.03	24.07	25.43
(C_2O_4)	45.0	2.46	54.2	38.2

The theoretical figures were calculated from the formulae:

Trioxalato $K_3\left[Cr(C_2O_4)_3\right] 3H_2O$

Succinatodioxalatochromiate $K_3\left[Cr(C_2O_4)_2(C_4H_4O_4)\right]$

It was considered that the solid obtained in this manner was not pure enough for physical tests and further attempts to prepare a product free from trioxalatochromiate were unsuccessful, so the succinate was not investigated further.

To summarise: It has been established that the succinate group is capable of coordinating with cis dioxalatodiaquochromiate, although apparently to a smaller extent than the malonate under the same physical conditions. A succinatodioxalato derivative free from trioxalatochromiate could not be isolated.

4. The Reaction of Adipate with cis Dioxalatodiaquochromiate

The adipate was investigated by the same procedure used for succinate, and it behaved similarly. In Fig. 37, Curve C, is shown the absorption spectrum for an equimolar mixture of adipic acid and potassium cis dioxalatodiaquochromiate which had been adjusted to pH 6.3, boiled and made to a concentration of

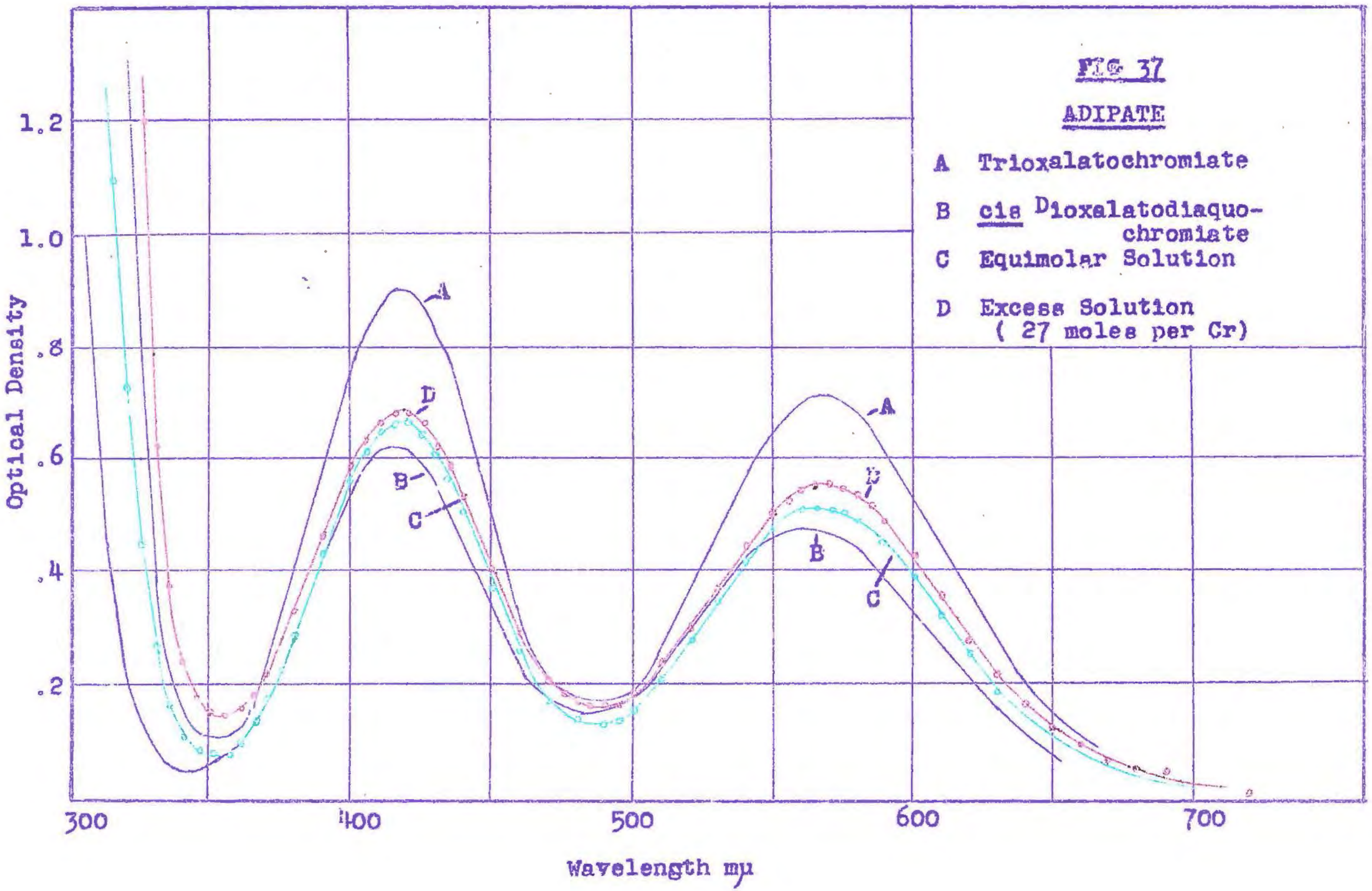
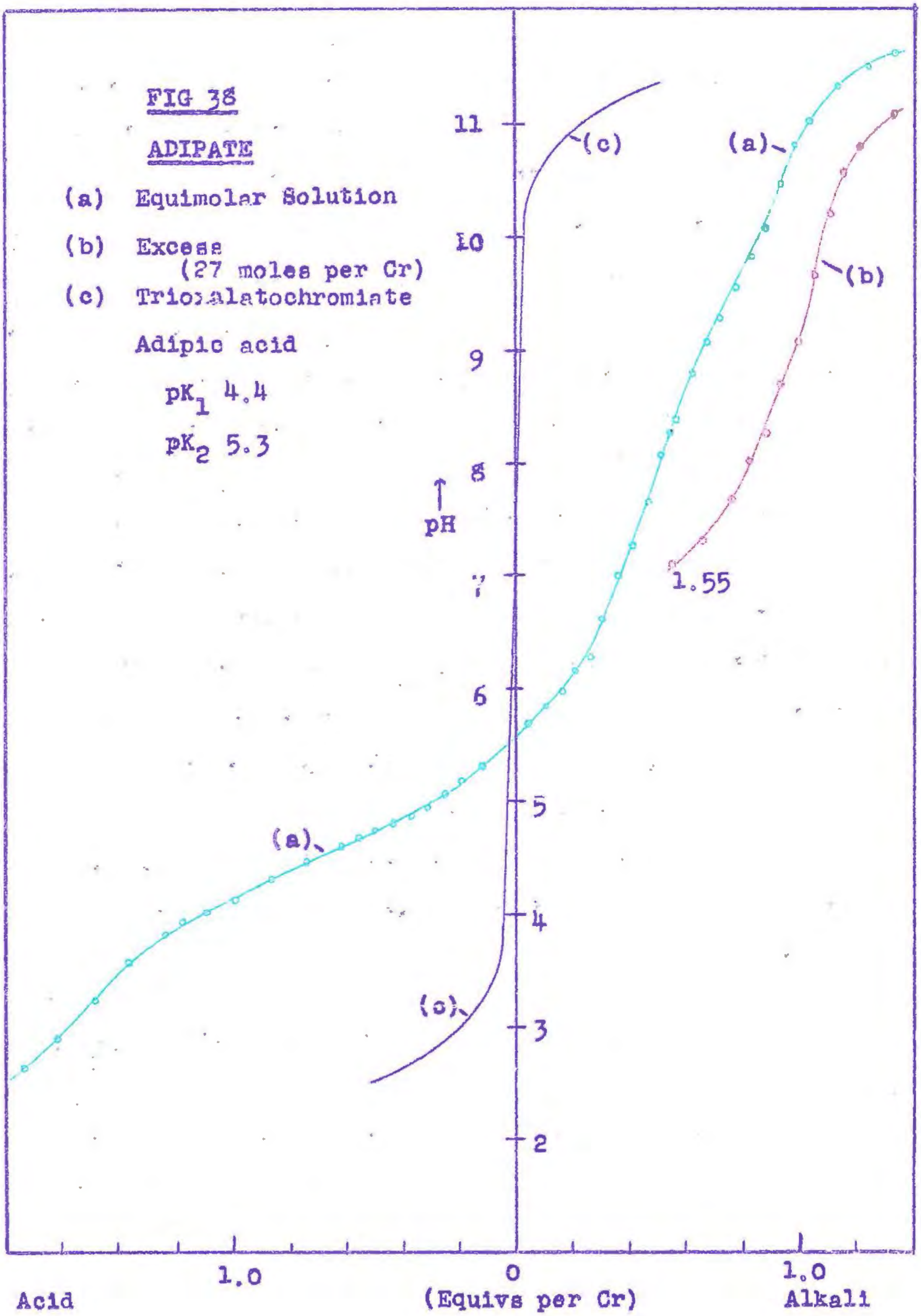


FIG 37

ADIPATE

FIG 38

ADIPATE



.07% Cr_2O_3 when cool. From this curve it is evident that some reaction occurred during boiling. The spectrum for a solution containing 27 moles per Cr of adipate is shown as Curve D in Fig. 37. The increase in light absorption for this solution is probably an indication that more penetration had occurred.

During boiling, the pH of the equimolar solution decreased from 6.3 to 5.55. The acid and alkali potentiometric curves of aliquots of this solution are shown as Curve (a), Fig. 38. This curve is rather like for the succinate (Fig. 36, Curve (a)). If the initial end point be taken at pH 3, then approximately 1.6 equivalents per Cr of moderately strong acid are titrating up to pH 6. A more detailed investigation would be necessary to reveal the nature of this acid. Above pH 6 it appears that free dioxalatodiaquochromiate was titrating and it is estimated that 49% of this ion remained unreacted.

The alkali pH curve for an aliquot of the boiled solution containing excess adipate is shown in Fig. 38, Curve (b).

As in the case of succinate, attempts to prepare an adipate derivative free from trioxalatochromiate were unsuccessful.

5. The Reaction of Fumarate and Maleate with cis Dioxalatodiaquochromiate

The reactions of maleate and fumarate were investigated as in previous cases. The absorption spectra of equimolar

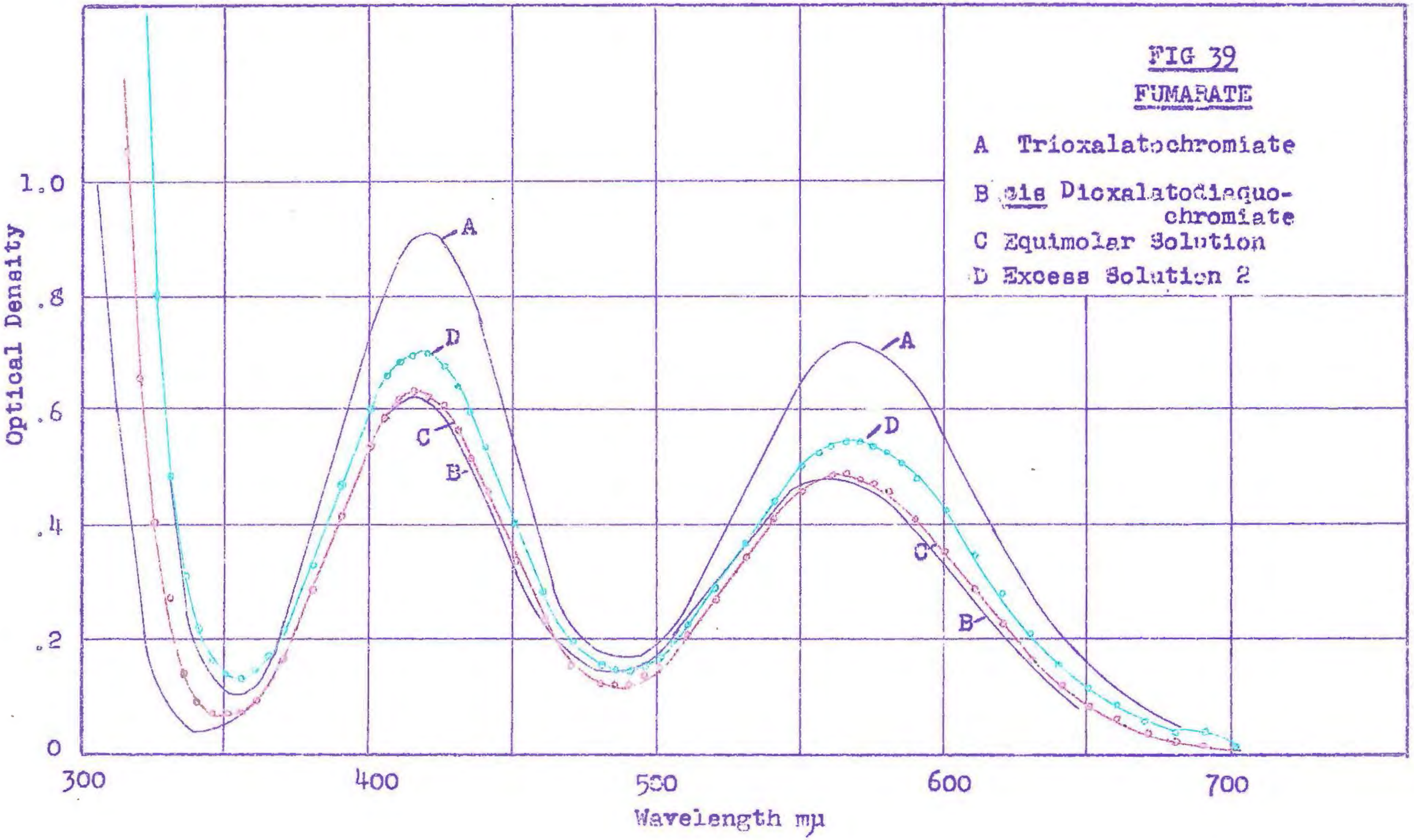
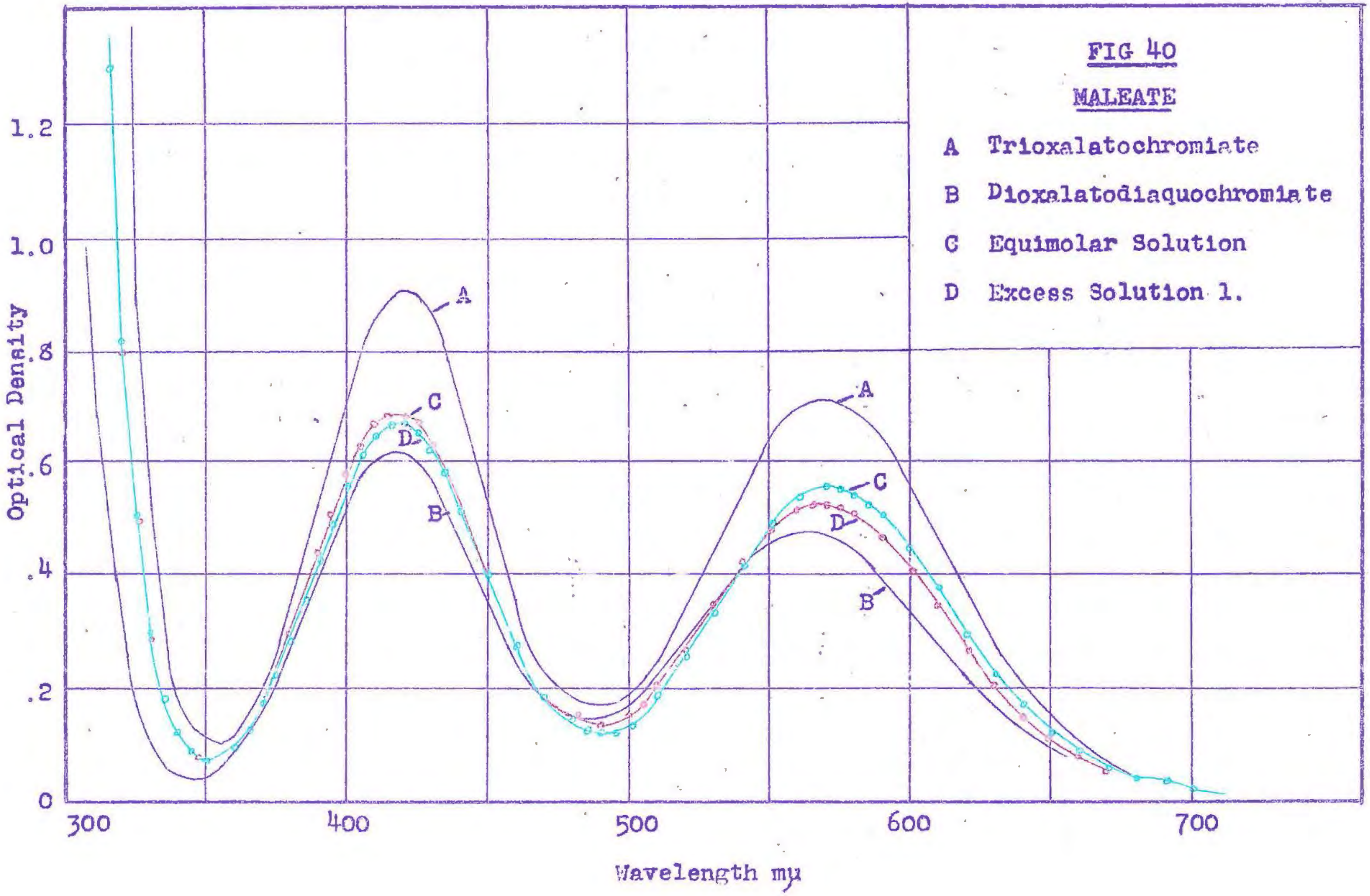


FIG 39

FUMARATE

FIG 40

MALEATE



series are shown as Curve C, Fig. 39 for the fumarate and Curve C Fig. 40 for the maleate. Solutions containing 9 and 25 moles per Cr in excess were also investigated for the fumarate, and one of these, that with 9 moles excess , is illustrated as Curve D, Fig. 39. The curve for the other solution had a similar shape and was very close to this, thus only one has been plotted. The readings are given in the Appendix Tables A 22 and A 23. For the maleate, the two excess solutions contained 9 and 38 moles per Cr respectively. That with 9 moles excess is shown in Fig. 40, Curve D.

It is clear from Figs 39 and 40 that both fumarate and maleate coordinate to some extent with *cis* dioxalatodiaquochromiate. The excess curve of fumarate has the same shape as that for equimolar quantities, but the excess curve for maleate is slightly different from the equimolar curve. This is better illustrated in Fig. 41 in which the peaks of the curves for equimolar, first excess (9 moles per Cr) and second excess (38 moles per Cr) are shown on an enlarged scale. The changes in the relative positions of the curves are reminiscent of the malonate curves (Section 2), and are not noticeable for the fumarate.

It will be noted that the equimolar solution of maleate has a higher absorption curve (Fig. 40, Curve C) than the corresponding fumarate solution (Fig. 39, Curve C).

