A COMPARATIVE KINETIC STUDY OF THE REACTION BETWEEN CHROMIUM NITRATE SOLUTIONS AND THE CARBOXYL GROUPS OF ACETATE AND COLLAGEN

by

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CONTENTS

SUMMARY AND CONCLUSIONS.

The kinetics of the coordination reaction between the carboxyl group of the acetate radical and the trivalent chromium ion has been examined by independent methods at a temperature selected to yield reasonably accurate rate data. The study has been extended to an examination of the rate of chromium "fixation" by the carboxyl groups of hide collagen in a series of miniature tannages carried out under similar conditions for comparative purposes. The effect of olation of the chromium ions in solution on the kinetics of the coordination reaction has also been examined.

The rate of coordination of the acetate radical was followed by solvent extraction and spectrophotometric techniques over a range of concentration and pH levels. The rate data revealed a reaction having typical mass-action characteristics, the rate of reaction depending on the concentration levels of the chromium ion and the ionised acetate radical. An attempt made to distinguish a differential reaction rate in the case of a parallel reaction series using boiled and aged chromium nitrate reactant solutions, failed to reveal any significant differences between the series.

The reactant solutions gave absorption spectra characteristic of the trivalent chromium ion with maxima in the 420 mμ and 570 mμ wavelength regions. The changes in optical density occurring in the vicinity of the maxima were followed spectrophotometrically, the height of the 570 mμ being found to increase during the course of reaction, while the height of the 420 mμ peak decreased.

The variation in optical density at the 570 mμ peak was found to

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be directly related to the increase in concentration of the product complex in solution in accordance with the Beer-Bougher law, while the decrease in the height of the 420 mμ peak, was related to the properties of unolated OH groups associated with the chromium complex as governed by pH and olation changes during the course of reaction.

Boiled and aged chromium nitrate solutions gave reactant solutions having initial optical densities greater than those of the corresponding fresh reactant solutions at the 570 mμ peak, and less than those of the fresh solutions at the 420 mμ peak. During the course of reaction, however, the two series converged to the same values.

The equilibrium reaction solutions were subjected to paper electrophoretic study which indicated that all the chromium was present in the form of cationic species. This finding was in accordance with stoicheiometric indications in the solvent extraction studies where coordination in a 1 : 1 ratio was reflected, giving rise to positively charged complex ions only. Making due allowance for band spreading the numbers of species predicted from the kinetic studies correspond with the electrophoretic patterns found.

Application of the classical second order kinetic expression to the solvent extraction rate data, yielded plots having two distinctly linear sections, apparently indicating consecutive second order processes occurring in solution, contrary to the findings of previous workers who assign a first order mechanism to the reaction. This finding was consistent with the view that in the case of both the fresh and aged series, reaction consisted of successive coordination of an acetate radical to

each/.....

each chromium atom of a diol complex. Second order rate "constants" were calculated for each step and their dependency on pH level demonstrated. The findings of Hamm et al[14] that these were first order reactions independent of acetate concentration are believed to be due to their use of a large excess of acetate in their experiments.

The kinetic study was further extended to an examination of the rate of "fixation" of trivalent chromium by the carboxyl groups of hide collagen under comparable conditions in a series of miniature tanning experiments in which the tannage substrate was provided in each of two physical forms:-

(a) As hide powder where surface development was large, and

(b) as prepared pelt pieces in which the fibrous weave pattern was retained.

In view of the heterogeneity of the tannage systems, remarkable similarity was observed in the reaction course when compared with that of the acetate coordination studies, particularly in the case of the hide powder tannages. The dependency of the tannage rate data upon concentration and pH conditions was also found to be the same as in the case of the pure chemical system.

The exact correlation between the rate data for the tannage and pure chemical systems was demonstrated by means of correlation plots. Close correlation was revealed in the case of hide powder tannage while the smaller degree of correlation observed in the case of the pelt tannage systems was attributed to the modifying effects of diffusion, particularly

on/.....

on the initial reaction velocity.

The effect of using boiled and aged chromium solutions in the tannages was to increase the initial rate of chromium "fixation" apparently due to the coordination of a diol species at each coordination site. After the initial reaction period, the two series showed a tendency to converge as in the case of the spectrophotometric studies on the acetate reaction. The convergence trend was regarded as indicative of the tendency for the chromium in fresh solutions to undergo rapid olation to the same level as in the boiled and aged solutions.

The experimental observations made on the various systems lead to the following conclusions:-

(a) The mechanism of coordination of the acetate radical to trivalent chromium appears to involve the successive coordination of ligand to each of the chromium atoms of a diol complex, both coordination steps proceeding by second order reaction mechanisms..

(b) At the pH levels at which the reaction is carried out, the formation of olated bodies is rapid so that reaction in the case of both fresh and aged solutions essentially occurs between an olated species and the ionised acetate radical.

(c) Modifications in the absorption spectrum of the reactant solution at the 570 mμ peak are directly related to coordination, while changes at the 420 mμ peak are related to the formation of loosely-bound hydroxo chromium compounds, the concentrations of which depend on the pH level.

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(d) The mechanism of chromium fixation in hide is essentially similar to that operating in the case of coordination of the acetate radical to chromium, involving attachment of chromium to the side chain acid residues of collagen.

(e) The effect of olation is to enhance the rate of chromium fixation by hide protein during the initial reaction stages and to render possible bridge formation between adjacent side chains by secondary coordination during the latter reaction stages.

(f) Where pelt pieces are used instead of hide powder, the initial rate of chromium fixation is dominated by the rate of diffusion of chromium into the fibrous structure.

It should be stressed that the observations made on the various reaction systems cannot be regarded as exhaustive and the conclusions are subject to further confirmation. Consequently, the present study is essentially of a preliminary nature, but it is felt that the need for further investigation along similar lines has been demonstrated.

CHAPTER 1.

INTRODUCTION.

COORDINATION KINETICS OF THE TRIVALENT CHROMIUM ION.

The coordination of ligands in the form of anions of organic and mineral acids to trivalent chromium has long been known to constitute an anomalous group of ionic reactions proceeding at measurable velocities at room temperatures. Study of precipitation points and other data has led to the establishment of a penetration order for a range of organic and inorganic anions. A comprehensive list[1] places the anions in order of their complex forming stability as follows:-

Hydroxyl, oxalate, citrate, malonate, maleate, lactate, glycollate, tartrate, succinate, acetate, formate, sulphate, chloride, nitrate, perchlorate.

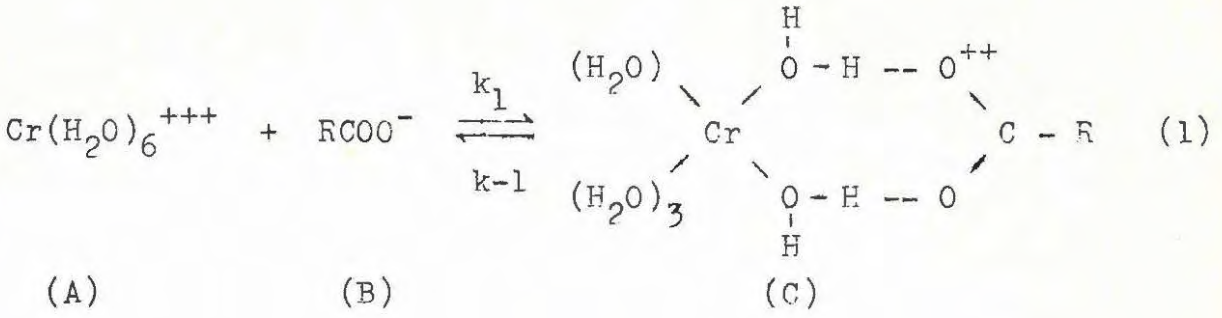
Shuttleworth has conducted studies in complex formation covering a range of organic acid anions, including monobasic,[2] dibasic[3,4] and hydroxy[5] acids by conductimetric techniques as a result of which a set of rules governing complex ion formation has been drawn up.[6] The stability of coordination of the simple monodendate acidic group to chromium was found to be inversely proportional to the ionisation constant of the acid while the formation of chelate rings greatly enhanced complex stability.

An extensive study of the complex ions of trivalent chromium has been undertaken by Hamm et al, the results of which have been published in a series of articles[7 - 14] in which particular attention has been given to the kinetic aspects of diol formation and complex formation with organic acid anions.

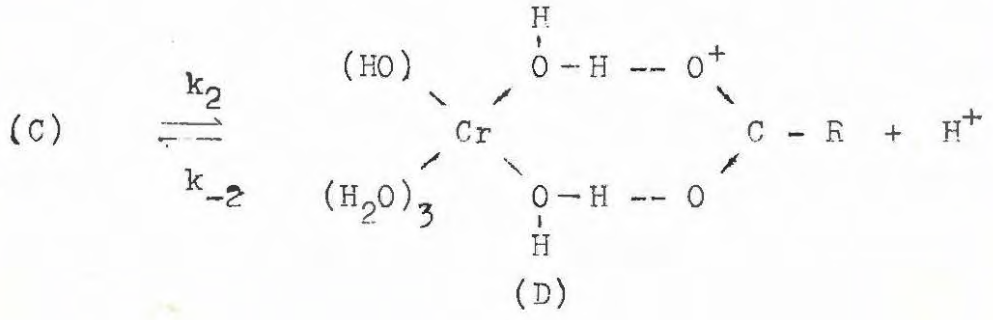
Hamm/.....

Hamm et al have confirmed the formation of mono- di- and tri-acido complexes in the case of the oxalate[9] and malonate[11] anions and have determined the reaction rates for the initial reaction step which was found to be of the first order in chromium ion concentration, by spectrophotometric means. Similarity in the reaction rates of the two ligands and the discovery that the reaction rate in the case of monodentate ligands such as acetate could be studied by polarographic means, led to the extension of this work to an examination of the coordination kinetics of a number of monobasic anions.[14] The experimental data indicated reactions of first order in chromium concentration over the range of anions studied with rates in each case approximating to that of the oxalate and malonate coordination. General similarities thus indicated that the rate determining step was not primarily concerned with the completion of a chelate ring as originally proposed by them[9] but was centred about the primary step to produce the first bond to the chromium atom.

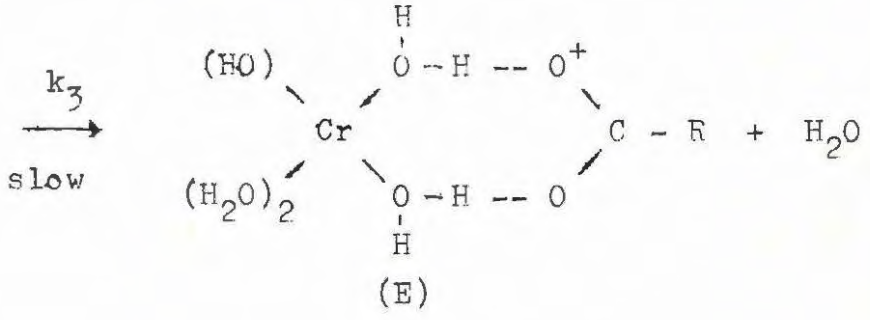
The investigations mentioned above were carried out using freshly prepared chromium nitrate reactant solutions at low concentration (0.002 M) and at mole ratios of ligand to chromium of 50 : 1. A general reaction mechanism applicable to both chelating as well as non-chelating anions has been proposed by them as follows:-



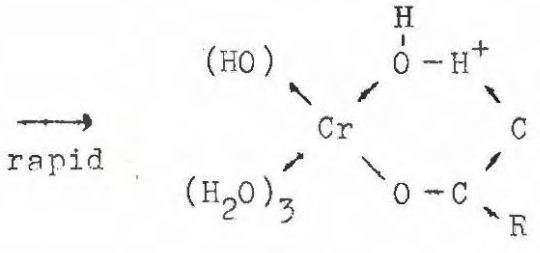
(A) (B) (C) (1)



(C) (D) (2)



(D) (E) (3)



(E) (4)

By the foregoing mechanism the primary reaction is assumed to occur between the ionised acid anion and the hexaquochromium ion present in freshly prepared solutions, with the formation of a loosely-bound, hydrogen-bonded complex. This is followed by protolysis to form the basic complex followed by the rate-determining slow step which involves the dissociation of a water molecule. The final rapid step according to Hamm et al then consists of ring closure with the formation of a six membered ring.

The assignment of a first order reaction mechanism to a bimolecular reaction by Hamm et al seems extremely unlikely. Hamm et al have attempted to justify this conclusion on the basis that all steps leading to the final coordination are rapid with the exception of a single slow step involving dissociation of a water molecule from the complex.

Examination of the concentration conditions under which the reaction was carried out indicate that an alternative explanation is possible. Anomalous behaviour has been noted in cases where one reactant species participating in a bimolecular reaction is present in large excess. Under these conditions the mathematical expression governing second order reactions can be shown to reduce to a form similar to that for first order reactions (cf. Appendix C) the reaction then being described as pseudo-unimolecular. Numerous examples (15) of such cases occur in organic chemistry as in the hydrolysis of esters in aqueous solution where water is a reactant. In the coordination studies conducted by Hamm the concentration of ligands was fifty times that of the chromium ion so that anomalous behaviour might be expected.

Accordingly/..

Accordingly it was proposed to re-examine the kinetics of coordination in the case of the acetate ion by independent methods over a range of concentration and pH conditions.

THE IMPORTANCE OF OLATION.

The processes of aggregation in chromium solutions by olation and complex formation by coordination are of interest to the leather chemist since accumulated evidence now indicates that it is on the basis of these mechanisms that the tanning action of chromium salts may be explained. The existence in solution of violet and green forms of chromium sulphate is well known. The violet form is obtained by dissolving crystals of the pure salt or chrome alum while the green form may be obtained by boiling the resultant solution. Similar, but less pronounced colour changes, indicative of structural change, are also observed in the case of chromium nitrate solutions, the blue colour of the freshly-prepared cold solution changing to green on boiling and/or ageing. Hall and Eyring[16] have shown by conductometric titration using ammonium paramolybdate reagent, that definite structural change accompanies the heating and ageing of a solution of chromium nitrate.

Stiasny[17] envisages the structural changes occurring as follows:-

$$Cr(H_2O)_6^{+++} \rightleftharpoons Cr(H_2O)_5OH^{++} + H^{+} \qquad (1)$$

$$2Cr(H_2O)_5OH^{++} \longrightarrow (H_2O)_4Cr\begin{matrix}OH\\ \diagup\ \diagdown\\ \diagdown\ \diagup\\ OH\end{matrix}Cr(H_2O)_4^{++++} + 2H_2O \qquad (2)$$

Initial/.....

Initial reaction consists of "protolysis" of the hexaquochromium ion accompanied by a fall in the pH of the solution. Protolysis is followed by "olation" of the chromium to form a "diol" complex. The nett effect of the process is to bring about aggregation of the chromium with the formation of polynuclear complexes. The formation of large aggregates containing four or more chromium atoms may be envisaged by a continuation of the process.

The hydroxo complex formed as a result of the protolysis equilibrium is titratable with acids, but the "ol" linkage represents a stable bond which resists strong acid attack. Evidence of this phenomenon is found in the classical titration curve of Bjerrum [18], in which chromium chloride of zero basicity is titrated to 33⅓% basicity and then back titrated with strong acid, (a) immediately, and (b) after standing for 24 hours to enable "ol" formation to occur.

The addition of alkali to such a system favours olation since the protolysis equilibrium (1) moves to the right to provide more product for further aggregation by process (2). The effect of alkali is of importance in the preparation of reactant solutions in coordination studies where the ligand is added in the form of its soluble sodium salt which undergoes appreciable hydrolysis in solution. Addition of sodium salts of ligands to chromium nitrate solutions thus brings about conditions which facilitate the aggregation of the chromium so that subsequent reaction is likely to occur between the anion and an olated species rather than the hexaquochromium ion.

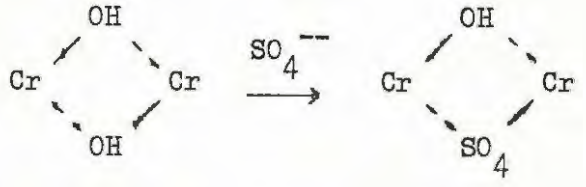
Studies on the kinetics of olation have been carried out by Riess [19, 20] and Shuttleworth [21] who have found that the rate data

fit/.....

fit the classical second order equations involving equivalent concentration and rates of removal of reactants. Shuttleworth[21] has studied the rate of olation as a function of the anion associated with the chromium and has found the olation to be rapid in the case of the nitrate ion and slow in the case of the sulphate ion; this differential rate is attributed to ligand competition. Similarity in the reaction rates of olation and coordination show that the olation process must be considered as a possible concurrent and complicating effect in the reaction of organic acid anions with chromium.

The effect of ligand competition on olation has been mentioned. Shuttleworth has carried out spectrophotometric investigations into the optical effects of sulphate coordination[22] and has found that in the case of chromium nitrate solutions containing a high percentage of olated complexes, an initial decrease in absorption with increasing sulphate penetration occurred. This was regarded as strong evidence of a structural change from an olated complex containing no sulphate to an olated complex containing coordinated sulphate incorporated into the ring.

Structurally,



In the case of ligands incorporated into the ring structure, the effect of olation would be to bring about favourable orientation of the chromium atoms and thus facilitate coordination of the ligand.

The carboxyl groups of organic acid anions constitute a type

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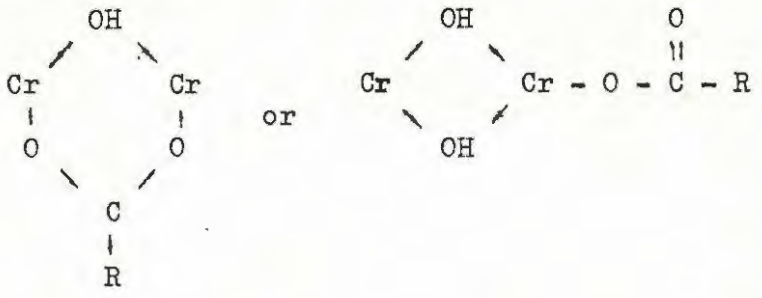
of ligand capable of coordination with formation of a six-membered ring or capable of attachment at one of the side positions unaffected by olation.

Structurally,



If coordination involves formation of a ring structure, an enhanced reaction rate might be expected in the case of boiled and aged reactant solutions in which favourable configurations occur due to olation. Differential reaction rates in the case of boiled solutions compared with fresh solutions where side coordination occurs might be expected. Previous indications are that olated complexes tan more rapidly.

This aspect of the coordination reaction appears to have been overlooked by Hamm et al in postulating their general reaction mechanism. Accordingly in the present study it was proposed to examine the kinetics of coordination in a parallel series of reactant solutions prepared from boiled chromium nitrate solutions in order to determine the influence of olated bodies on the rate determining step.

KINETICS OF CHROME TANNAGE.

A survey of the literature reveals that relatively little work has been carried out on the kinetics of the chrome tanning process,

attention/....

attention being rather focussed on the end product, the tanned leather. Some work was carried out in 1920 by Thomas, Baldwin and Kelly[23] who tanned quantities of hide powder using excesses of water and chrome tanning salt. They found that the amount of chromium fixation could not be determined by the difference in initial and final chromium concentrations in the external phase. Application of the classical rate equations to the rate data obtained from direct determination of chromium fixation was found to be impossible.

In a series of articles presented over the period 1945 to 1950, P.S. Briggs[24 - 29] has attempted to place the kinetics of chrome tannage on a mathematical basis. Rate data derived from the study of the exhaustion of the chrome tanning bath was found to be resolveable upon an empirical equation of the following form:

$$[Cr]^{-n} = K't + 1$$

where t is the time lapse and K' and n are arbitrary constants. In applying the equation initially to semi-chrome tanning systems, Briggs expressed [Cr] as a decimal fraction of the initial chromium concentration.

In extending the equation to pure chrome tannage systems, Briggs found that the initial chromium concentration of the "float" or external phase required correction to give an effective concentration, the value for this correction being referred to as the "contact drop". The existance of the contact drop was attributed to factors such as the passage of water from the internal to the external phase, diffusion effects and the adsorption of chromium on pelt surfaces on contact. Substitution of the appropriate values for the constants k' and n in the "exhaustion formula" yielded linear plots. Attempts were made to determine the dependency of the constants on reaction conditions.

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While the development of the exhaustion formula served to provide a means of approach to kinetics in a complex system, the empirical nature of the equation and difficulties experienced in attaching physical significance to its associated constants, limited its usefulness.

The exhaustion equation has been subsequently criticised by Gustavson (30) and von Thaden (31) who have pointed out that while the exhaustion of chrome tanning liquors can be foretold on the basis of an exponential function, this expression is not meant to represent a simple reaction process since the course followed is the result of various complicating factors. von Thaden (31) has suggested modifications to the original exhaustion equation in the case of diffusion limited and coordination limited reactions and in the case where the rates of both are similar.

The failure of the classical mathematical expression to describe the kinetic behaviour of the tannage reaction is due to the fact that several kinetic factors are involved. According to Shuttleworth (32) the following processes must be considered:-

(1) Rate of penetration of the chrome tanning liquor into the fibres.

(2) Rate of coordination of the chromium complex to the protein carboxyl groups.

The rate of coordination of chromium will itself be dependant upon a number of factors:-

(a) Occupation of available coordination positions by stable ligands tending to reduce the rate of coordination.

(b) Rate of coordination of masking agents whose time factor for coordination would be of the same order as that for protein carboxyl groups.

(c) Rate of achievement of pH equilibrium in the pelt after

making basic, the equilibrium value serving to govern the number of ionised carboxyl groups in the hide.

It is evident that there is a need for comparative study of reaction rates in simply systems (where reaction occurs between chromium ions and organic acid anions, hide powder, and pelt, respectively) if the effect of the various factors operative is to be separately gauged. Accordingly it was proposed to extend the preliminary kinetic study on acetate coordination in a simple chemical system to a study of the reaction between chromium and collagen by means of a series of miniature tanning experiments designed to demonstrate the importance of diffusion processes.

THEORY OF CHROME TANNING.

Early theories of chrome tanning regarded the process as consisting of the coating of the collagen fibres due to the deposition of the tanning agent on the fibre surfaces by an adsorption process. This was the viewpoint of Knapp who has been credited with the discovery of the tanning process in 1857 (33).

Cobb and Hunt(34) envisaged chromium fixation by residual valence forces operative in collagen. The basic hydroxy groups common to a range of tanning reagents including chromium complexes, were considered to constitute the chief attractive centres (35, 36). The discovery that chromium complexes containing no unolated hydroxy groups retain their tanning action has served to discredit this theory (37).

Wilson(38) believed that chromium fixation resulted from the formation of mono-, di-, and tri-, acid salts with collagen, the stepwise formation of which accounted for the time factor in tannage. Revision of views concerning the exact equivalent weight of collagen removed apparent stoicheiometric support for the theory however. Although the possibility of adsorption processes, residual valence forces and salt links participating in the tannage mechanism

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is not excluded, these processes are not considered to constitute the main mechanism according to the modern view-point. By far the most tenable theory proposed has been that of coordination of collagen reactive groups to chromium although some confusion has arisen due to the polyfunctional character of the collagen molecule.

Collagen contains a number of functional groups capable of coordination to chromium under suitable conditions. Credence has been given to the coordination of amino groups in the protein side chains as a possible mechanism, particularly in the case of tannage with anionic chromium complexes (39, 40). Evidence in support of this theory, however, has been shown to be capable of alternative interpretation (41). In a comprehensive study of the coordination of a series of amino acids, Shuttleworth and Sykes (42) and Ellis (43) have failed to detect any indications of amino group coordination under pH conditions similar to chromium tannage. These considerations would also appear to eliminate the possibility of bridge formation between amino and carboxyl groups as an explanation for thermal stability of tanned collagen.

Consideration has also been given to possible coordination of protein hydroxyl and peptide groups, but again lack of analogy in simple chemical systems under comparable conditions (44) has prevented further development of the theory.

The only functional group remaining to be considered is the side chain carboxyl group. According to Shuttleworth, "cases of carboxyl groups incapable of coordinating to chromium under conditions similar to normal chrome tannage do not seem to exist" and hence it must be concluded that the side chain carboxyl groups will play a part in tannage. The importance of carboxyl group coordination has been further demonstrated as a result of accumulated experimental evidence based on miniature tannages on modified collagen (45, 46, 47) where large reductions in chromium fixation have resulted from inactivation of

carboxyl / ...

carboxyl groups by esterfication. Striking correlation has also been demonstrated by Shuttleworth[48] in a series of kinetic studies in which chromium fixation by hide powder was compared with coordination of acetate ions under similar conditions. Experiments involving ion exchange resins have also revealed remarkable correlation between the uptake of complexes by carboxyl type resins and the thermal stability imparted by the complexes in tannage experiments[49].

The high degree of dimensional stability imparted to the protein structure by chrome tannage has led to the concept of bridge formation between the carboxyl groups of neighbouring side chains, the resulting cross linkage conferring rigidity which is retained even at relatively high temperatures ($\pm 100^{\circ}C$). Opinions are divided concerning the average distance between carboxyl groups of neighbouring side chains, but it would appear that a single chromium atom would be unable to achieve a bridging effect due to dimensional incompatibility. However, since the conditions of chrome tannage are those of such pH range (4.0) as to favour both the ionisation of carboxyl groups and the aggregation of chromium ions to form large complexes, bridging of the inter-carboxyl distances becomes feasible.

The historical theories and modern concepts of chrome tannage outlined above have been presented in greater detail by Shuttleworth in Volume 2 of A.C.S. Monograph 134, entitled "The Chemistry and Technology of Leather" (Chap. 23).

Further understanding of the tanning process involves a more detailed study of the particle size of the chromium aggregates in tanning solutions, the effect of penetration rate on the speed of tannage and greater understanding of the structure of the collagen molecule. The

obscuring/.....

obscuring effects of these factors on the reaction data have thus far prevented the application of mathematical expressions to a description of the tannage mechanism.

Reference has been made to kinetic studies carried out by Shuttleworth[48] in which reaction rates of chromium fixation by hide powder were compared with the rates of coordination of acetate ions to chromium sulphate. Remarkable similarity in the curves obtained served to emphasize the importance of carboxyl group coordination and the need for further investigation along these lines. In the present investigation a more exact and extensive study was proposed in which the coordination of acetate and collagen carboxyl groups to chromium nitrate was to be examined under controlled conditions. Furthermore by extending the study to tannage of prepared pelt pieces, it was hoped to demonstrate the effects of diffusion of complexes through the tannage substrate, and to add to the available evidence on the mechanism of chrome tannage.