Acid and alkali potentiometric titrations were performed on aliquots of the equimolar solutions for both the fumarate

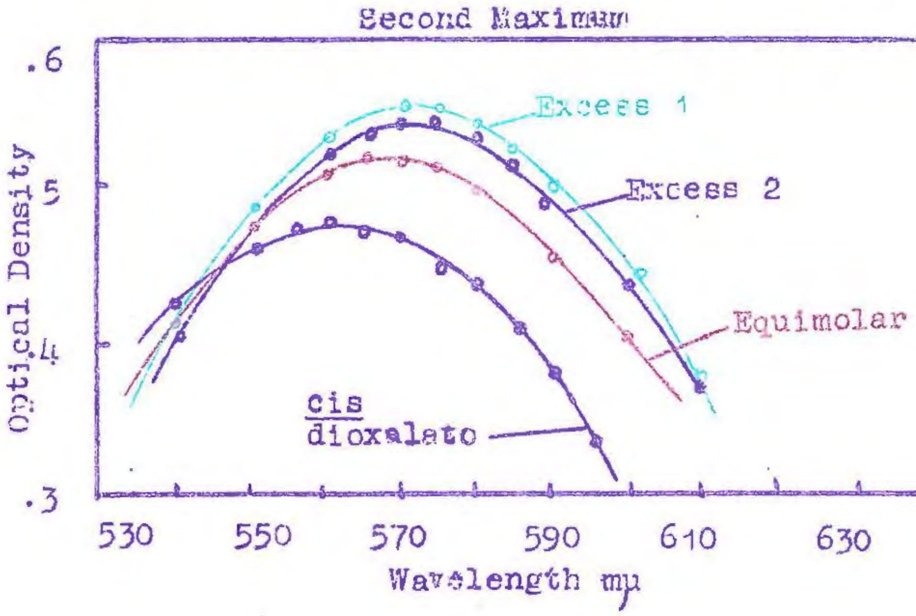


FIG 41. (MALEATE)

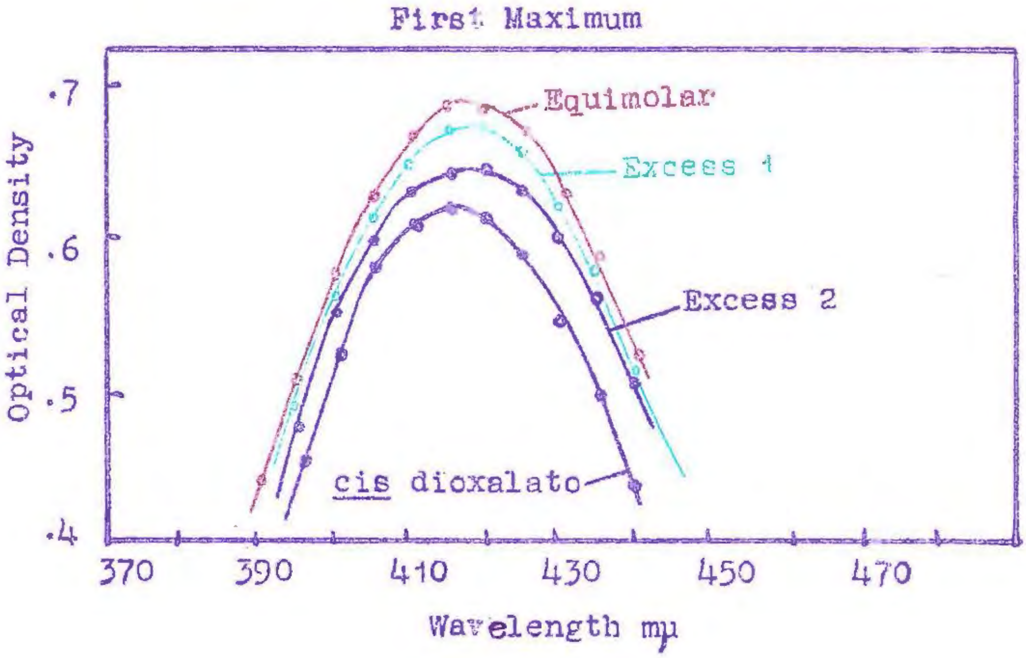


FIG 42

FUMARATE

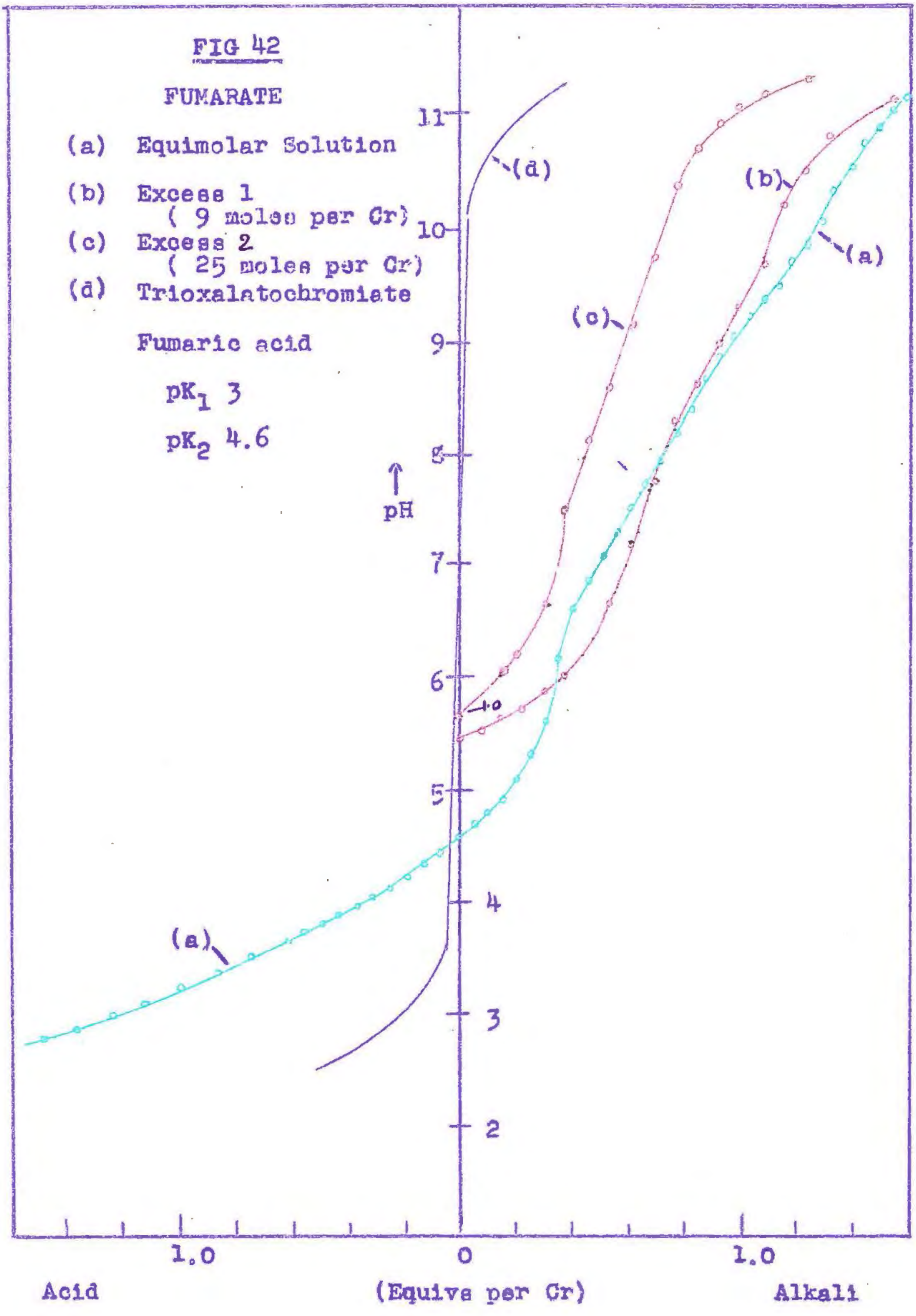
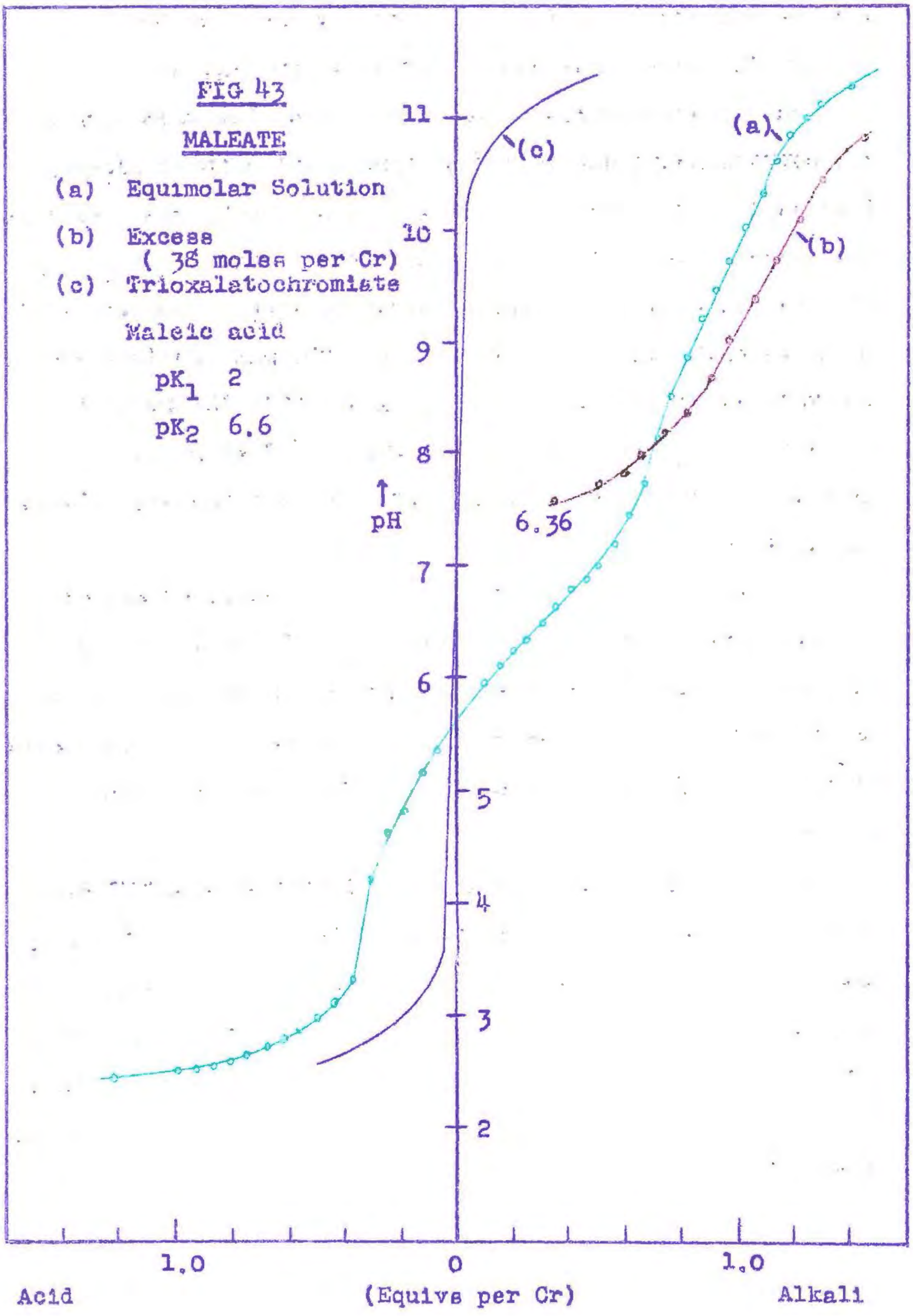


FIG 43

MALEATE



and the maleate. The fumarate curve is shown as Curve (a) in Fig. 42 and the maleate as Curve (a) in Fig. 43.

The fumarate curve up to pH 6.5 is of the same form as the corresponding curves for succinate and adipate already discussed. If it be assumed that above pH 6.5 free dioxalatodiaquochromiate is titrating, then it is estimated that 60% of this ion remained unreacted after boiling. However, it is probable that other ions, for example the monoaquofumarato derivatives were present in this case, since the point of inflexion occurred at about pH 9 instead of at pH 8.27 corresponding to the first aquo group of the dioxalatodiaquochromiate ion.

The alkali pH curves for the two excess solutions of fumarate are illustrated as Curves (b) and (c) in Fig. 42. Once again, the quantitative interpretation of these curves is not easy, but it appears that only slightly less weak acid is titrating above p^H 8 than was found for the equimolar solution.

The acid and alkali potentiometric titrations for the equimolar maleate solutions are shown in Fig. 43, Curve (a). The important thing about this is the end point at about pH 3.7. Since the pK values of maleic acid are sufficiently far apart, the curve of this acid shows a similar end point. It is not possible to infer from this that Curve (a) shows the titration of free maleic acid, but it may be stated that if

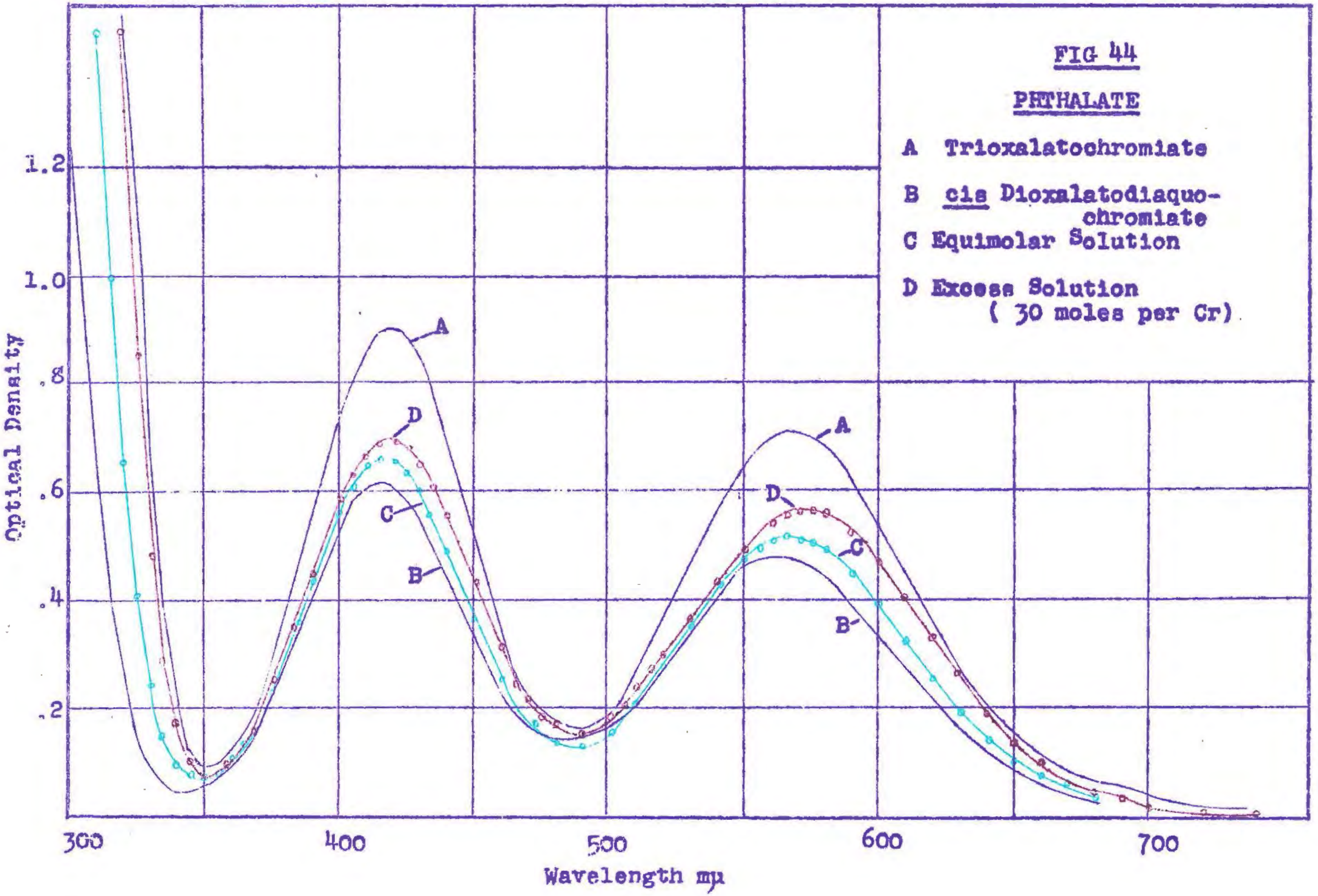
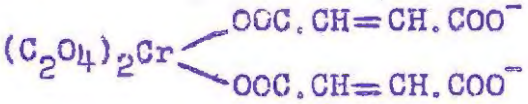


FIG 44

PHTHALATE

this curve represented the titration of appreciable amounts of ions of the type:



$$(C_2O_4)_2Cr\begin{array}{l}\diagup OOC.CH{=}CH.COO^-\\ \diagdown OOC.CH{=}CH.COO^-\end{array}$$

then the pK values of the free carboxyl groups did not differ greatly from those of maleic acid.

On the assumption that free dioxalatodiaquochromiate was titrating above pH 7, it was estimated that 40% of this ion remained in solution.

The curve showing the alkali titration of the second excess solution is given in Fig. 43 as Curve (b).

Attempts were made to separate fumarato and maleato derivatives free from trioxalatochromiate but without success.

6. The Reaction of Phthalate with cis Dioxalatodiaquochromiate

The reactions of the phthalate group were investigated in a manner similar to that used for the other groups discussed in this chapter. The potassium hydrogen salt was used as the starting material.

Absorption curves of solutions containing equimolar and excess (30 moles per Cr) quantities of phthalate, after boiling, are shown in Fig. 44, Curves C and D respectively. It is apparent that some reaction has occurred on boiling the equimolar solution, but the reaction proceeded further in the case where excess of phthalate was employed.

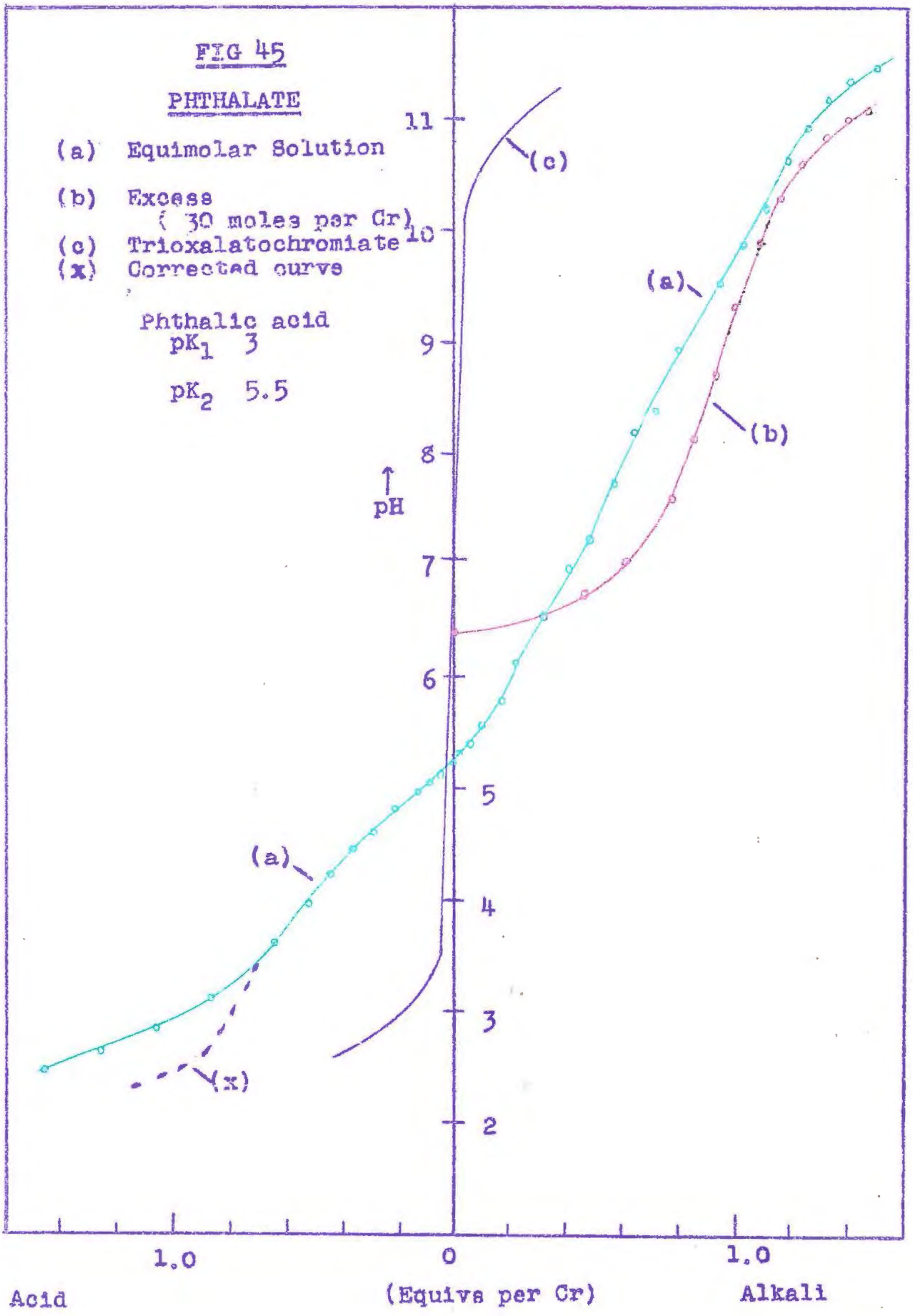


FIG 45

PHTHALATE

The acid and alkali potentiometric titrations of aliquots of the equimolar and excess phthalate solutions are shown in Fig. 45, as Curves (a) and (b) respectively. The equimolar curve, (a), has been corrected for the blank titration at the end of the curve, the corrected curve being indicated as Curve (x). From this it is apparent that acid is still titrating below pH 3. The second pK value for phthalic acid is 5.5, which means that if a large amount of free phthalic acid were present in solution, a point of inflexion or region of buffering should be discernable between pH 5 and 6. Unfortunately this region is so close to that at which the coordinated H_2O groups commence to titrate that considerable uncertainty arises in the interpretation. Obviously a more thorough investigation is required in the case of the phthalate complex, but it is possible that very little free phthalate remained in solution.

If the titration above pH 7 is taken as dioxalatodiaquochromiate, then it is estimated that about 52% of this ion remained unreacted. This means that if the solution really contained very little phthalate after reaction, then more than one phthalate group must have coordinated to each dioxalatodiaquochromiate ion which reacted.

All attempts to isolate a phthalate derivative were unsuccessful owing to the interference of trioxalatochromiate.