EXPERIMENTAL OBJECTIVE.

Consideration of the four preceding sections of this introduction suggested the need for a comparative study of the kinetics of coordination of trivalent chromium to the carboxyl groups of acid anions and collagen. Accordingly it was proposed to undertake the study of the coordination of a typical monodentate ligand, the acetate ion, in a simple chemical system under controlled conditions and subsequently to extend the study to the more complex tannage system by conducting a series of miniature tanning experiments on hide substance, provided in each of two physical forms:-

(a)/.....

(a) as hide powder in which surface development was at a maximum, and

(b) as prepared pelt pieces in which the fibrous weave pattern was retained and diffusion effects large.

Chromium nitrate was chosen as the source of chromium (III) ion in order to eliminate competing ligands from the system as far as possible. Reference to the list of complex stabilities (page 1) indicates the small tendency for the nitrate ion to coordinate while complex ions containing coordinated nitrate are unknown[16].

It should be emphasized that the present study is of a restricted nature and as such can only be regarded as preliminary. The need for further investigation along similar lines has been suggested and it is felt that such studies will prove rewarding and are likely to contribute in no small measure to the final elucidation of the tanning process.

CHAPTER II.

EXPERIMENTAL TECHNIQUES.

The methods of classical research preferably involve the isolation and analysis of pure compounds. However, difficulties encountered in the preparation of chromium complexes, particularly the basic salts, have led to a different approach on the part of the leather chemist whereby the compounds are studied in solution in which they form complex systems in equilibrium dependent upon factors such as pH level, concentration of reactants, temperature and neutral salt concentration. Change in one or more of the above conditions, leads to changes in complex formation, so that the experimental techniques chosen should be those which involve minimum disturbance of the reactant system. The techniques employed have included chemical methods such as solvent extraction and precipitation procedures, and instrumental methods such as spectrophotometry, polarography and conductimetry[50].

In the present study interest has centred upon determining the course of reaction over a range of pH and concentration conditions using independent chemical and spectrophotometric techniques.

(1) PREPARATION OF CHROMIUM SOLUTIONS.

Chrome nitrate was chosen as the source of chromium (III) ion owing to the small tendency for the nitrate ion to coordinate[16] hereby eliminating from the system as far as possible, anions which might compete strongly with the ligand under investigation.

All/.....

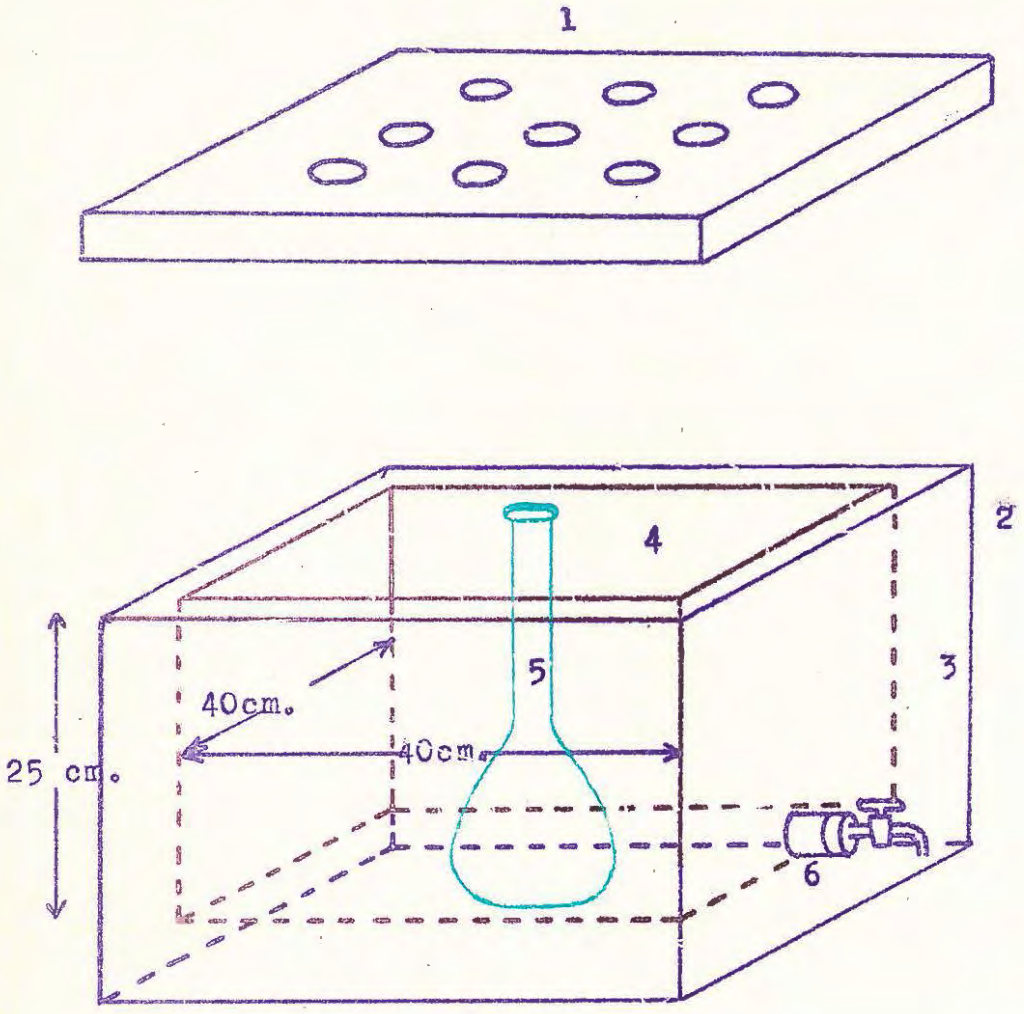
All chromium solutions were prepared by weighing out the appropriate amount of laboratory grade chromium nitrate which had previously been dried in a dessicator over silica gel at atmospheric pressure. Weighings were carried out as quickly as possible to reduce errors due to the extremely hygroscopic nature of the salt. After completion of a series of studies, aliquots of the reactant solutions were analysed for total chrome content by the official "wet oxidation" method of the Society of Leather Trades' Chemists [51].

In the preparation of "fresh" solutions, the weighed quantity of chrome nitrate was transferred to a litre volumetric flask which served as reaction vessel, and diluted to a suitable volume using de-ionised, distilled water precooled to the reaction temperature. The ligand in the form of its soluble sodium salt was added immediately and the reactant solution adjusted to the mark.

In the case of "olated" solutions, the weighed quantity of chrome nitrate was dissolved in a small volume of distilled water and brought to the boil. The solution was allowed to cool, diluted to large volume (750 ml.) in a litre flask and aged at reaction temperature for a minimum period of three days before use.

In the case of the miniature tanning experiments (section 7) where pH adjustment of the chrome solutions was necessary, this was effected by dropwise addition of 50% caustic soda solution or concentrated nitric acid to the diluted solution before adjustment to the mark.

Temperature/.....



1. Wooden lid with series of 4 cm. holes.
2. Wooden outer box.
3. Cavity between inner and outer walls "lagged" with glass wool.
4. Galvanised iron tank.
5. Volumetric flask.
6. Drainage pipe fitted with tap.

Fig. 2.1. Temperature control tank.

(2) TEMPERATURE CONTROL.

The entire series of studies was carried out at the same fixed temperature. Preliminary investigation indicated a relatively rapid reaction at room temperature and in view of the inherent limited accuracy of the techniques used, it was proposed to carry out the reaction in a low temperature environment to increase accuracy and hence, the degree of differentiation between reaction rates, particularly during the initial stages.

Temperature control was established by immersing the reaction vessels in water containing melting ice. A galvanised iron tank was constructed for this purpose of dimensions and design shown in the sketch (Fig. 2. 1.). The capacity of the tank was such as to enable a total of nine litre volumetric flasks to be accommodated for the solvent extraction and spectrophotometric studies or alternatively to contain the series of reaction tubes used in the miniative tanning studies. Insulation of the tank was achieved by means of glass wool "lagging" on the outer surfaces, the whole being enclosed in a wooden box fitted with a lid having a series of holes bored to accommodate the necks of the volumetric flasks.

As expected, under static conditions, a temperature gradient was established in the tank. However, provided replenishment of the ice was carried out at 24 hour intervals, depending on ambient temperature, the layer of water at the bottom of the tank remained constant at a temperature of $4.0 \pm 0.5^{\circ}$ C while its depth was sufficient to provide an environment for the solutions under investigation.

Solvent/.....

(3) SOLVENT EXTRACTION STUDIES.

Since the solvent extraction technique does not permit a distinction to be drawn between coordination of two or more groups of the same polyfunctional molecule, it should be limited strictly to monofunctional molecules.[52] The monobasic acetate ion with fairly high acid pK value (4.63), lends itself to estimation by the solvent extraction technique which may be applied to suitable aliquots with minimum disturbance of the bulk reactant system.

The technique was applied to a series of reactant solutions in which the molar concentrations of the two reactants and the pH levels of the reactant solutions were varied in turn as shown in the following table:-

Table 2.1.

Solution	Moles chromium nitrate/litre	Moles sodium acetate/litre	Moles acid added
1	0.02	0.02	-
2	0.02	0.04	-
3	0.02	0.08	-
4	0.01	0.08	-
5	0.04	0.08	-
6	0.02	0.08	0.04
7	0.02	0.08	0.06

No pH adjustment was carried out on solutions 1 to 5 of the series/.....

series, the reaction being allowed to proceed at the natural pH level of the reactant system. In order to study the effect of pH, two further solutions (6 and 7) were prepared at molar concentrations of 0.02 with respect to chrome nitrate and 0.08 with respect to sodium acetate. An amount of normal hydrochloric acid equivalent to half and three-quarters respectively of the total acetate content, was added to the chrome nitrate solution before addition of the sodium acetate reagent and adjustment to the mark.

In applying the technique, a suitable aliquot (20 ml) of the reactant solution was withdrawn (in duplicate) at zero time, and pipetted into a separating funnel containing sufficient excess of normal hydrochloric acid (20 ml) to convert non-complex bound acetate to acetic acid. An equal volume of ether was added and the acetic acid extracted by shaking vigorously for a five minute period. The aqueous phase was carefully run out, the ether layer remaining decanted as quantitatively as possible into a conical flask and subsequently titrated against standard 0.02 molar sodium hydroxide, using phenolphthalein indicator and shaking vigorously after each addition of alkali until the aqueous phase showed a faint, permanent pink colouration.

Similar aliquots were withdrawn at intervals over the first seven hours and then continued less frequently for a total period of 6 days. The amount of acetate ion coordinated was calculated as follows:-

Let titre after zero hours = x_o

Let titre after t hours = x_t

Let/.....

Let molarity with respect to sodium acetate = M

Let number of gm-ions acetate coordinated = n

Then

$$n = M \frac{x_o - x_t}{x_o} \qquad (a)$$

The solvent extraction technique was applied to a second series of reactant solutions in which the mole ratios were varied in the same way as indicated in Table 2.1., but in which the chrome nitrate solutions were treated as described in section 1 in order to bring about aggregation of the chromium by the phenomenon of olation.

Accuracy.

The method is subject to inherent errors arising out of the partitioning effect of the acetic acid between the two phases, inability on the part of the operator to quantitatively decant the ethereal extract and the presence of hydrochloric acid held in fine suspension in the decanted ether layer. Useful results can, however, be obtained by avoiding the use of stopcock grease which tends to be distributed by the ether over the inner surface of the separating funnel preventing optimum drainage and by performing the sequence of operations in exactly the same manner for each determination. The experimentally measured values then contain some small, constant error which can be shown to cancel from the numerator of the expression (a), but not from the denominator where, however, it will be sufficiently small to be neglected.

Spectrophotometry/...

(4) SPECTROPHOTOMETRY.

Chromium exhibits properties peculiar to the transitional series of which it is a member, such as paramagnetism, variable valence and colour, the latter due to spectral absorption in the visible region. Colour changes, both quantitative and qualitative, accompanying basicity change and complex formation, were readily visible in the case of the reactant solutions studied by solvent extraction and prompted investigation by spectrophotometric means in order to provide an independent approach. In addition, the solutions were sufficiently dilute to enable optical density to be determined directly in most cases.

The absorption spectrum of the chromium (III) ion with characteristic maxima in the "blue" (420 mμ) and "yellow" (570 mμ) wavelength regions, is well-known (53, 54).

Changes in colour intensity and hence in optical density at a particular wavelength are associated with changes in concentration of the absorbing species. In practice, measurements are made at the wavelength of maximum absorption and related to concentration using the Beer-Bougher Law.

$$I = I_0 . 10^{-\varepsilon . c . t .}$$

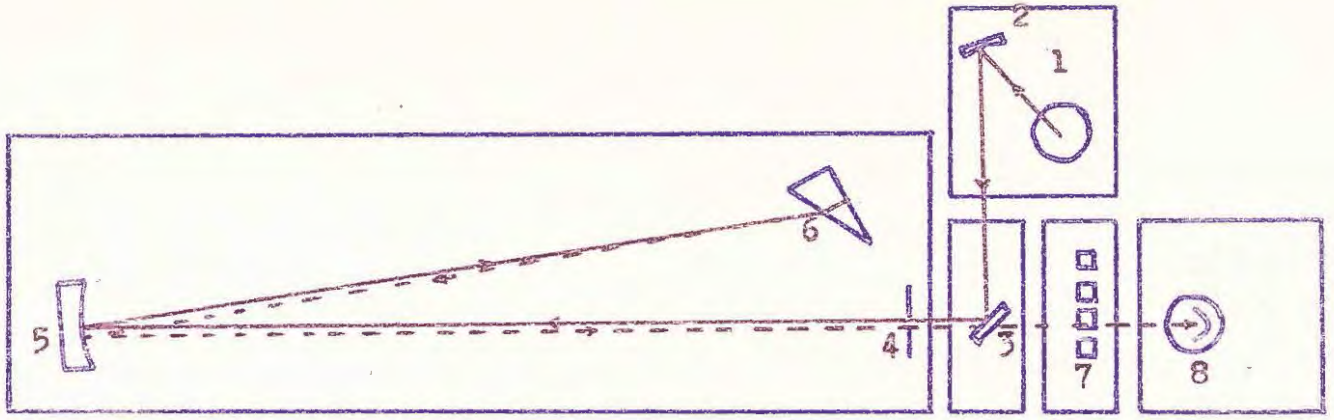
where I = light transmitted through solution

I_0 = light transmitted through an equal thickness of solvent

t = thickness of absorbing solution

c = concentration of absorbing species in moles per litre.

molar/.....



1. Tungsten lamp.
2. Condensing mirror.
3. Diagonal slit entrance mirror.
4. Entrance and exit slits.
5. Collimating mirror.
6. Quartz prism, rotated to select desired wavelength.
7. Corex cells containing solutions under investigation.
8. Photo-electric cell whose amplified output signal is measured by a potentiometer.

Fig. 2.2. Optical System of the Beckman Model DU Spectrophotometer.

ϵ = molar extinction coefficient of solute

and $\epsilon.c$ = optical density of solution.

Qualitative colour changes in a solution corresponding to shifts in the positions of absorption maxima, may be attributed to structural changes in the absorbing species such as might result from the penetration of other ions into a complex.

In the present investigation, measurements of optical density were made using the Beckman Model D U Spectrophotometer, the optical system of which is shown diagramatically in Fig. 2.2.

A series of reactant solutions was prepared according to the pattern indicated in Table 2.1. Except in the case of the solution 0.04 molar in chrome nitrate which required 1 : 1 dilution (to 0.02 molar), the remaining solutions were sufficiently dilute for direct spectrophotometric examination. Portions of the reactant solutions were withdrawn after suitable time intervals and transferred to Corex resistance glass absorption cells of 1 cm. light path whose cell blank had previously been determined using pure water. Each cell was flushed out with small portions of the reactant solution before filling, after which it was allowed to stand for 3 minutes to enable the temperature of the solution to rise above the dew point in order to avoid condensation of moisture on the optical surfaces while taking readings. The error due to the delay was unavoidable, but except during the initially rapid reaction period, was considered to be relatively small.

In/.....

In each case readings were taken at 10 mμ intervals in the vicinity of the two absorption peaks in order to reveal the position of these peaks and hence the absorption density at the wavelength of maximum absorption. In order to approximate as closely as possible to monochromatic light, the instrument was operated at maximum sensitivity which enabled a slit-width of 0.06 - 0.01 mm. to be used, giving a spectral band-pass of about 0.5 mμ (55).

The values for the absorption densities at the two peaks, corrected using the appropriate cell blank in each case, were plotted graphically as a function of time for purposes of comparative study in conjunction with the curves obtained from solvent extraction data.

(5) pH MEASUREMENT.

The course of complex formation is marked by a decrease in pH, while increase in pH brings about an increase in the rate of coordination of the anion.

A time study of the pH variation during the course of reaction was undertaken using the bench type Cambridge pH meter with a wide range spear type glass electrode covering pH values from 1.0 to 13.0. As the temperature compensation control allowed for adjustment only down to 10°C, the temperature of the solution under investigation was allowed to rise to this value before taking the reading.

In the case of the chrome nitrate-sodium acetate reaction, pH measurements were carried out on portions withdrawn from the reactant solutions used in the spectrophotometric studies. In the

miniature/.....

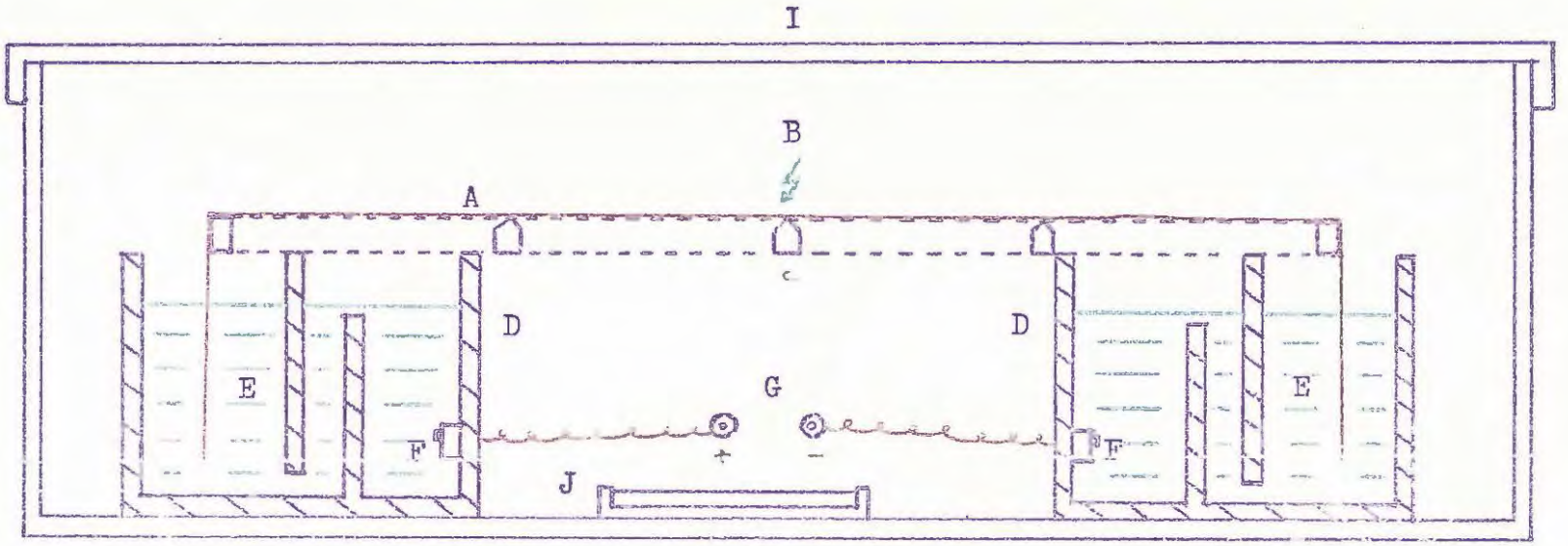


Fig. 2.3. Paper Electrophoresis Apparatus.

A. Filter paper strips.

B. Point of application of reactant solution.

C. Perspex supporting grid.

D. Electrode vessels.

E. Background electrolyte.

F. Platinum wire electrodes.

G. Terminals for connection to external current source.

H. Perspex box.

I. Perspex lid.

J. Shallow dish containing background electrolyte.

miniature tanning series (section 7), the supernatant liquor in each reaction tube was decanted and subjected to pH measurement before discarding.

(6) PAPER ELECTROPHORESIS.

The apparatus of "Perspex" construction was comprised essentially of two electrode vessels and a grid contained in a "Perspex" box fitted with a lid. The side of the box carried two terminals for connection to the external current source. A longitudinal cross-section of the apparatus is shown in Fig. 2. 3. A maximum of 6 strips of Whatman No. 3 M M filter paper, 2.5 cm. x 40 cm., was laid horizontally over the supporting grid which consisted of five cross pieces shaped to knife edges at the points of contact with the paper. The grid was placed in position above the electrode vessels, each of which was partially divided into two main compartments by means of a double partition. Platinum wire electrodes were located in one section of the electrode vessel, while the ends of the filter paper strips were allowed to dip into the remote compartment thereby isolating the paper from contact with electrolysis products in the vicinity of the electrode during the electrophoresis.

In order to reduce evaporation from the paper strips, a saturated atmosphere was maintained by placing flat dishes containing water within the box. A stablised current source was derived from the output terminals of an adjoining Perkin-Elmer-Tiselius solution electrophoresis apparatus.

Procedure/.....

PROCEDURE.

Two litres of 0.1 M sodium nitrate was made up and the pH adjusted to the equilibrium value of the reactant solution to be investigated by dropwise addition of concentrated nitric acid or 50% sodium hydroxide solution. The electrode vessels were twice rinsed with portions of the sodium nitrate solution, subsequently filled to a level about $\frac{1}{4}$ inch above the central partition and placed in position in the box with their long axes about 25 cms. apart. The electrolyte levels in the two vessels were equalised by connecting a syphon tube between the two and leaving the apparatus undisturbed for ten minutes.

Six paper strips having their centres marked with a faint pencil line, were soaked in the balance of the sodium nitrate solution which served as background electrolyte after which the strips were blotted lightly over their entire lengths in order to remove the excess solution. The strips were then stretched lightly over the grid which was placed in the position indicated previously with the overhanging ends of the strips suspended beneath the surface of the electrolyte in the vessels.

Equal volumes (0.05 ml.) of the reactant solution under investigation were uniformly applied along the central line on four strips using a micropipette. A similar volume of pure chrome solution was applied to the remaining two strips to serve as a control.

A current of 0.06 mA per centimetre width of paper was applied across the strips at 60 volts D.C. for a four hour period after which the strips were removed and air dried.

Colour/.....

Colour Development.

The air dried strips were sprayed evenly over their entire lengths with 5% ammoniacal hydrogen peroxide solution in order to oxidise the chromium to the hexavalent state when the position of the band was revealed by the faint yellow colouration of the chromate. The band was then further intensified by spraying with a saturated solution of lead acetate to form chrome yellow.

The above electrophoretic technique was applied to the series of solutions used in the spectrophotometric studies after the elapse of six week time period when it was considered that equilibrium had been established within the various reaction systems.

(7) MINIATURE TANNING EXPERIMENTS.

The tanning of normal and modified collagens on a test tube scale in the laboratory has yielded valuable information regarding the participation of reactive groups within the hide and the tanning properties of complexes. In the present investigation, the technique was applied to a rate study of chromium fixation by normal collagen of hide substance provided in two physical states. In the first series, tannage was carried out on standard hide powder in which surface development of the material was at a maximum and time "lag" due to penetration effects small, while in the second series prepared pelt pieces were tanned in which the weave pattern of the collagen fibres was retained resulting in reduced accessibility of reactive centres to the tanning reagent.

Hide/.....

(a) HIDE POWDER STUDIES.

Standard hide powder of the same batch and pH 5.48, prepared by Baird and Tatlock (London) Ltd., was used in the present study. Making due allowance for the moisture content specified and on a basis of a carboxyl group content of 0.9 milli-equivalents per gram[56], the quantities of moist hide powder equivalent in respect of carboxyl group content to that contained in the weights of sodium acetate used in the solvent extraction studies, were calculated in accordance with the scheme indicated in Table 2.1. These calculated weights were scaled down by a suitable factor (i.e. a fiftieth) in order to give convenient quantities of hide powder (i.e. 0.5 to 2 g.) for subsequent digestion and analysis for fixed chrome by the official method of the Society of Leather Trades' chemists[51].

In order to obtain a minimum of eight points for each reaction curve, the appropriate amount of hide powder was weighed into each of nine 1 inch diameter specimen tubes (in duplicate) which served as reaction vessels. An amount of distilled water chilled to the reaction temperature and equal to half the final volume of the float to be used (i.e. 10 ml), was pipetted into each of the tubes which were then stoppered with rubber bungs and immersed in the constant temperature tank overnight in order to enable the hide powder to "wet back". The dimensions of the specimen tubes were such as to enable the solid phase to be completely immersed beneath the surface of the float during the reaction, and at the same time to ensure negative buoyancy after addition of the float to permit the reaction tubes to be arranged in an orderly fashion on the bottom of the tank.

The/.....

The chrome tannage solutions to be used were prepared in each case as described in section 2, but were of double the chrome concentration. In the case of fresh solutions, the chromium nitrate crystals were dissolved, diluted to large volume and pH adjustment carried out immediately before use. The pH level was adjusted to coincide as closely as possible with the natural initial pH of the chrome nitrate-sodium acetate reactant solution of corresponding mole ratio and concentration, used in the solvent extraction studies. A preliminary check on the initial pH was made by pipetting into one of the reaction tubes, a volume of chrome solution equal to the volume of water used to "wet back" the hide powder, shaking vigorously and taking a pH reading. Any further small adjustments required were effected by dropwise additions of concentrated acid or alkali to the double strength chrome solution as before.

When pH adjustment of the chrome solution had been completed to give a satisfactory initial pH in the reactant mixture, the addition of chromium nitrate solution to eight of the remaining reaction tubes was completed (in duplicate), each tube being stoppered, and shaken well after each addition. Each tube was gently tapped in order to dislodge any hide powder adhering to the sides of the vessel to ensure total submersion of the bulk of the material before immersing the reaction tube in position in the tank. The time of commencement of the additions was noted.