7. Discussion

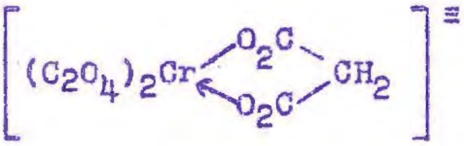
It is contended that the data presented in the preceeding sections prove that the malonate, succinate, adipate, fumarate, maleate and phthalate groups are capable of coordinating with the cis dioxalatodiaquochromiate ion, although, except in the case of malonate, it is not certain to what extent reaction proceeded. In the table below, the percentages of dioxalatodiaquochromiate ion remaining unreacted in the equimolar solutions after boiling , are recorded:

TABLE 17

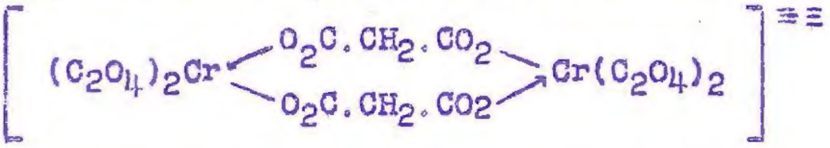
Group	Dioxalato-
Malonate	15%
Succinate	48%
Adipate	40%
Fumarate	60%
Maleate	40%
Phthalate	52%

These figures are based on the titration of the two aquo groups of the dioxalatodiaquochromiate ion and are liable to error if other ions were present which titrated in the same pH region. With this reservation, it may be seen that much less dioxalatodiaquochromiate remained unreacted for the malonate series that for the other dibasic groups studied.

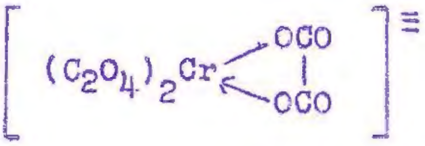
In no case could the structure of the complex formed be established with certainty and there is evidence that in many cases more than one complex was present. However, there is circumstantial evidence that the malonate group coordinates to form a ring:



Thus, in Section 2 it was shown that malonate coordinates with dioxalatodiaquochromiate to the extent of about 80% to produce a complex with no weak acidic or basic groups. From this evidence it appears that two structures are possible for this complex; that shown above, and the structure:



The absorption curves (Fig. 33) indicate a similarity between the malonato complex and the trioxalatochromiate, both in the positions of the maxima and in the shapes of the curves. This similarity does not occur for the other dibasic groups studied. Thus an analogy with the structure of the trioxalatochromiate is indicated:



It should be noted, however, that for reasons discussed in

Chapter 10, too much importance cannot be attached to the exact shapes of absorption curves. Fortunately, other evidence is available and this tends to confirm the view that malonate coordinates with chromium(III) to form a six-membered ring:

(i) It has been proved (59) that malonate coordinates with cobalt(III) to form a six-membered ring.

(ii) Conductometric measurements (67) are in favour of the existence of a six-membered ring for malonato complexes of chromium.

The question of the greater stability of five- and six-membered rings is discussed in Chapter 11.

Chapter 9

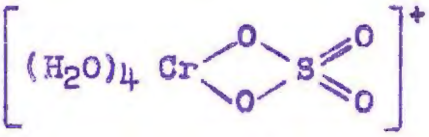
AN INVESTIGATION OF THE SULPHATODIOXALATOCHROMIATE COMPLEXES

1. Introductory

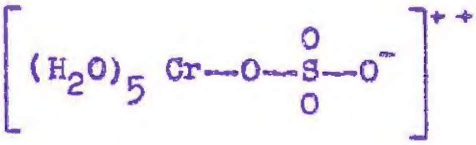
The widespread use of chrome sulphate liquors in tanning processes has resulted in numerous investigations on the sulphato chromium complexes. The earlier work in this field is reviewed by Atkin and Chollet (25) and several discussions are available (68).

As the sulphato complexes appear to be relatively less stable than the oxalato complexes, the investigation of the former has been extremely difficult and the problem is complicated by the fact that sulphato complex ions olate readily (69). It is, therefore, not suppriaing that our knowledge of these ions is incomplete.

Various structures have been proposed for the chromium sulphate complexes; Gustavson (68) considered the ions:



and



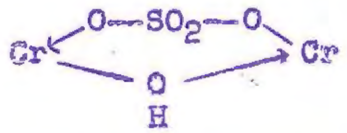
$$\left[(H_2O)_5\ Cr-O-\overset{O}{\underset{O}{S}}-O^-\right]^{++}$$

for the monosulphato complex.

Stiasny and Balanyi (70) mentioned the possibility of SO_4 forming a bridge between two Cr atoms i.e.

$$Cr-O-SO_2-O-Cr$$

and Atkin (71) favoured the existence of rings involving two or more chromium atoms, e.g.



Most past investigations on sulphato complexes have dealt with chrome alum or chrome sulphate in which each of the six coordination positions are available for substitution by sulphate. This complicates the interpretation of the experimental data and so it was thought desirable to attempt a more simple investigation starting from the cis dioxalatodiaquochromiate ion, in which only two coordination positions are available.

The results of the experiments described in Chapter 8 showed that the data obtained from the reaction of groups which appear to coordinate less readily with dioxalatodiaquochromiate in dilute solution, were not easy to interpret. Consequently, the method of evaporating mixtures to dryness, originally proposed by Stiasny, was tried. This method depends on the fact that coordinated water molecules tend to be removed from the complex as the solution becomes more concentrated. This tendency is increased if another, non-volatile group like SO_4 is available to fill the vacated positions.

2. Procedure

To a 50% (w/v) solution of potassium cis dioxalatodiaquochromiate, prepared by weighing a known quantity of the trans potassium salt, dissolving in water and ageing to convert to the cis isomer, an exactly equimolar quantity of pure potassium sulphate was added. After boiling for 20 minutes the colour of the solution had changed from pink to dark green. Unsuccessful attempts were made to separate a solid from the cooled solution, by leaving to stand for several days at a low temperature (5°C), and by further evaporation. The addition of alcohol merely precipitated a dark, tarry liquid, together with potassium sulphate crystals. No crystals of potassium trioxalatochromiate were observed at any time during the preparation. The original solution was then evaporated to dryness in an air oven at 90°C for 12 hours, during which time a dark-green, glassy solid formed. This was pulverised with great difficulty since it was extremely hard.

The pulverised solid was heated for periods of several hours at progressively higher temperatures until the chromium content, as determined by analysis, became constant. This occurred at 130°C and heating for 12 hours at 170°C did not cause any further loss in weight. If the solid were heated from 250 to 350°C, the powder puffed up and became light green in colour. This was apparently caused by the oxidation of the chromium, since on shaking with water this solid gave yellow, chromate-like solutions, though it was not all soluble. That this solution did contain chromate was confirmed by acidifying and testing with diphenyl carbazide. It was found that chrome alum also oxidised at about the same temperature.

It is considered that, during heating to 130°C, almost every one of the dioxalatodiaquochromiate complexes in the solid became coordinated with sulphate by the displacement of coordinated water.

In other words the solid contained no dioxalatodiaquochromiate. This deduction follows from the following considerations:

Firstly, close examination of the solid after heating to 130°C revealed no evidence for the independent existence of potassium dioxalatodiaquochromiate and potassium sulphate crystals in the material.

Secondly, a solution of potassium cis dioxalatodiaquochromiate after evaporating to dryness and heating at 130°C for several hours, formed a dark-green, glassy solid which on analysis was found to have lost about half of its coordinated water. This solid, unlike that obtained in the presence of potassium sulphate, was quite insoluble in cold water, even after vigorous shaking. On boiling in water, the familiar pink colour of the cis dioxalatodiaquochromiate was regenerated and the solid passed into solution - evidently due to recoordination of water lost during heating. The behaviour of this substance was quite unlike that of the product obtained by heating the same salt in the presence of an equimolar quantity of potassium sulphate, where the resulting solid was instantly soluble in cold water to give a bright green solution. Clearly, if an appreciable amount of dioxalatodiaquochromiate complex had not reacted with sulphate, an insoluble residue would have been observed, as in the case of the cis dioxalatodiaquo salt alone.

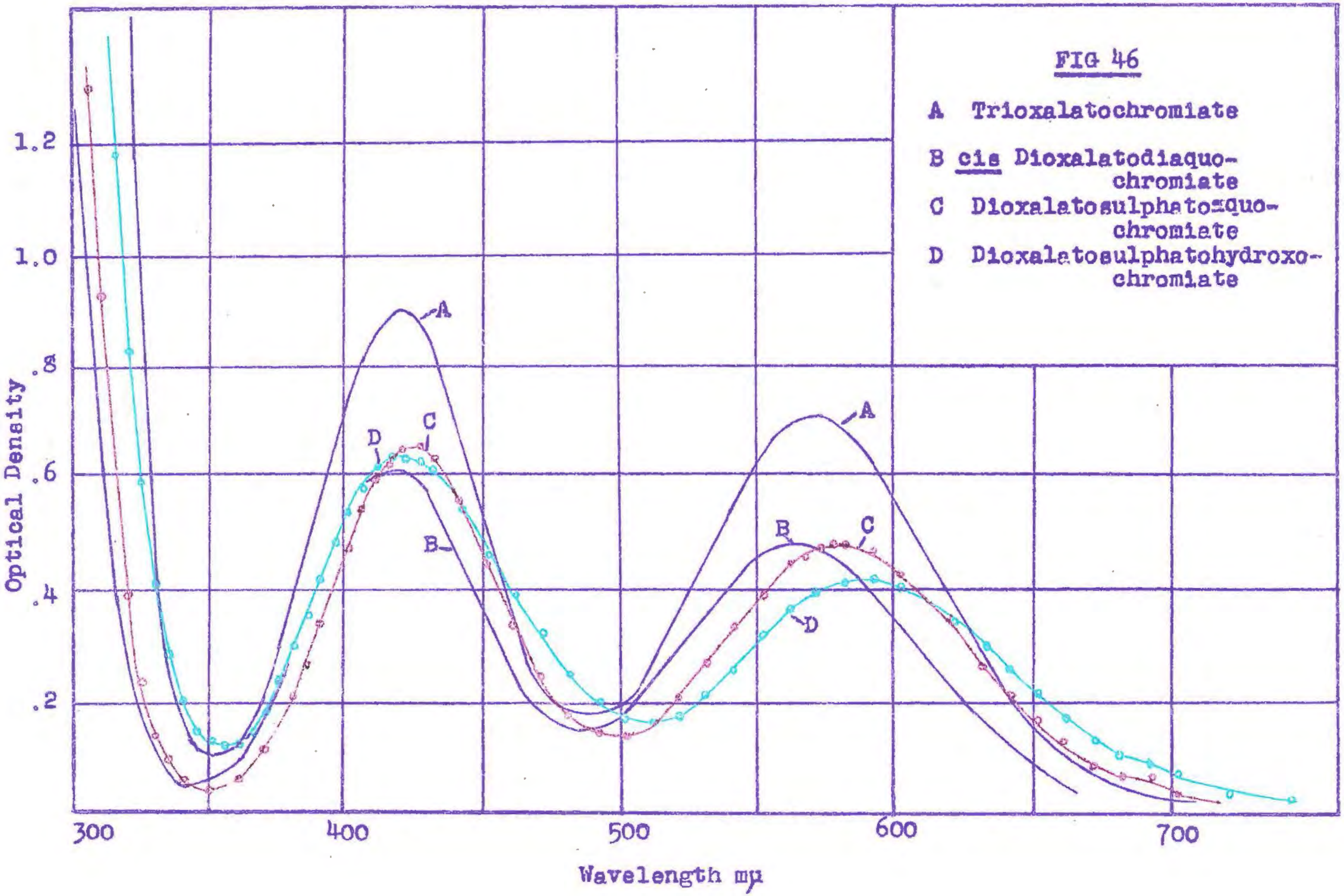


FIG 46
A Trioxalatochromiate
B cis Dioxalatodiaquochromiate
C Dioxalatosulphatoaquochromiate
D Dioxalatosulphatohydroxochromiate
A
A
B
B
C
C
D
D
Optical Density
1.2
1.0
.8
.6
.4
.2
300
400
500
600
700
Wavelength mμ

The analytical figures for the sulphatodioxalato derivative are recorded in Table 18 where also are given calculated values for a number of theoretically possible empirical formulae:

TABLE 18

	Empirical Formula	Chromium	Oxalate
1	$[Cr(C_2O_4)_2(H_2O)_2]K + K_2SO_4$	10.90%	36.87%
2	$[Cr(C_2O_4)_2(SO_4)]K_3$	11.79	39.87
3	$[Cr_2(C_2O_4)_4(SO_4)_2(H_2O)]K_6$	11.55	39.09
4	$[Cr(C_2O_4)_2(SO_4)(H_2O)]K_3$	11.32	38.33
	Experimental	11.32	38.2

It is evident from this table that the experimental figures are in close agreement with those for the hypothetical structure which contains one SO_4 and one H_2O per Cr (i.e. No 4). It appears, therefore, that half of the coordinated water molecules originally present in the diaquo salt had been driven off by heating and replaced by sulphate.

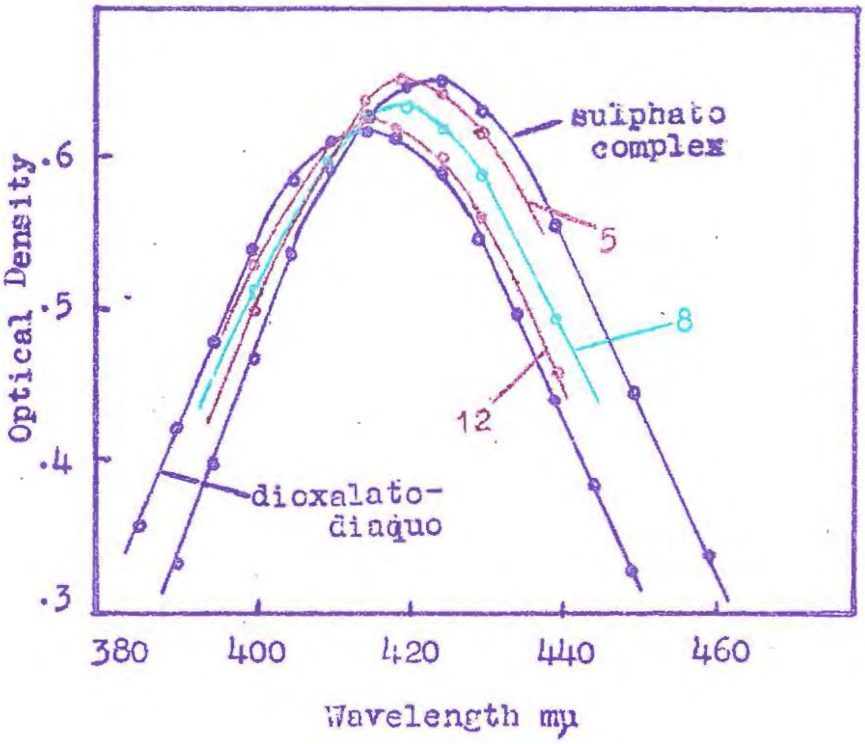
A number of preliminary tests were performed on the sulphato solid prepared as above. It was found that the optical density, at a number of wavelengths, of a solution containing .07% Cr_2O_3 changed rapidly with time at room temperature but at a low temperature (8°C) it remained constant long enough to enable an a absorption curve to be measured. This is shown in Fig 46, Curve C. The pH of this .07% Cr_2O_3 solution immediately on dissolving at room temperature was found to be about 3.8 but rose to about 4.2 on standing.

In order to throw further light on the nature of the sulphato product, a measure of the amount of free sulphate in a solution of the solid was desirable. The use of barium chloride is known to give erroneous results in the presence of coordinated sulphate since it is capable of removing SO_4 from the complex. However, the method of precipitation by benzidine hydrochloride, originally proposed by W. Müller (72) has been recommended for the determination of free sulphate in these cases (36). This method depends on the precipitation of the $SO_4^{=}$ as the sparingly soluble benzidine sulphate (See page 24 for details of method).

Preliminary additions of benzidine hydrochloride solution to freshly prepared solutions of the sulphato solid produced copious precipitates. This indicated that the solid contained a large amount of free sulphate and appeared to contradict the earlier deduction that most of the complex had coordinated with sulphate. For this reason, a thorough investigation of the decomposition of the sulphato solid was undertaken.

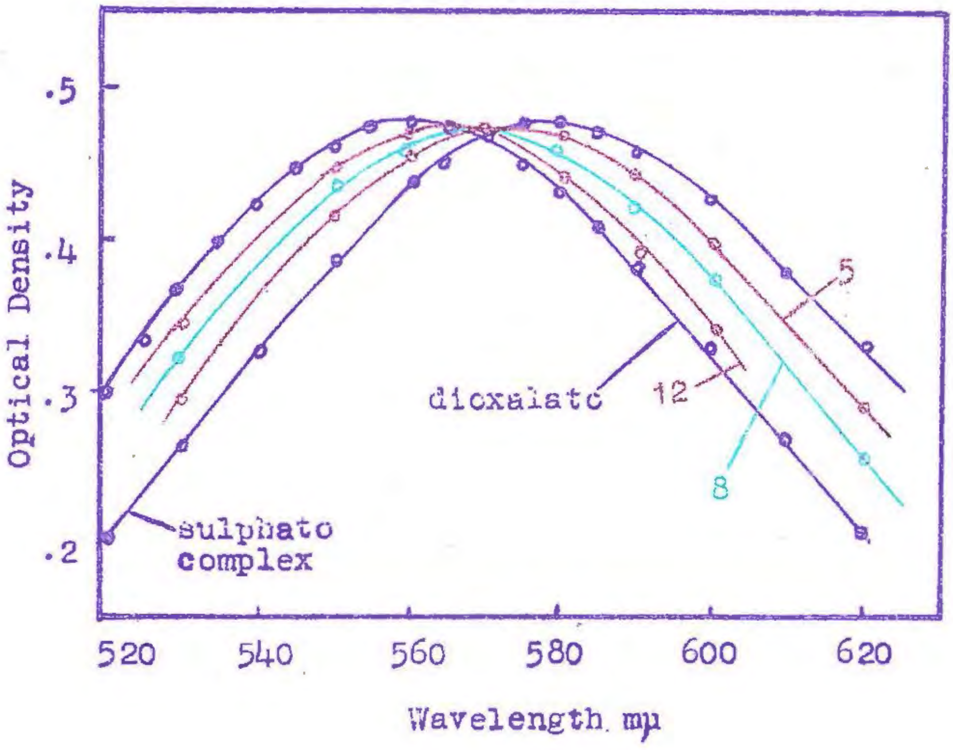
3. The Decomposition of the Sulphatodioxalatochromiate Complex in Dilute Solution

One litre of a .07% Cr_2O_3 solution of the sulphato solid, freshly prepared, was kept in a constant temperature water bath at 21.7°C. At intervals of time over a period of about 15 hours, portions of the solution were withdrawn by pipette. A number of tests to be described below, were performed on these aliquots:



sulphato complex
5
8
12
dioxalato-diaquo
Optical Density
.6
.5
.4
.3
380
400
420
440
460
Wavelength mμ

Fig 48



Optical Density
.5
.4
.3
.2
5
12
8
dioxalato
sulphato complex
520
540
560
580
600
620
Wavelength mμ

(a) A 20 ml aliquot was used to determine the percentage of sulphate by the benzidine method. The results are recorded in Table 19, Column 3, and they are expressed graphically in Fig. 47 where the amount of benzidine precipitate, calculated as apparent percentage sulphate on the dry weight, has been plotted against the time in minutes. The horizontal line represents the actual percentage of sulphate added, calculated on the same basis.

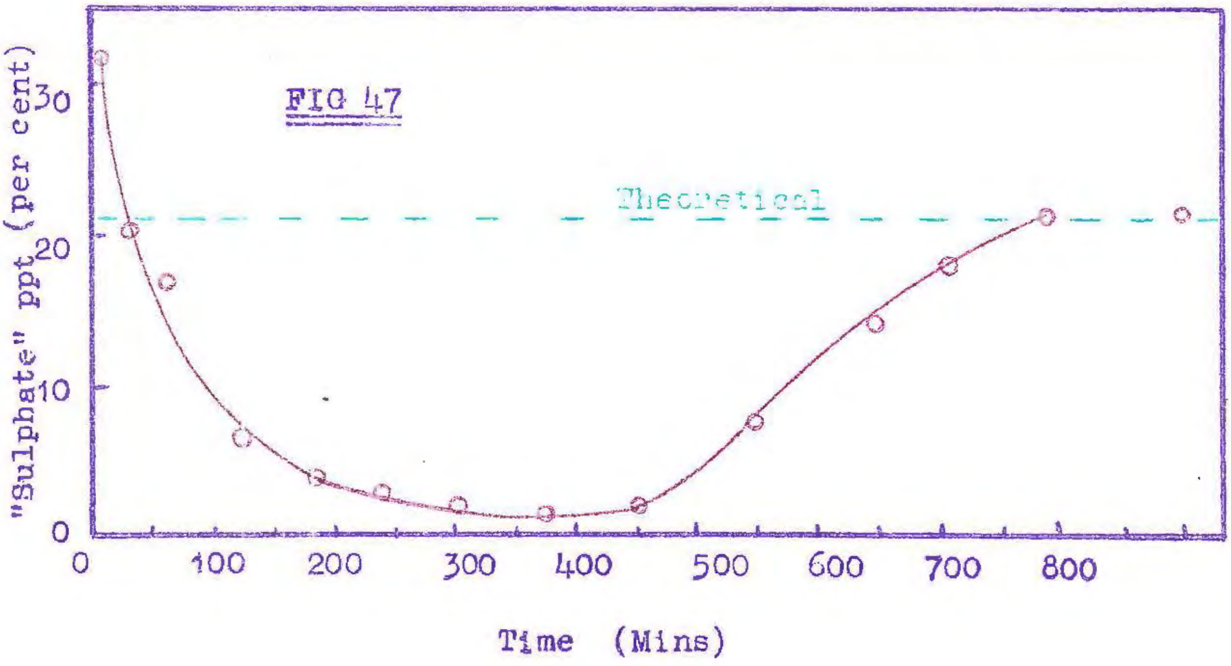


FIG 47

(b) Small portions of the solution were used to measure the optical density at a number of wavelengths in the vicinity of the maxima. Three of these curves, numbered according to Table 19, are shown in Fig. 48 and the actual readings are recorded in the Appendix Table A 32. The curves for pure <u>cis</u> dioxalatodiaquochromiate and for the sulphato solution at a low temperature (from Fig. 46) are also given.