Reaction vessels were withdrawn from the tank (in duplicate) after time intervals of 1, 3, 5, 7, 24, 48, 96 and 144 hours. In each case the contents of the tube were washed quantitatively

into/.....

into a "split" Buchner funnel with decinormal hydrochloric acid in order to stop the reaction and the hide powder was then filtered off on Whatman No. 41 "fast" grade filter paper. The hide powder was washed a further ten times with portions of distilled water in order to remove "unfixed" chrome. The hide powder was then transferred on the filter paper to a Kjeldahl flask and retained for subsequent chrome analysis.

The series of hide powder studies was repeated under the same conditions of temperature, concentration and pH, using "olated" double strength chrome solutions prepared as described in section 1.

(b) TANNAGE OF PELT PIECES.

1) Preparation of material.

The material used in this study was prepared according to the method of T.I. Pound and F.H. Quinn for the production of "Drypelt"(57). The pelt pieces were prepared from grain layer of 2 millimetre thickness, split from a portion of medium hide which had been limed, depilated and subsequently "freeze-dried" by sublimation of water vapour from the frozen hide. The material was cut into approximately two hundred 5 centimetre squares, which were soaked in decinormal hydrochloric acid for 24 hours in order to remove surface calcium carbonate and neutralise any residual lime. The pieces were then washed free of acid by immersing in running tap water for a period of 48 hours.

Five litres of acetic acid/sodium acetate buffer at pH

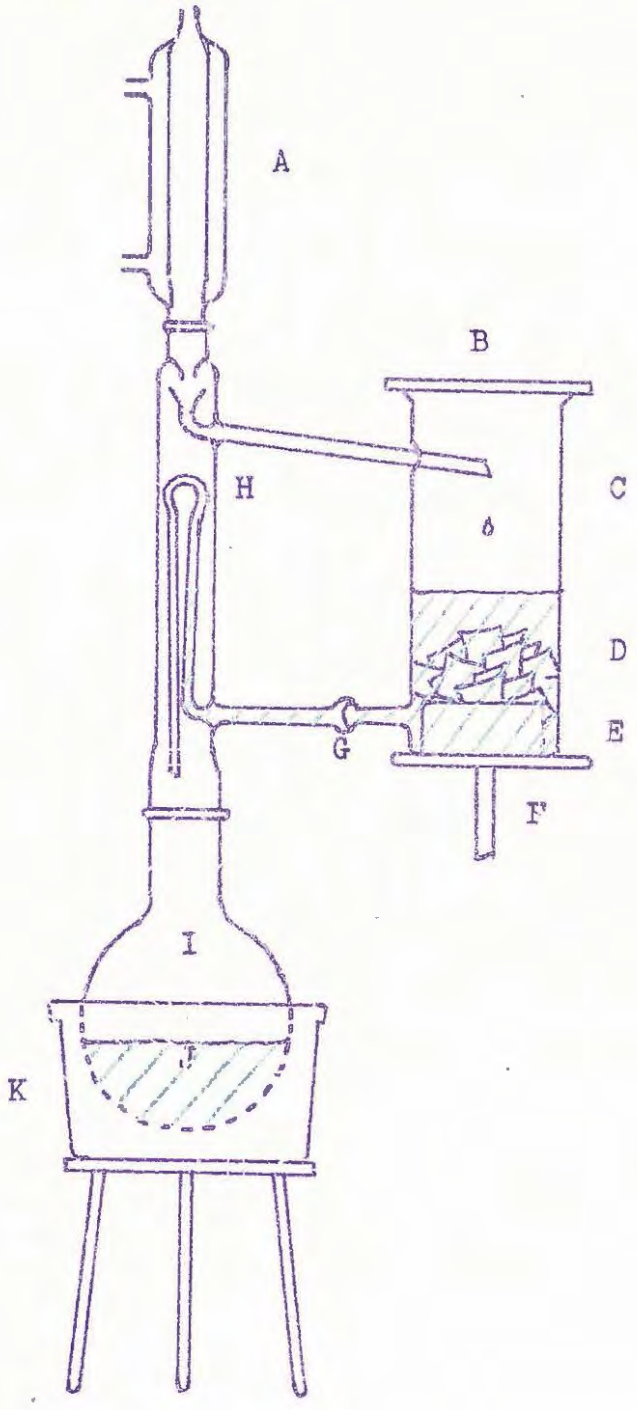


Fig. 2.4. Large Capacity Soxhlet Apparatus.

A. Reflux condenser.
B. Glass plate.
C. Side chamber.
D. Felt pieces.
E. Perforated shelf.
F. Retort stand.
G. Flexible joint.
H. Siphon tube.
I. Round bottom flask.
J. Acetone.
K. Water bath.

4.64 and $^{N}/_{3}$ with respect to acid radicle were added to the raw pelt pieces in a glass churn, the ratio of float to pelt being adjusted to about 5 to 1. The pieces were then drummed in buffer which was changed at intervals during a total period of 72 hours.

The buffer was then washed out of the pieces by drumming for a further period of 72 hours with frequent changes of distilled water. At the end of this period, the pieces were found to buffer at pH 4.74.

The pieces were removed from the churn, drained and subsequently acetone degreased in a low temperature, large capacity Soxhlet apparatus of the design shown in Fig. 2.4. The degreasing was continued for 36 hours after which the pieces were air dried under normal atmospheric conditions of temperature and humidity when the pieces were found to have the appearance and feel of a white leather.

The moisture content of the prepared material was determined by the official method of the International Society of Leather Trades' Chemists[58]. The pieces were stored in a glass jar with a screw top until required.

2) Tanning experiments.

The prepared pelt pieces were utilised in a similar series of tanning experiments, as in the case of the hide powder studies. The carboxyl group content per gram of the pelt was assumed to be the same as for hide powder, and the amounts of conditioned pelt to be used in each experimental series were calculated on this basis

allowing/.....

allowing for the moisture content as determined. The pieces were weighed directly on the balance pan after resetting the zero adjustment, the weight adjustment to the material being carried out by cutting away portions of the pelt with a pair of scissors until the actual weight was within $\pm$ 5 milligrams of the required value.

Reaction series were set up at the same mole ratios and concentrations with respect to total carboxyl group and chromium nitrate as in the preceeding studies and the necessary pH adjustment was carried out as in section 7 (a).

Reaction tubes were withdrawn from the constant temperature bath (in duplicate) after suitable time intervals. The float in each case was decanted into a 30 ml beaker and a pH reading taken. The pelt pieces were washed 5 times with portions of decinormal hydrochloric acid to stop the reaction after which they were pressed between layers of blotting paper in a hydraulic press. The pieces were then washed in running water (pH 7.5 - 8.0) for 2 hours to remove the remaining excess chromium[59]. The pieces were then transferred to a Kjeldahl flask and retained for subsequent analysis to determine "fixed" chrome by the official method.

The results were recorded graphically by plotting "fixed" chrome content as a function of time for comparison with similar plots obtained from the solvent extraction, spectrophotometric and hide powder studies.

CHAPTER III.

COORDINATION OF THE ACETATE RADICAL BY CHROMIUM NITRATE UNDER AQUEOUS ACID CONDITIONS.

The coordination of the acetate radical to trivalent chromium has been studied previously in these laboratories[60] and by other workers.[14]. In the present investigation a more detailed re-examination of the kinetics of the process was proposed, in which the course of reaction was followed under various conditions using independent chemical (solvent extraction) and instrumental (spectrophotometric) techniques. The various reactant solutions at equilibrium were also subjected to electrophoretic examination. Details of these techniques and the method of preparation of solutions are as described in Chapter II.

RESULTS.

(a) Solvent Extraction Studies.

Figs. 3.1., 3.2. and 3.3. show the results obtained when the extent of coordination as determined by this technique is plotted as a function of time over a reaction period of 144 hours.

The effect of alteration in the mole ratio of reactants according to the pattern indicated in Table 2.1., page 19, is shown in Figs. 3.1. and 3.2. in which the sodium acetate and chromium nitrate concentrations are varied respectively. No pH adjustment was carried out in these cases, but the reactions were allowed to proceed at their natural pH levels.

Fig. 3.3 shows the effect of pH adjustment on the reaction course,

the/.....

Fig. 3.1. Effect of variation in acetate concentration on the coordination of acetate radical by chromium nitrate in 0.02 M solution.

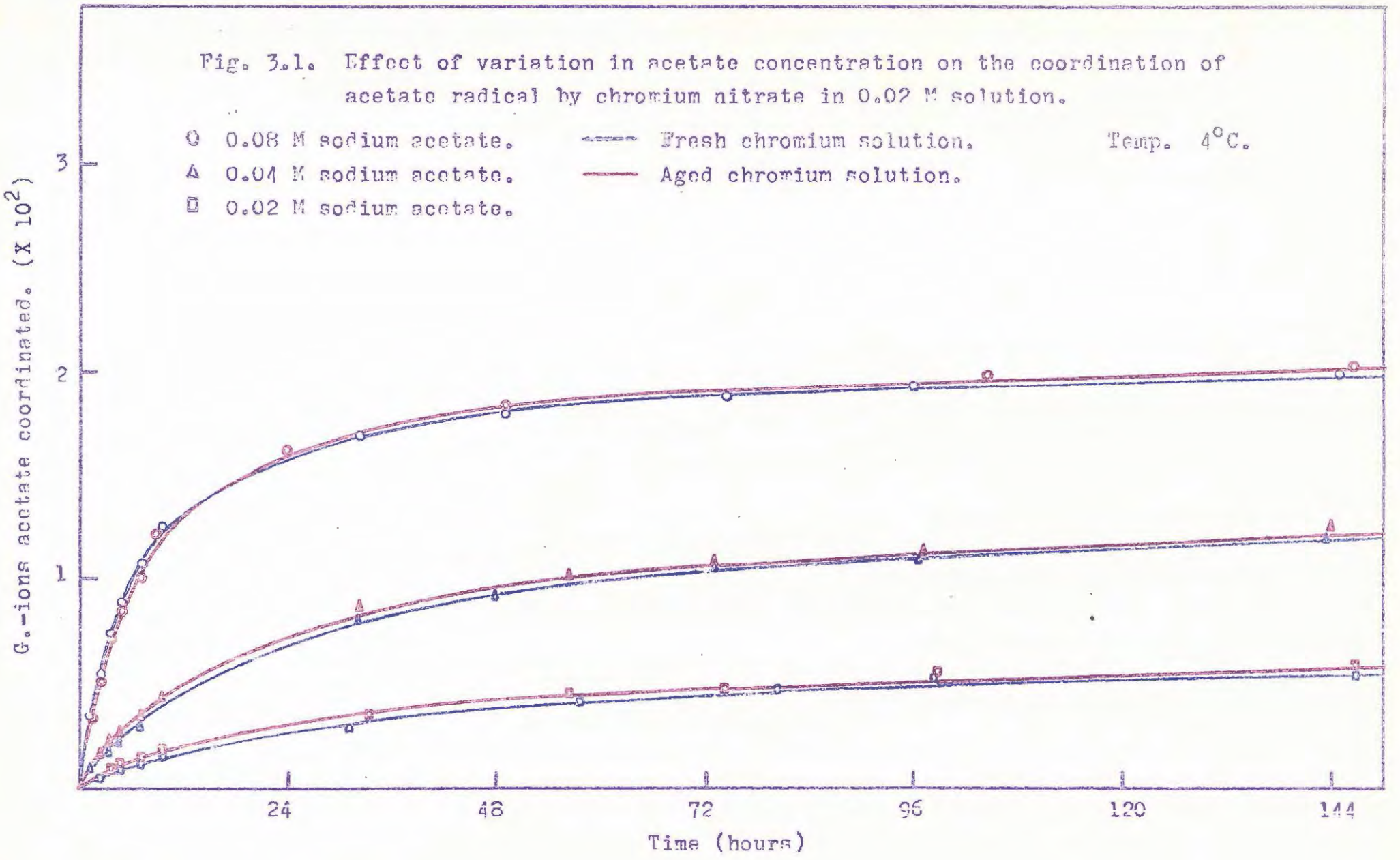


Fig. 3.2. Effect of variation in chromium concentration on the coordination of acetate radical from 0.08 M sodium acetate solution.

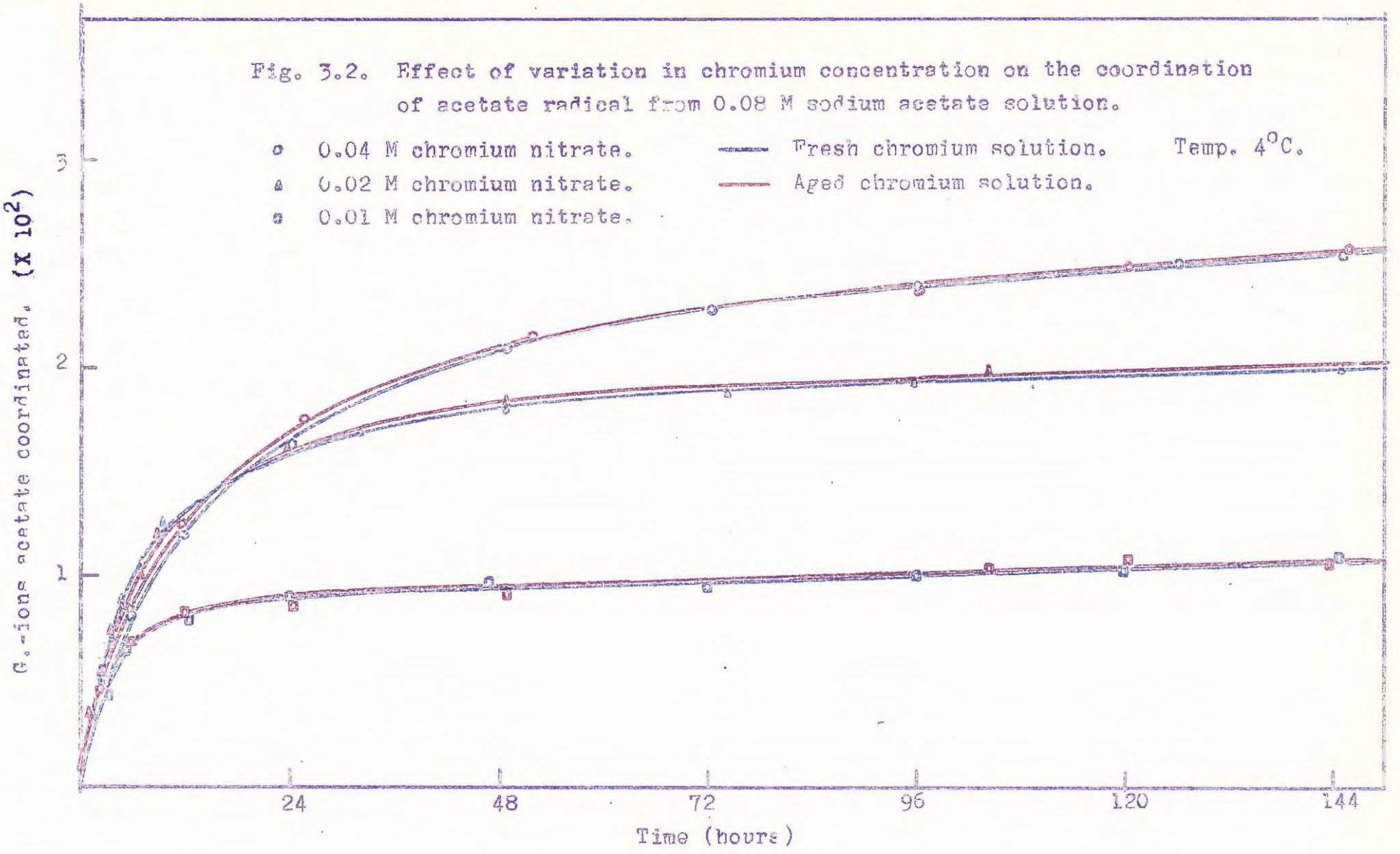
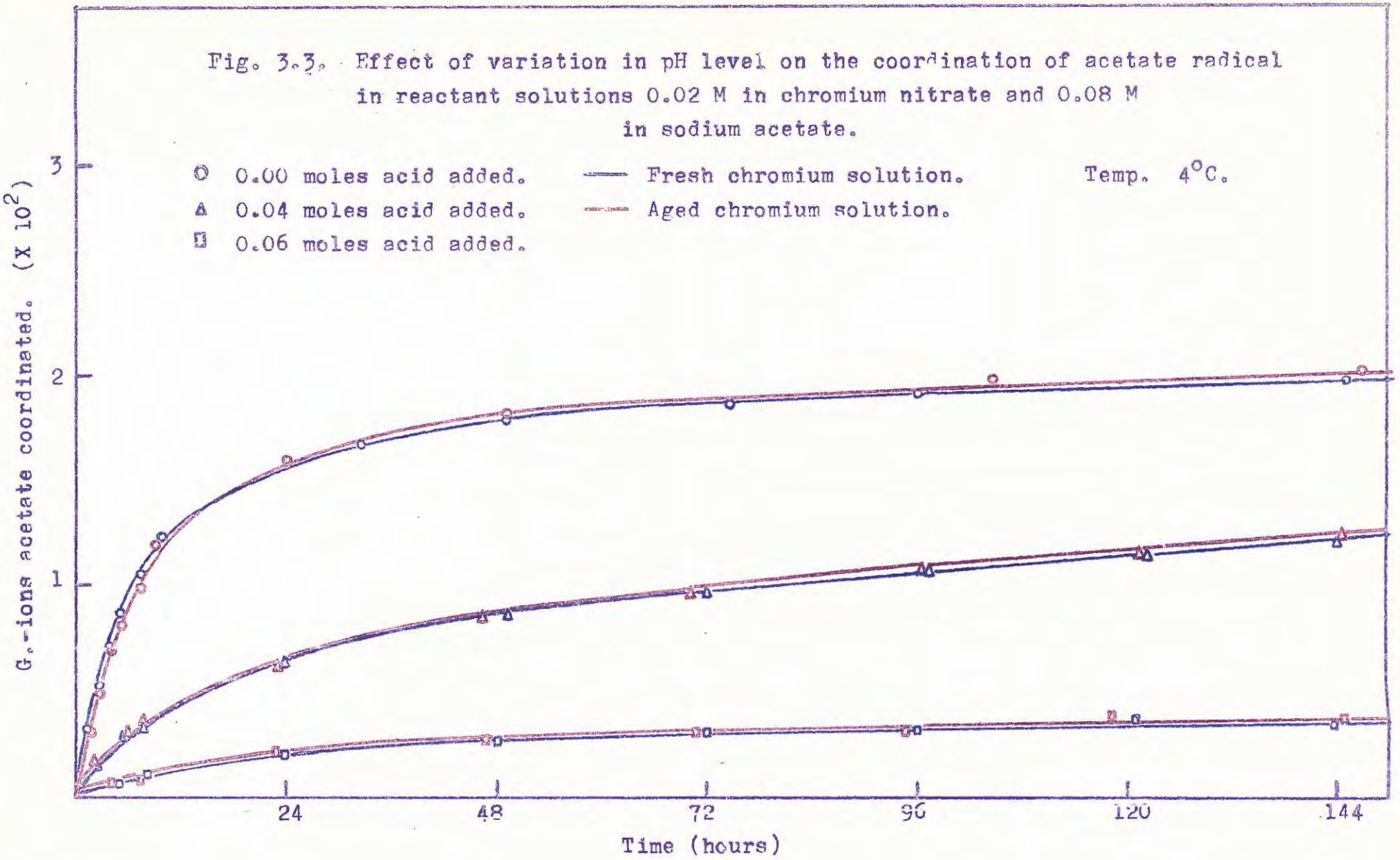


Fig. 3.3. Effect of variation in pH level on the coordination of acetate radical in reactant solutions 0.02 M in chromium nitrate and 0.08 M in sodium acetate.



the adjustment being effected by addition of calculated volumes of normal hydrochloric acid chemically equivalent to half and threequarters of the total acetate present, to solutions containing reactants at a constant mole ratio (0.08M in sodium acetate and 0.02M in chromium nitrate).

An attempt was made to distinguish differences in the reaction course using freshly prepared chromium nitrate solutions (blue graphs) and the reaction course using boiled and aged chromium nitrate solutions (red graphs).

In general the resulting plots have the shape of typical mass-action curves with rapidly rising initial portions which "turn over" and appear to approach an equilibrium value assymptotically. Increase in the sodium acetate (fig. 3.1.) and chromium nitrate (Fig. 3.2.) concentrations brings about an increase in coordination while decrease in the reaction pH level as a result of acid additions, serves to reduce the rate and extent of coordination (Fig. 3.3.). These observations are in accordance with the findings of previous workers.[61].

The stoicheiometry of the reaction appears to be indefinite except in the case of the solutions containing the higher sodium acetate to chromium nitrate ratios (i.e. mole ratios of 8 : 1 and 8 : 2, Fig. 3.2.), where there is a marked decrease in the coordination rate, the curves turning over sharply, at the 0.01 and 0.02 mole levels. This is an indication of an equimolecular reaction between the two reactants.

At lower mole ratios (i.e. ratios of 4 : 2, 2: 2 and 8 : 4, Figs. 3.1. and 3.2.), no definite combining proportions are apparent; this departure may be accounted for on the basis that high mole ratios bring about

conditions/.....

conditions of (a) high acetate concentration and (b) elevated pH due to acetate hydrolysis, both of which favour completion of the reaction, while at lower mole ratios the relatively larger proportions of chromium nitrate serve to bring about conditions of (a) high chromium ion concentration and (b) lower pH level due to hydrolysis of the chromium nitrate; in this case the effect of (a) and (b) are contrary and the reaction would be expected to be less complete.

Similarity between the curves obtained at various pH levels (Fig. 3.3.) and those obtained at various levels of sodium acetate concentration (Fig. 3.1.) indicates that the concentration of ionised acetate, and not total acetate concentration, is the operative factor in determining the reaction course, the effect of addition of half and threequarters the equivalent amount of acid being thus to reduce the acetate ion concentration by repression of the ionisation of the acetic acid present.

No significant differences in the course of reaction were detected in the case of the fresh and olated chromium nitrate reactant solutions when the rate data as determined by the solvent extraction technique were compared graphically.

The implications of these results are discussed in Chapter VI.

(b) pH Studies.

Figs. 3.4., 3.5. and 3.6. reflect the variation in pH level with time during the course of reaction. The effect of variation in reactant proportions on the rate of the pH variation is shown in Figs. 3.4. and 3.5., while the effect of initial pH adjustment in reactant solutions of the same mole ratio is shown in Fig. 3.6. pH curves obtained with fresh chromium

Fig. 3.4. Effect of variation in acetate concentration on the rate of pH change accompanying the coordination of acetate radical in 0.02 M chromium nitrate solution.

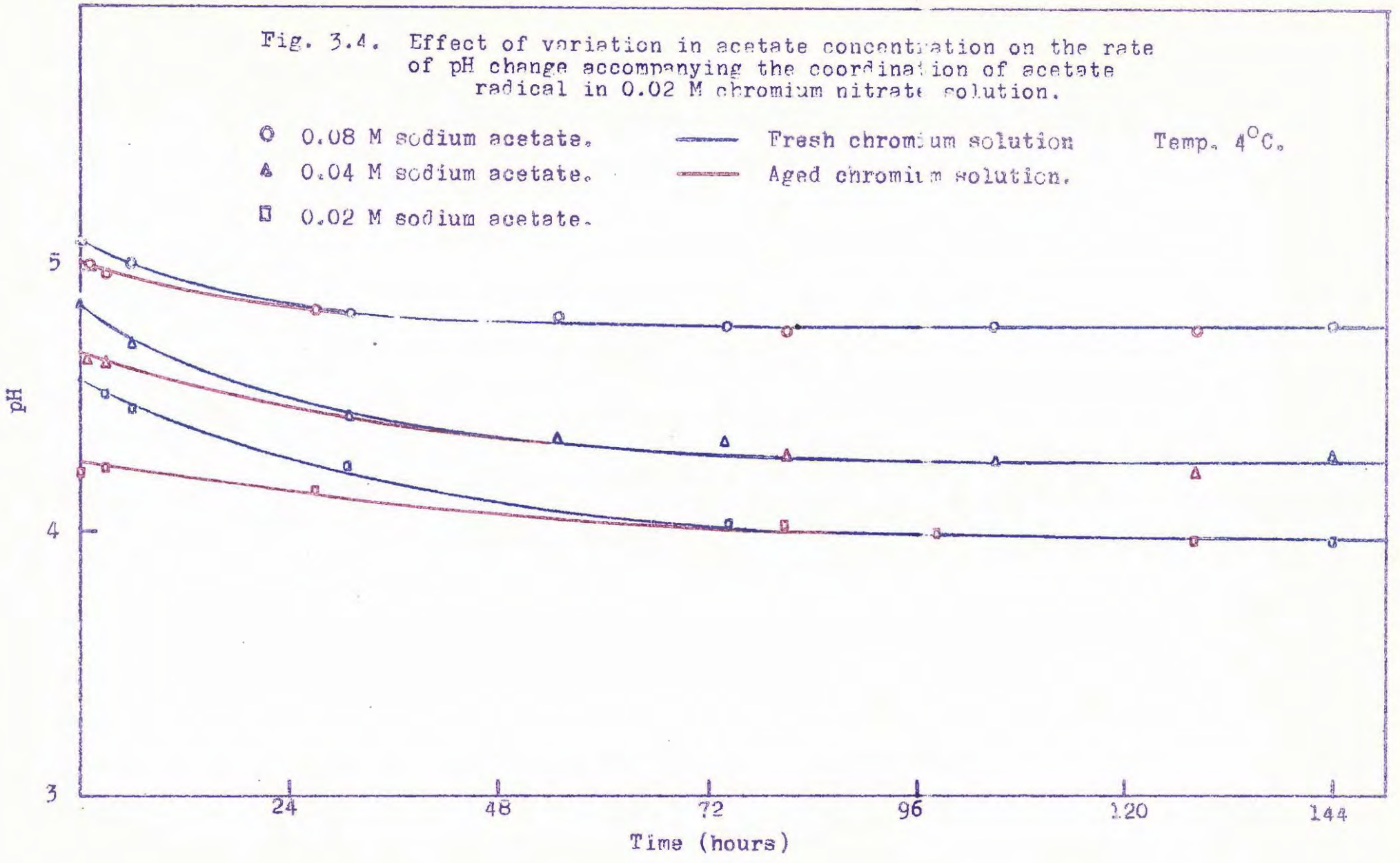


Fig. 3.5. Effect of variation in chromium concentration on the rate of pH change accompanying the coordination of ligand in 0.08 M sodium acetate solution.

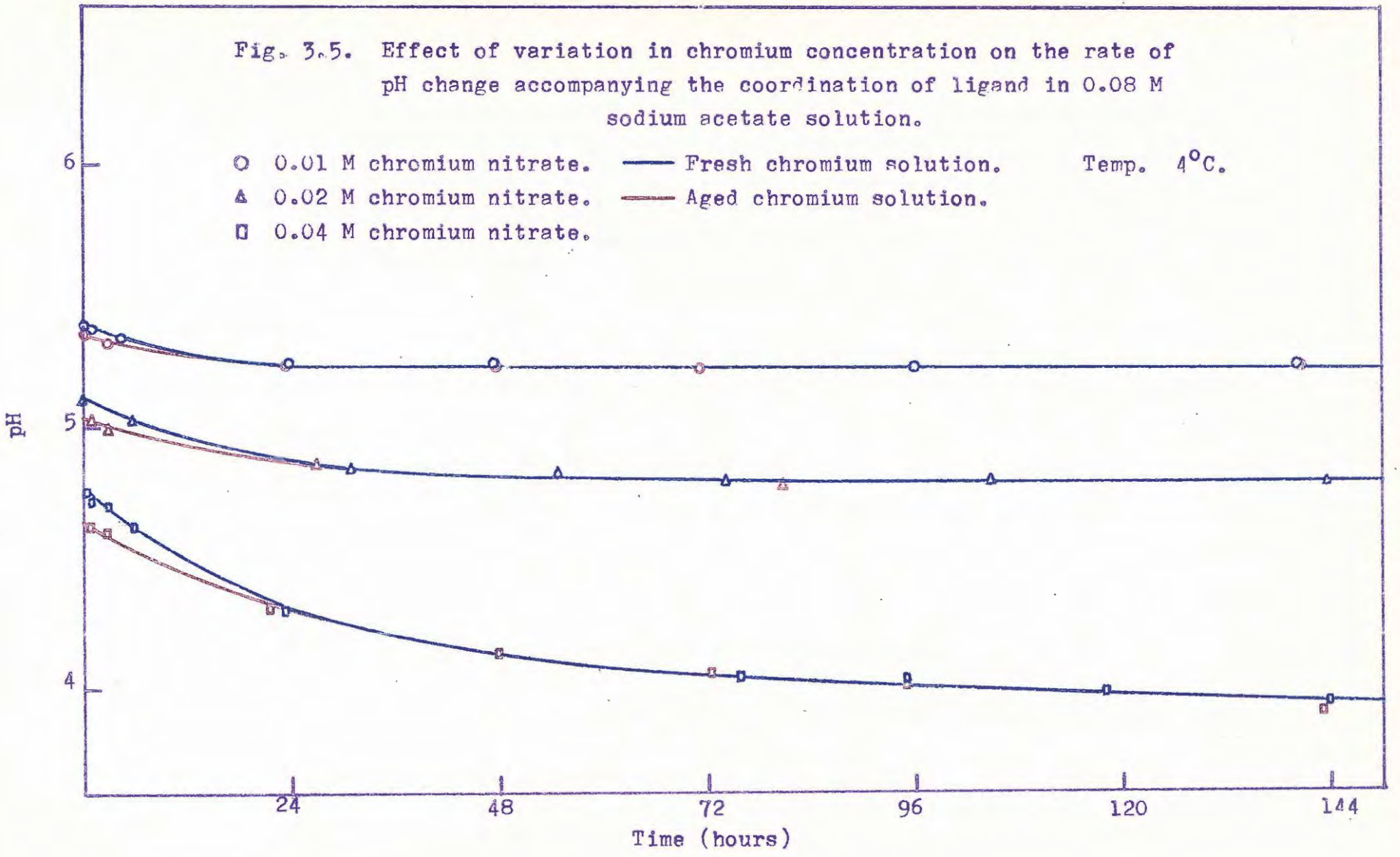
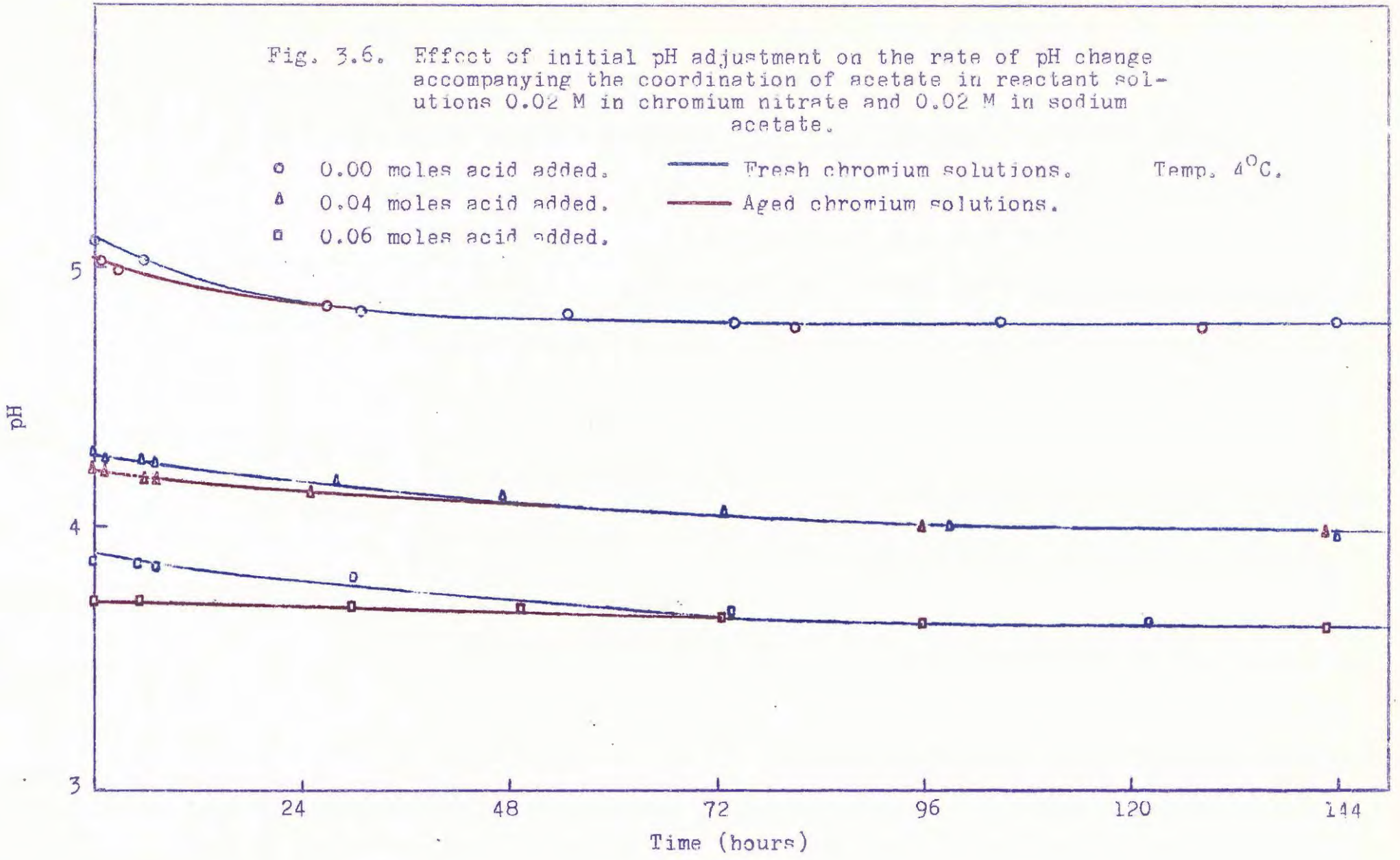


Fig. 3.6. Effect of initial pH adjustment on the rate of pH change accompanying the coordination of acetate in reactant solutions 0.02 M in chromium nitrate and 0.02 M in sodium acetate.



nitrate solutions are shown in blue, while those obtained with boiled and aged chromium nitrate are shown in red.

In each case penetration of the ligand into the chromium complex was accompanied by a decrease in the pH level of the reactant solution, the rate of the decrease varying directly with the reaction rate. The initial pH values in the case of the boiled and aged chromium nitrate solutions were lower than those of the corresponding fresh solutions, indicating the presence of a larger amount of "free" acid due to olation (cf. Chapter I, page 5); these pH differences were most pronounced at the lower pH levels (Figs. 3. 4 and 3. 6.) The rate of fall in pH over the initial reaction period was greater in the case of the fresh solutions, however, so that the ultimate pH levels in the case of the corresponding fresh and aged solutions merged to the same limiting values.

The implications of these results are discussed in Chapter VI.

(c) Spectrophotometric Examination.

(i) Changes in the Absorption Spectrum of the Chromium (III) Ion

Colour changes occurring in solution were readily visible during the preparation of the reactant solutions and also accompanying the course of reaction. Boiling of the pure, freshly-prepared chromium nitrate solutions to bring about olation, was accompanied by a marked colour change from blue to green, the original blue being partly restored on ageing. Preparation of the reactant solutions by addition of sodium acetate to the blue chromium nitrate solutions resulted in an immediate colour change to green apparently due to elevation of the pH of the solution by the hydrolysed sodium acetate. During the reaction penetration of the ligand

was / ...

was accompanied by a colour change from green to blue-violet.

These changes were subjected to accurate optical density measurement in the Beckman Model DU Spectrophotometer as described in Chapter II, in the vicinity of the two peaks which characterise the absorption spectrum of the trivalent chromium ion. Figs. A.1. to A.14. of the Appendix reflect the qualitative and quantitative changes occurring in the vicinity of the absorption peaks during the reaction. The absorption spectra of chromium nitrate solutions of the same concentration as the reactant solutions, but without added ligand, are included for reference.

Initially, the effect of elevation of the pH level as a result of addition of the sodium salt of the ligand, is to immediately increase the absorption at both the 420 mμ and 570 mμ peaks by amounts proportional to the pH change, the effect being greatest at the 420 mμ peak. This effect corresponds to the marked change in the initial colour of the chromium nitrate solution from blue to green, observed visually, thus due to the greatly increased absorption in the blue region of the spectrum. The increase in absorption at both peaks is also accompanied by shifts in the positions of the peaks to longer wavelengths.

During the course of reaction, ligand penetration is accompanied by an increase in absorption at the 570 mμ peak and a decrease in absorption at the 420 mμ peak. These changes are also accompanied by shifts in the positions of both peaks back to shorter wavelengths. These effects are in accordance with visual observation, the increased absorption in the 570 mμ or "yellow" region together with the decreased absorption in the 420 mμ or "blue" region accounting for the shift in the colour of the reactant solution back to the original blue. The final colour of the reactant

solution/.....

solution borders on the blue-violet region as a result of the additional tendency of the maxima to migrate to shorter wavelengths as the reaction proceeds.

The various optical effects described are evidence of structural change taking place in solution. Quantitative changes in the absorption spectra of species in solution, such as variation in peak height, are normally related to variation in the concentration of the absorbing species by means of the Beer-Bougher relation (cf. page 22). Qualitative changes in the spectra such as shifts in the wavelengths of absorption maxima, are usually ascribed to changes in vibrational energy of the molecule due to structural changes such as might result from the penetration of new ligands into a chromium complex structure. This effect has been noted by Colmar and Schwartz in their study of the coordination of ammonia to trivalent chromium.(62)

(ii) Quantitative Changes at the 570 mμ Absorption Peak.

Figs. 3.7., 3.8 and 3.9. reflect the variation in optical density at the 570 mμ peak plotted as a function of time over a reaction period of 144 hours. The effect of variation in the mole ratio of reactants is shown in Figs. 3.7. and 3.8. in which the sodium acetate and chromium nitrate concentrations are varied respectively, as in the solvent extraction studies, while the effect of pH variation at constant mole ratio is shown in Fig. 3.9. The reaction curves obtained in the case of the reactant solutions containing olated chromium nitrate (red graphs) are shown together with the curves obtained using fresh chromium nitrate solutions (blue graphs) for purposes of comparison.

The resulting curves have the characteristic mass-action form

and/.....

Fig. 3.7. Effect of variation in acetate concentration on the rate of change in optical density of 0.02 M chromium nitrate solution at the 570 mu absorption peak.

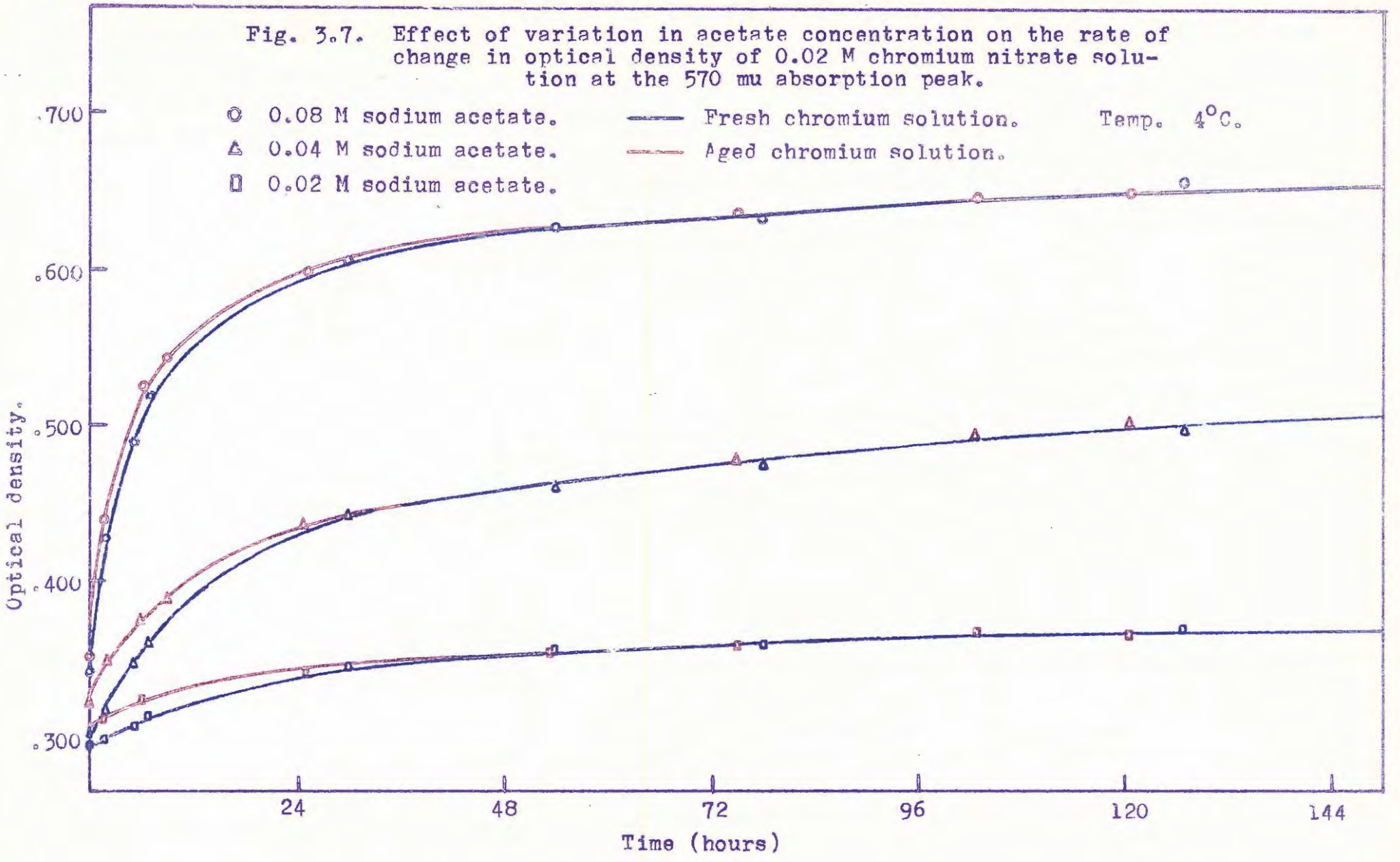


Fig. 3.8. Effect of variation in chromium concentration on the rate of change in optical density at the 570 mμ absorption peak in 0.08 M sodium acetate solution.

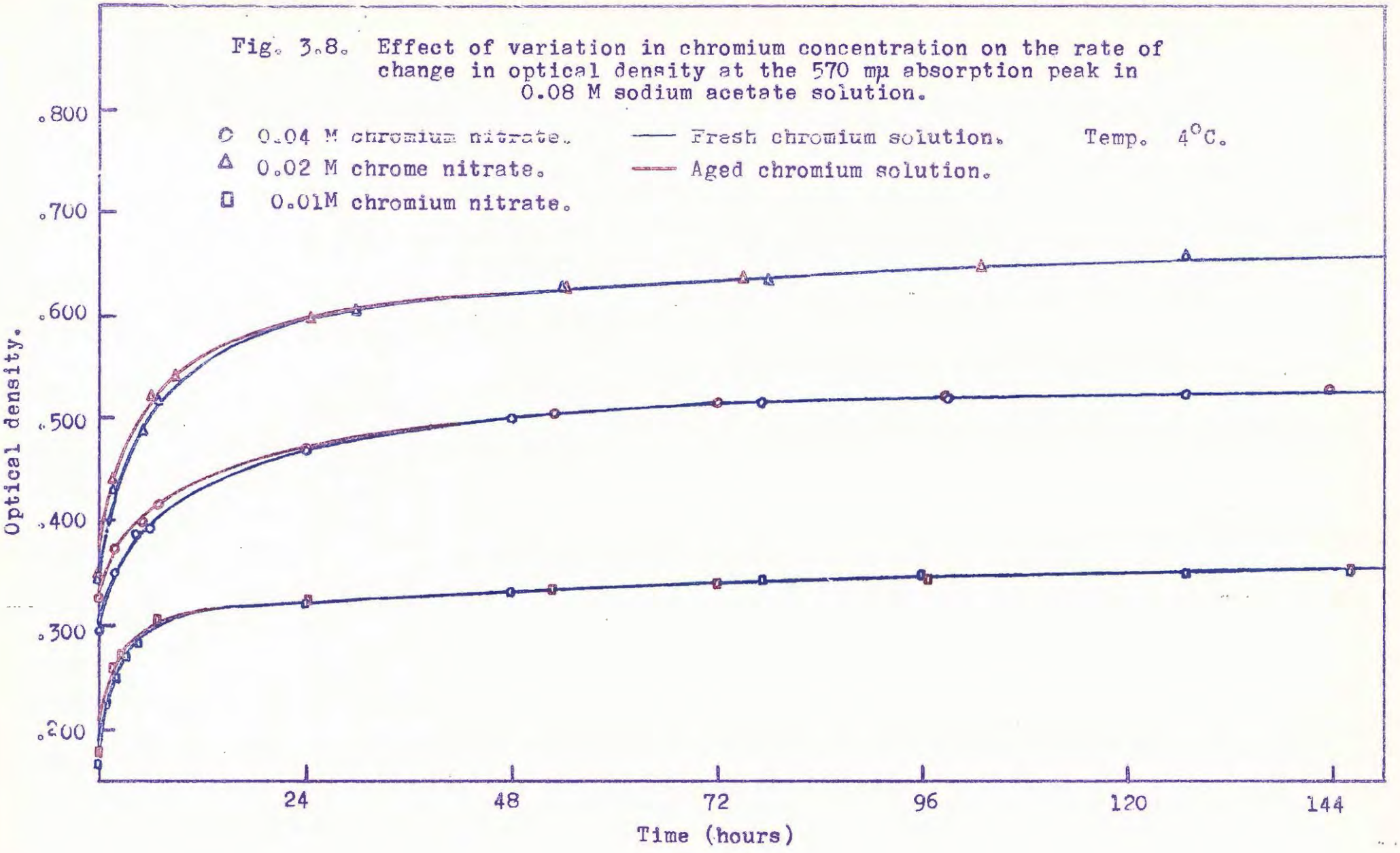
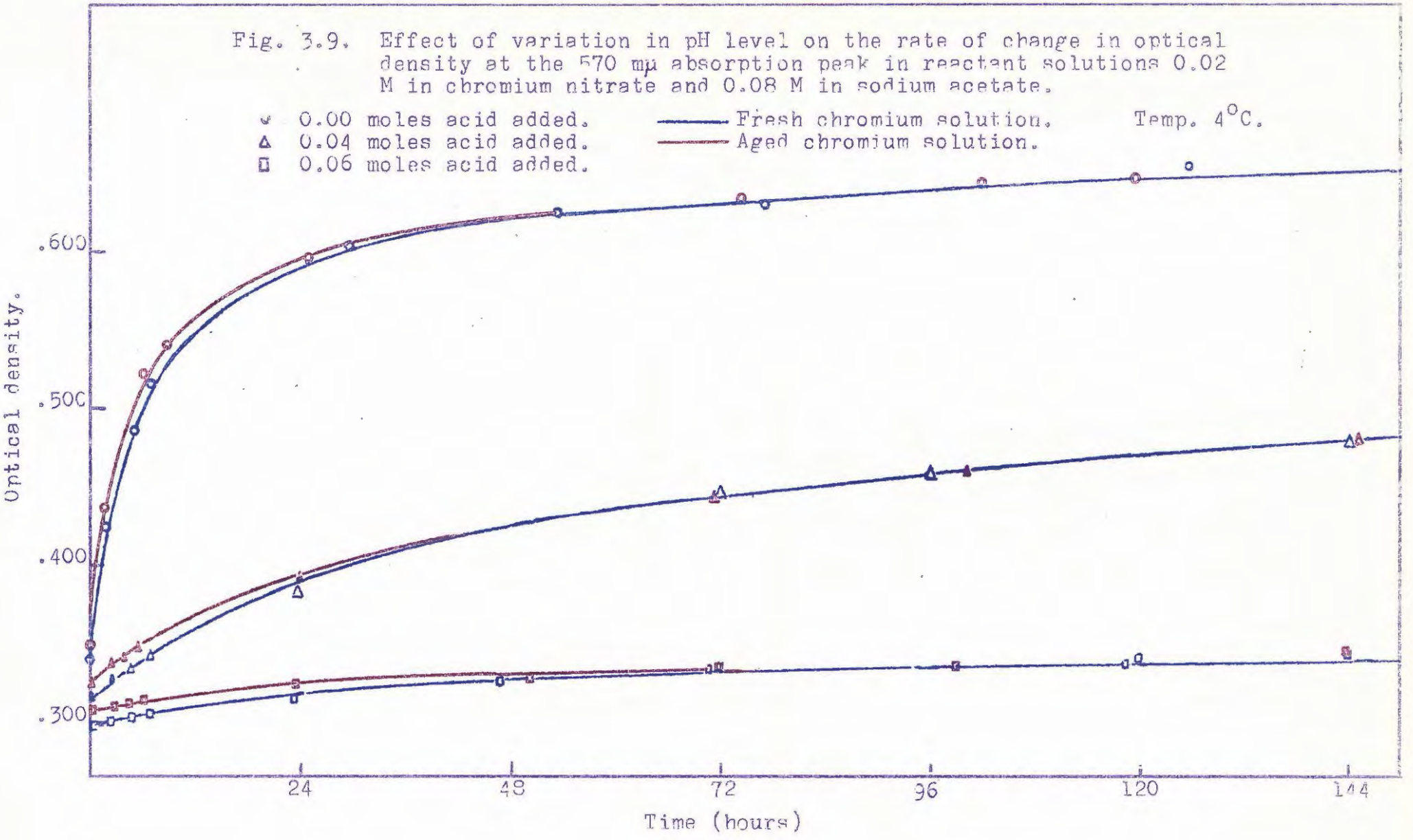


Fig. 3.9. Effect of variation in pH level on the rate of change in optical density at the 570 mμ absorption peak in reactant solutions 0.02 M in chromium nitrate and 0.08 M in sodium acetate.



and correspond closely to the plots obtained in the solvent extraction studies, the shape of the plots showing similar dependency upon concentration and pH conditions. The variations in absorption at the 570 mμ peak appear to be directly related to the concentration of the complex in solution; the quantitative nature of the relationship is discussed in the following section. These observations are in accordance with the findings of previous workers who have associated changes in the height of the 570 mμ peak with coordination of ligands to the chromium complex ion.(63)

In general, the olated chromium nitrate solutions gave reactant solutions whose initial absorption was slightly greater than that of the corresponding fresh chromium nitrate reactant solutions. As the coordination reaction proceeded, however, the corresponding curves tended to merge so that the final absorption values were the same. The general shapes of the reaction curves were, nevertheless, essentially similar in the case of both fresh and olated chromium solutions.

Applicability of the Beer-Bougher Relationship.