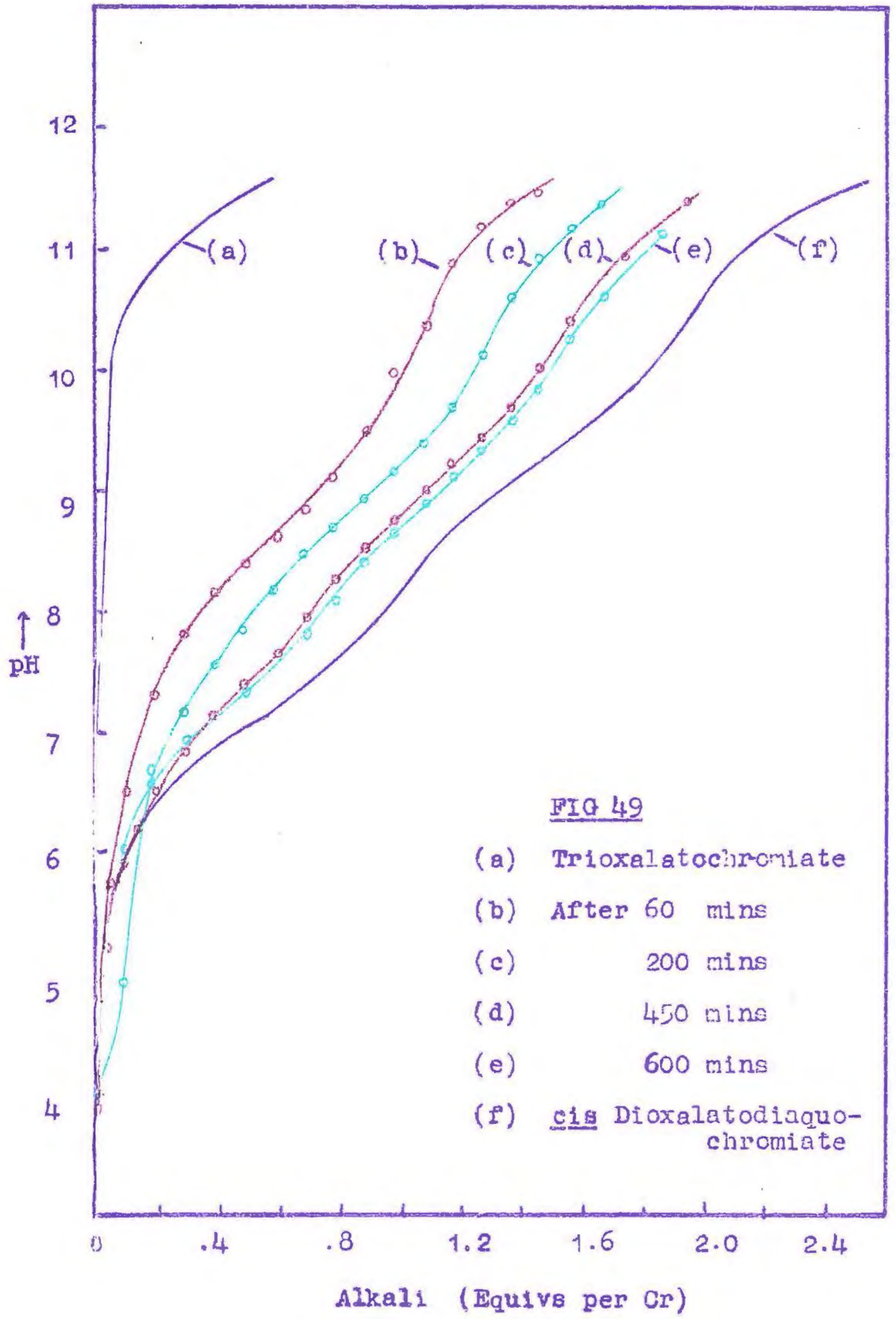


FIG 49

12
11
10
9
8
7
6
5
4
pH
0
.4
.8
1.2
1.6
2.0
2.4
Alkali (Equivs per Cr)
(a)
(b)
(c)
(d)
(e)
(f)
(a) Trioxalatochromiate
(b) After 60 mins
(c) 200 mins
(d) 450 mins
(e) 600 mins
(f) cis Dioxalatodiaquochromiate

(c) The pH of another portion was measured and recorded in Table 19, Column 4.

(d) Alkali potentiometric titrations were performed on 40 ml aliquots. Four of these titrations were performed at times corresponding to 60, 200, 450 and 600 minutes after dissolving the solid. The curves are shown in Fig. 49 together with the curve for pure dioxalatodiaquochromiate and trioxalatochromiate. These titrations each took about 15 minutes to complete so that slight decomposition probably occurred during measurement. A similar titration was also performed when the decomposition had gone to completion. This curve coincided exactly with the curve for pure dioxalatodiaquochromiate (Fig. 49).

An examination of both the absorption curves (Fig. 48) and the potentiometric curves (Fig. 49) indicates that during the experiment, the sulphato solution underwent a gradual change , becoming a solution of cis dioxalatodiaquochromiate and potassium sulphate. However, the results of the benzidine determinations (Fig. 47) indicate that a large amount of free sulphate was present initially and that this gradually decreased. The fact that the amount of this "free sulphate" initially present in solution was larger than that added in the first instance, showed that the benzidine results could not be taken literally. A closer examination of the first benzidine precipitates revealed that they were flocculent and light green in colour, unlike benzidine sulphate which crystallises characteristically as colourless plates. Some of the green precipitate was dried at 100°C and analysed. It was found to contain about 7.4% of chromium, indicating an insoluble chrome complex containing benzidine.

Though the filtrate from this precipitation was generally green in colour it was found that if the solid were dissolved at a lower temperature (5°C) and the process repeated, all of the chromium could be precipitated and the filtrate was colourless. This appeared to indicate that some of the sulphate complex changed immediately into another green complex when dissolved at room temperature, the latter complex not being precipitatable by benzidine. The green precititate was quite insoluble in water at room temperature.

Evidently owing to the presence of a benzidine precipitable complex, the benzidine method cannot be used to determine the amount of free sulphate initially present in this solution. Moreover, from Fig. 47 it is apparent that the amount of benzidine precipitate, whether sulphate or chromiate complex, decreases to a minimum corresponding to about 2% of sulphate, during the decomposition. On the other hand, the spectrophotometric curves (Fig. 48) and the pH titrations (Fig. 49) both indicate qualitatively that at this stage the sulphato complex has decomposed to a considerable extent, so that the solution should contain much more than 2% of free sulphate.

In order to obtain more exact data on this matter, an attempt was made to determine the progress of the decomposition quantitatively from the absorption data. To do this it was necessary to assume (i) that the sulphato solid dissolved at a low temperature to give a solution containing no dioxalatodiaquochromiate ions, (ii) that equations based on Beer's law were applicable to the solution during the decomposition. These assumptions are both quite reasonable.

Let Dd be the optical density at 600 mμ of a solution of pure cis dioxalatodiaquochromiate having a concentration corresponding to .07% Cr_2O_3 and let Ds be the optical density of the sulphato solid at a low temperature also at 600 mμ and at the same concentration.

Then if D is the optical density of a solution of concentration .07% Cr_2O_3 consisting of a mixture of these complexes, the percentage of the sulphato complex (Cs) — taking the theoretically possible maximum as 100% — will be given by:

$$Cs = \frac{(D - Dd).100}{(Ds - Dd)} \; \%$$

The derivation of similar equations for mixtures of two absorbing substances has already been discussed in detail in Chapters 4 and 6.

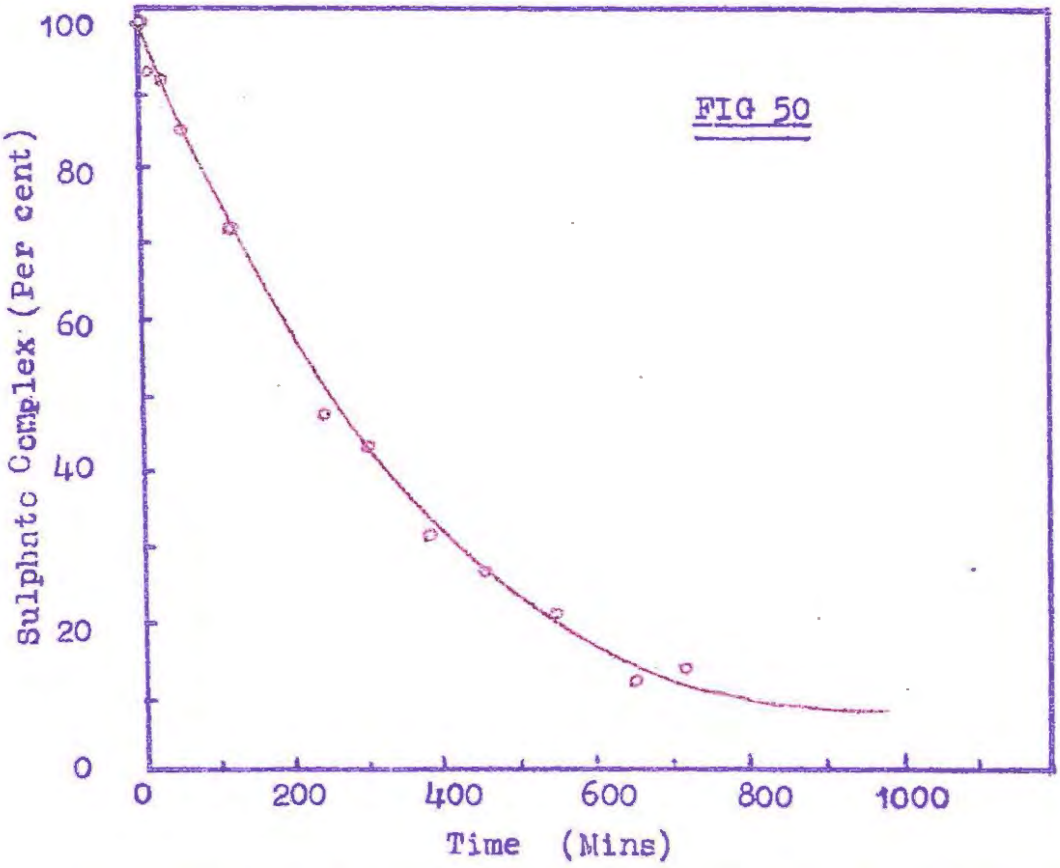
Using the values: Dd = .326

Ds = .103 at 600 mμ

TABLE 19

No	Time	Benzidine ppt "Sulphate"	pH	Sulphato Complex Ce
1	0 mins	-	-	100%
2	6	31.9%	3.80	93.2%
3	30	20.4%	3.82	92.2%
4	60	10.7%	3.89	85.4%
5	120	6.8%	3.94	71.8%
6	180	4.28%	4.00	51.5%
7	240	3.26%	3.97	47.6%
8	300	2.33%	3.95	43.7%
9	375	1.63%	3.94	30.1%
10	450	2.24%	3.97	26.2%
11	540	7.74%	3.97	20.4%
12	645	15.3%	4.01	11.7%
13	705	18.1%	4.00	13.6%
14	790	21.2%	4.10	
15	900	21.4%		

the percentage of sulphato complex in solution at a number of time intervals during decomposition was calculated. The results have been recorded in Table 19, Column 5, and are expressed graphically in Fig. 50:



In spite of the scatter of the points, it is evident that the sulphato complex decomposes with time, although the decomposition is not exponential. At the time corresponding to the minimum in Fig. 47, about 70% of the sulphate should be free in solution according to Fig. 50. This is consistent with the observation made from the absorption curves in Fig. 48 earlier.

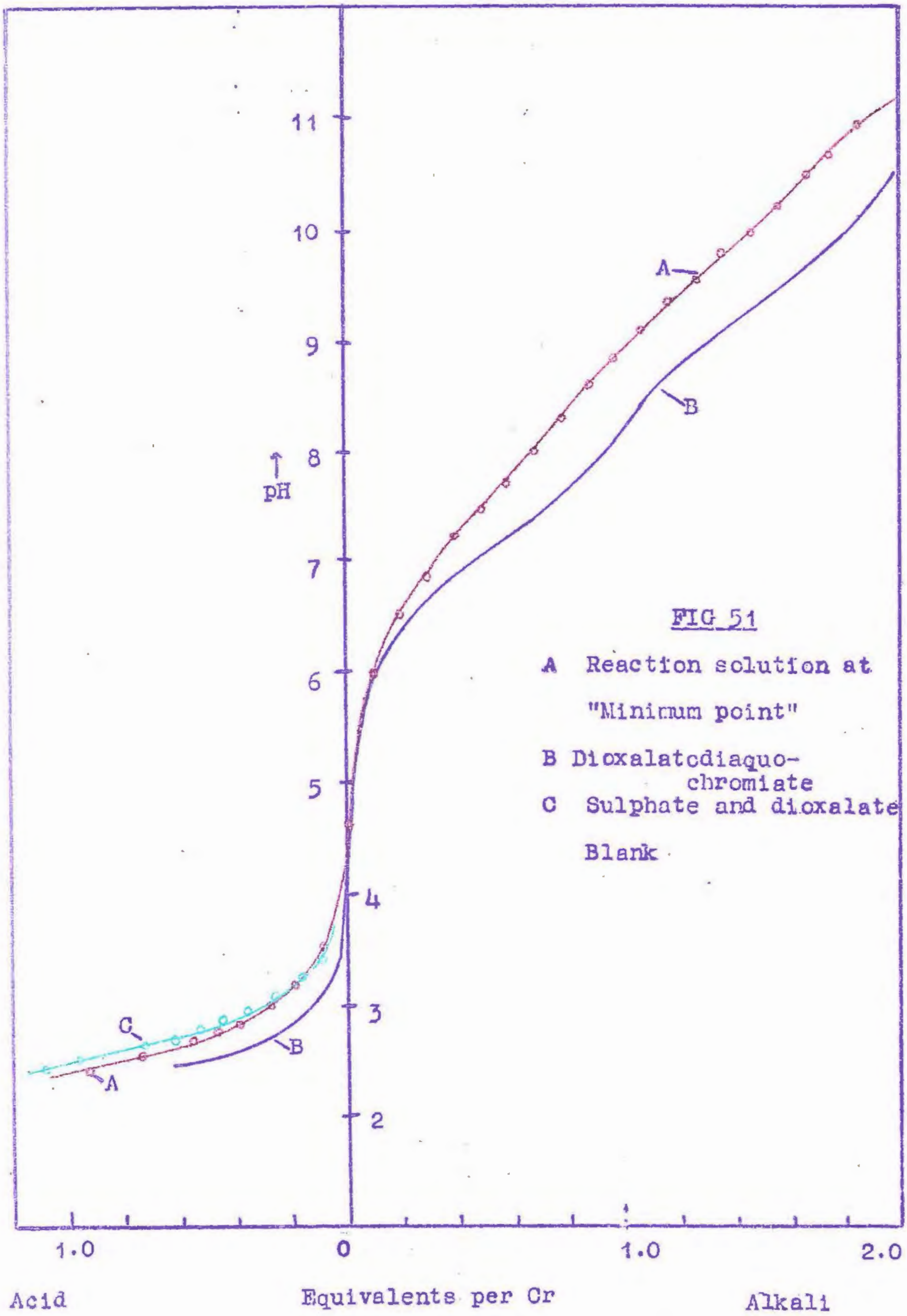


FIG 51

A Reaction solution at "Minimum point"

B Dioxalatodiaquo-chromiate

C Sulphate and dioxalate Blank

A more detailed potentiometric investigation of the reaction solution at the time corresponding to the minimum in Fig. 47 was undertaken. Another solution, of the same concentration as that used previously was allowed to age at the same temperature. After 350 minutes the solution was tested with benzidine and, once again a negligible precipitate was obtained. More accurate alkali and acid potentiometric titrations were then performed on aliquots of this solution and the curves are plotted in Fig. 51, Curve A. For comparison, the curve for pure dioxalatodiaquochromiate (Curve B) and the acid curve for a solution containing equimolar quantities of dioxalatodiaquochromiate and potassium sulphate (Curve C) at the same concentrations (about .01M) are given.

The acid section of Curve A shows that, potentiometrically, the solution at the "minimum point" behaves like a mixture of potassium sulphate and dioxalatodiaquochromiate, while the alkali titration indicates that a large percentage of the dioxalatodiaquochromiate was titrating, although the decomposition had not gone quite to completion. This is in agreement with the spectrophotometric data discussed above, and confirms the earlier potentiometric curves (Fig. 49).

Thus, there can be no doubt that the results of the benzidine sulphate method are in disagreement with the spectrophotometric and potentiometric evidence. In order to attempt to resolve this dilemma, some simple tests were performed on the sulphate solution at the "minimum point".

To a sample of this solution in a test-tube, about half as much benzidine hydrochloride solution was added; no visible precipitate was obtained. Then some .01M potassium sulphate was added; again no precipitate was visible. More potassium sulphate solution was added and precipitation of benzidine sulphate occurred only when the volume added was about three times the volume used initially. A blank test was performed in which the sulphato complex solution was replaced by an equal volume of distilled water. A large precipitate was obtained on the first addition of the .01M potassium sulphate solution. It was determined that an equimolar mixture of potassium sulphate and potassium dioxalatodiaquochromiate instantly precipitated benzidine sulphate on addition of benzidine hydrochloride solution.

These observations suggested that although the solution contained a large amount of free $SO_4^=$ at the "minimum point", this was not precipitated by benzidine owing to some peculiar physical property of the solution. The importance of this finding requires no emphasis and is discussed at a later stage (Section 4).