Basic similarity has already been pointed out in the curves obtained by plotting absorption changes at the 570 mμ or "yellow" peak and coordination of acetate radical as functions of time. In order to establish the degree of accuracy with which the spectrophotometric data quantitatively reflect the course of reaction as indicated by the analytical technique, the applicability of the Beer-Bougher Law was examined. According to the Law, the absorption of monochromatic light by a particular species in solution, is related to its concentration as follows:-

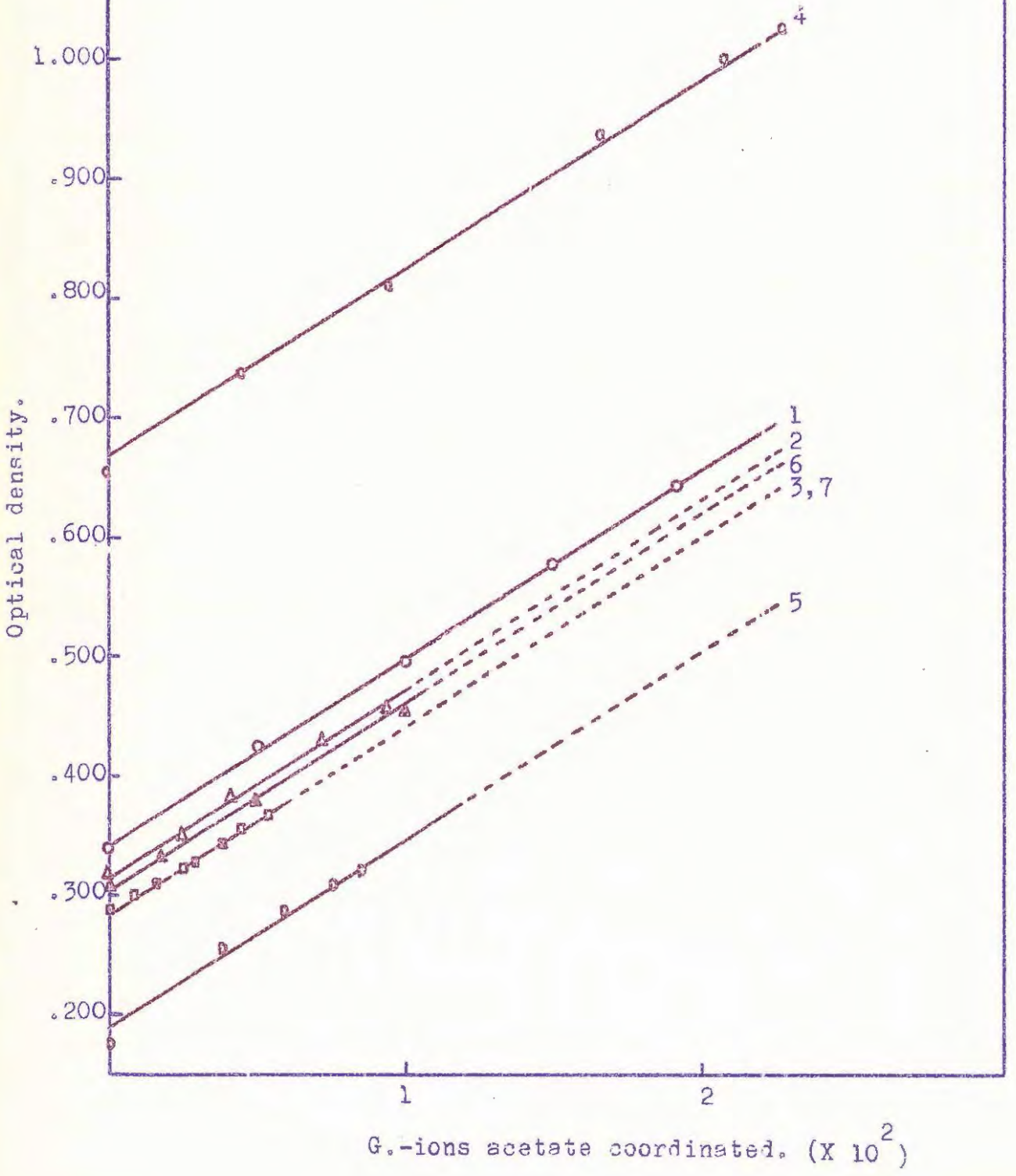
$$I = I_0 . 10^{-E.c.t}$$

where/.....

Fig. 3.10.

Correlation between optical density of aged chromium nitrate reactant solutions at the 570 mμ absorption peak and the extent of acetate coordination after comparable reaction times.

1. 2 Cr : 8 Ac (pH=5.1)
2. 2 Cr : 4 Ac (pH=4.6)
3. 2 Cr : 2 Ac (pH=4.3)
4. 4 Cr : 8 Ac (pH=4.7)
5. 1 Cr : 8 Ac (pH=5.4)
6. 2 Cr : 8 Ac (pH=4.2)
7. 2 Cr : 8 Ac (pH=3.8)



where the symbols have the significance indicated previously (page 22).

Hence,

$$\text{Log } \frac{I_o}{I} = - E.c.t$$

i.e. Optical density = E.c.t

Since all readings are taken on the same "thickness" of solution and E is a constant, it follows that:-

Optical density $\propto$ concentration.

Fig. 3.10. shows the result of plotting absorption data against concentration data obtained under comparable conditions and after similar reaction times. All the plots are straight lines, with the same gradient, demonstrating the linear relationship between optical density and concentration in accordance with the law. The plots were obtained using the absorption readings for the aged reactant solutions since these were considered to reflect the true course of reaction over the initial reaction periods. (cf. Chapter VI).

It should be pointed out that strict comparison of the data obtained in the solvent extraction and spectrophotometric studies was limited due to the unavailability of pure chromium nitrate reagent and the extreme hygroscopic nature of the salt which made accurate duplication of concentrations difficult. This difficulty was partly overcome in the spectrophotometric series by preparing a stock chromium solution.

Large vertical displacements between graphs 1, 4 and 5 are in accordance with the Beer-Bougher Law being proportioned to the initial levels of chromium nitrate (0.01, 0.02 and 0.04 molar, respectively). In the case of graph 4, the reactant solutions were diluted in 1 : 1 ratio

prior/.....

Fig. 3.11. Effect of variation in acetate concentration on the rate of change in optical density at the 420 mμ absorption peak in 0.02 M chromium nitrate solution.

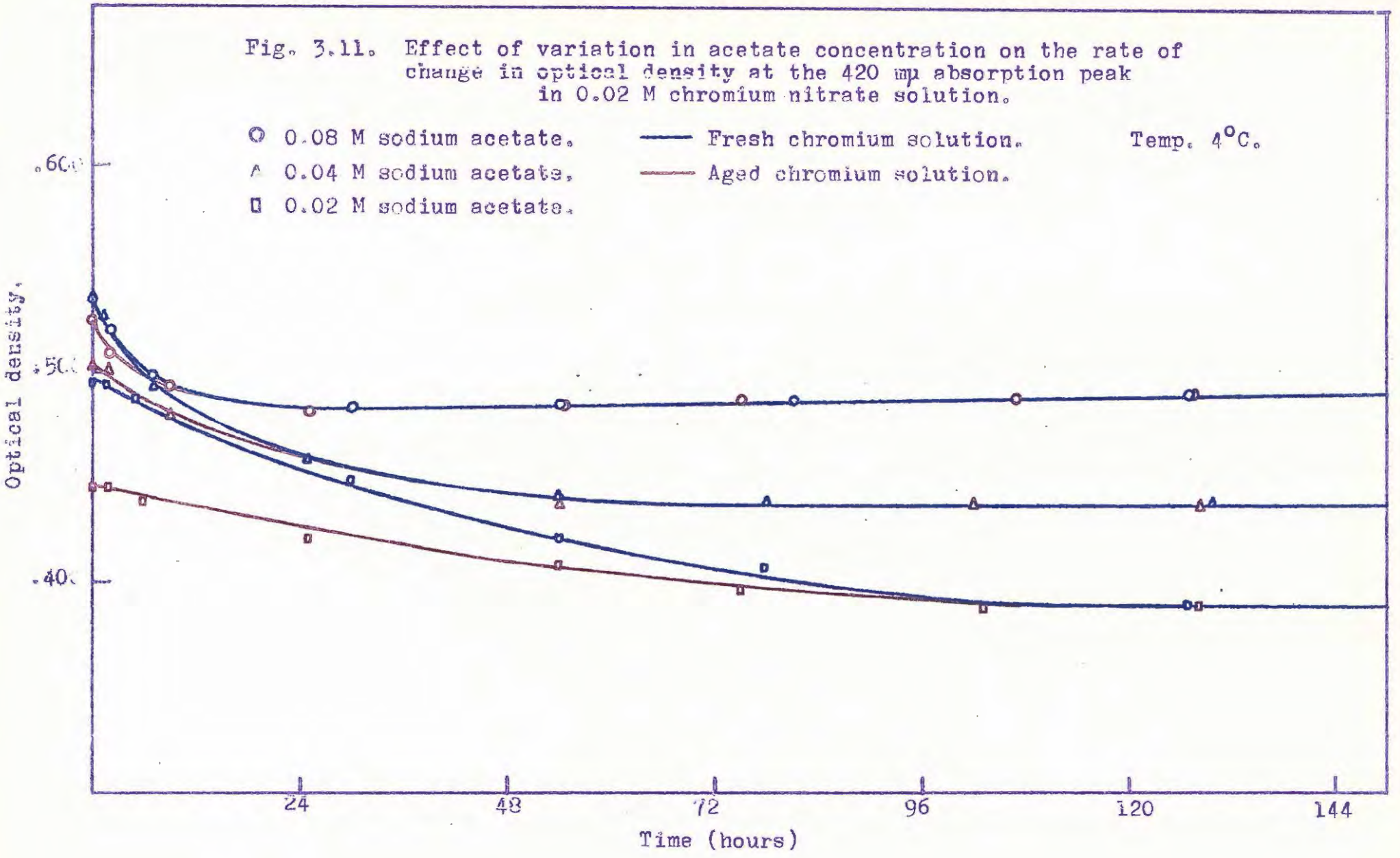


Fig. 3.12. Effect of variation in chromium concentration on the rate of change in optical density at the 420 mμ absorption peak in 0.08 M sodium acetate solution.

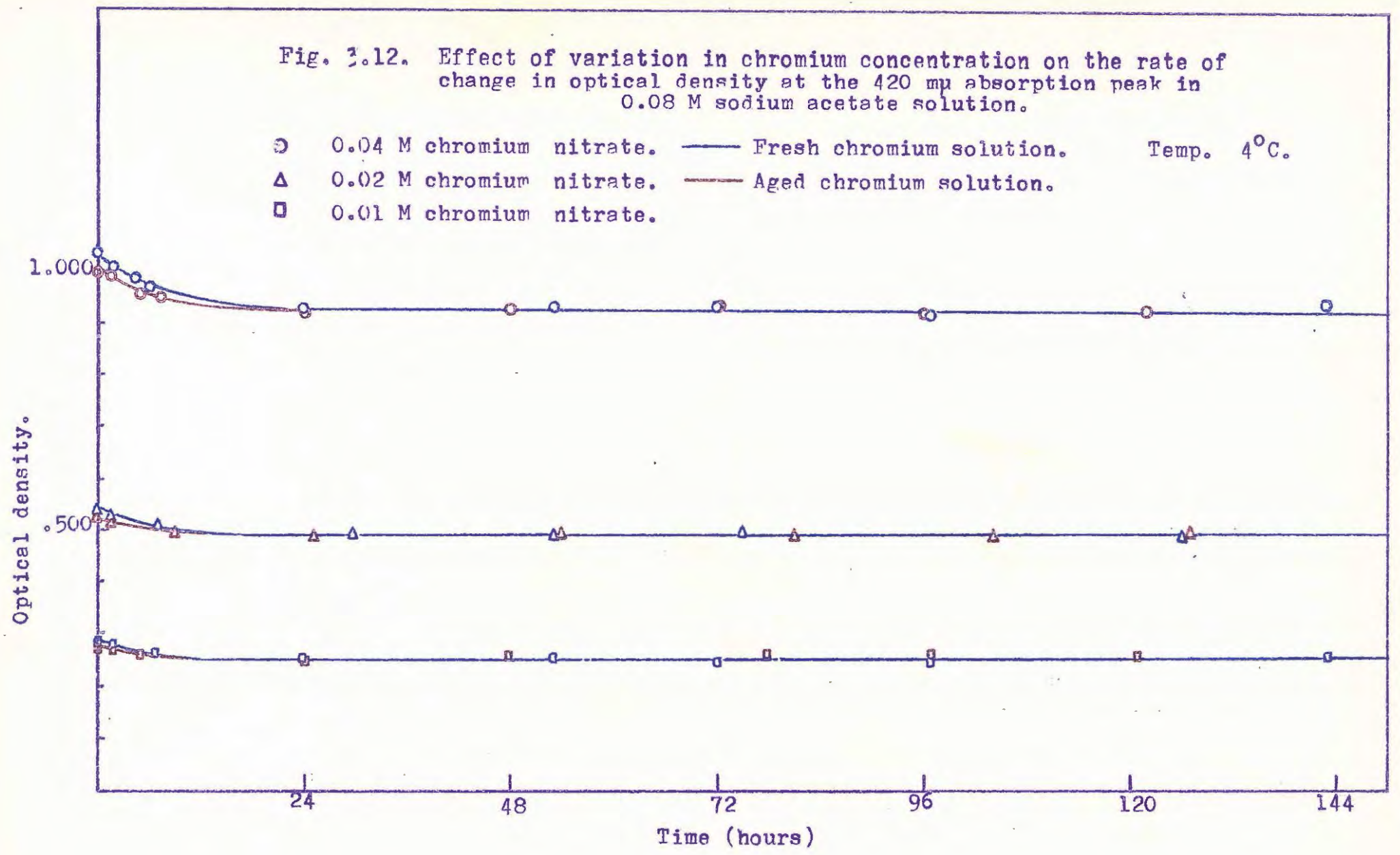
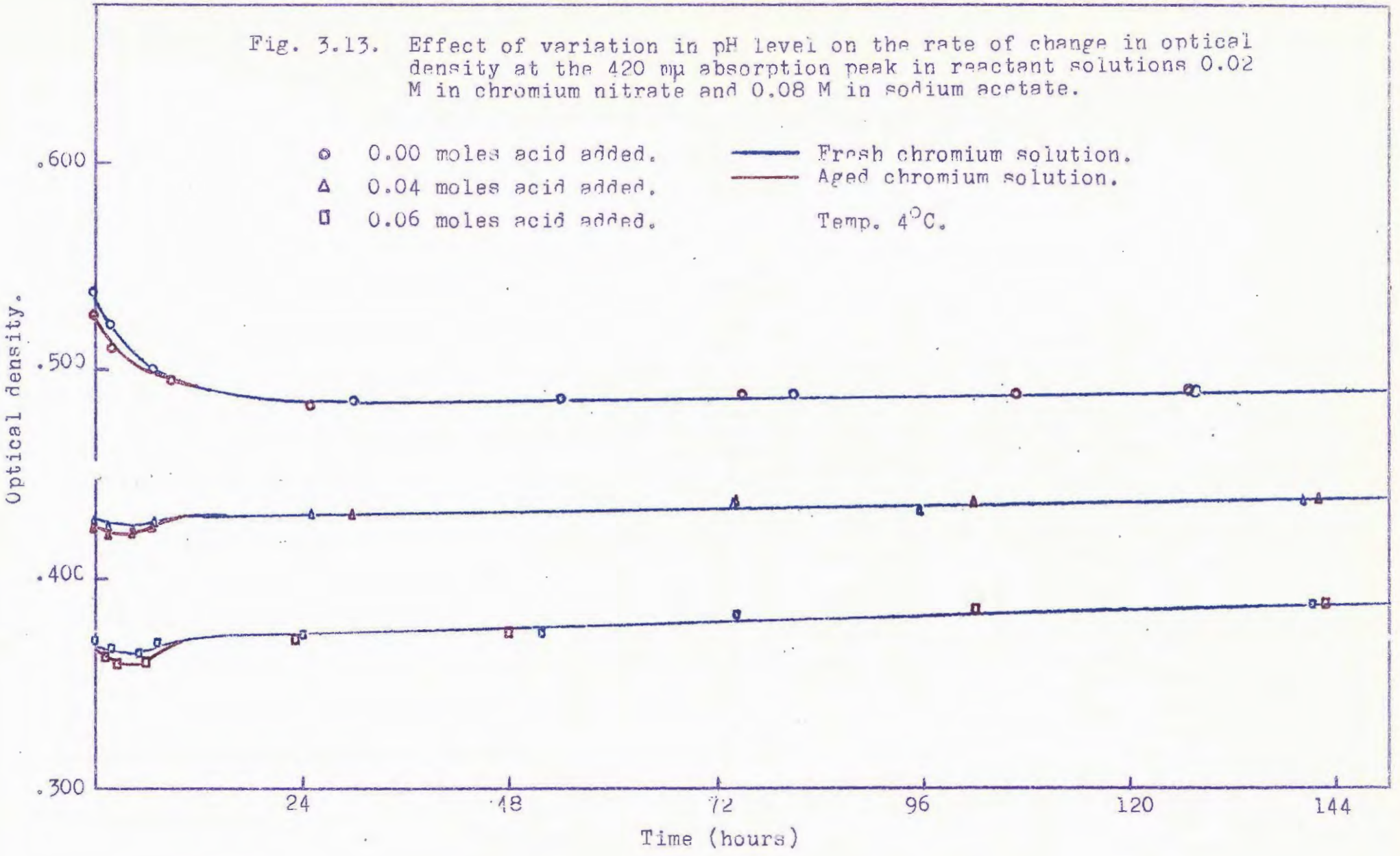


Fig. 3.13. Effect of variation in pH level on the rate of change in optical density at the 420 mμ absorption peak in reactant solutions 0.02 M in chromium nitrate and 0.08 M in sodium acetate.



prior to taking spectrophotometric readings; the values obtained were then doubled for purposes of plotting in Fig. 3.10.

Small vertical shifts in the relative positions of graphs 1, 2, 3, 6 and 7, all of which have the same initial chromium nitrate concentration (0.02M), may be attributed to the small effect of pH differences upon the height of the 570 mμ peak, the displacement of the graphs above the horizontal axis being greatest at the higher pH values.

The extinction coefficient of boiled and aged chromium nitrate solution at the 570 mμ peak, calculated from the absorption spectra of the pure solutions (cf. Appendix, Figs. A.1. to A.14.), is of the order 14.5 litre mole^{-1}. Intercepts on the vertical axis of Fig. 3.10. indicate that the initial chromium reactant species formed as a result of pH elevation due to ligand addition, has an extinction coefficient of approximately 17 litre mole^{-1}; however, this is not a true constant being partially susceptible to pH change. All the graphs have a common gradient of 16 litre mole^{-1}. This appears to indicate that during the course of reaction, structural change due to coordination of ligands, results in the replacement of the chromium complex ion responsible for the initial absorption, by a species having 100% greater absorption.

The implications of these results are discussed in Chapter VI.

(iii) Quantitative changes at the 420 mμ Absorption Peak.

Figs. 3.11., 3.12. and 3.13 reflect the variation in optical density at the 420 mμ peak plotted as a function of time over a reaction period of 144 hours. The effects of variation in reactant proportions are shown in Figs. 3.11. and 3.12. while the effect of pH variation is shown

in/.....

in Fig. 3.13. Reaction curves obtained with fresh chromium nitrate solutions are shown in blue, while those obtained in the case of boiled and aged solutions are shown in red.

In general, the absorption decreased to limiting values as the reaction proceeded, the time rate of the variation corresponding to that of the 570 mμ peak and hence to the coordination of acetate. In the case of the faster reactions (i.e. mole ratios of 8 : 1 and 8 : 2), there was a further tendency for the absorption to increase with time towards the end of the reaction period, and this trend was confirmed in the case of the faster reactions by comparing absorption values after "infinite" time. These observations are in accordance with previous studies on the coordination of sulphate radical to chromium nitrate[22], where initial decreases in absorption values at the 420 mμ peak were followed by increases in absorption accompanying further coordination.

In contrast to the observations made at the 570 mμ peak, the reactant solutions containing fresh chromium nitrate showed an initial absorption greater than that of the corresponding boiled and aged solutions, the absorption differences being more pronounced at the lower pH levels. The corresponding curves tended to merge, however, as the reaction proceeded so that the ultimate values were the same.

The implications of the above absorption changes at the 420 mμ peak are discussed in Chapter VI.

(d) Electrophoretic Studies.

The results of paper electrophoretic studies carried out as described in Chapter II, page 25, are shown in Table 3.1., in which the

band/.....

band velocities are expressed in cm./sec./ unit voltage gradient.

Detailed quantitative interpretation of electrophoretic data is difficult owing to the experimental limitations of the method. Evaporation of solvent due to electrical heating effects in the strips results in concentration changes which in turn may lead to structural changes in the complexes under study. Resulting changes in electrical resistance across the strips also leads to fluctuation in voltage gradient, while temperative changes also have a direct effect on mobilities. These considerations limit direct comparison between successive runs of the same duration; useful information can be obtained however, by running control strips.

Qualitatively, migration in all cases was in the direction of the cathode indicating the presence in solution of positively charged chromium ions only. Maxima of two to three bands were visible at intermediate mole ratios and low pH levels, while at the highest (1 and 2) and lowest (7) mole ratios single bands only were detected. The more rapidly migrating bands had mobilities comparable to those of the chromium bands in the control strips without added ligand.

Generally, no significant differences were detected in the mobilities of the various bands obtained from the fresh and aged series.

The implications of these results are discussed in Chapter VI.

CHAPTER IV

MINIATURE TANNING EXPERIMENTS. THE COORDINATION OF CARBOXYL GROUPS OF HIDE COLLAGEN TO CHROMIUM NITRATE UNDER AQUEOUS ACID CONDITIONS.

Hide collagen is considered[64] to contain a number of different types of side chain carboxyl groups varying in acid strength, but all capable of coordination to chromium under conditions similar to those of normal chrome tannage. Reference has already been made to the importance of the dissociation constant of the participating acid in determining complex stability in the case of the non-ring forming acids (cf. chapter 1) and in addition the dissociation constant, by controlling the extent of acid ionisation at various pH levels, is an important factor in determining the rate and extent of coordination.

The average pK value of the side-chain carboxyl groups of wool has been shown to be of the order 4.3[65] and the value for collagen having a slightly higher proportion of strong acid residues (aspartic and glutamic), should be somewhat lower[66]. The actual value is presumed to be of an order intermediate between those of formic and acetic acids and in fact, lying closer to that of acetic acid. The validity of this assumption has been demonstrated in tanning experiments with formate and acetate complexes, the former giving good fixation while the latter show poor tanning properties owing to unfavourable competition from the acetate ion with its higher acid dissociation constant.[67]

If carboxyl group coordination is one of the main mechanisms underlying the tanning process, the above considerations make it reasonable to expect similarities in reaction course when the fixation of chromium by hide substance, is compared with the coordination of carboxy acid anions

of/.....

of similar acid strength under equivalent conditions. Minor differences between the two processes might then be attributed to penetration effects. The results of such miniative tanning studies are shown in the following sections in which tannages were carried out on hide substance provided in the form of (a) standard hide powder, and (b) prepared pelt pieces, under reaction conditions approximating closely to those obtaining in the acetate ion coordination studies. Experimental details of the procedures used are as described in Chapter II, section 7.

RESULTS.

(a) Hide Powder Studies.

Figs. 4.1., 4.2. and 4.3. reflect the extent of chromium "fixation", as determined directly by "wet oxidation" and volumetric procedures, after various time intervals during a reaction period of 144 hours. Reaction curves obtained with fresh chromium nitrate solutions are shown in blue, while those obtained with boiled and aged chromium nitrate solutions are coloured red.

Figs. 4.1. and 4.2. show the effect of varying the quantities of the two reactants, the amount of hide powder and concentration of the chromium nitrate solution being varied separately according to the scheme indicated in the acetate coordination studies (Table 2.1.). The equivalent weight of collagen was taken as 900 for this purpose[68, 69]. Adjustment of pH to the same initial level as in the case of the corresponding fresh chromium nitrate-sodium acetate reactant solutions, was effected by dropwise addition of concentrated alkali to the chrome tanning solution. The

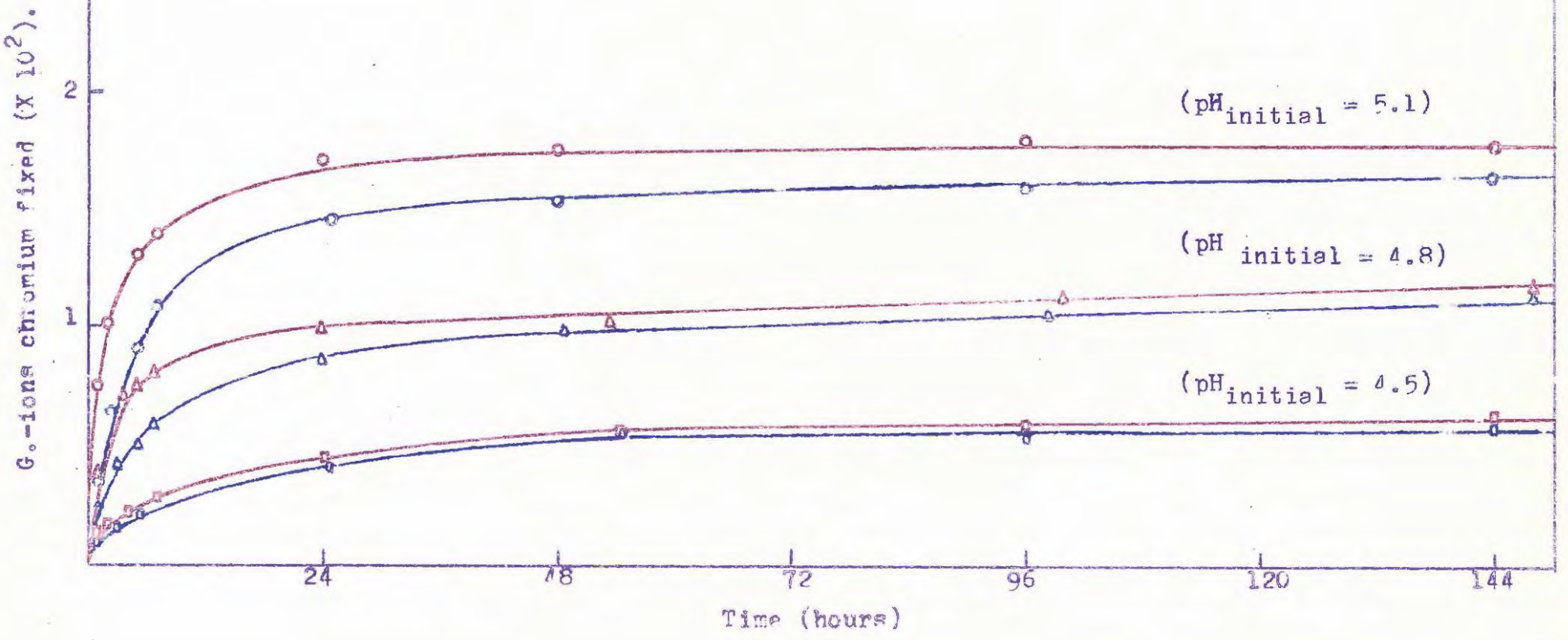
initial/.....

Fig. 4.1. Rate of chromium fixation by various amounts of hide powder in 0.02 M chromium nitrate solution.

○ 0.08 "equivalents" hide powder. —— Fresh chromium solution. Temp. 4°C.

△ 0.04 "equivalents" hide powder. —— Aged chromium solution.

□ 0.02 "equivalents" hide powder.



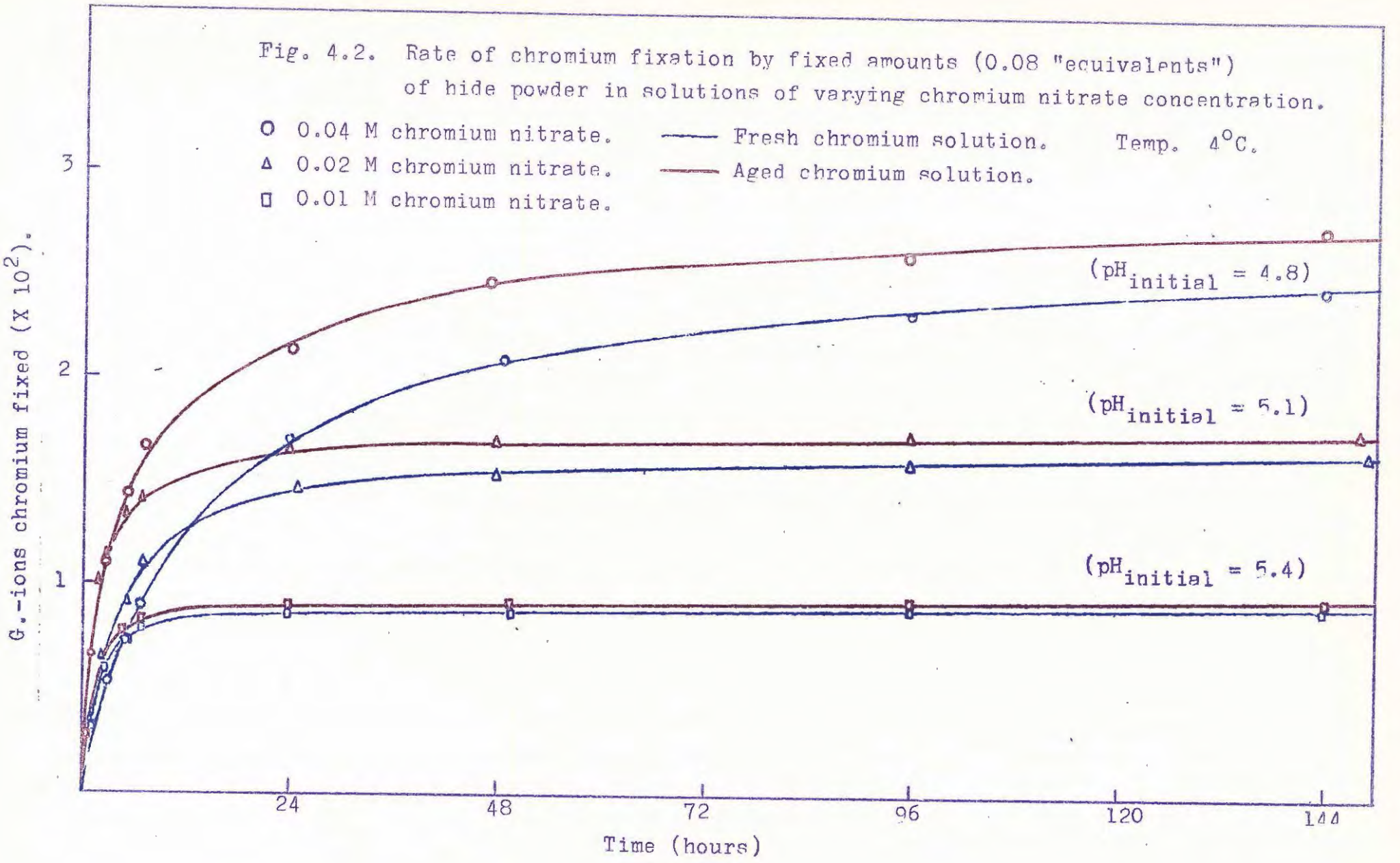
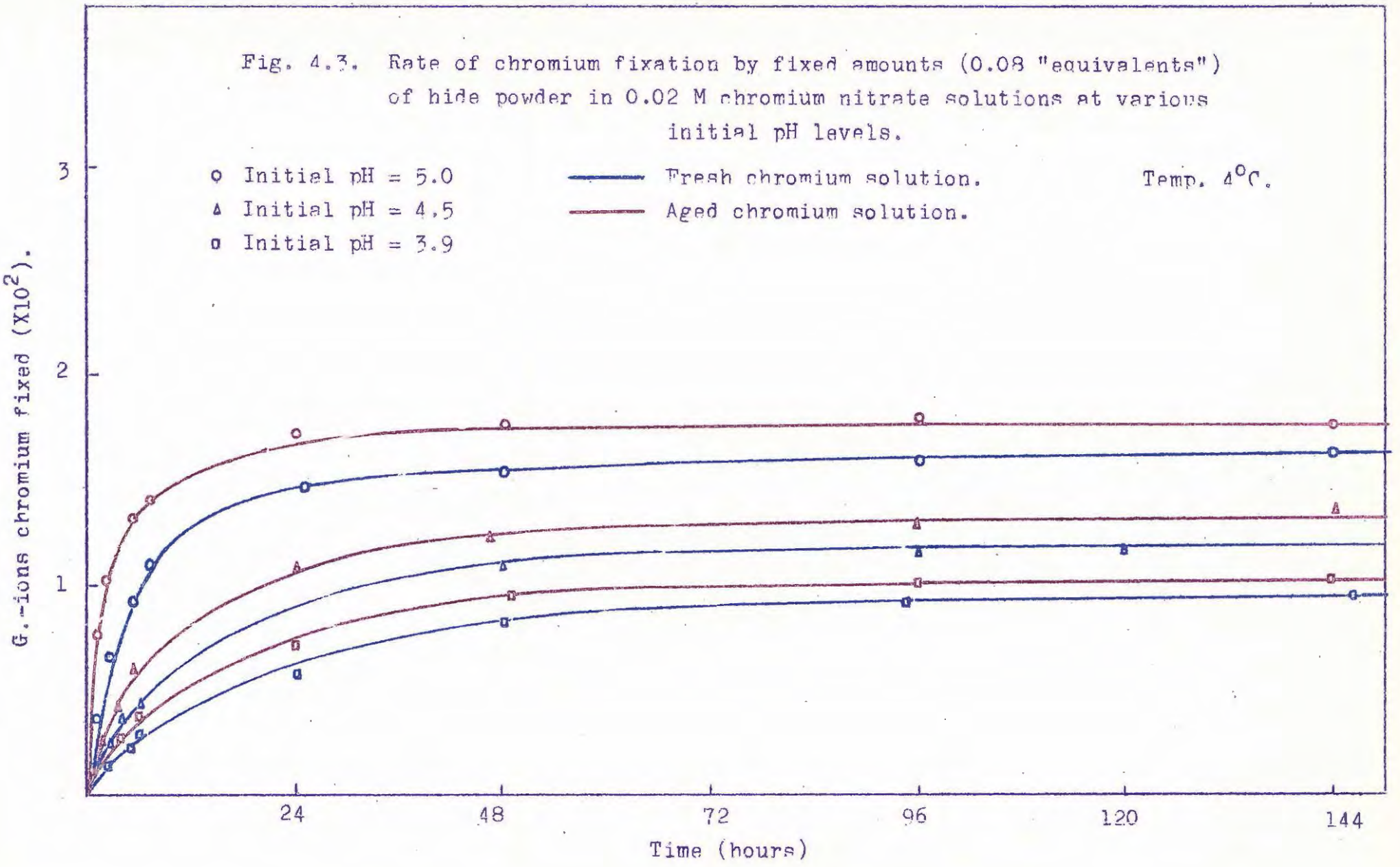


Fig. 4.2. Rate of chromium fixation by fixed amounts (0.08 "equivalents") of hide powder in solutions of varying chromium nitrate concentration.
O 0.04 M chromium nitrate.
Δ 0.02 M chromium nitrate.
□ 0.01 M chromium nitrate.
—— Fresh chromium solution.
—— Aged chromium solution.
Temp. 4°C.
(pH initial = 4.8)
(pH initial = 5.1)
(pH initial = 5.4)
G.-ions chromium fixed (X 10²).
3
2
1
24
48
72
96
120
144
Time (hours)

Fig. 4.3. Rate of chromium fixation by fixed amounts (0.08 "equivalents") of hide powder in 0.02 M chromium nitrate solutions at various initial pH levels.



initial pH level in the case of the boiled chromium nitrate solutions was adjusted to the same level as that of the fresh solutions.

Fig. 4.3. shows the effect of varying the initial reaction pH level while keeping the reactant ratio constant. Adjustment was carried out to the same initial value obtaining in the case of the pH adjusted, acetate coordination studies.

In general, the curves obtained in the case of the fresh chromium nitrate solutions show remarkable resemblance to the curves obtained in the acetate coordination studies (Figs. 3.1., 3.2 and 3.3). In the case of the boiled and aged chromium nitrate solutions, however, the initial reaction rate is greater than that of the corresponding fresh reactant solution although the two curves later tend to merge so that the ultimate result is the same.

Changes in reactant proportions (Figs. 4.1. and 4.2.) and reaction pH (Fig. 4.3.) are seen to have the same effect on the rate and extent of coordination as noted in the acetate coordination studies, chrome fixation increasing with concentration and pH level.

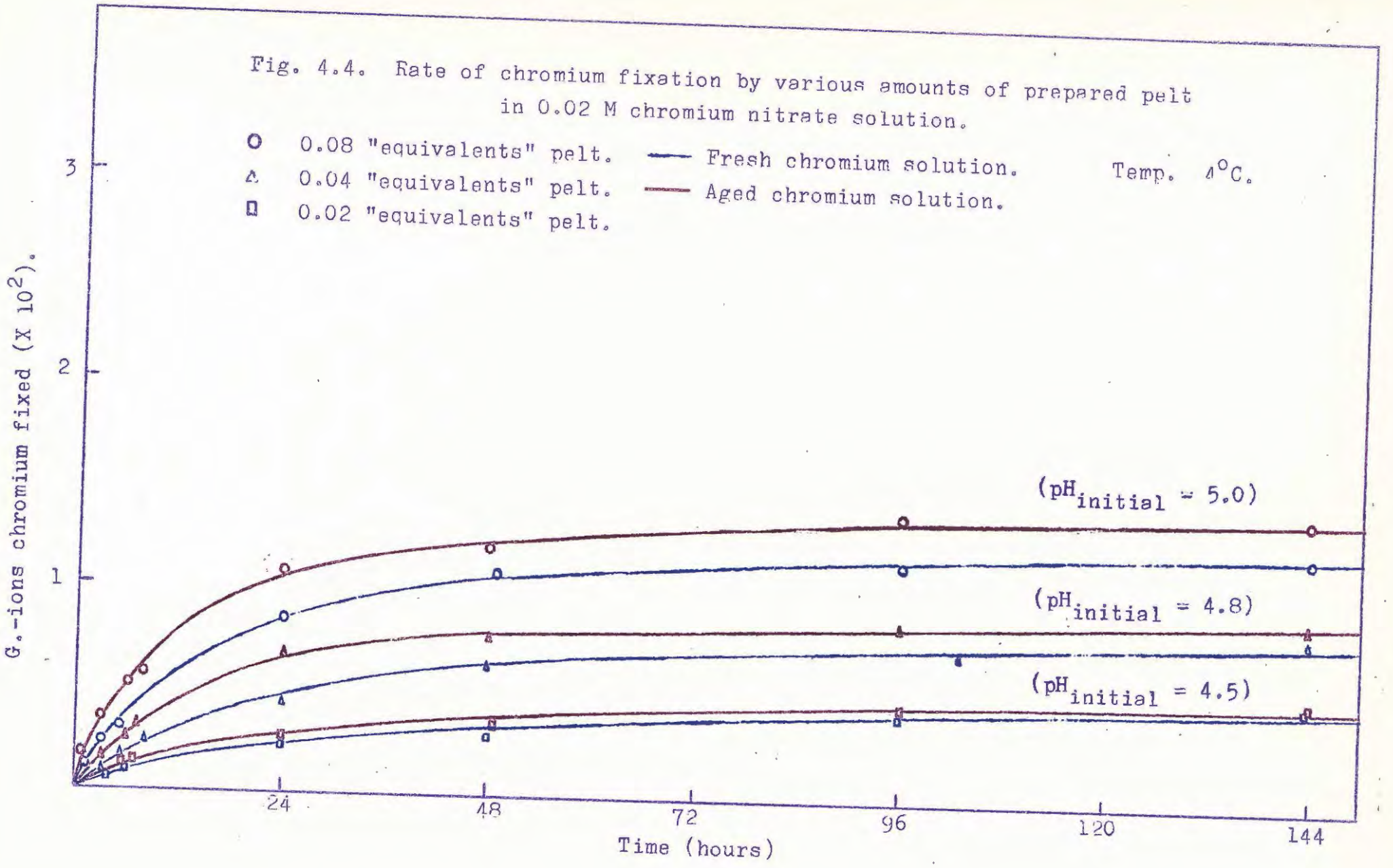
The above similarities serve to demonstrate the close analogy between the two reaction systems studied and indicate that under the experimental conditions the tannage mechanism is essentially the same as that operating in the case of coordination of acetate ions to chromium, involving the attachment to the chromium of acid residues whose acid strenths approximate closely to that of acetic acid.

Minor differences in the curves are shown in the tendency towards slightly less overall chrome fixation at the end of the reaction period

particularly/.....

Fig. 4.4. Rate of chromium fixation by various amounts of prepared pelt in 0.02 M chromium nitrate solution.

○ 0.08 "equivalents" pelt. —— Fresh chromium solution. Temp. 4°C.
△ 0.04 "equivalents" pelt. —— Aged chromium solution.
□ 0.02 "equivalents" pelt.



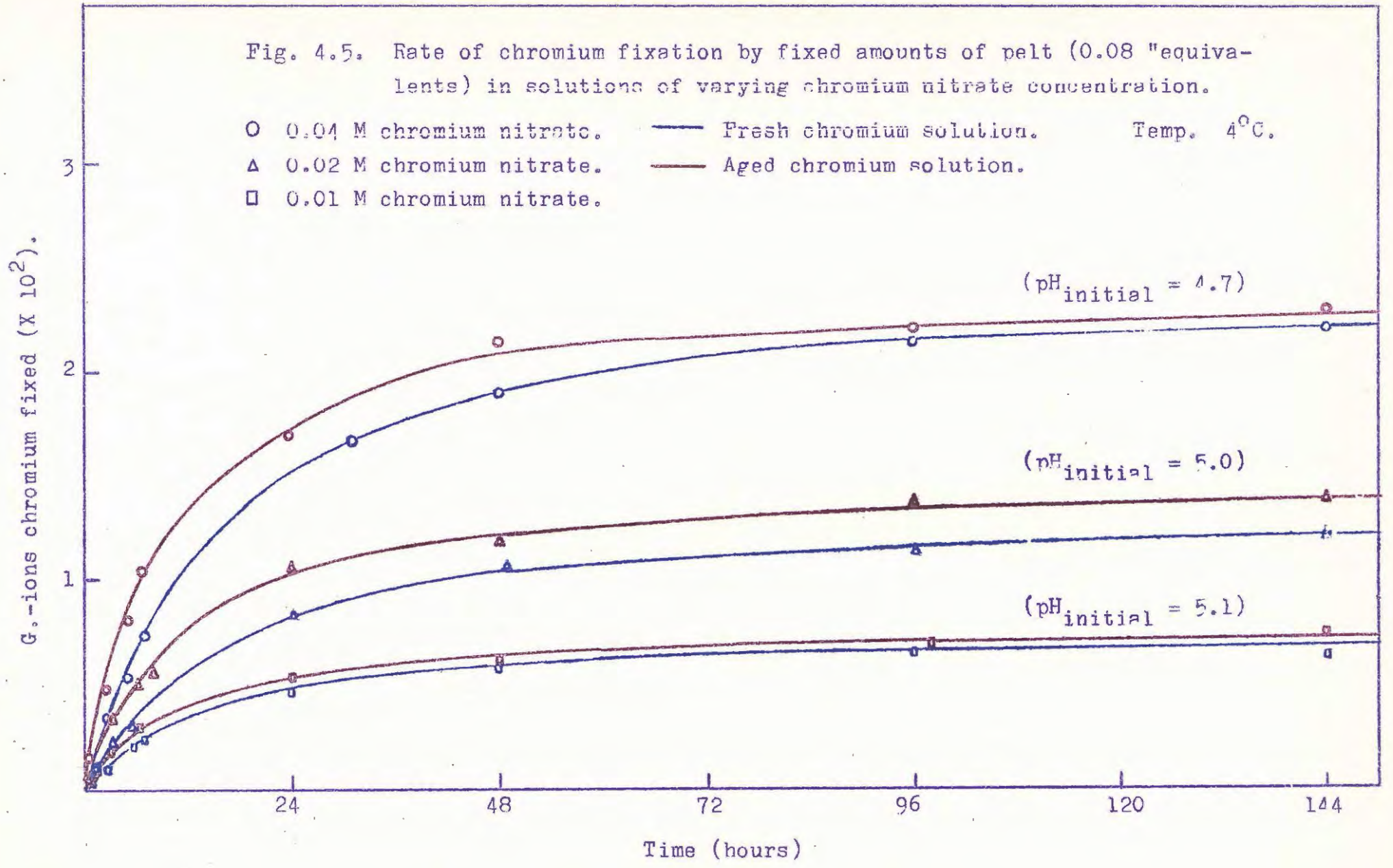
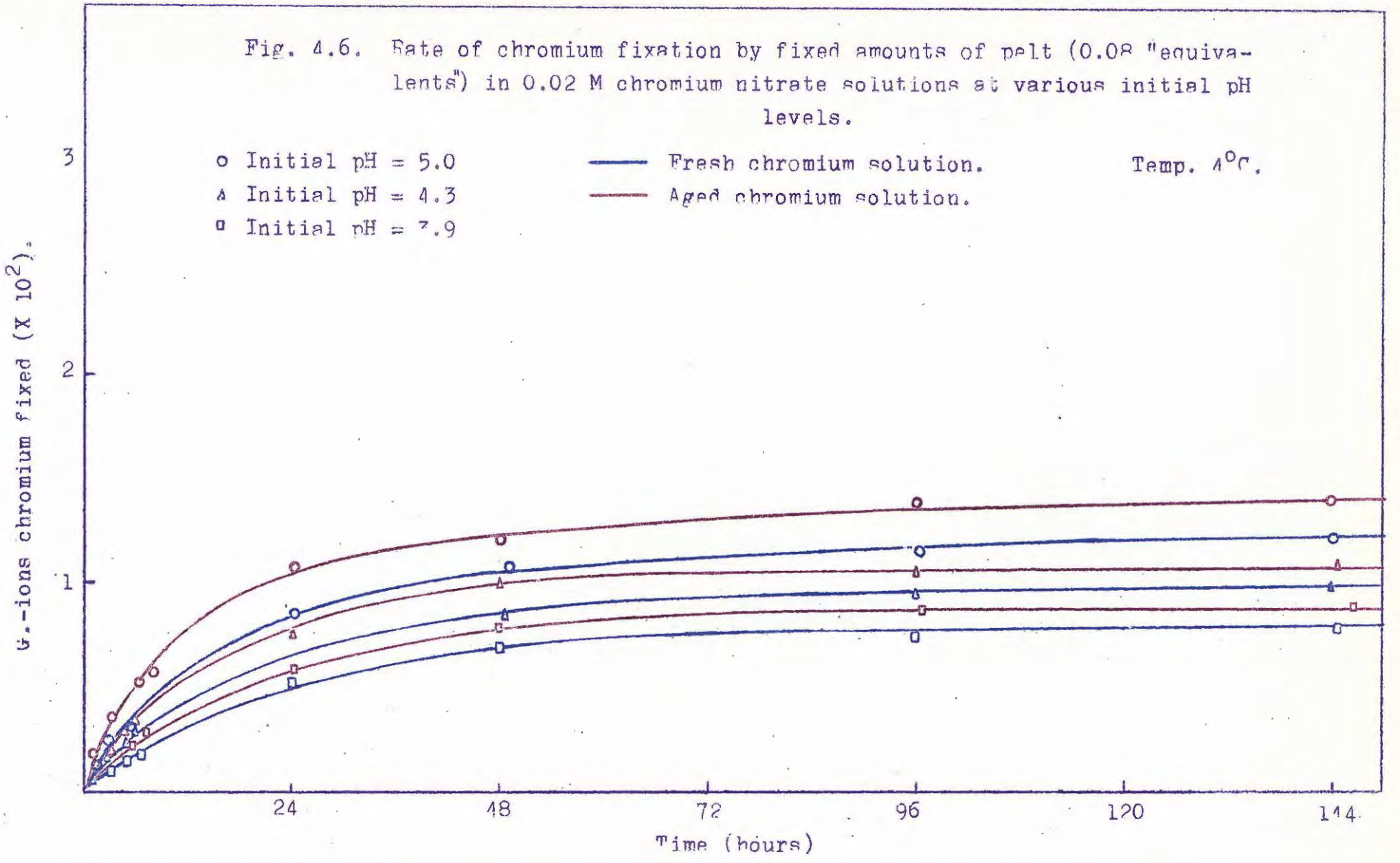


Fig. 4.5. Rate of chromium fixation by fixed amounts of pelt (0.08 "equivalents) in solutions of varying chromium nitrate concentration.
O 0.04 M chromium nitrate.
Δ 0.02 M chromium nitrate.
□ 0.01 M chromium nitrate.
Fresh chromium solution.
Aged chromium solution.
Temp. 4°C.
(pH initial = 4.7)
(pH initial = 5.0)
(pH initial = 5.1)
G.-ions chromium fixed (X 10²).
1
2
3
24
48
72
96
120
144
Time (hours)

Fig. 4.6. Rate of chromium fixation by fixed amounts of pelt (0.08 "equivalents") in 0.02 M chromium nitrate solutions at various initial pH levels.



particularly in the case of the faster reactions; however, in view of the differences in carboxyl group accessibility which must exist between soluble sodium acetate and the insoluble hide substance as well as the heterogeneity of acid residues present in collagen, the actual differences are surprisingly small. An unusual tendency is shown in that the initial reaction rates in the case of the hide powder studies are greater than those of the corresponding acetate studies, particularly in the case of the faster reactions. This difference is discussed in greater detail in Chapter VI.

(b) Pelt tannage studies.

The material in the form of rectangular pelt pieces split from the grain layer of medium hide, was prepared as described in Chapter II, in order to produce a tannage substrate with properties comparable to those of hide powder, particularly with regard to the iso-electric point of the material. The resultant substrate was subjected to stationary tannage under reaction conditions similar to those of the previous studies with a view to comparing results, particularly with regard to the effect which occlusion of carboxyl reactive centres within the weave pattern of the pelt, might have upon the kinetics of the reaction. Experimental details are as described in Chapter II.

Figs. 4.4, 4.5 and 4.6 reflect the extent of chrome fixation by raw pelt under varying reaction conditions over an initial period of 144 hours. Curves obtained using fresh chromium nitrate solutions are shown in blue while those obtained with boiled and aged chromium nitrate are shown in red.

The /...

The effect of variation in reactant proportions (Fig. 4.4 and 4.5) and reaction pH (Fig. 4.6.) is seen to be the same as in the previous studies. As in the case of the hide powder studies, the reaction rate is greater initially in the case of the boiled and aged chromium nitrate solutions. General similarity between the various curves obtained in the present study and those obtained in the hide powder study, is evident in spite of pronounced differences due to diffusion and penetration effects. These effects bring about (a) reduction in the initial rate of reaction and (b) reduction in the overall chrome fixation at the end of the 144 hour reaction period, both these effects being more pronounced in the case of the more rapid reactions. The correlation between these curves and those of the preceeding study is discussed later (Chapters V and VI).

CHAPTER V

REACTION KINETICS

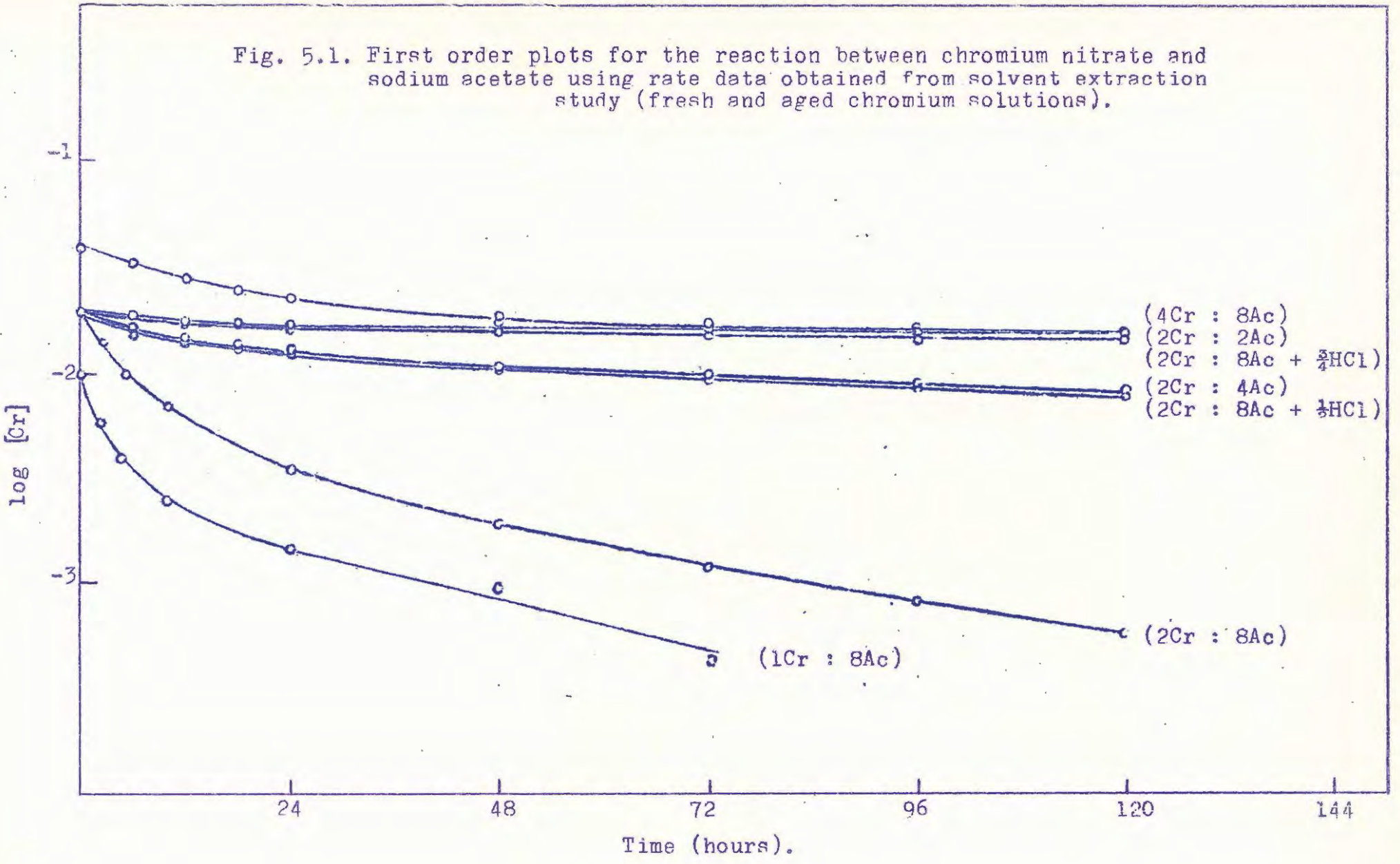
The province of chemical kinetics is concerned with the measurement of the reaction rates of processes proceeding at measurable velocities at laboratory temperatures. These reactions comprise a relatively small group of processes intermediate between the large group comprised of those reactions whose velocities are too great to be measured and those whose velocities are too low to be detected. Amongst the measurable minority are included the reactions of the trivalent chromium ion involving the coordination of a range of neutral molecules and the anions of both organic and mineral acids.