The pH values recorded in Table 19, Column 4, show that initially the solution had a pH of about 3.8 at 21.7°C but the pH curves do not show the titration of a

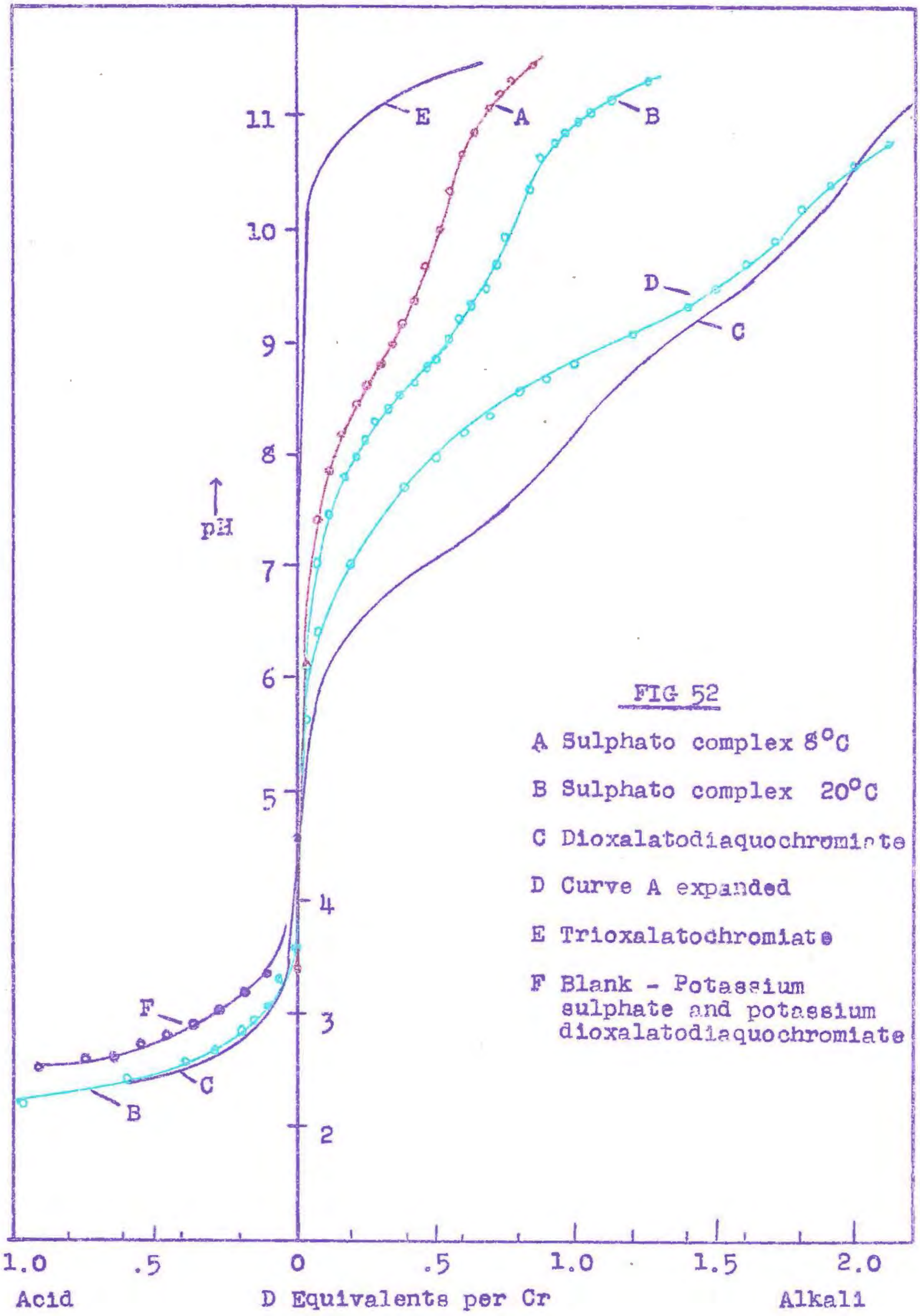


FIG 52

A Sulphato complex 8°C
B Sulphato complex 20°C
C Dioxalatodiaquochromiate
D Curve A expanded
E Trioxalatochromiate
F Blank - Potassium sulphate and potassium dioxalatodiaquochromiate
pH
11
10
9
8
7
6
5
4
3
2
E
A
B
D
C
F
C
B
1.0
.5
0
.5
1.0
1.5
2.0
Acid
D Equivalents per Cr
Alkali

large amount of strong acid, so it was decided to study the potentiometry of the sulphato complex more thoroughly. First, more accurate acid and alkali potentiometric titrations were performed on freshly prepared solutions of the solid at room temperature (20°C) and a concentration of about .1% Cr_2O_3. These are shown as Curve B in Fig. 52. The alkali curve at a lower temperature (8°C) is also shown (Curve A) and it is apparent that, while the initial pH is lower at the lower temperature, there is less acid titrating. Comparison with Curve C for pure dioxalatodiaquochromiate, shows that Curves A and B might represent the titration of smaller amounts of dioxalatodiaquochromiate ion, In other words, the solution might contain a certain amount of free dioxalatodiaquochromiate initially or this might be produced during titration with alkali. To check this, Curve A was transformed so that an exact comparison with the dioxalatodiaquochromiate curve was possible. This was achieved by assuming that the acid titrating in Curve A had approximately the same end point as dioxalatodiaquochromiate i.e. pH 10.6. Curve A was then expanded so that the alkali reading at 10.6 occurred at 2.0, the same as the dioxalatodiaquochromiate curve. The expanded curve has been plotted as Curve D, Fig. 52. The expansion of Curve B by the same procedure gave a curve of shape similar to D, while expansion of Curves (b) and (c) in Fig. 49 gave curves which lay between C and D, in Fig. 52.

It is evident that curves C and D show a considerable difference, especially in the region between pH 4 and 9. This indicates that the solutions titrated at 20° and 8° contained an acid other than dioxalatodiaquochromiate, which decomposed on ageing. This acid is weaker than the first aquo group of the dioxalatodiaquochromiate ion since most of it appears to titrate above pH 8.

Below pH 4, Curve B (measured at 20°) is compared with the dioxalatodiaquochromiate curve, (C), and with the curve for the titration of an equimolar mixture of potassium sulphate and potassium dioxalatodiaquochromiate, (F), at the same concentration. Since it appears that the curve for the sulphato complex is close to that of the dioxalatodiaquochromiate, there can be no doubt that a large amount of free sulphate ion was not initially present in solution. This also shows that titration with acid does not remove coordinated SO_4.

The pH of a solution of the sulphato complex was then measured at nearly 0°C. At this temperature the solid did not dissolve immediately but absorbed water to form an oily syrup on the bottom of the vessel. This syrup had to be stirred vigorously before it dispersed. The pH meter available could not compensate for temperatures below 10°C and so differences in the readings of a standard buffer solution with a small temperature coefficient between

10 and 0°C was used as an indication of the error involved. Fortunately, this was negligible.

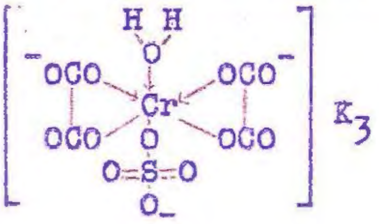
The pH values of freshly prepared sulphato complex solutions at the same concentrations (.1% Cr_2O_3) are compared below:

Temperature	pH
1°C	3.35
8°C	3.46
20°C	3.66

Evidently a moderately strong acid was present at low temperatures which decomposed as the temperature rose. However, this acid must have been present in very small amount since it did not show appreciably on the titration curves (Curve A, Fig. 52, for example).

4. Discussion

The foregoing experimental work does not establish the structure of the sulphato complex with certainty. It is known that the solid had the empirical formula $K_3\left[Cr(C_2O_4)_2(SO_4)(H_2O)\right]$ but there are indications that it contained a mixture of complexes. One complex having this empirical formula has the constitution:



No importance should be attached to the exact positions of the double and coordinate bonds in this diagram : they have been included merely to show a possible charge distribution.

In order to prove the existence of this complex, it is necessary to obtain evidence for the presence of a single coordinated water molecule and a sulphato group coordinated by one position only.

Now a complex possessing a single aquo group should act as a weak acid, even weaker than the dioxalatodiaquochromiate ion. The potentiometric data indicated that the sulphato solid contained an acid weaker than dioxalatodiaquochromiate, but they also indicated that less than one equivalent of this acid was present per Cr and that the exact amount appeared to vary with the temperature at which the solid was dissolved (See Fig. 52).

Evidence for the existence of a singly bound sulphato group is obtained from the fact that all of the complex could be precipitated with benzidine when freshly dissolved. Experience shows that sulphato complexes in which the sulphate occupies two coordination positions do not give a precipitate with benzidine and it was determined that a solution of a complex having three negative charges, namely, potassium trioxalatochromiate, did not give a precipitate with benzidine either, therefore, the triple negative charge could not be the factor causing a precipitate with benzidine.

Thus it is reasonable to suppose that the sulphatodioxalato complex is capable of forming an insoluble compound with benzidine because the sulphate is bound by one coordination link only. This evidence is only indicative in view of numerous other factors which determine solubility.

It seems likely, therefore, that the sulphato solid contained some potassium sulphatodioxalatoaquochromiate. Without more data, further deductions would be unjustified and a number of problems, such as the reason why all of the coordinated water molecules - that is if all the water molecules were coordinated - did not titrate as weak acid (Cf Fig. 52), and the reason for the presence of a small amount of strong acid at low temperatures, must be left in abeyance.

It must be assumed that the sulphatodioxalatochromiate ion undergoes a gradual decomposition with time and liberates the coordinated sulphate group, its place being taken by H_2O. An important problem to be considered, is why, at some stage during this decomposition, does benzidine hydrochloride give no precipitate ? It was proposed in the preceeding section that, although at this stage the solution contains free sulphate, the benzidine sulphate does not precipitate on account of some physical property of the solution at the "minimum point". For example, at this point the precipitate may exist as an invisible, non-filterable colloid. This explanation is consistent with the spectrophotometric and potentiometric data and is supported by the fact that under these conditions some additional sulphate can be added to the solution without causing precipitation.

An alternative, but less reasonable, explanation is that the sulphato complex (I) converts to another complex (II) which still contains sulphate but which has the spectrophotometric and potentiometric properties of the cis dioxalatodiaquochromiate ion. Complex (II), unlike (I), is not precipitated by benzidine. At the point corresponding to minimum precipitation by benzidine, (I) has been converted almost entirely into (II) which then decays to give dioxalatodiaquochromiate and free sulphate. On this hypothesis, extra sulphate added at the minimum point would have to coordinate instantly to prevent precipitation. This does not seem feasible.

5. The Sulphatodioxalatohydroxochromiate Complex

Since there was evidence that the sulphato complex contained a single coordinated water molecule, it was decided to attempt to form a hydroxo derivative.

To a freshly prepared, concentrated solution of the sulphato solid at about 5°C, one equivalent of potassium hydroxide per Cr was added. The solution, which was light green in colour, was then made to standard volume with cold water, such that the concentration was .07% Cr_2O_3. The solution had a pH of about 11 as indicated by the glass electrode.

A complete absorption spectrum of this solution was measured at about 8°C. The measurements had to be done in three sections using three fresh samples of a solution prepared at 5°C, since decomposition occurred during readings. The curve is shown in Fig. 46, Curve D.

The fact that the shape of the absorption curve has been altered considerably by the addition of alkali is a sign that a reaction involving the complex has occurred. The new curve is quite unlike that of the dioxalato-dihydroxochromiate (Fig. 14, Chapter 5) so it is apparent that an appreciable amount of this ion could not have been present in solution. This also proves that the addition of alkali did not remove an appreciable quantity of the sulphate from the complex, or else the dihydroxo derivative would have been formed at pH 11. The curve has a slight resemblence to that of the hydroxoaquo derivative (Fig. 14) but this ion cannot exist at pH 11. Thus it may be accepted that the absorption curve is due to the dioxalato-sulphatohydroxochromiate ion; with the probable addition of small amounts of other, unknown, sulphato complexes.

The decomposition of the sulphatohydroxo solution was studied and it was determined that, even at about 1°C, this ion gradually changed to the dioxalatohydroxoaquochromiate ion. This was determined by observing that the pH dropped from 11 to 8 in about 12 hours by which time the optical density at a number of wavelengths was close to that of the hydroxoaquo derivative.

6. Summary

Evidence in favour of the existence of the ions:

$\left[Cr(C_2O_4)_2(SO_4)(H_2O)\right]^{\equiv}$

and $\left[Cr(C_2O_4)_2(SO_4)(OH)\right]^{==}$

has been presented, although they have not been isolated as pure salts.

It has been shown that the benzidine method for determining free $SO_4^{=}$ in the presence of coordinately bound sulphate is liable to give entirely false results under certain conditions: (i) when the sulphato complex is itself capable of precipitation and (ii) when no precipitate forms despite the fact that the solution contains free sulphate.

Chapter 10

THE SIGNIFICANCE OF THE ABSORPTION SPECTRA OF COMPLEX TRIVALENT CHROMIUM COMPOUNDS IN AQUEOUS SOLUTION

1. Introductory

In the course of the preceeding seven chapters, about twelve absorption spectra of complex chromium compounds, and a number of spectra of mixtures of complexes, have been measured. Of these, only that of potassium trioxalatochromiate has been published hitherto, as far as is known.

It has been found by previous investigators, (40, 73), that the absorption spectra of chromium(III) and cobalt(III) complexes exhibit two or more maxima between 300 mμ and 700 mμ. This is confirmed by the spectra illustrated in the present work. Thus in all cases a maximum is shown in the yellow region at about 550 mμ, another in the near ultra-violet at about 420 mμ and a third below 300 mμ. Those complexes containing oxalate show total absorption below 300 mμ.

Previous investigators (73) have found that the nature of absorption curves, especially as regards the positions and shapes of the peaks, is dependent upon the character of the groups coordinated to the complexes. The most important aim of any investigation in this field is to find the relationships between the properties of the coordinated groups and their influence on the absorption spectra. In the present chapter, it is proposed to discuss this aspect in some detail.

First, it is desirable to consider what sort of information we may expect to obtain from an absorption spectrum. Even for a diatomic molecule in the vapour state, the interpretation of the absorption spectrum is very difficult although in some cases quantities like dissociation energies and moments of inertia can be obtained. Now for an ion having 19 atoms, like the trioxalatochromiate ion, it is apparent that, even if the absorption spectrum for the vapour state could be obtained, the elucidation of its fine structure would be almost impossible. It has already been mentioned (page 9) that, owing to phenomena like the Stark Effect, the spectra of solutions do not exhibit fine structure. Thus it is evident that we must expect to obtain less exact data from the absorption curves of complex ions in solution.

For many organic molecules in solution, it has been possible to associate different parts of the absorption spectra with definite atomic groupings and linkages, and the earlier attempts to interpret the absorption spectra of complex ions were along the same lines. For example, Shibata and co-workers (74) and also Lifschitz and Rosenbohm (75) proposed that each of the absorption peaks could be associated with a definite part of the complex. The maximum associated with the longest wavelength was thought to be due to the central atom while the next maximum was assumed to be connected with the coordinated groups. However, we now possess evidence which shows this theory to be quite incorrect (40). Thus it appears that the spectra of complex ions may not be interpreted in the same way as has sometimes proved successful in the case of certain organic substances.

In 1934 Mead (40) proposed that the maxima observed for chromium and cobalt complex ions represent different states of excitation of the coordination electrons.

In 1936 Mathieu (73) supported this view from evidence based on photochemical experiments. Thus it may be accepted that the large absorption peaks in the spectra of complex chromium and cobalt ions in the visible and near ultra-violet are due to electronic transitions involving the hybridised 4s, 4p and 3d electrons. A recent suggestion by von Kiss et al. (76) that lower electron levels may be inolved is unconvincing.

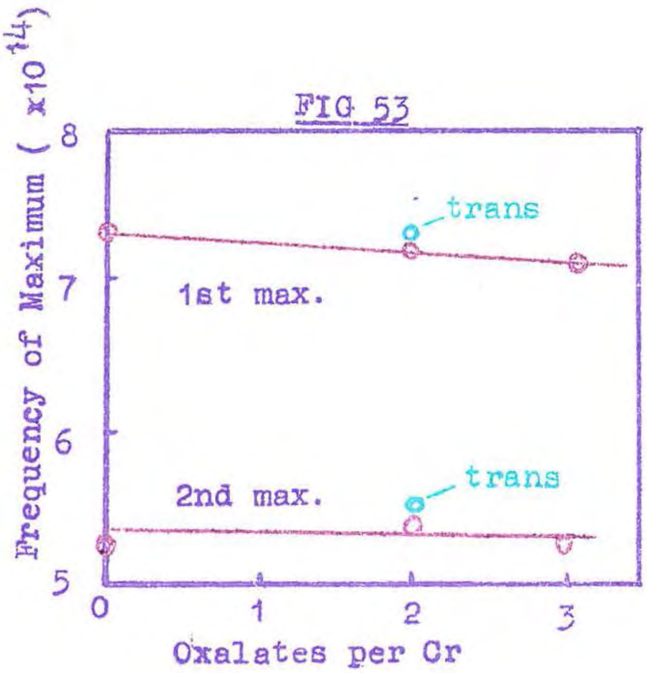
Mathieu (73) found that when one or two of the coordinated groups of a given complex ion were replaced by a group or groups which coordinated less strongly with the central atom, then the positions of the maxima in the visible region are displaced towards the red. He made this deduction from series such as; $[Co\ en_2(NH_3)A]$ where A represents any of the groups: Cl, NCS, H_2O, NH_3, NO_2. As a measure of the strengths of the bonds formed with these groups, he used their relative stabilities in aqueous solution.

In addition, Mathieu tried to correlate physical properties of the coordinated groups, such as molar refraction and magnetic properties, with the displacements in the absorption maxima, but without success.

Mead (40) measured the absorption spectra in aqueous solution of a number of complex chromium and cobalt compounds, using a Hilger - Nutting photometer and a Hilger medium quartz spectrograph. He found that, for the series $[Cren_3]^{+++}$, $[Cr(C_2O_4)en_2]^{+}$ $[Cr(C_2O_4)_2en]^{-}$, $[Cr(C_2O_4)_3]^{---}$, a linear relation exists between the frequencies at which the absorption maxima occur, and the number of oxalate groups in the complex. This result is somewhat similar to that obtained earlier by Colmar and Schwartz (77). The latter workers carried out a thorough investigation of the differences in the shapes of the absorption curves of the series: $[Cr(NH_3)_6]$, $[Cr(NH_3)_5(H_2O)]$, $[Cr(NH_3)_4(H_2O)_2]$, $[Cr(NH_3)_3(H_2O)_3]$, $[Cr(NH_3)_2(H_2O)_4]$, $[Cr(NH_3)(H_2O)_5]$, $[Cr(H_2O)_6]$, between wavelengths 400 mμ and 600 mμ. They found a linear decrease,,both in the frequency at which maximum occurs and in the molar extinction coefficient at that frequency, as the number of coordinated water molecules per Cr increased. A similar linear relation was also observed for the corresponding cobalt series.

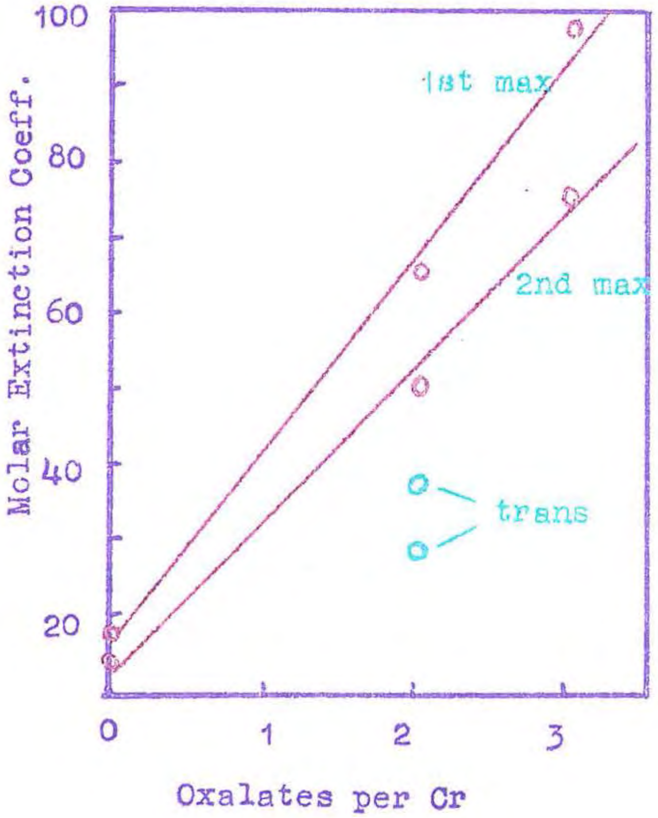
In order to ascertain whether relations similar to those found by Colmar and Schwartz and by Mead hold for some of the absorption spectra reported in the previous chapters, data for the series: $[Cr(C_2O_4)_3]^{---}$, $[Cr(C_2O_4)_2(H_2O)_2]^{-}$, $[Cr(H_2O)_6]^{+++}$ were examined. The frequencies and molar extinction coefficients of the first and second maxima for these ions are shown in Table 20.

FIG 53



Frequency of Maximum (x10^14)
8
7
6
5
trans
1st max.
2nd max.
trans
0
1
2
3
Oxalates per Cr

FIG 54



Molar Extinction Coeff.
100
80
60
40
20
1st max
2nd max
trans
0
1
2
3
Oxalates per Cr

TABLE 20

Ion	Frequency		Molar Ext. Coeff	
	1st max.	2nd max.	1st max	2nd max
$Cr(C_2O_4)_3^{---}$	$7.16x10^{14}$	5.27×10^{14} sec^{-1}	98.3	76.0
cis $Cr(C_2O_4)_2(H_2O)_2^-$	7.23 "	5.36 "	65.9.	50.5
trans $Cr(C_2O_4)_2(H_2O)_2^-$	7.29 "	5,52 "	37.5	28.2
$Cr(H_2O)_6^{+++}$	7.32 "	5.26 "	17.4	14.1

In Figs 53 and 54 the frequency and molar extinction coefficient have been plotted against the number of oxalate groups per Cr. Two points have been plotted in each case for the $[Cr(C_2O_4)_2(H_2O)_2]^-$ ion, one for the cis and the other for the trans isomer. Though only three points are involved if the data for the trans form of the dioxalatodiaquochromiate ion be excluded, it is apparent that approximately linear relations exist, in agreement with the work of previous investigators.

In order to account for the linear relationship between the number of similar coordinated groups on the one hand, and the extinction coefficients and the positions of the maxima, on the other, Colmar and Schwartz proposed that the energy levels of the coordination electrons remained constant for a given metal and that the changes in absorption were due to changes in the vibrational levels brought about by changing the coordinated groups. For example, when an H_2O molecule replaces an NH_3 group from the complex $[Cr(NH_3)_6]$ giving the complex $[Cr(NH_3)_5(H_2O)]$, then the absorption peak in the visible region decreases in height, becomes wider, and the position of the maximum is displaced towards the red. According to the Colmar and Schwartz explanation, the H_2O and NH_3 groups are fixed to the Cr atom by bonds of different strengths, so that different modes of vibration will be possible for the two complexes, with a resulting change in the absorption spectra. It was assumed that this effect is additive in view of the linearity observed for the series; $[Cr(NH_3)_6]$,$[Cr(NH_3)_5 (H_2O)]$, $[Cr(NH_3)_4(H_2O)_2]$, etc.