Chemical kinetics classifies reactions according to molecularity which is defined as"the number of species participating in each act leading to reaction", and by the order of reaction, defined by"the number of species whose concentrations determine the reaction rate." In practice, the assignment of a general rate to a reaction is difficult since the absolute rate varies continuously during the course of reaction. However, mathematical treatment of the experimentally determined rate data permits the calculation of a proportionality constant, referred to as the rate constant for the reaction. The derivation of the various mathematical expressions used in calculating the rate constant is outlined in the Appendix C.

The result of substitution of the rate data obtained by solvent extraction study on the reaction between trivalent chromium and acetate ions, into the various expressions is presented in the following sections.

THE / ...

Fig. 5.1. First order plots for the reaction between chromium nitrate and sodium acetate using rate data obtained from solvent extraction study (fresh and aged chromium solutions).



THE ORDER OF REACTION

(a) FIRST ORDER PLOTS

Fig. 5.1. reflects the result of plots of $\log_{10}$ of the unreacted chromium ion concentration as a function of time in accordance with the classical first order equation (cf. Appendix C, page (i)):-

$$t = \frac{2.303}{k} \log \frac{a}{a-x} \qquad (1)$$

where t = time

k = first order rate constant

a = initial concentration of reactant

x = moles reactant coordinated

The applicability of the classical expression was tested on the rate data obtained from the solvent extraction study (Figs. 3.1., 3.2. and 3.3.) and reflects the application of the equation to both the fresh and aged reactant solutions since no significant differences were detected in the rate data obtained from corresponding curves. The plots reveal no simple linear relationship between reaction time and Log_{10} chromium ion concentration as suggested by the expression I, and are thus at variance with the findings of Hamm et al who assign a first order mechanism to the reaction. (cf. Chapter I) page 2.

Non-applicability of a first order reaction mechanism is to be expected since:-

(a) the reaction is bimolecular, and

(b) previous indications are that the concentration of each reactant species is an operative factor in determining the reaction rate (Figs. 3.1. and 3.2.)

contrary to/.....

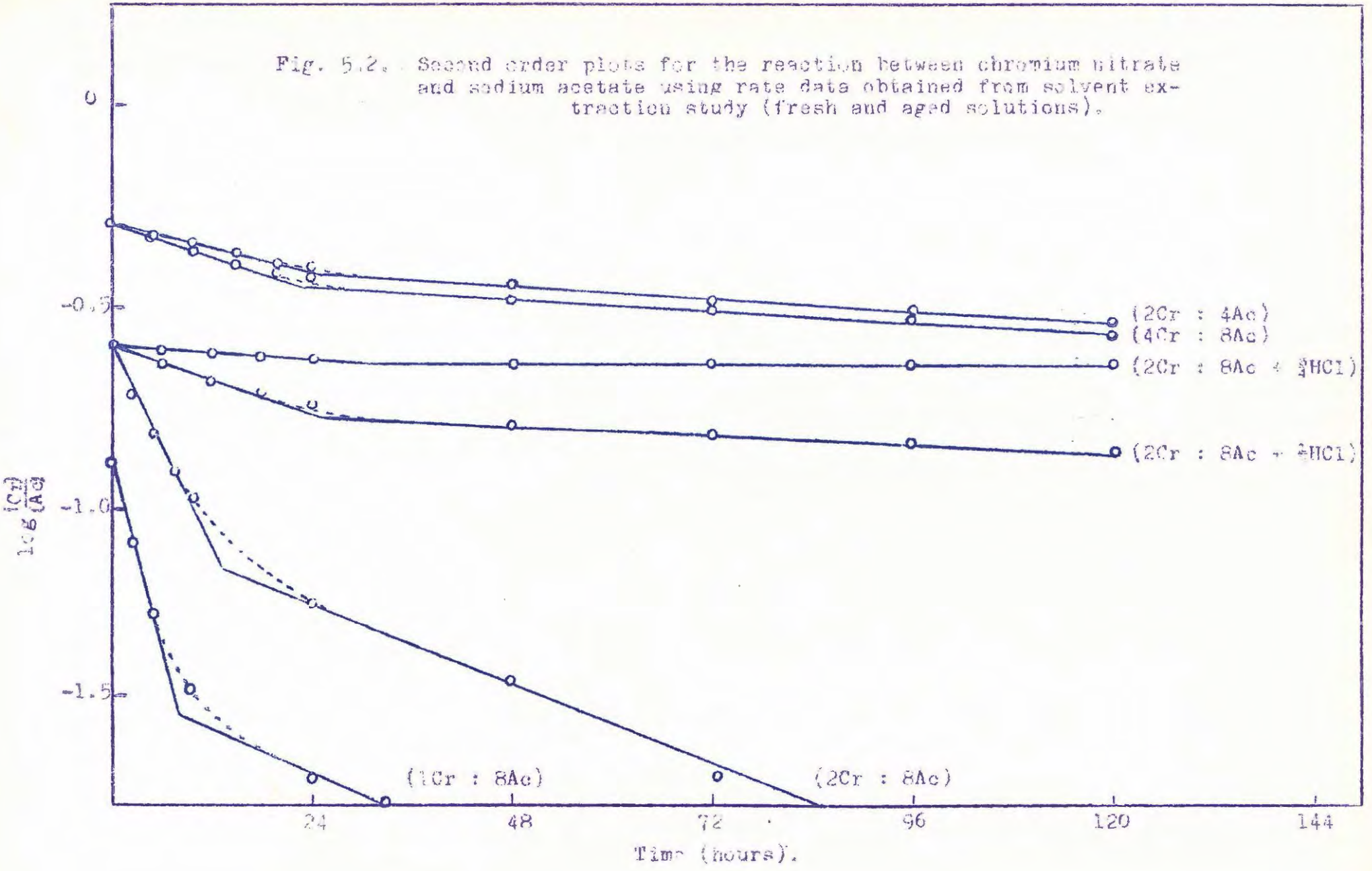


Fig. 5.2. Second order plots for the reaction between chromium nitrate and sodium acetate using rate data obtained from solvent extraction study (fresh and aged solutions).

to the findings of Hamm et al who regard chromium ion concentration as the only operative concentration factor.

A tentative explanation for the findings of Hamm et al has been suggested to ~~be~~ lie in the choice of reactant ratio which was of the order of 50 moles of acetate per mole of chromium. Under these conditions a bimolecular reaction assumes pseudo-unimolecularity (page 4). In the present study lower mole ratios were chosen, the highest ratio being of the order, 8 : 1. Under these conditions the reacting systems might be expected to exhibit true reaction order.

(b) Second Order Plots.

Fig. 5.2. shows the result of plots of $\log_{10}$ of the ratio of unreacted species as a function of time in accordance with the classical expression governing second order reactions. (cf. Appendix C, page iii):-

$$t = \frac{2.303}{k\,(a-b)} \log \frac{b}{a} + \frac{2.303}{k\,(a-b)} \log \frac{(a-x)}{(b-x)} \qquad \text{(II) a}$$

where t = time

k = second order rate constant

a = initial concentration of reactant A.

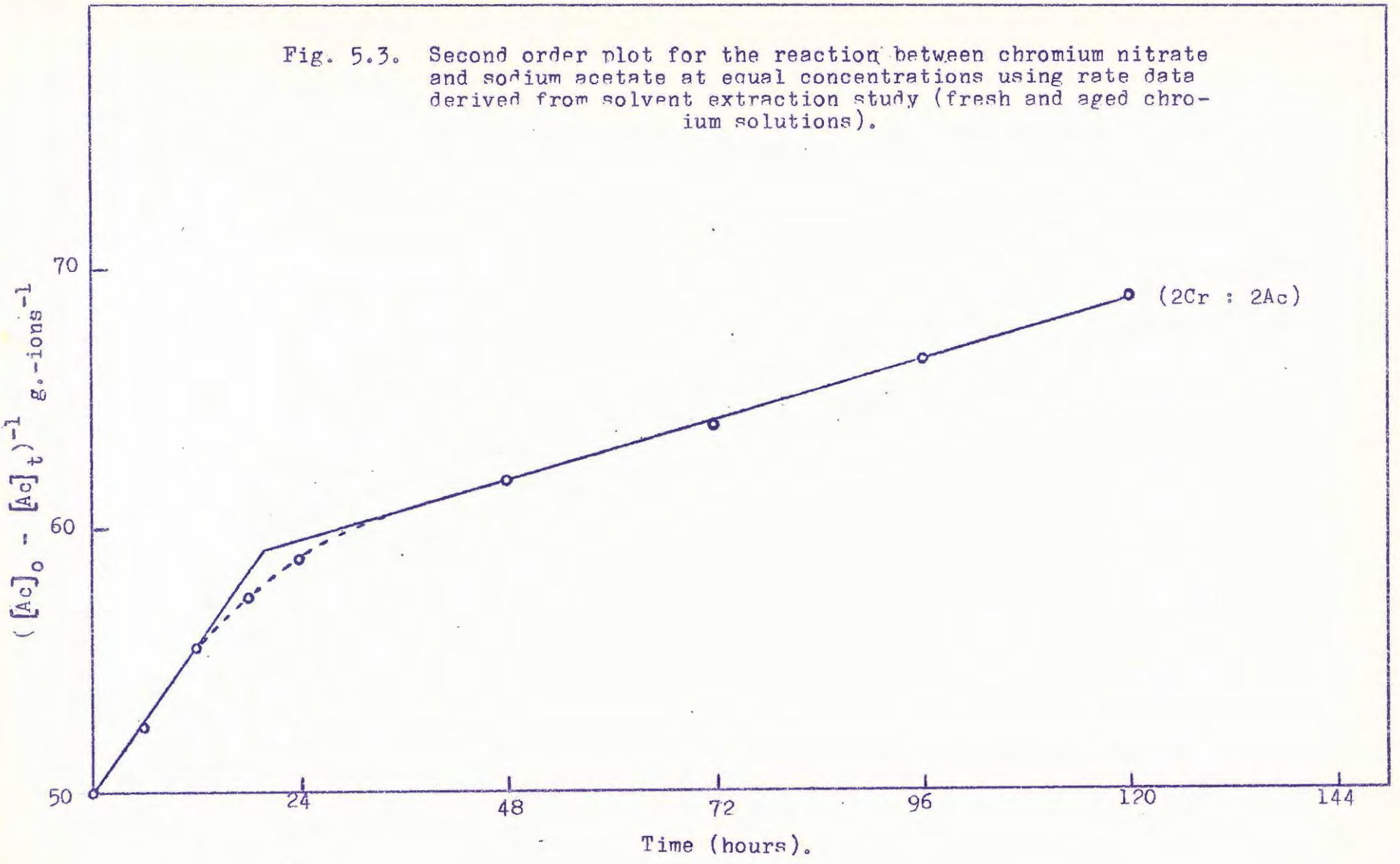
b = initial concentration of reactant B.

x = moles A or B reacted.

By the above expression a linear relationship should exist between t and $\log_{10} \left(\frac{a-x}{b-x}\right)$ for a second order, bimolecular process.

Modification of expression (II) a is necessary in the case where two reactants are initially present at equivalent concentrations (i.e. $a = b$).

Fig. 5.3. Second order plot for the reaction between chromium nitrate and sodium acetate at equal concentrations using rate data derived from solvent extraction study (fresh and aged chromium solutions).



a = b). Under these conditions, expression (II) b can be shown to reduce to (cf. Appendix C page (iii)):-

$$t = \frac{1}{k\,(a-x)} - \frac{1}{ka} \qquad \text{(II)b}$$

By the above expression a linear relationship should exist between t and the reciprocal of the unreacted chromium concentration. The result of such a plot is shown in Fig. 5.3.

Application of the appropriate expressions to the experimentally determined rata data obtained by solvent extraction study, are seen to yield plots which show two distinctly linear portions. The pattern was essentially similar for the series of reaction solutions investigated, indicating a similar mechanism over the range of concentration and pH conditions chosen.

The dual linearity of the plots is presumably indicative of successive second order reactions and is consistent with the view that a reaction mechanism essentially similar for both the fresh and aged series, is operative consisting of stepwise coordination of acetate ions to an olated species.

CALCULATION OF RATE CONSTANTS.

From equation (II)a, the gradient of a second order plot is given by:-

$$\text{Gradient} = \frac{2.303}{k(a - b)} \qquad \text{(a)}$$

Hence the second order rate constant, k, may be calculated.

For equation (II) b, applicable to systems containing equimolecular

quantities/.....

Fig. 5.4. Negative logarithm of first "apparent" rate constant for the reaction between chromium nitrate and sodium acetate plotted as a function of pH.

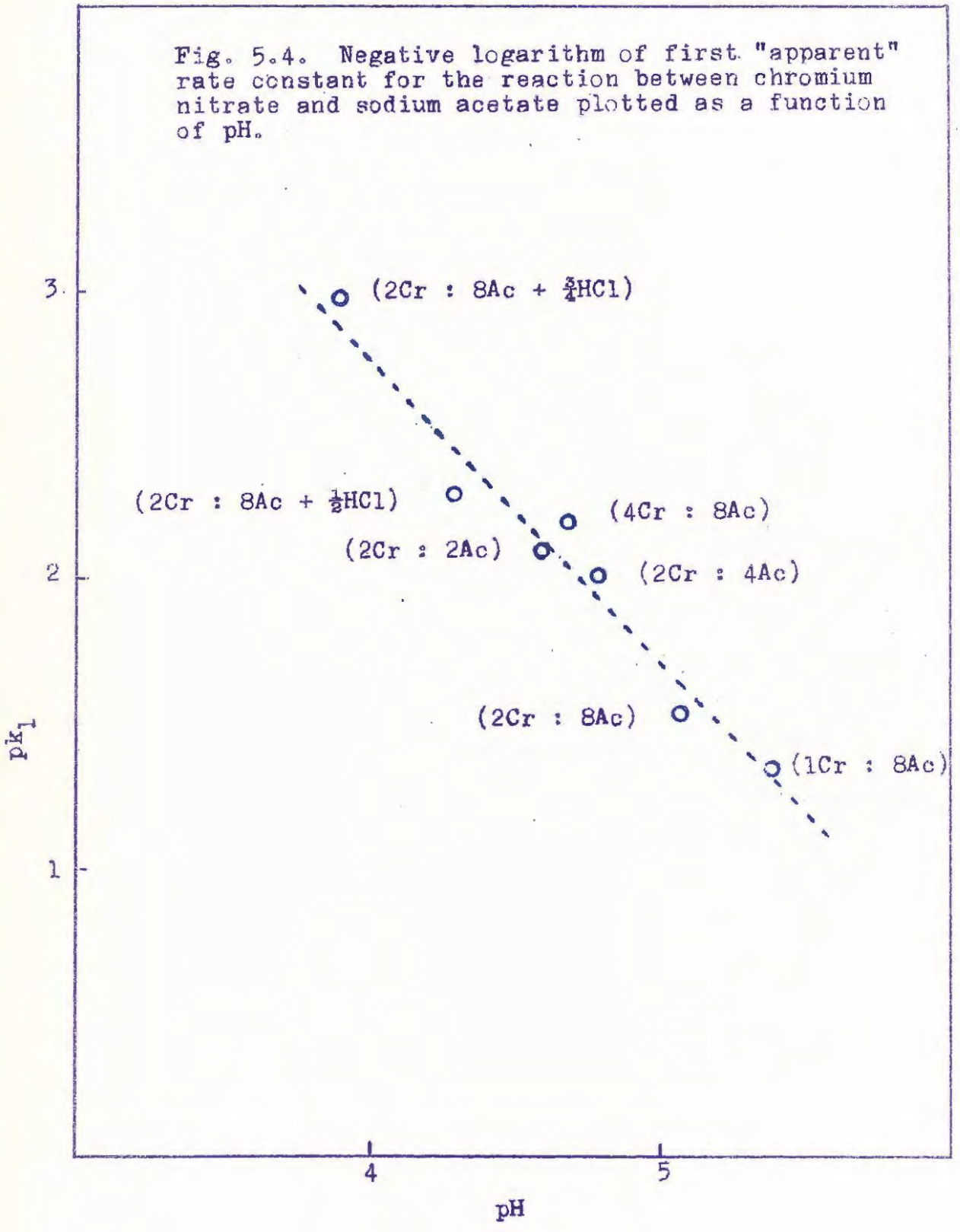
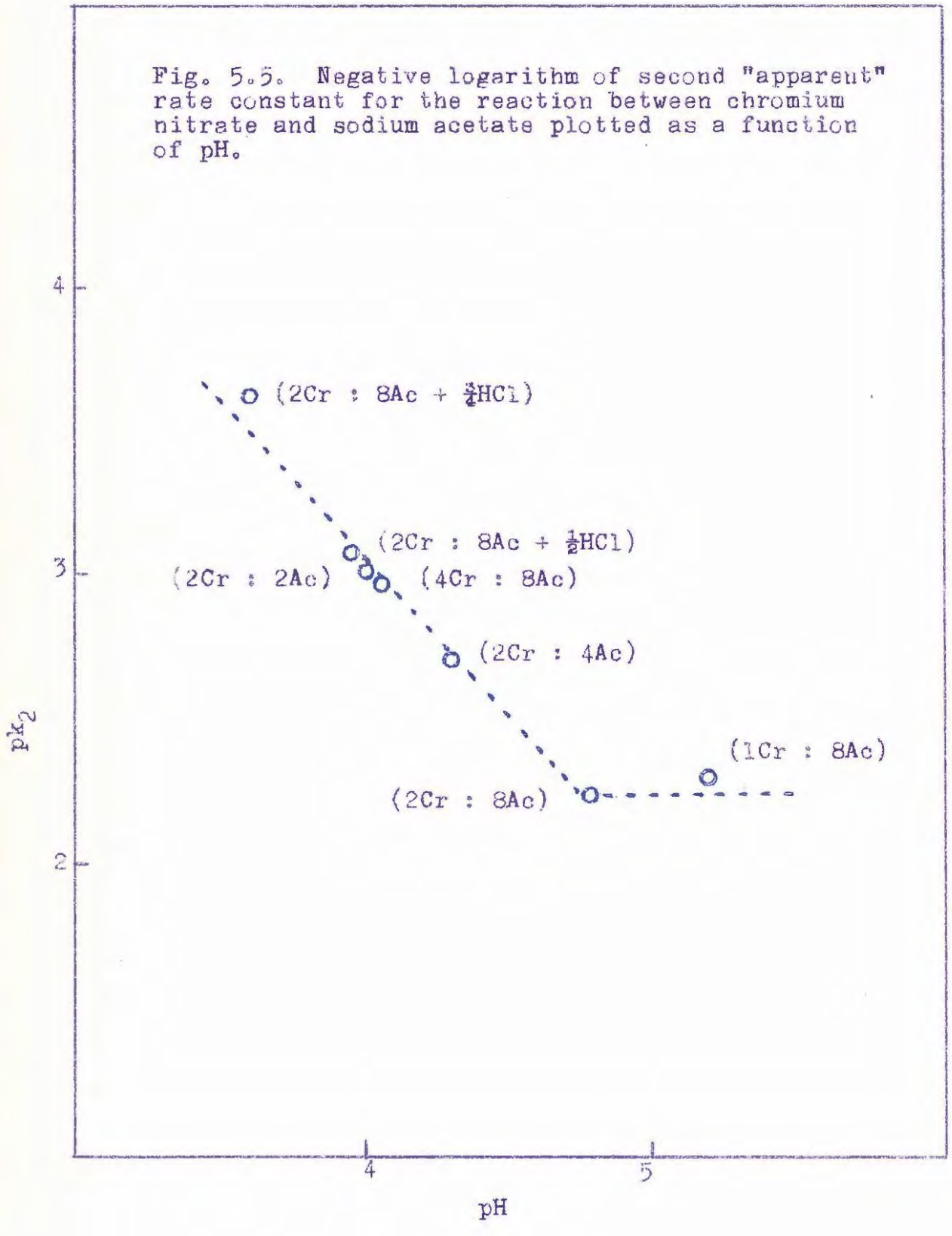


Fig. 5.5. Negative logarithm of second "apparent" rate constant for the reaction between chromium nitrate and sodium acetate plotted as a function of pH.



quantities of reactants, the rate constant may be calculated from the relationship:-

$$\text{Gradient} = \frac{1}{k} \qquad (b)$$

The appropriate expressions were applied to a determination of rate constants corresponding to the linear portions of the second order reaction plots; the constants obtained are shown tabulated in Table 5.1. with the associated pH values. The rate "constants" determined in this way, were not found to be true constants, but were pH dependant, the "constants" obtained from both linear portions of the plots, decreasing with pH. The "apparent rate constants" are shown arranged in descending order of pH in the tabulation.

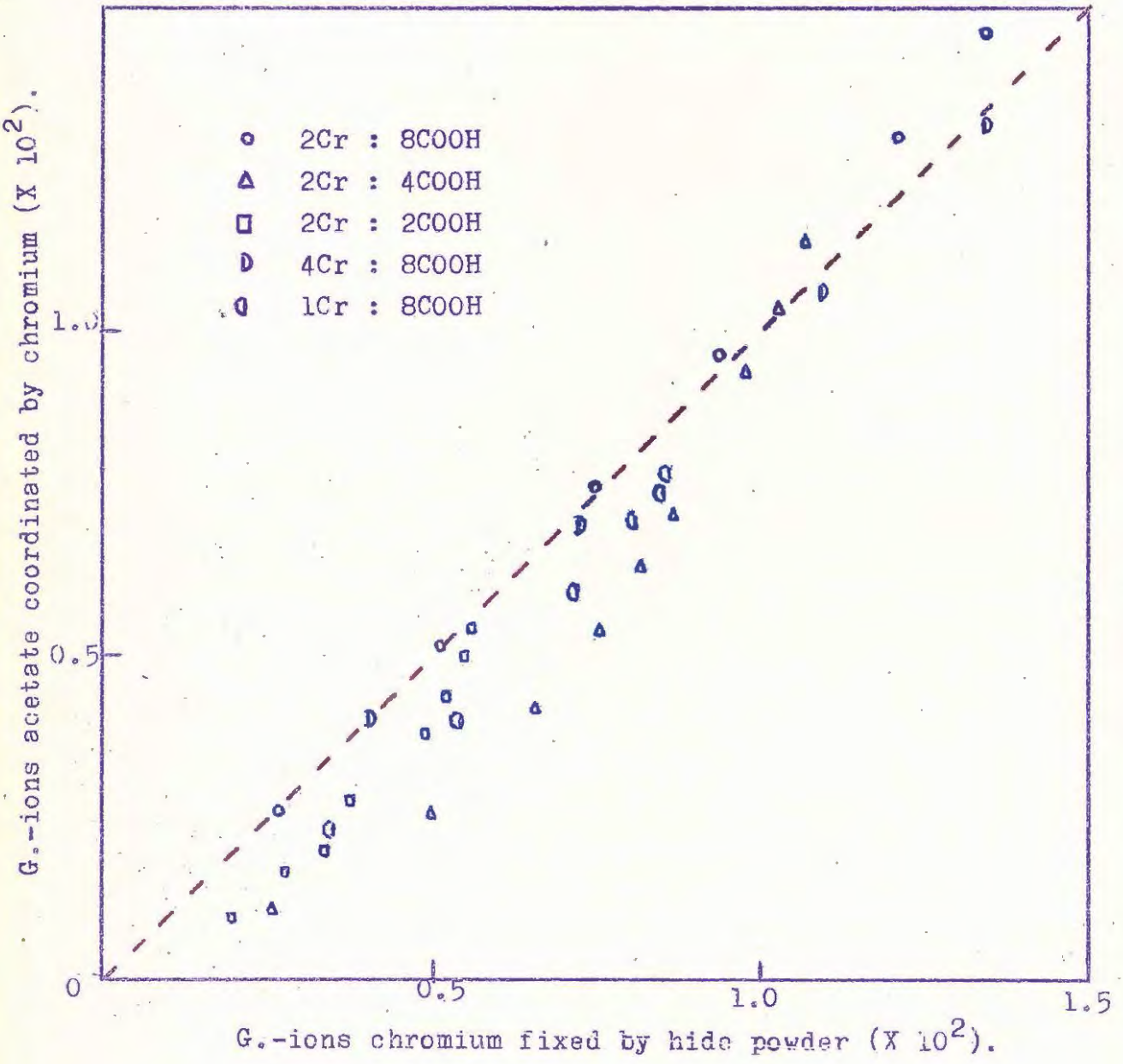
Hamm et al [14] have found that the apparent rate constants are inversely proportional to the hydrogen ion concentration for a wide range of organic acid anions. In order to test the validity of this observation in the present context, the negative logarithm of the apparent rate constant was plotted as a function of pH. The results of such plots for rate constants calculated from initial linear portions of plots, are shown in Fig. 5.4., while similar plots in the case of constants derived from the second linear portions are shown in Fig. 5.5.

Dotted blue lines of gradient -1, are shown for reference purposes. In general the large deviation from the theoretical line in the case of the second order rate constant obtained at the highest acetate to chromium level (1 : 8), may indicate that the rate constant is independent of pH at the higher pH levels approaching the precipitation point of the chromium nitrate. Lack of further experimental data at this level

prevented/.....

Fig. 5.6.

Correlation between chromium fixation by hide powder and acetate coordination by fresh chromium nitrate solutions under similar reaction conditions and after comparable reaction times.



prevented confirmation.

Comparison of the "apparent" rate constants, k_1 and k_2, at the same pH levels, by means of the graphs, indicated that:-

$$\frac{k_1}{k_2} = 5 \quad \text{(approximately)}$$

Since the absolute reaction rate at any instant is directly proportioned to the rate constant, this indicates that the initial coordination step has a reaction velocity 5 times greater than that of the subsequent step at the same pH values ~~and concentration levels~~.

The implications of this observation are further discussed in Capter VI.

COMPARATIVE KINETICS.

(a) Hide Powder Studies.