This theory deserves careful consideration since it explains the results obtained by Mead, and ,as shown above, it appears to be supported by some of the measurements recorded in the present work. Mathieu (73) has pointed out that it is fallacious to think of the electronic and vibrational energy levels separately and he prefered to consider the energy of the system as a whole. This is clear enough when it is recalled that the vibrational energy levels are merely additional permissible positions for the electrons; similarly for the rotational levels, although the effects of these are much smaller. Nevertheless, only a change in the fundamental electronic levels can cause an appreciable shift in the position of the band system as a whole; vibrational changes can merely alter the numbers and positions of the bands in the system.

Another point to be considered is whether changing the coordinated groups of a complex ion can alter the fundamental electronic energy levels, apart from changes in vibrational and rotational energy. An answer to this may be possible from the following considerations:

Chromium complex ions exhibit an extremely small band in their absorption spectra in the region between 660 and 700 mμ. This band is just visible in some of the spectra recorded in this work (e.g. Fig. 14, Curve D). Johnson and Mead (26) have studied these bands or "characteristic bands" as they termed them, and found that, like the larger absorption peaks, these bands change in position when the coordinated groups are changed. One explanation for these minute bands is that they are due to transitions of the coordination electrons, in a manner similar to that of the larger maxima. However, Johnson and Mead proposed that the "characteristic bands" are due to transitions involving electrons other than the hybridised electrons. The electronic configuration of Cr^{+++} is considered to be:

4p OOO
3d OO⊙⊙⊙
4s O

It is the three unpaired d electrons which, according to Johnson and Mead, give rise to the "characteristic bands". They also considered that these bands represent pure electronic transitions, not influenced by vibrational or rotational changes.

Now Co^{+++} has the configuration:

4p 000
3d 00⊙⊙⊙
4s 0

This ion has no unpaired electrons so that, if this theory is correct, "characteristic bands" should not be found in the corresponding cobalt complexes. Johnson and Mead found that cobalt complexes do not exhibit these bands, in confirmation of the theory.

It has been mentioned that the positions of the "characteristic bands" depend on the coordinated groups. For example, the band is at 669.5 mμ for the $[Cr(H_2O)_6]^{+++}$ ion and at 684.5 mμ for the $[Cr(C_2O_4)en_2]^{+}$ ion. This is important in view of the theory of the origin of these bands because it indicates that the coordinated groups can influence the energy levels of those 3d electrons which are not involved in bond formation. It is, therefore, not unreasonable to assume that the coordinated groups can alter the energy levels of the electrons which form the bonds.

In the case of the various series of complex ions studied by Colmar and Schwartz, by Mead and by the author, it is unnecessary to postulate large changes in the electronic energy levels to account for the changes in the absorption spectra. Most of the spectra which have been published seem to be of this type. However, for certain complexes, very large displacements in the maxima, on changing the coordinated groups, have been reported.

For example, the visible maximum for $[Coen_2BrCl]$ is at about 560 mμ while that for $[Coen_2(NO_2)_2]$ is at about 440 mμ - a difference of over 100 mμ (73). In these cases it is likely that the coordinated groups have a more profound influence on the electronic energy levels than merely altering the vibrational bands.

In general, therefore, it may be stated that the positions of the absorption maxima depend, firstly on the positions of the fundamental electronic levels and secondly on vibrational changes to these levels. The existence of linear relations such as those found by Colmar and Schwartz, cited above, may be taken as an indication that the coordinated groups influence only the vibrational bands.

Attention may now be directed towards the question of the significance of the difference in heights between corresponding absorption peaks of the various complexes. In 1936 Mathieu (73) found that for the series; $Cl_3[Co(NH_3)_6]$, $Cl_3[Coen_2(NH_3)_2]$, $Cl_3[Co\ en_3]$, $Cl_3[Co\ pn_3]$, where en and pn refer to ethylene diamine and propylenediamine respectively, the height of the maximum between 400 and 500 mμ increased as the molecular weights increased. Only very small changes in the frequencies of the maxima occurred at the same time. The complex ions all possess the same charge, and Mathieu considered that all of the coordinated groups had approximately the same chemical affinity. From these results he concluded that, other things being equal, an increase in the molecular weights of the coordinated groups can cause an increase in the light absorption at a given maximum.

Since in general it is found that a change in the coordinated groups which causes a frequency displacement in one or more maxima also changes the heights of the maxima, it is desirable to consider whether the vibrational changes which may occur on subsititution are sufficient to account for these variations in height. Now for a given frequency, absorption only occurs if the difference in energy between two permissible energy levels is equal to the energy of the quanta of this frequency. An increase in absorption can only be brought about by an increase in the number of pairs of levels having the right energy difference. Complex chromium ions have at least twelve electrons which can be regarded as taking part in absorption in the visible and near ultra-violet. Thus it is evident that an enormous number of energy levels are possible and probably a large number of permissible transitions will correspond to the same energy value. It is impossible to pursue this problem further in view of our present limited knowledge, but it is certain that changes in vibrational levels occurring on replacing coordinated groups are capable of changing the heights as well as the positions of the absorption peaks.

It is convenient at this stage to attempt to formulate some general rules based on the investigations which have been reviewed above:

(1) The absorption spectra of chromium(III) and cobalt(III) complex ions in solution possess a number of peaks or maxima in the visible and near ultra-violet regions.

(ii) These peaks are due to transitions involving the hybridised electrons.

(iii) A large change in the positions of the peaks can occur only if a group coordinated to the metal is replaced by another which is capable of altering the fundamental frequencies due to electronic transitions.

(iv) In general, changing the coordinated groups merely causes small alterations to the heights and positions of the peaks owing to alterations to the modes of vibration and rotation of the system.

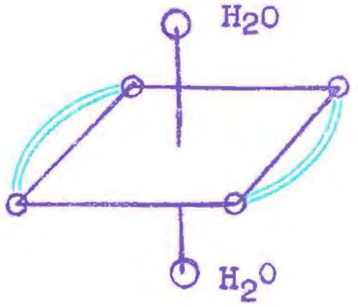
Rule (iv) can be amplified by two further rules which have been found to hold in a few cases (73) ;

(v) If in a given complex, a coordinated group is replaced by another which is less firmly coordinated, then the positions of the maxima are displaced towards the longer wavelengths.

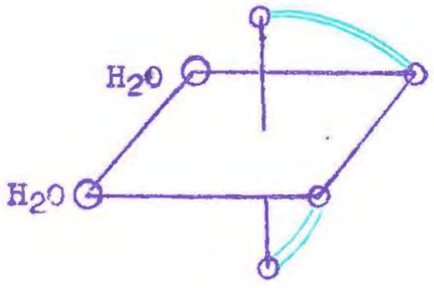
(vi) If a group is replaced by another with similar properties but larger molecular or ionic weight, then an increase in absorption occurs with very little shift in the wavelengths of the maxima.

To return to the spectra recorded in the present work. The first two of the above rules are obviously in accord with these curves since they all possess three maxima in the spectral range considered. Rule (iii) does not apply because in all cases only very small shifts in the positions of the maxima were noted. Thus it may be concluded that the differences noted amongst the spectra in this work are all explicable in terms of the changes in the modes of vibration and rotation brought about by changing the coordinated groups (Rule (iv)).

The differences between the spectra of the <u>cis</u> and the <u>trans</u> forms of the dioxalatodiaquochromiate ion (Fig. 12) are very noticeable. The same phenomenon has been observed qualitatively for other complexes, but as far as is known, no actual absorption curves have been published. It has already been mentioned that the two isomers are:



<u>trans</u>



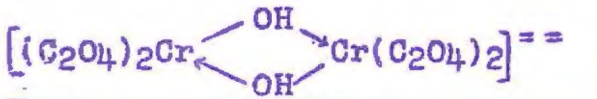
<u>cis</u>

These structures are sure to have different modes of vibration in view of the different positions of the aquo groups, so that from Rule (iv) above, different absorption spectra are to be expected. This is found in practice.

The application of the empirical rules (v) and (vi) is not possible in this case since there is no question of a single group being replaced by another, but rather a complete rearrangement of the groups.

In Chapter 5 the absorption curves of a number of closely related complex ions are illustrated (Fig. 14). These complexes all possess the grouping $Cr(C_2O_4)_2$, their formulae being:

$[Cr(C_2O_4)_2(H_2O)_2]^-$ Dioxalatodiaquochromiate
$[Cr(C_2O_4)_2(H_2O)(OH)]^{--}$ Dioxalatohydroxoaquochromiate
$[Cr(C_2O_4)_2(OH)_2]^{==}$ Dioxalatodihydroxochromiate



$$\left[(C_2O_4)_2Cr\begin{smallmatrix}OH\\ \\OH\end{smallmatrix}Cr(C_2O_4)_2\right]^{==}$$ (Olated Complex)

$[Cr(C_2O_4)_2(C_2O_4)]^{---}$ Trioxalatochromiate.

The spectra of these complexes exhibit rather striking differences - espeially in the relative heights of the peaks - and at first it was thought possible to apply Rule (v) above to this system. From this rule it would be expected that the most stable complexes would have their maxima nearest to the shorter wavelengths. This does not appear to be true, either at the visible or at the ultra-violet maximum, since there seems to be no relation between the stability of the complexes and the relative positions of the peaks. This does not mean that the rule is valueless, but it does imply that it is not applicable to complicated cases such as the above system.

Rule (vi) is also inapplicable since the coordinated groups do not have the same properties.

Before leaving this system, it should be mentioned that the curve for the dioxalatohydroxoaquochromiate has a much wider peak in the ultra-violet than the corresponding diaquo complex, while the visible peak is displaced towards the red. In Chapter 9 Fig. 46, it was seen that a similar relation exists between the hydroxo and aquo derivatives of the sulphato complex i.e.

$$[Cr(C_2O_4)_2(SO_4)(H_2O)]^{---}$$

and $$[Cr(C_2O_4)_2(SO_4)(OH)]^{==}$$

although the composition of the solutions was not known with such certainty in this case. These similarities suggest that, for this system, the conversion of an aquo group to hydroxo has a more or less constant effect on the shapes of the curves.

It will be recalled that in Chapter 8, Fig 33 the curves for the malonatodioxalato and trioxalatochromiates;

$$[Cr(C_2O_4)_2(C_3H_2O_4)]^{---}$$
$$[Cr(C_2O_4)_2(C_2O_4)]^{---}$$

had maxima at about the same wavelengths. The curve for the trioxalatochromiate is considerable higher than that for the malonato derivative, even taking into account the fact that the malonato solutions contained a small amount of impurity. Now from Rule (vi) above it would seem that, if we regard malonate and oxalate as having approximately similar properties, the curve for malonate should be higher than that for oxalate, since the former group has the higher molecular weight. The fact that this is not the case shows, once again, that the empirical rules given above cannot be applied to more complicated systems. The reactions of the other dibasic groups investigated in Chapter 8 all caused the positions of the maxima to be shifted slightly towards the red. For the same reason, the exact significance of these displacements is not clear.

In considering the question of correlations between the positions and heights of the absorption peaks and the properties of the coordinated groups, mention should be made of the fact that certain quantitative relations have been suggested in the past (78). For the curves of chromium complexes, the most successful has been that of Mead (40) which fits the curve for potassium trioxalatochromiate extremely well between wavelengths 500 and 650 mμ, that is, the second peak. The equation is of the form:

$$k = k_m e^{-\beta(\lambda - \lambda_m)^2}$$

where k_m is the extinction coefficient at the wavelength of maximum absorption λ_m,

k is the extinction coefficient at wavelength λ and

β is a parameter depending on the semi-width of the band.

Further elaborations have been made by Mathieu (73) but it is difficult to see the value of such equations in view of the nature of these absorption spectra.

In addition, Mead (40) used the frequency shift occurring between the maxima when one group is replaced by another to calculate the difference in energy involved. At first it was thought that this would provide a useful method for finding the energy involved when one coordinated group is replaced by another and that this value could be compared with the activation energy obtained kinetically. However, consideration shows that this is impossible. The position of the highest point of the absorption peak has no real theoretical significance and is dependent upon alterations in the modes of vibration of the system and not on the reaction energy or activation energy alone. This can readily be proved by considering a specific case. For example, the reaction studied in Chapter 7:

cis dioxalatodiaquochromiate + oxalate ⟶
trioxalatochromiate + water.

It has been shown that a tentative value for the activation energy of this reaction is 30,000 calories per mole. Now the difference between the highest points in the visible absorption peak for cis dioxalatodiaquochromiate and trioxalatochromiate is 9 mμ which corresponds to about 890 calories per mole. It is apparent that these energy values have little relation to each other even allowing for corrections which may be necessary. If instead, the shift in the wavelength for the ultra-violet peak is considered, the result is even more ridiculous since this difference is only about 4 mμ. In fact, the wavelength differences between the corresponding maxima for the trans and cis forms of dioxalatodiaquochromiate are actually larger than the differences between those of the cis isomer and the trioxalatochromiate. It has been shown in Chapters 4 and 7 that less energy is involved in the conversion from trans to cis than for the reaction between the cis isomer and oxalate, the activation energies being 17,600 and 30,000 cals per mole respectively.

Finally, it should be noted that Samuel and co-workers (79) have shown that slight differences in absorption occur when a given complex ion is present in solution with different kations (or anions). For this reason only the potassium salts have been considered throughout this work and previous workers have usually restricted investigations to potassium or sodium salts.

To conclude: At the present time the absorption spectra of aqueous solutions of chromium complexes are useful for investigations on the stability of the ions, for studying the progress of reactions involving complex ions and for estimating quantitatively the amounts present, but more fundamental data cannot be expected from the shapes of the curves or from the relative positions of the maxima.

Chapter 11

CONCLUSION

In previous chapters a number of specific topics have been dealt with in some detail, together with the theoretical discussion considered necessary for the exposition of the experiments. In conclusion, two aspects of this work as a whole may be considered.

1. The Stability of Chromium Complex Ions in Aqueous Solution

The results obtained for the individual complex ions are summarised in Table 21 below, in which the stability is indicated qualitatively for .00921M solutions at room temperature (about 20°C). Werner's observations for the acetatodioxalatochromiate derivatives (13) are included:

TABLE 21

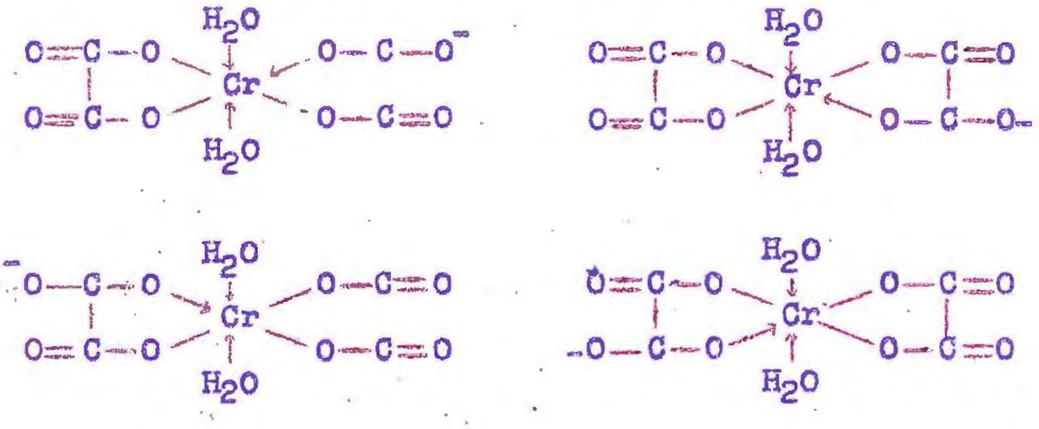
Ion	Stability	Resomers
Trioxalatochromiate	Quite stable in neutral, decomposes in acid solution to give oxalate and the dioxalatodiaquochromiate	40
cis Dioxalatodiaquo chromiate	Stable above about pH 1	4
trans Dioxalato-diaquo-chromiate	Converts to cis form in about 3 hours	4
cis Dioxalatohydroxo aquochromiate	Olates slowly at 20°C and in about 2 hours at the boil	6

Cis Dioxalatodihydroxochromiate	Decomposes rapidly to give oxalate and other, unidentified ions	4
Sulphatodioxalatoaquochromiate (?)	Decomposes in about 20 hours to give sulphate and dioxalatochromiate	(70)
Malonatodioxalatochromiate	Of the same order of stability as the trioxalatochromiate	(40)
Dioxalatoacetatochromiates (Werner (13))	Quite unstable even in strong solution; liberate acetic acid.	?

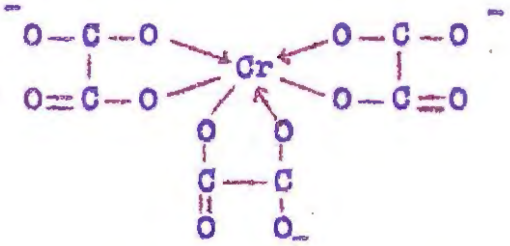
It is apparent that the strength of the coordinative bonds involving a given group depends on the complex to which the group is attached. For example, the oxalate groups are not readily discharged from the cis dioxalatodiaquochromiate complex in dilute solution, but one or both similar groups in the cis dioxalatodihydroxochromiate ion are rapidly liberated in solutions of the same concentration. This indicates that results deduced from one system are not necessarily applicable to another system, and — more important — that in order to obtain a correct picture, the complex must be considered as a whole.

Unfortunately, quantitative data on bond strengths for complicated atomic systems such as the complexes under discussion, cannot be calculated, even by the methods of wave mechanics. For organic molecules, the Resonance Theory has been of great value in explaining the stability of a number of molecules. This quasi-quantitative method has not been applied to chromium coordination compounds, as far as is known, and it is considered beyond the scope of this work to undertake a prolonged study of this subject. Nevertheless, several suggestions can be made:

A dioxalatodiaquochromiate ion is capable of the following resonance structures:



Calculation shows that the trioxalatochromiate ion has 40 resomers, one of which may be written:

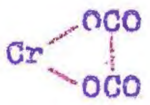


It is, therefore, probable that these ions are resonance hybrids and this is supported by the fact that they are highly dissociated in aqueous solution, indicating that the negative charges are distributed over the ion as a whole and not confined to particular atoms.

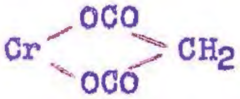
In Table 21 above, the number of possible resonance structures for some of the complex ions have been tabulated. It is apparant that other factors have a more important influence on the stability of these complexes than the number of resonance structures. (For example, compare the stabilities of the dioxalatodiaquochromiate and the trioxalatochromiate with the number of resomers).

It appears that the stability of groups attached to a given complex under identical conditions depends upon two factors; (a) what may be called the "inherent coordinative power" of the group, which is due to its electronic arrangement and (b) spatial considerations.

The latter does not play a very large part in the case of monatomic or singly charged groups like Cl^- or OH^- , but it is probably the most important single factor in the case of dibasic groups such as oxalate, malonate, etc (81). Thus the reason why the oxalate group is more stable than most other groups, is because it is capable of forming a five-membered ring:



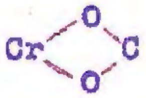
which is very stable on account of its steric arrangement. It may be inferred that the reason why the malonate group appears to have more coordinative power than other dicarboxylic groups, but less than the oxalate, is because it can form a six-membered ring:



which is more stable than higher rings, but not quite as stable as the ring with five atoms.

It is to be noted that the acetate group, although it possesses a carboxyl, forms complexes with dioxalatochromiate which are not as stable as those of the dibasic acids. According to the above argument, this is because acetate is incapable of forming such stable rings.

The question as to whether a carboxyl group can coordinate to form a four membered ring:



cannot be regarded as settled. (See for example the discussion by Sidgwick(82)). However, if this does occur it must be very much less stable than the five-membered or six-membered rings for the anionic dioxalatochromiate system.

The aquo and hydroxo groups occupy a unique position in chromium coordination chemistry. There is ample evidence that the hydroxo group is the most firmly held of all the coordinated groups, even oxalate being displaced by excess alkali. On the other hand, the aquo group is one of the weakest as regards coordinating power. Thus, to displace a hydroxo group, it must first be converted, by means of acid, to an aquo group which can then be substituted directly. When olation occurs, even this may not be readily accomplished, because the hydroxo group is not directly titratable with acid, in this case.

2. The Importance of the Physical Methods Used

It is useful to discuss the value of the combined physical methods adopted throughout this work. It must be emphasised that, although spectrophotometry was considered the most important method employed, very little could have been achieved without the confirmatory evidence provided by the potentiometric measurements. This is well illustrated by the investigation of the conversion from trans to cis dioxalatodiaquochromiate described in Chapter 4. The spectrophotometric measurements showed that the complex changed its light absorbtion properties by a first order mechanism in solution; while the constancy of the pH readings during this change showed that this change was not just a step in a type of olation.

But perhaps the advantages of the combined spectrophotometric and potentiometric measurements are best exemplified by the study of the sulphatodioxalato complexes described in Chapter 9; especially in view of the fact that a well-tried method — the benzidine method for sulphate — gave anomalous results in this case. The potentiometric curves indicated the presence of a single titratable aquo group in the complex. This evidence could not have been taken alone since the complex might have undergone decomposition during the titration. However, the spectrophotometric measurements showed that the addition of alkali during titration changed the shape of the absorption curve and similar changes had been shown to occur when aquo groups are titrated with alkali (Cf Chapter 5).

It is obvious from the discussions in this thesis that much remains to be done in the study of chromium coordination chemistry, even in the very small field which has been dealt with. Several of the topics investigated require further study, for example, the coordinative properties of the dicarboxylic acids (Chapter 8) and the problems connected with olation (Chapter 5). It is also considered that much valuable information would be obtained by the application of the spectrophotometric and potentiometric methods, developed here, to systems other than the dioxalatochromiate complexes.

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APPENDIX

In this Appendix, the following symbols are used:

D = Optical Density

λ = Wavelength in millimicrons

In Table A 1 the slit widths recorded are the same as those used throughout the rest of the work.

S.W. - Slit Width in millimetres.

TABLE A 1

The absorption Curve of potassium trioxalatochromiate in .00921M solution - Fig. 2, Curve A

λ	S.W	D	λ	S.W	D	λ	S.W	D
740	.05	.001	550	.04	.641	435	.04	.774
730	.05	.002	545	.04	.608	430	.04	.837
720	.05	.005	540	.04	.559	425	.05	.881
710	.05	.012	535	.04	.510	419	.05	.903
700	.05	.022	530	.03	.461	417	.05	.899
690	.05	.037	525	.03	.403	415	.05	.896
680	.05	.041	520	.03	.355	413	.05	.884
670	.05	.065	515	.03	.307	410	.05	.860
660	.06	.100	510	.03	.264	405	.05	.811
650	.06	.137	505	.03	.223	400	.06	.738
640	.06	.193	500	.03	.195	395	.08	.650
630	.06	.267	495	.03	.171	390	.10	.561
620	.06	.352	490	.03	.165	385	.10	.461
610	.06	.447	485	.03	.164	380	.10	.378
600	.06	.538	480	.03	.172	375	.10	.296
590	.06	.618	475	.03	.185	370	.10	.228
585	.06	.656	470	.03	.197	365	.10	.147
580	.05	.680	465	.03	.248	360	.10	.130
575	.04	.700	460	.03	.336	355	.15	.097
570	.04	.707	455	.03	.422	350	.15	.104
						345	.15	.120
565	.04	.707	450	.03	.501	340	.15	.175
560	.04	.700	445	.04	.608	335	.20	.277
555	.04	.675	440	.04	.692	330	.20	.488
						325	.20	.857
						320	.20	1.45

TABLE A 2

Potassium chrome alum, .00921M solution, Fig. 2, Curve B. The curve below 300 mμ has not been plotted in this figure.

λ	D	λ	D	λ	D	λ	D
740	.004	570	.129	470	.047	370	.081
730	.005	565	.128	465	.055	365	.069
720	.007	560	.126	460	.063	360	.059
710	.008	555	.121	455	.072	355	.054
700	.009	550	.115	450	.082	350	.048
690	.013	545	.108	445	.092	345	.046
680	.017	540	.100	440	.105	340	.047
675	.020	535	.093	435	.117	335	.048
670	.025	530	.085	430	.130	330	.048
660	.028	525	.076	425	.143	325	.050
650	.038	520	.067	419	.153	320	.055
640	.051	515	.063	417	.155	315	.065
630	.065	510	.057	415	.156	310	.067
620	.080	505	.051	413	.163	305	.075
610	.096	500	.047	410	.164	300	.081
600	.110	495	.047	405	.159	290	.100
590	.122	490	.043	400	.155	280	.124
585	.125	485	.042	395	.147	270	.145
580	.128	480	.042	390	.136	260	.157
575	.128	475	.045	385	.124	250	.177
				380	.110	240	.241
				375	.096	230	.447
						220	1.30

TABLE A 3

The kinetics of the <u>trans-cis</u> conversion. Figs 6 and 7.

In this table, $\log = \log_{10}(Dc - D)$

and t = time in minutes.

For this experiment the slit width used was .07 mm.

(1)

Temp. 34.5°C

Conc. .00921M

t	D	log
0	-	-
6.5	.273	-.475
8.75	.316	-.535
12.75	.383	-.648
15.75	.424	-.735
19.5	.466	-.848
25.0	.508	-1.00
30.25	.549	-1.23
35.5	.559	-1.31
46.0	.588	
60	.597	
79	.608	
133	.609	
150	.609	
170	.608	
190	.609	
220	.609	

Dc= .609

(2)

Temp. 32.9°C

Conc. .00921M

t	D	log
0	-	
7.7	.262	-.458
10.2	.304	-.514
14.75	.364	-.609
19.0	.421	-.724
25.1	.477	-.876
31.0	.513	-1.013
35	.536	-1.131
40.5	.559	-1.29
46.5	.572	
59	.592	
78	.604	
109	.610	
119	.610	
131	.610	
141	.610	
160	.610	
180	.610	

Dc = .610

(3)

Temp. 27.0°C

Conc. .00921M

t	D	log
0		
9	.271	-.469
13.5	.342	-.570
18	.393	-.662
21.25	.413	-.703
29.5	.486	-.903
44.5	.540	-1.15
52.5	.569	-1.37
95	.592	
125	.601	
155	.610	
185	.611	
245	.611	
305	.611	

Dc = .611

(4)

Temp. 27.0°C

Conc. .00921M

15	.267	-.466
21.25	.321	-.539
25	.353	-.590
30	.395	-.668
34.25	.423	-.728
39.75	.451	-.799
44	.472	-.860
50	.498	-.951
59	.525	-1.071
75	.561	-1.31
109	.598	
129	.602	
146	.606	
165	.607	
184	.608	
230	.609	
285	.610	
315	.610	
350	.611	

Dc = .611

(5)

Temp. 24.25°C

Conc. .00921M

13	.286	-.490
17.5	.318	-.535
25	.371	-.622
35	.422	-.725
43.8	.458	-.818
53.8	.491	-.925
62.5	.511	-1.044
77	.542	-1.168
89	.560	-1.30
140	.597	
158	.601	
183	.606	
210	.607	
243	.609	
283	.609	
303	.612	
333	.611	
345	.611	
363	.611	

Dc = .611

(6)

Temp. 20.3°C

Conc. .00921M

19	.293	-.484
24.5	.331	-.538
33	.367	-.595
40.5	.400	-.656
44.5	.431	-.721
75	.498	-.910
86.5	.520	-.967
97	.539	-1.086
86.5	.568	
97	.583	
118	.612	
145	.612	
265	.612	
295	.612	

Dc = .612

(7)
Temp. 56.7°C
Conc. .00921M

t	D
3	.512
6	.568
10	.595
14.5	.609
20	.610
26	.610
35	.610
48	.610
60	.610
112	.610
142	.610
183	.610
224	.610
350	.610
420	.612

Dc = .610

(8)
Temp. 27.0°C
Conc. .00549M

t	D	log
4.5	.155	-.660
7	.166	-.682
28	.229	-.839
33	.253	-.917
37.75	.271	-.987
53.75	.315	-1.229
64	.336	-1.420
79.5	.351	
120	.374	
145	.374	
155	.374	
180	.374	
190	.374	

Dc = .374

(9)
Temp. 27.0°C
Conc. .00702M

t	D	log
13.5	.210	-.570
18.75	.261	-.662
23	.287	-.717
29.5	.327	-.791
34	.348	-.883
39.25	.368	-.955
44.25	.386	-1.032
66	.430	-1.309
76	.441	
90	.453	
110	.464	
125	.471	
130	.480	
150	.480	
170	.479	
175	.479	
190	.479	

Dc = .479

(10)
Temp. 27.0°C
Conc. .00702M

t	D	log
4.75	.219	-.506
11	.273	-.588
17	.323	-.682
27	.383	-.830
34	.412	-.925
43	.441	-1.046
54.2	.471	-1.222
70	.521	
100	.526	
130	.530	
150	.530	
170	.529	
180	.531	
205	.531	
223	.531	
280	.531	

(Dc = .531)

(11)
Temp. 27.0°C
Conc. .0157M

t	D	log
7.75	.431	-.207
13.75	.536	-.287
19.5	.620	-.365
28.25	.725	-.486
37	.802	-.602
47	.875	-.752
60	.925	-.896
87	.995	-1.244
135	1.043	
148	1.044	
160	1.050	
180	1.052	
190	1.052	
205	1.052	

(Dc = 1.052)

TABLE A 4

Potassium *cis* dioxalatodiaquochromiate, Fig. 12, Curve B.

λ	D	λ	D	λ	D	λ	D
740	.003	545	.447	419	.615	305	1.00
730	.004	540	.424	417	.619	300	1.3
720	.006	535	.397	415	.620		
710	.008	530	.364	413	.618		
700	.013	525	.332	410	.611		
690	.025	520	.297	405	.583		
680	.032	515	.266	400	.540		
675	.033	510	.234	395	.480		
670	.040	505	.203	390	.421		
660	.060	500	.181	385	.355		
650	.086	495	.158	380	.290		
640	.117	490	.146	375	.230		
630	.155	485	.142	370	.176		
620	.209	480	.143	365	.131		
610	.269	475	.153	360	.095		
600	.329	470	.173	355	.074		
590	.383	465	.203	350	.057		
585	.411	460	.237	345	.048		
580	.435	455	.280	340	.047		
575	.452	450	.327	335	.057		
570	.467	445	.385	330	.089		
565	.475	440	.440	325	.154		
560	.478	435	.498	320	.270		
555	.475	430	.546	315	.446		
550	.460	425	.590	310	.688		

TABLE A 5

Potassium trans dioxalatodiaquochromiate, Fig. 12, Curve C.

λ	D	λ	D	λ	D	λ	D
740	.029	590	.192	470	.137	355	.114
730	.030	580	.213	460	.155	350	.098
720	.031	570	.232	450	.192	345	.089
710	.033	565	.241	440	.241	340	.085
700	.035	560	.247	435	.271	335	.093
690	.043	555	.254	430	.296	330	.104
680	.047	550	.258	425	.319	325	.135
670	.051	545	.262	420	.334	320	.210
660	.053	540	.262	415	.343	315	.330
650	.070	530	.253	410	.344	310	.495
640	.085	520	.232	400	.321	305	.740
630	.102	510	.205	390	.298	300	1.075
620	.125	500	.178	380	.249		
610	.147	490	.153	370	.188		
600	.170	480	.137	360	.133		

TABLE A 6

Potassium cis dioxalatohydroxoaquodioxalatochromiate,

Fig. 14, Curve C.

λ	D	λ	D	λ	D	λ	D
740	.015	590	.418	490	.267	400	.565
730	.022	585	.424	485	.295	395	.541
720	.030	580	.427	480	.325	390	.501
710	.037	575	.427	470	.393	380	.407
700	.062	570	.422	460	.455	370	.283
690	.079	565	.414	450	.504	365	.227
680	.092	560	.402	445	.525	360	.183
670	.121	555	.384	440	.541	355	.153
660	.157	550	.364	435	.559	350	.145
650	.194	545	.345	430	.570	345	.164
640	.237	540	.321	425	.581	340	.215
630	.277	535	.299	420	.588	335	.298
620	.327	530	.277	418	.590	330	.433
610	.361	520	.240	416	.590	325	.632
605	.381	510	.220	414	.589	320	.900
600	.397	500	.227	410	.588	316	1.15
595	.408	495	.243	405	.578	314	1.30

TABLE A 7

Potassium cis dioxalatodihydoxochromiate, Fig. 14, Curve D.

λ	D	λ	D	λ	D	λ	D
740	.043	585	.374	460	.380	390	.780
730	.061	580	.373	455	.440	385	.660
720	.070	575	.368	450	.498	380	.541
710	.088	570	.363	445	.570	375	.439
700	.108	565	.356	440	.648	370	.351
690	.124	560	.345	435	.473	360	.265
680	.143	555	.331	430	.820	350	.308
670	.178	550	.315	425	.918	345	.388
660	.208	540	.273	420	.987	340	.530
650	.240	530	.232	418	1.003	335	.715
630	.302	520	.194	415	1.025	330	.990
620	.328	510	.172	413	1.040	327	1.17
610	.348	500	.164	410	1.040	325	1.32
600	.363	490	.182	405	1.020	322	1.55
595	.371	480	.227	400	.980		
590	.373	470	.297	395	.880		

TABLE A8

Olated complex, .07% Cr_2O_3 solution, Fig. 14, Curve E.

λ	D	λ	D	λ	D	λ	D
740	.018	580	.494	440	.530	355	.115
720	.023	575	.502	435	.587	350	.127
710	.030	570	.504	430	.628	345	.155
700	.035	565	.501	425	.658	340	.203
690	.047	550	.450	422	.665	335	.280
680	.056	540	.393	420	.670	330	.423
670	.074	530	.324	418	.670	325	.648
660	.103	520	.252	415	.662	320	.990
650	.133	510	.195	410	.642	318	1.15
640	.173	500	.155	405	.607		
630	.221	490	.143	400	.553		
620	.288	480	.155	390	.425		
610	.349	470	.203	380	.293		
600	.412	460	.288	370	.186		
590	.454	450	.407	360	.123		

TABLE A 9

Formation of trioxalatochromiate, Series 1 and 5, Table 11, Fig. 18, Curves III and IV.

λ	1	5	λ	1	5	λ	1	5
740	.002	.000	590	.462	.552	505	.208	.215
730	.004	.003	580	.516	.612	500	.185	.187
720	.006	.006	575	.535	.628	495	.162	.165
710	.008	.009	570	.548	.648	490	.151	.155
700	.017	.019	565	.555	.647	480	.151	.160
690	.030	.031	560	.552	.632	475	.163	.173
680	.035	.033	555	.541	.618	470	.186	.197
670	.047	.057	550	.552	.592	460	.270	.306
660	.074	.088	545	.500	.561	450	.384	.452
650	.104	.121	540	.466	.518	440	.525	.620
640	.143	.170	535	.433	.475	435	.592	.693
630	.196	.233	530	.397	.433	430	.643	.753
620	.257	.313	520	.318	.337	425	,690	.800
610	.327	.397	510	.243	.253	419	.712	.816
600	.398	.473	510	.243	.253	415	.713	.812
413	.711	.808	395	.538	.599	365	.124	130
395	.538	.599	390	.465	.512	360	.107	.114
410	.695	.790	380	.319	.345	350	.076	.087
405	.660	.745	375	.249	.268	345	.075	.097
400	.607	.679	370	.193	.205	340	.092	.135
						335	.135	.215
						330	.224	.377
						325	.387	.670

TABLE A 10

The kinetics of the reaction between oxalate and cis dioxalatodiaquochromiate.. Figs 26 to 30.

Wavelength 420 mμ
Slit width .05 mm

t = time in minutes
r = 1/(Dt - D)

(1) Temp. 56.0°C

1			2			4		
$\sqrt{\mu}$ = .177			$\sqrt{\mu}$ = .223			$\sqrt{u}$ = .302		
t	D	r	t	D	r	t	D	r
0	.531	4.02	0	.531	4.02	0	.531	4.02
46	.552	4.39	75	.565	4.65	73	.575	4.88
88	.567	4.70	110	.577	4.93	113	.581	5.03
132	.581	5.03	161	.591	5.29	163	.599	5.53
166	.592	5.32	183	.597	5.46	185	.606	5.75
183	.596	5.44	210	.605	5.71	213	.613	5.99
214	.605	5.71	238	.611	5.92	240	.621	6.29
244	.613	5.99	278	.619	6.21	281	.628	6.58

3

$\sqrt{\mu}$ = .302

t	D	r
0		4.02
75	.570	4.77
112	.581	5.03
162	.597	5.46
184	.601	5.52
212	.611	5.92
239	.619	6.21
280	.625	6.45

N.B.

Dd .531

Dt .780

(2) Temp. 54.0°C

1			2			3		
$\sqrt{\mu}$ = .177			$\sqrt{\mu}$ = .223			$\sqrt{\mu}$ = .258		
t	D	r	t	D	r	t	D	r
0	.531	4.02	0	.531	4.02	0	.531	4.02
56	.553	4.40	59	.557	4.48	61	.558	4.50
101	.566	4.68	93	.565	4.67	105	.576	4.91
148	.578	4.96	148	.585	5.13	152	.590	5.26
182	.586	5.15	184	.592	5,32	184	.597	5.46
239	.598	5.50	240	.605	5.71	242	.610	5.88
319	.612	5.95	320	.620	6.25	323	.622	6.33

4			5			6		
$\sqrt{\mu}$ = .302			$\sqrt{\mu}$ = .342			$\sqrt{\mu}$ = .399		
t	D	r	t	D	r	t	D	r
0	.531	4.02	0	.531	4.02	0	.531	4.02
62	.559	4.53	63	.565	4.65	67	.566	4.68
106	.574	4.86	112	.580	5.01	108	.586	5.15
153	.589	5.24	154	.592	5.32	155	.597	5.46
192	602	5.62	193	.606	5.75	194	.610	5.88
306	.626	6.49	242	.614	6.02	239	.618	6.17
346	.629	6.62	306	.630	6.67	310	.635	6.96
			341	.632	6.76	339	.641	7.19

(3) Temp. 52.0°C

1			2			3		
$\sqrt{\mu}$ .177			$\sqrt{\mu}$ .223			$\sqrt{\mu}$ .258		
t	D	r	t	D	r	t	D	r
0	.531	4.02	0	.531	4.02	0	.531	4.02
61	.542	4.20	62	.548	4.31	64	.550	4.35
108	.559	4.53	109	.561	4.57	112	.564	4.63
166	.571	4.79	166	.576	4.91	168	.579	4.98
220	.582	5.06	220	.588	5.21	222	.591	5.29
280	.595	5.41	280	.598	5.50	282	.601	5.59
310	.600	5.56	332	.608	5.81	334	.610	5.88
342	.604	5.68	379	.613	5.99	380	.618	6.17
379	.610	5.88						

4			5			6		
$\sqrt{\mu}$ .302			$\sqrt{\mu}$ .342			$\sqrt{\mu}$ .399		
t	D	r	t	D	r	t	D	r
0	.531	4.02	0	.531	4.02	0	.531	4.02
65	.553	4.40	68	.557	4.48	74	.561	4.57
113	.569	4.74	114	.571	4.79	116	.578	4.96
170	.585	5.13	171	.588	5.21	173	.598	5.50
223	.596	5.44	224	.599	5.53	226	.609	5.85
285	.608	5.81	286	.610	5.88	286	.620	6.25
336	.616	6.04	308	.613	5.99	309	.626	6.48
381	.623	6.37	341	.620	6.25	342	.631	6.71
			382	.627	6.54	384	.640	7.14

(4) Temp. 50°C

1 $\sqrt{\mu}$ .177			2 $\sqrt{\mu}$ .223			3 $\sqrt{\mu}$ .258		
t	D	r	t	D	r	t	D	r
0	.531	4.02	0	.531	4.02	0	.531	4.02
37	.540	4.15	58	.540	4.15	107	.554	4.43
103	.551	4.37	106	.552	4.39	161	.566	4.68
157	.560	4.55	159	.563	4.61	218	.574	4.86
215	.569	4.74	215	.572	4.81	266	.583	5.08
262	.577	4.93	264	.581	5.03	335	.594	5.37
332	.589	5.24	333	.592	5.32	375	.600	5.56
374	.592	5.32	375	.597	5.46			
403	.596	5.44						
4 $\sqrt{\mu}$ .302			5 $\sqrt{\mu}$ .342			6 $\sqrt{\mu}$ .399		
t	D	r	t	D	r	t	D	r
0	.531	4.02	0	.531	4.02	0	.531	4.02
113	.557	4.48	40	.540	4.15	36	.540	4.15
162	.569	4.74	109	.560	4.55	110	.565	4.65
218	.579	4.98	164	.572	4.81	164	.577	4.93
266	.588	5.21	220	.586	5.15	219	.591	5.29
337	.599	5.53	260	.593	5.35	267	.599	5.53
						338	.609	5.85

(5) Temp. 48°C

1			2			3		
$\sqrt{\mu}$ .177			$\sqrt{\mu}$ .223			$\sqrt{\mu}$ .258		
t	D	r	t	D	r	t	D	r
0	.531	4.02	0	.531	4.02	0	.531	4.02
155	.554	4.43	112	.545	4.26	157	.559	4.53
222	.565	4.65	155	.554	4.42	224	.573	4.81
276	.573	4.83	220	.560	4.55	283	.581	5.03
328	.578	4.96	276	.569	4.73	320	.586	5.16
357	.585	5.13	329	.578	4.94	435	.605	5.70
444	.597	5.46						

4			5			6		
$\sqrt{\mu}$ .302			$\sqrt{\mu}$ .342			$\sqrt{\mu}$ .399		
t	D	r	t	D	r	t	D	r
0	.531	4.02	0	.531	4.02	0	.531	4.02
85	.552	4.38	102	.552	4.39	96	.554	4.43
153	.563	4.61	160	.566	4.68	162	.568	4.72
219	.575	4.87	225	.577	4.93	219	.582	5.06
270	.583	5.07	282	.587	5.18	268	.589	5.24
331	.591	5.28	332	.598	5.44	295	.595	5.47
			450	.610	5.88	386	.607	5.68

TABLE A 11

The kinetics of the oxalate-dioxalatodiaquochromiate reaction.

Figs 26 to 30.

Temp. 56.0°C   T = 329°A   1/T = .003040

	$\sqrt{\mu}$	slope	k	$\log_{10}k$
1	.177	.00779	4.12 x 10^{-3}	-2.39
2	.223	.00834	4.41 "	-2.36
3	.258	.00893	4.72 "	-2.33
4	.302	.00937	4.95 "	-2.31

Temp. 54.0°C   T = 327°A   1/T = .003056

	$\sqrt{\mu}$	slope	k	log k
1	.177	.00646	3.42 x 10^{-3}	-2,47
2	.223	.00702	3.71 "	-2,43
3	.258	.00757	3.99 "	-2,40
4	.302	.00825	4.36 "	-2,36
5	.342	.00863	4.56 "	-2,34
6	.399	.00922	4.89 "	-2,31

Temp. 52.0°C   T = 325°A   1/T = .003077

	$\sqrt{\mu}$	slope	k	log k
1	.177	.00497	2,63 x 10^{-3}	-2,58
2	.223	.00535	2,83 "	-2,55
3	.258	.00561	3,00 "	-2,53
4	.302	.00638	3,37 "	-2,47
5	.342	.00685	3,62 "	-2.44
6	.399	.00794	4,20 "	-2,38

Temp. 50.0°C   T = 323°A   1/T = .003096

	$\sqrt{\mu}$	slope	k	log k
1	.177	.00352	1.86 x 10^{-3}	-2.73
2	.223	.00384	2.03 "	-2.69
3	.258	.00411	2.17 "	-2.66
4	.302	.00450	2.38 "	-2.62
5	.342	.00506	2.67 "	-2.57
6	.399	.00585	3.09 "	-2.51

Temp. 48.0°C   T = 321°A   1/T = .003115

	$\sqrt{\mu}$	slope	k	log k
1	.177	.00256	1.35 x 10^{-3}	-2.87
2	.223	.00296	1.56 "	-2.81
3	.258	.00348	1.84 "	-2.74
4	.302	.00388	2.05 "	-2.69
5	.342	.00415	2.19 "	-2.66
6	.399	.00460	2.43 "	-2.61

TABLE A 12

Malonate equimolar
Fig. 33 Curve C

λ	D	λ	D	λ	D	λ	D
720	.005	560	.621	425	.728	340	.064
700	.015	550	.576	420	.741	335	.129
690	.032	540	.492	415	.740	330	.225
680	.031	530	.407	410	.718	325	.393
670	.047	520	.304	405	.679	320	.641
660	.076	510	.221	400	.618	315	1.00
650	.111	500	.159	395	.547	305	
640	.157	495	.137	390	.470		
630	.216	490	.129	385	.393		
620	.304	485	.129	380	.317		
610	.389	490	.135	375	.241		
600	.470	470	.171	370	.181		
590	.548	460	.268	365	.133		
580	.608	450	.405	360	.091		
575	.625	440	.561	355	.067		
570	.631	435	.630	350	.061		
565	.631	430	.685	345	.062		

TABLE A 13

Malonate Excess 1

700	.019	575	.649	490	.123	390	.463
690	.033	570	.659	485	.123	385	.396
680	.031	565	.660	480	.127	380	.314
670	.047	560	.648	470	.158	375	.248
660	.074	555	.630	460	.253	370	.174
650	.107	550	.600	450	.390	365	.134
640	.153	540	.518	440	.544	360	.097
630	.217	530	.420	435	.612	355	.068
620	.306	525	.355	430	.670	350	.061
610	.395	520	.314	425	.706	345	.068
600	.493	515	.265	420	.725	340	.071
595	.528	510	.233	415	.723	335	.104
590	.570	505	.186	410	.700	330	.173
585	.606	500	.156	405	.670	325	.295
580	.630	495	.135	400	.607	320	.495
575	.649					315	.770
						300	2.0

TABLE A 14

Malonate Excess 2
Fig. 33, Curve D

λ	D	λ	D	λ	D	λ	D
700	.015	570	.665	470	.165	365	.144
690	.036	565	.668	460.	.258	360	.109
680	.032	560	.657	450	.395	355	.083
670	.050	555	.632	440	.551	350	.069
660	.080	550	.608	435	.619	345	.067
650	.109	540	.522	430	.671	340	.080
640	.155	530	.422	425	.715	335	.114
630	.218	520	.321	420	.732	330	1184
620	.309	510	.232	415	.733	325	.314
610	.398	505	.193	410	.711	320	.515
600	.490	500	.164	405	.671	315	.790
590	.571	495	.140	400	.616	310	1.30
585	.609	490	.130	390	.479	305	α
580	.637	485	.129	380	.327		
575	.656	480	.132	370	.197		

TABLE A 15

Malonatodioxalato solid
.07% Cr_2O_3 solution
Fig. 33 Curve E

λ	D	λ	D	λ	D	λ	D
720	.01	570	.650	440	.570	360	.165
700	.023	565	.650	435	.641	355	.130
690	.036	560	.638	430	.700	350	.117
680	.048	550	.591	425	.745	345	.110
670	.057	540	.503	420	.768	340	.123
660	.089	530	.410	415	.765	335	.163
650	.119	520	.310	410	.748	330	.347
640	.165	510	.225	405	.710	325	.400
630	.230	500	.163	400	.654	320	.640
620	.316	495	.140	390	.530	315	.970
610	.402	490	.130	385	.459	310	1.40
600	.490	480	.135	380	.387	305	α
590	.570	470	.172	375	.321		
580	.626	460	.270	370	.266		
575	.642	450	.410	365	.307		

TABLE A 16

Succinate Equimolar

Fig. 35, Curve C

λ	D	λ	D	λ	D	λ	D
720	.008	570	.500	440	.490	355	.067
700	.015	565	.501	435	.551	350	.065
690	.028	560	.497	430	.599	345	.069
680	.032	550	.463	425	.631	340	.092
670	.046	540	.410	420	.649	335	.143
660	.071	530	.343	415	.649	330	.240
650	.097	520	.270	410	.631	325	.409
640	.131	510	.203	405	.600	320	.660
630	.183	500	.153	400	.550	315	1.03
620	.247	495	.136	390	.422	310	1.45
610	.314	490	.128	380	.311	305	∞
600	.378	480	.134	375	.221		
590	.437	470	.170	370	.163		
580	.480	460	.254	365	.123		
575	.493	450	.363	360	.091		

TABLE A 17

Succinate Excess 1

λ	D	λ	D	λ	D	λ	D
700	.030	565	.537	440	.532	355	.113
690	.045	560	.527	435	.587	350	.117
680	.052	550	.481	430	.628	345	.128
670	.070	540	.420	425	.658	340	.158
660	.100	530	.348	420	.672	335	.216
650	.131	520	.271	415	.671	330	.325
640	.177	510	.210	410	.651	325	.503
630	.229	500	.165	405	.613	320	.770
620	.300	495	.153	400	.563	316	1.05
610	.365	490	.152	390	.438	310	1.6
600	.443	485	.156	380	.303		
590	.491	480	.167	375	.244		
585	.530	470	.210	370	.194		
575	.538	460	.299	365	.155		
570	.541	450	.407	360	.127		

TABLE A 18

Succinate Excess 2

λ	D	λ	D	λ	D	λ	D
720	.020	565	.546	435	.587	355	.114
700	.031	560	.533	430	.622	350	.121
690	.048	550	.488	425	.652	345	.132
680	.053	540,	.421	420	.666	340	.146
670	.074	530	.344	415	.661	335	.231
660	.106	520	.269	410	.641	330	.366
650	.141	510	.207	405	.602	325	.611
640	.186	500	.165	400	.552	320	.980
630	.240	495	.157	395	.491	315	1.45
620	.316	490	.151	390	.428	310	
610	.383	485	.157	385	.360		
				380	.299		
600	.448	480	.171	380	.299		
590	.501	470	.216	375	.243		
580	.541	460	.304	370	.194		
575	.551	450	.414	365	.156		
570	.551	440	.531	360	.129		

TABLE A 19

Adipate Equimolar
Fig. 37, Curve C

λ	D	λ	D	λ	D	λ	D
720	.006	570	.510,	440	.502	360	.095
700	.019	565	.510	435	.568	355	.075
690	.031	560	.505	430	.610	350	.075
680	.035	550	.473	425	.648	345	.085
670	.050	540	.417	420	.667	340	.112
660	.076	530	.346	415	.662	335	.166
650	.101	520	.270	410	.648	330	.270
640	.140	510	.204	405	.610	325	.450
630	.190	500	.153	400	.560	320	.730
620	.255	495	.139	390	.430	315	1.10
						310	1.60
610	.321	490	.130	385	.358		
600	.387	480	.136	380	.290		
590	.447	470	.173	375	.226		
580	.490	460	.260	370	.173		
575	.501	450	.372	365	.127		

TABLE A 20

Adipate Excess.
Fig. 37, Curve D

λ	D	λ	D	λ	D	λ	D
700	.020	570	.551	470	.207	365	.179
690	.043	565	.551	460	.291	360	.154
680	.048	560	.541	450	.401	355	.144
670	.065	555	.522	440	.529	350	.151
660	.096	550	.501	435	.583	345	.179
650	.123	540	.440	430	.618	340	.240
640	.163	530	.365	425	.661	335	.376
630	.217	520	.291	420	.679	330	.621
620	.277	510	.225	415	.680	325	1.2
610	.354	505	.197	410	.661	320	1.8
600	.428	500	.177	405	.629		
590	.486	495	.153	400	.580		
585	.511	490	.159	390	.458		
580	.532	485	.161	380	.327		
575	.545	480	.170	370	.217		

TABLE A 21

Fumarate Equimolar

Fig. 39, Curve C.

λ	D	λ	D	λ	D	λ	D
700	.010	565	.483	440	.459	360	.093
690	.020	560	.480	435	.518	355	.072
680	.025	550	.454	430	.564	350	.070
670	.036	540	.407	425	.602	345	.073
660	.060	530	.342	420	.621	340	.097
650	.084	520	.270	415	.625	335	.143
640	.121	510	.204	410	.612	330	.237
630	.163	500	.152	405	.582	325	.400
620	.222	495	.134	400	.537	320	.653
610	.287	490	.124	390	.413	315	1.05
600	.352	485	.122	385	.347	310	1.55
590	.407	480	.125	380	.283		
580	.453	470	.156	375	.223		
575	.470	460	.233	370	.169		
570	.478	450	.459	365	.126		

TABLE A 22

Fumarate Excess 1

λ	D	λ	D	λ	D	λ	D
700	.020	570	.549	440	.512	365	.177
690	.035	560	.542	435	.587	360	.147
680	.040	550	.500	430	.632	355	.132
670	.057	540	.441	425	.672	350	.140
660	.081	530	.371	420	.691	345	.153
650	.111	520	.297	415	.691	340	.196
640	.151	510	.227	410	.678	335	.275
630	.198	500	.177	405	.642	330	.420
620	.267	495	.157	400	.597	325	.700
610	.340	490	.152	395	.531	320	1.15
600	.408	485	.152	390	.468	315	1 90
590	.469	480	.158	385	.400		
585	.493	470	.194	380	.332		
580	.514	460	.277	375	.273		
575	.531	450	.393	370	.247		

TABLE A 23

Fumarate Excess 2
Fig. 39, Curve D

λ	D	λ	D	λ	D	λ	D
700	.020	570	.543	485	.150	380	.330
690	.040	565	.544	480	.157	370	.216
680	.045	560	.538	470	.196	365	.178
670	.060	555	.521	460	.483	360	.151
660	.085	550	.499	450	.400	355	.137
650	.120	540	.438	440	.532	350	.147
640	.159	530	.366	435	.593	345	.166
630	.208	525	.325	430	.640	340	.216
620	.278	520	.287	425	.679	335	.306
610	.348	515	.253	420	.698	330	.482
600	.422	510	.218	415	.698	325	.800
590	.478	505	.191	410	.682	320	1.33
585	.502	500	.170	405	.654	315	
580	.525	495	.153	400	.600		
575	.538	490	.147	390	.468		

TABLE A 24

Maleate Equimolar

Fig. 40, Curve C

λ	D	λ	D	λ	D	λ	D
720	.005	565	.522	440	.524	360	.100
690	.033	560	.512	435	.588	355	.080
680	.037	550	.476	430	.630	350	.080
670	.054	540	.418	425	.670	345	.093
660	.083	530	.334	420	.687	340	.125
650	.112	520	.266	415	.687	335	.187
640	.151	510	.199	410	.665	330	.300
630	.202	505	.170	405	.627	325	.500
620	.273	500	.150	400	.575	320	.800
610	.341	495	.135	395	.507	315	£
600	.406	490	.131	390	.440		
590	.460	480	.141	380	.295		
580	.504	470	.183	375	.231		
575	.519	460	.274	370	.176		
570	.522	450	.393	365	.123		

TABLE A 25

Maleate Excess 1

Fig. 40, Curve D

λ	D	λ	D	λ	D	λ	D
700	.017	570	.557	440	.513	365	.127
690	.034	560	.534	435	.582	360	.097
680	.037	550	.484	430	.626	355	.077
670	.057	540	.416	425	.658	350	.078
660	.087	530	.334	420	1673	345	.089
650	.121	520	.251	415	.670	340	.121
640	.170	510	.187	410	.650	335	.183
630	.225	500	.137	405	.613	330	.300
620	.298	495	.124	400	.561	325	.506
610	.375	490	.123	395	.493	320	.823
600	.443	485	.126	390	.428	315	1.30
590	.503	480	.147	385	.354		
585	.525	470	.184	380	.286		
580	.543	460	.277	375	.225		
575	.553	450	.400	370	.171		

TABLE A 26

Maleate Excess 2

λ	D	λ	D	λ	D	λ	D
720	.010	570	.550	450	.397	360	.122
700	.023	565	.542	440	.510	355	.110
690	.038	560	.530	435	.565	350	.120
680	.041	550	.480	430	.602	345	.125
670	.061	540	.411	425	.632	340	.167
660	.093	530	.335	420	.647	335	.241
650	.125	520	.255	415	.642	330	.393
640	.170	510	.189	410	.630	325	.660
630	.225	505	.153	405	.598	320	1.08
620	.301	500	.145	400	.550	315	
610	.374	495	.133	395	.491		
600	.440	490	.132	390	.430		
590	.500	480	.149	380	.300		
580	.538	470	.195	375	.240		
575	.548	460	.284	370	.190		

TABLE A 27

Phthalate Equimolar

Fig. 44, Curve C

λ	D	λ	D	λ	D	λ	D
740	.000	575	.508	460	.255	375	.223
720	.005	570	.516	440	.494	370	.168
700	.016	565	.518	435	.559	365	.126
690	.031	560	.510	430	.607	360	.101
680	.034	555	.497	425	.642	355	.073
670	.048	550	.475	422	.656	350	.073
660	.076	545	.452	420	.660	345	.077
650	.102	540	.420	418	.662	340	.100
640	.140	530	.349	415	.660	335	.147
630	.193	520	.272	410	.653	330	.242
620	.257	510	.204	405	.609	325	.408
610	.327	500	.153	400	.558	322	.547
600	.391	490	.127	390	.422	320	.656
590	.450	480	.135	385	.353	318	.707
580	.496	470	.171	380	.284	315	1.00
						310	1.45

TABLE A 28

Phthalate Excess 1

λ	D	λ	D	λ	D	λ	D
740	.000	575	.577	465	.242	385	.345
700	.023	570	.578	460	.294	380	.275
690	.040	565	.569	455	.355	375	.213
680	.044	560	.553	450	.418	370	.161
670	.063	550	.497	445	.488	365	.122
660	.097	540	.423	440	.550	360	.094
650	.135	530	.342	435	.608	355	.077
640	.184	520	.256	430	.651	350	.078
630	.247	510	.189	425	.683	345	.087
620	.327	500	.143	420	.695	340	.113
610	.408	495	.131	415	.690	335	.162
600	.470	490	.130	410	.667	330	.255
590	.530	485	.136	405	.622	325	.421
585	.554	480	.147	400	.562	320	.663
580	.569	470	.196	390	.421	316	.940
						314	1.10

TABLE A 29

Phthalate Excess 2

Fig. 44, Curve D

λ	D	λ	D	λ	D	λ	D
720	.020	570	.565	440	.559	355	.154
700	.037	565	.558	435	.611	350	.173
690	.057	560	.541	430	.651	345	.203
680	.064	550	.487	425	.684	340	.267
670	.080	540	.420	420	.695	335	.394
660	.119	530	.343	415	.691	330	.650
650	.151	520	.268	410	.670	325	1.13
640	.201	510	.206	405	.631	320	1.80
630	.263	500	.167	400	.581		
620	.334	495	.157	390	.447		
610	.403	490	.157	380	.283		
600	.470	480	.177	375	.256		
590	.525	470	.226	370	.210		
580	.560	460	.319	365	.178		
575	.568	450	.433	360	.159		

TABLE A 30

Potassium sulphatodioxalatoaquochromiate (?) .00921M solution

Fig. 46, Curve C.

λ	D	λ	D	λ	D	λ	D
720	.011	570	.467	425	.651	330	.132
700	.032	565	.453	420	.648	325	.229
690	.061	560	.439	415	.628	320	.390
680	.062	550	.386	410	.593	315	.618
670	.083	540	.326	405	.538	310	.930
660	.126	530	.264	400	.470	305	1.30
650	.164	520	.201	395	.401		
640	.207	510	.156	390	.334		
630	.261	500	.135	385	.267		
620	.330	490	.141	380	.206		
610	.380	480	.178	370	.113		
600	.429	470	.244	360	.057		
590	.461	460	.336	350	.034		
585	.471	450	.447	345	.043		
580	.477	440	.559	340	.053		
575	.476	430	.633	335	.077		

TABLE A 31

Potassium sulphatohydroxochromiate (?) .00921M solution
Fig 46, Curve D.

λ	D	λ	D	λ	D	λ	D
740	.015	570	.390	425	.632	350	.121
720	.030	560	.360	420	.638	345	.145
700	.063	550	.311	415	.631	340	.197
690	.087	540	.259	410	.614	335	.280
680	.097	530	.213	405	.581	330	.403
670	.127	520	.177	400	.537	325	.592
660	.169	510	.160	395	.480	320	.830
650	.208	500	.165	390	.420	315	1.18
640	.251	490	.196	385	.355	310	∞
630	.295	480	.249	380	.293		
620	.340	470	.313	375	.233		
610	.375	460	.386	370	.183		
6							
600	.402	450	.466	365	.146		
590	.415	440	.550	360	.121		
580	.411	430	.612	355	.112		

TABLE A 32

Decomposition of the "sulphato solution". Fig. 48.

	time	OPTICAL DENSITY														
	min	400	410	415	420	425	430	440	530	550	560	570	580	590	600	620 mμ
1	0															
2	6		.580	.618	.640		.630		.233	.385	.433	.463	.471	.456	.422	.316
3	30		.595	.630	.649		.630		.269	.395	.441	.469	.472	.453	.421	.313
4	60		.601	.632	.649		.630		.277	.401	.449	.472	.472	.451	.414	.303
5	120	.499	.608	.638	.650	.645	.619		.294	.416	.457	.474	.470	.441	.400	.287
6	180	.507	.610	.637	.642	.638	.610	517	.305	.422	.460	.472	.463	.432	.389	.274
7	240	.509	.610	.632	.640	.640	.601	.503	.314	.428	.461	.471	.457	.426	.375	.265
8	300	.511	.610	.630	.637	.621	.591	493	.321	.431	.463	.471	.449	.420	.371	.254
9	375	.520	.610	.628	.630	.614	.581	479	.328	.438	.467	.469	.448	.411	.357	.243
10	450	.521	.610	.625	.626	.610	.575	475	.331	.439	.468	.469	.441	.409	.353	.237
11	540	.528	.610	.624	.622	.607	.570	464	.337	.445	.468	.468	.439	.440	.347	.233
12	645	.531	.608	.621	.618	.599	.562	458	.343	.448	.468	.464	.439	.393	.340	.217
13	705	.530	.609	.620	.619	.599	.560	.453	.347	.450	.470	.465	.439	.393	.340	.217
14	790															
15	900	.532	.607	.617	.610	.589	.543	.440	.353	.451	.470	.460	.430	.380	.325	.304

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