General similarity between reaction curves obtained under comparable conditions in the case of acetate ion coordination in fresh chromium nitrate solutions and chromium fixation by hide powder in fresh solution, is evident from inspection of the various curves (Figs. 3.1., 3.2., 3.3. and 4.1., 4.2., 4.3.) and similar dependency of the reaction rate on change in conditions has already been referred to (page 46). The exact correlation can be more readily demonstrated by means of a correlation plot the result of which is shown in Fig. 5.6., where the extent of acetate coordination by chromium is compared as ordinate with the extent of chromium fixation by hide powder as abscissa, after similar time intervals under comparable conditions. Rate data obtained

in/.....

in the case of fresh chromium nitrate solutions was used in the correlation plot since this was considered to reflect the course of the reaction more accurately (cf. Chapter VI). The dotted red line of gradient +1 represents the theoretical plot for exact correlation between the variables.

Considering the various factors operative, particularly the heterogeneous nature of the hide powder tannage system in comparison with the pure chemical system, the points show remarkably little "scatter" tendency and lie close to the theoretical line. This agreement must be regarded as strong evidence of the basic similarity of the reaction mechanisms underlying the two processes.

A general trend exhibited lies in the fact that the deviations from ideality are on the side of increased chromium fixation by the hide powder and that these deviations tend to decrease over the latter portion of the reaction period studied i.e. the reaction rate in the case of the hide powder appears to be greater initially than that of the acetate coordination. The explanation for this trend appears to be connected with the adoption of different criteria to gauge the extent of reaction in the case of the pure chemical system and the tannage system, namely acetate coordinated and chromium fixed. The reasons for the difference are more fully discussed in Chapter VI.

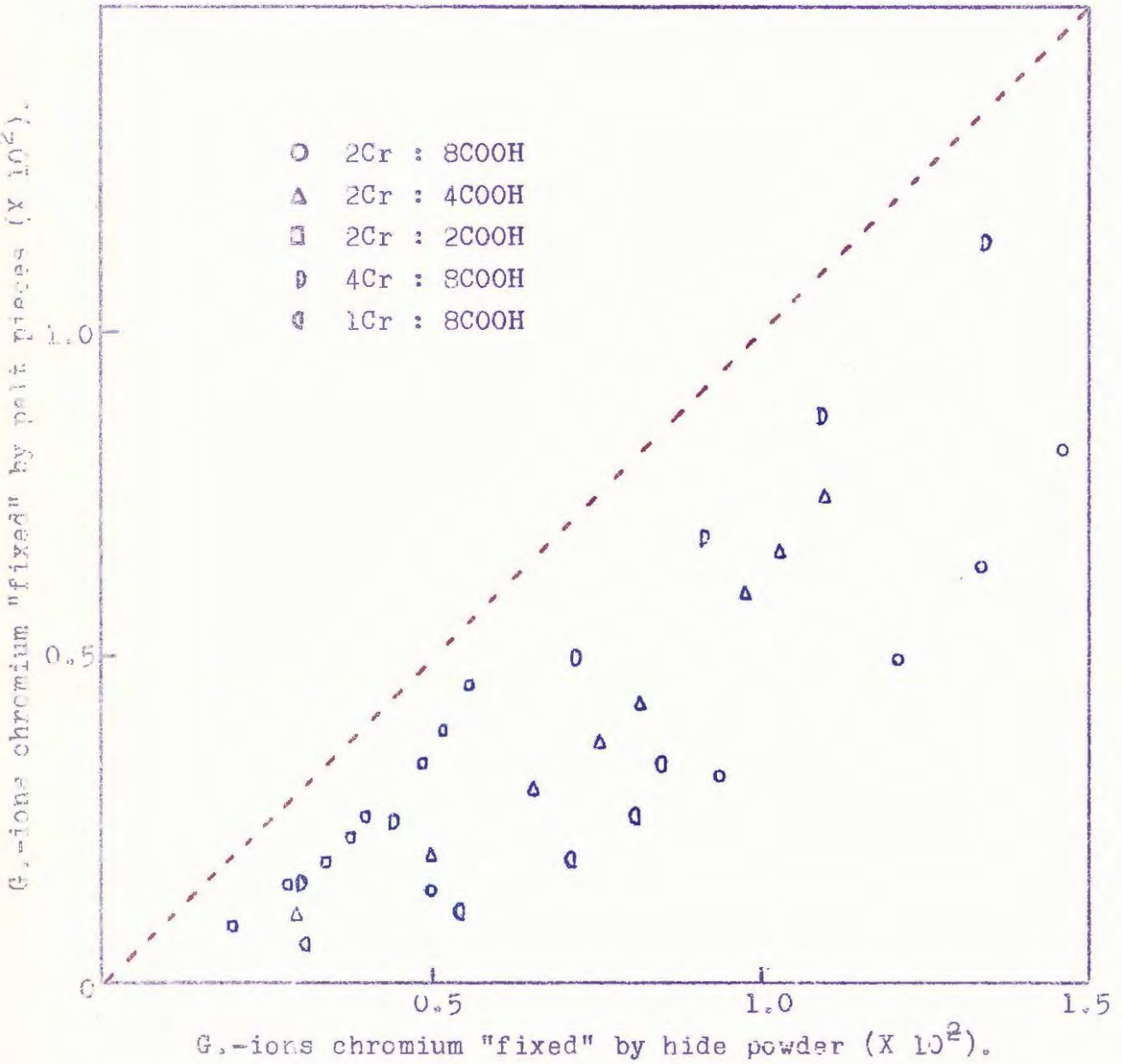
(b) Pelt Piece Tannage.

In order to simulate practical conditions with regard to the physical condition of the tannage substrate and thus to determine the effect of diffusion on the rate of reaction, a series of miniature tannages was performed as described in the experimental section on pelt

pieces/.....

Fig. 5.7.

Correlation between chromium "fixation" by hide powder and chromium "fixation" by pelt pieces under similar reaction conditions and after comparable reaction times.



pieces prepared by a standard method (cf. page 30). The degree of correlation between the rate data obtained in this series and that obtained in the hide powder series, was again investigated by means of a correlation plot the result of which is shown in Fig. 5.7. The dotted red line of gradient +1 indicates the theoretical plot for true parallelism between the series. Comparison is restricted to the rate data obtained in the case of the fresh reactant solutions at various mole ratios since the high buffering capacity of the hide powder and pelt pieces made control of pH at the lower levels difficult. Qualitative similarities between the corresponding reaction curves (Figs. 4.3. & 4.6.) are evident, however.

The large effects of diffusion on the reaction rate are evident in the reduction in degree of correlation apparent in Fig. 5.7. compared with Fig. 5.6. In general the deviations from the theoretical plot are towards the side of greater chromium fixation by the hide powder system after similar reaction times. The magnitude of the deviations is seen to be greatest in the case of the "fastor" reactions (mole ratios of 8 : 1 and 8 : 2) for the points obtained from the initial reaction period; towards the latter portion of the reaction period studied the deviations tend to decrease. In the case of the slower reactions, deviations from ideality are much less pronounced.

When due allowance is made for the effects of diffusion, correlation between the hide powder and pelt piece studies is apparent and moreover the dependency of the rate data on change of conditions is similar to that noted in the case of acetate coordination.

The part played by diffusion in producing deviations from ideality is discussed in Chapter VI.

Table 5.1./.....

TABLE 5. 1.

Mole Ratios Cr : Ac.	$pH_{initial.}$	k, (litre $mole^{-1}$ $min.^{-1}$)
1 : 8	5.3	44.0×10^{-3}
2 : 8	5.0	29.0×10^{-3}
2 : 4	4.7	9.3×10^{-3}
4 : 8	4.6	6.4×10^{-3}
2 : 2	4.5	7.5×10^{-3}
2 : 8 ($\frac{1}{2}$)	4.3	5.1×10^{-3}
2 : 8 ($\frac{3}{4}$)	3.9	1.0×10^{-3}
Mole Ratios Cr: Ac	**pH_{final}**	**k_2 (litre $mole^{-1}$ $min.^{-1}$)**
1 : 8	5.2	5.0×10^{-3}
2 : 8	4.8	5.8×10^{-3}
2 : 4	4.4	2.0×10^{-3}
4 : 8	4.1	1.1×10^{-3}
2 : 2	4.0	1.0×10^{-3}
2 : 8 ($\frac{1}{2}$)	3.9	0.86×10^{-3}
2 : 8 ($\frac{3}{4}$)	3.7	0.22×10^{-3}

(Fractions in parenthesis denote solutions containing half and threequarters neutralised sodium acetate, respectively.).

CHAPTER VI.

DISCUSSION AND CONCLUSIONS.

COORDINATION OF THE CARBOXYL GROUP OF THE ACETATE RADICAL TO TRIVALENT CHROMIUM ION UNDER AQUEOUS ACID CONDITIONS.

(a) Order of Reaction.

The assignment of a first order reaction mechanism by Hamm et al, to the bimolecular coordination reaction between trivalent chromium ion and a range of organic acid anions, has been discussed previously (page 1). Detailed examination of this reaction in the case of a typical monodentate ligand, the acetate radical, by means of the independent techniques of solvent extraction and spectrophotometry, reveals that the reaction is typically mass-action in nature, having a reaction velocity dependent upon the concentrations of each of the two reactants (Figs. 3.1. and 3.2.) as well as on the pH level at which the reaction is carried out (Fig. 3.3.).

The observed dependency of the reaction velocity upon the concentration of both reactants is at variance with the findings of Hamm et al who regard the chromium ion concentration as the only concentration factor governing the reaction rate. Further examination of the rate data by substitution into the classical expressions governing first and second order reaction mechanisms, revealed poor fit in the case of the first order expression (Fig. 5.1.), no simple linear relationship arising. A tentative explanation has been advanced to account for the apparent resolution of the rate data when the polarographic readings were substituted into the first order expression by Hamm et al in which the apparent "fit" obtained is ascribed to the choice of reactant mole ratios, the acetate ion being present in large excess (cf. page 4).

In/.....

In the case of the expression governing second order reactions, substitution of the rate data obtained from solvent extraction study, yielded plots having two marked linear portions (Figs. 5.2. and 5.3.). The pattern of the plots was found to be essentially similar over the range of reaction conditions chosen, the initial linear portion of each plot being followed by a second linear portion of lesser gradient. This pattern is taken to be indicative of the occurrence of two consecutive second order reactions in solution over the time period considered.

The rate constants corresponding to the linear portions of the plots have been calculated (cf. Table 5.1.), and show dependency upon the pH level of the reactant solution. The calculated "constants" can thus only be regarded as apparent rate constants and dependance upon pH level has been demonstrated in Figs. 5.4. and 5.5. where the apparent rate constant in each has been shown to be inversely proportional to the hydrogen ion concentration.

Comparison of the values reveals that the initial rate constants (k_1) are approximately 5 times greater than the subsequent rate constants (k_2) at similar pH levels. This observation would account for the discreteness of the two reaction steps as indicated by the dual linearity of the second order plots. Strictly, both coordination reactions are occurring simultaneously, however, since the velocity of the second step is small compared with that of the initial step and the concentration of the intermediate product is low, the rate data obtained initially are due almost entirely to the initial reaction process which proceeds rapidly to relative completion, after which further rate data obtained are determined by the second slow reaction step.

Comparison/.....

Comparison of the solvent extraction curves (Figs. 3.1., 3.2. and 3.3.) and their corresponding second order plots (Figs. 5.2. and 5.3.) indicates that deviations from initial linearity occur at times corresponding roughly to the half-reaction times, i.e. there is a change in the kinetic character of the system after the coordination of one acetate group per two chromium atoms is complete. The formation of such an intermediate is discussed in the following sections.

(b) The Importance of Olation.

The phenomenon of aggregation of chromium ions in solution by olation and the factors governing the process, have been reviewed in Chapter I, page 5. Olation processes appear to have been ignored completely by Hamm et al in postulating their general reaction mechanism in spite of the fact that the conditions under which the coordination reaction is carried out are those which favour olation of the chromium ions.

In order to examine the kinetic significance of olation, a parallel series of reaction solutions was prepared from chromium nitrate solutions which had been previously boiled and equilibrated at reaction temperative in order to bring about the formation of olated bodies. The reaction occurring within solution was followed by independent techniques, namely solvent extraction and spectrophotometry, each of which relies on different criteria to gauge the extent of reaction. The solvent extraction procedure, depending on the removal of free acetate from solution, reflects the variation of acetate concentration with time, while the spectrophotometric studies reveal directly the changes in optical density resulting from the penetration of ligands into the chromium complex.

Since/.....

Since olated chromium complexes are known to have greater optical density than the corresponding unolated complexes (cf. page 7), due to the increased absorbance of light energy associated with the ring structure, the spectrophotometric technique could be expected to provide a more sensitive means of distinguishing between reactions involving olated bodies and those involving unolated bodies in solution.

A comparison of the rate data obtained (Figs. 3.1., 3.2. and 3.3.) by solvent extraction study in the case of fresh (blue graphs) and aged (red graphs) chromium nitrate solutions, reveals no significant differences in the rate of removal of free acetate from solution. This observation appears to be indicative of essential similarity of reaction mechanism in both fresh and aged reactant solutions.

The greater sensitivity of the spectrophotometric method has already been mentioned. Comparison of the rate data showing the variation in optical density with time at the 570 mμ peak (Figs. 3.4., 3.5. and 3.6.) in the case of fresh (blue graphs) and aged (red graphs) solutions, reveals that initial absorption is greater in the case of the aged reactant solutions. This observation is in accordance with the expected greater optical density exhibited by olated bodies. The absorption differences appear to be most pronounced at the lower pH levels. In all cases, the graphs obtained in the case of the aged chromium nitrate reactant solutions (red) converge with those obtained in the case of the fresh series (blue) after varying time periods depending on the initial reaction rate.

Comparison of the rate data reflecting the variation in optical density with time at the 420 mμ peak (Figs. 3.11., 3.12. and 3.13.) in

the/.....

the case of fresh (blue) and aged (red) reactant solutions, reveals greater initial absorption in the case of the fresh solutions. The actual differences are most pronounced at the lower pH levels and, as in the case of the curves obtained at the 570 mμ peak, the absorption values for the fresh and aged solutions converge with time, the time periods for the convergence being proportional to the initial reaction rate.

pH studies were carried out in conjunction with the spectrophotometric studies and the variation in pH during the course of reaction is recorded in Figs. 3.4., 3.5. and 3.6. In all cases the initial pH levels of the solutions containing aged chromium nitrate reactant were lower than those of the corresponding fresh reactant solutions. This effect might be anticipated from the known greater proportion of free acid present in chromium solutions in which olation processes have occurred (cf. page 5). The actual pH differences are most pronounced at the lower pH levels. As in the case of the spectrophotometric studies, there was a tendency for the corresponding curves from the fresh and aged series to converge after time periods which are shorter in the case of the faster reactions.

The tendency for the corresponding curves obtained in the case of fresh and aged reactant solutions by spectrophotometric and pH study, to merge to common values after the elapse of an initial time interval, is regarded as indicative of the essential similarity of reaction mechanism in both the fresh and aged series. Since the reaction is carried out under conditions of pH which favour olation, the basic reaction in each case is assumed to occur between an olated chromium complex and acetate ions. Hence in the case of the fresh reactant solutions, the elevation

of/.....

of the solution pH level due to the addition of the sodium salt of the ligand, would appear to favour rapid olation of the chromium ions to the same levels as in the case of the previously boiled solutions, resulting in the convergence of the experimentally determined absorption and pH values during the initial period of the reaction after which further reaction occurs between the same species in each series.

Mention has been made previously of the twofold possibility of attachment of ligand by:-

(a) coordination at a side position unaffected by olation, and

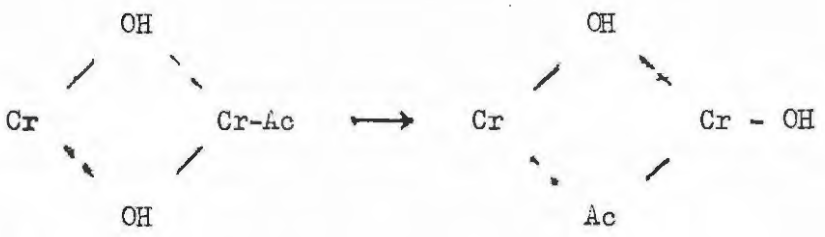
(b) incorporation into the ring structure of an olated complex by replacement of a hydroxyl group participating in the -ol linkage (page 7).

If the mechanism described under (b) is favoured, the effect of olation might be to bring about either a differing or enhanced reaction rate compared with that observed in fresh solutions where coordination must either proceed by mechanism (a) or otherwise first be preceeded by olation.

The obvious similarity in the general shape of curves obtained for the fresh and aged series where minor initial differences in absorption and pH level could be directly attributed to olation effects, lead to the conclusion that olation is of minor importance as a rate determining factor and that the coordination mechanism is that of side attachment as in (a) in the case of both olated and unolated species. It should be noted, however, that this conclusion does not exclude the possibility of subsequent rearrangement with incorporation of ligand into the ring structure.

Hence/.....

Hence,



Indications of such rearrangement occurring after initial coordination at a side position have been observed in the tendency for the optical density at both the 420 mμ and 570 mμ absorption peaks to increase to larger values at "infinite" time particularly in the case of the more complete reactions (cf. Appendix A, Figs. A.1. - A.14.). This is in accordance with the known greater absorbancy shown by the ring structure.

The anomalous lower absorption exhibited initially by the aged reactant solutions at the 420 mμ peak is discussed in the following section.

(c) General Theory.

The various effects described in the preceeding two sections ~~have~~ lead to the conclusions that -

(a) the reaction appears to proceed by two consecutive second order mechanisms, and

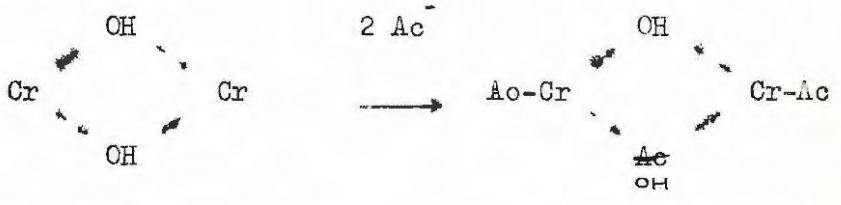
(b) olation is rapid under the experimental conditions so that in the case of both fresh and aged reactant solutions, reaction occurs between an olated chromium species and the acetate ion.

The/.....

The above two conclusions may be reconciled by assuming that the olated species formed in the reactant solutions by boiling and ageing or by elevation of the pH, is of the diol type, containing two chromium atoms per complex. Although the possibility of further aggregation by continuation of the olation processes may be envisaged to give complex ions containing four or more chromium atoms, the time factor involved is considerably greater. Moreover, the diol complex which represents a fairly stable entity, is regarded as an important olation product [70] in the literature.

The formation of diol complexes is partly confirmed in the present context, by comparison of the curves obtained by solvent extraction (Figs. 3.1., 3.2. and 3.3.) and spectrophotometric (Figs. 3. 7, 3.8. and 3.9) study where similarity im the rates of reaction of both the acetate and chromium ions indicated the occurrence of an equimolecular reaction between chromium nitrate and sodium acetate. A reaction of this type may be readily envisaged in the case of a diol complex, the mechanism involving the coordination of an acetate radical to each of the two chromium atoms in order to achieve the stoicheiometry indicated above.

Structurally,



In the case of larger olated aggregates coordination of acetate radicals to the "inner" chromium atoms is likely to be hindered due to the steric effects of the chromium atoms attached on either side by olation bonds.

Assuming /...

Assuming a diol species to be the chief reactant entity formed, the mechanism of coordination would thus appear to consist of the stepwise attachment of two acetate radicals per chromium species. This conclusion is in accordance with the findings of the reaction kinetic studies (Chapter V, page 52) which indicated the occurrence of two consecutive second order reactions having differing rate constants, during the reaction period considered. Slower reaction rate observed in the case of the second coordination step may be accounted for on the basis of a reduction in affinity between the mono-aceto-chromium complex and the second coordinating acetate radical due to structural changes introduced by the first coordination.

Electrophoretic studies carried out on reaction solutions at "equilibrium" support the above conclusions (cf. Chapter III, page 42). In all cases migration took place in the direction of the cathode indicating the presence of cationic bodies only. The formation of cationic product complexes is to be expected in the case of reaction involving stepwise coordination of two acetate radicals to a diol species, the attachment of each univalent acetate radical serving to reduce the positive charge on the chromium complex by unity in each combination. The formation of product complexes carrying positive charges of 5 (2 x 3 - 1) and 4 (2 x 3 - 2) corresponding to coordination of one and two acetate radicals respectively, may be envisaged.

No significant differences in band pattern and mobilities were detected between the fresh and aged reactant solution series, indicating that the products formed are essentially similar in both series.

A maximum / ...

A maximum of three cationic bands was detected in the case of three of the reactant solutions at intermediate mole ratios and pH levels, presumably due to migration of the residual chromium ions and the two product complexes formed. At other intermediate levels, considerable spreading of the bands made discernment of three bands difficult although at least two bands were distinguishable.

In the case of the more complete reactions at the higher pH levels, single bands only were detected having mobilities differing from that of the control and which are thus attributed to migration of the final product complex. Reference to the curves obtained by solvent extraction study indicates that the residual chromium concentration is low in these cases.

Similarly, single bands detected in reaction solutions at the lower pH levels and mole ratios are attributed to migration of the residual chromium nitrate only, the concentration levels of the product complexes in these solutions being too low to permit detection.

The mobilities of the more rapidly migrating bands were comparable to those of the chromium ions in the control without added ligand so that these bands could be attributed to the residual chromium nitrate and the mobilities of the product complexes were thus less than that of chromium nitrate. The smaller mobilities of the product complexes may be accounted for on the basis that entry of acetate groups into the chromium ion has the twofold effect of:-

(a) lowering the charge on the complex ion, and

(b) reducing the structural compactness,

both / ...

both of which give rise to a complex of reduced mobility.

The colour changes observed in the various chromium solutions following immediately on addition of the sodium salt of the ligand and during the course of reaction and the subjection of these changes to spectrophotometric examination, have been discussed in Chapter III, (page 36). The modifications to the absorption spectrum of the chromium reactant solution are recorded in Figs. A. 1 to A. 14. of Appendix A. Since the optical densities measured are those of reactant solutions which contain a number of chromium species, the absorption spectra recorded represent the result of the interaction of the spectra of all the species present. Modification in the resultant absorption spectrum such as variation in peak heights and positions may thus be attributed to modification in the component spectra of the various chromium species present.

Examination of the various absorption spectra reveals that the effect of addition of sodium acetate is to increase immediately the absorption at both the 420 mμ and 570 mμ peaks, the effect being most pronounced at the 420 mμ peak. Since the rate of coordination is slow, this effect is attributed entirely to the interaction between the chromium species present and hydroxyl ion formed as a result of the hydrolysis of the sodium acetate in solution.

Attention has been drawn previously to apparently anomalous behaviour observed at the 420 mμ peak (page 41) where higher initial absorption was recorded in the case of fresh reactant solutions immediately after addition of the sodium acetate reactant. The anomaly may be explained on the basis that the pH elevation which determines the increase in optical density, is not as great in the case of olated

solutions /...

solutions due to greater partial neutralisation of the hydroxyl ions by the larger amount of free acid present in these solutions arising out of protolysis of the hexaquochromium ion prior to olation (cf. page 5). The same consideration would also apply to the 570 mμ peak, where, however, the effect of pH elevation is much smaller and is presumed to be overshadowed by the effect of increased optical density due to olation so that the initial absorption is greater in the case of olated solutions, as normally expected.

The greater degree of differentiation between the initial absorption values of the fresh and aged reactant solutions at the lower acetate levels may be attributed to the larger proportion of free hydroxyl group neutralisation in the case of the olated solutions since at low acetate levels the total amount of hydroxyl radical produced is correspondingly smaller.

During the course of reaction, modifications in the absorption spectrum of the reactant solution were readily detectable, the 420 mμ peak decreasing, and the 570 mμ peak increasing, with time. The increase in optical density at the 570 mμ peak during the course of reaction has been conclusively shown to be directly related to the increase in concentration of the product complex$^{es}_{A}$ formed in solution (cf Chapter III, page 39).

The explanation for the fall in optical density at the 420 mμ peak is not as apparent, but attention should be drawn to the remarkable similarity of this variation (Figs. 3. 11 and 3. 12) and the pH drop (Figs. 3. 4 and 3. 5) at corresponding mole ratios and concentrations. This similarity would appear to indicate that the hydroxo compound formed initially due to pH elevation is a loosely-bound compound of high optical

density / ...

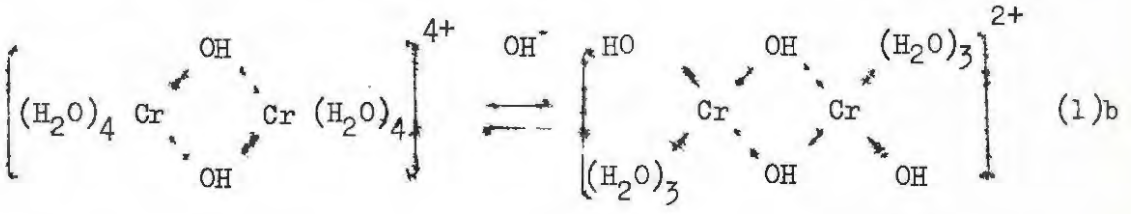
density at 420mμ in equilibrium with hexaquochromium ions in the case of fresh chromium nitrate solutions and with the olated chromium species in the case of aged chromium nitrate solutions.

Structurally,

Fresh solutions:-

$$Cr\ (H_2O)_6^{+++} \rightleftharpoons^{OH^-} (H_2O)_5\ Cr\ OH^{++} \qquad (1)\ a.$$

Aged solutions:-



(1)b

Addition of sodium acetate reactant results in the setting up of the following equilibrium between associated and dissociated acetic acid:-

$$HAc \rightleftharpoons H^+ + Ac^- \qquad (2)$$

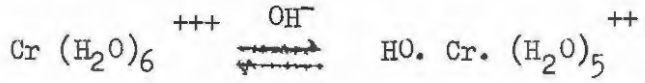
During the course of reaction, removal of acetate ions by coordination results in displacement of equilibrium (2) to the right with resultant fall in pH level of the reactant solution. The effect of fall in pH level would then be to displace equilibrium reactions (1)a and (1)b to the left resulting in the reformation of species having lower absorption at the 420mμ peak so that the absorption spectrum of the solution decreases in height at the 420mμ peak.

It should be noted that the formation of a loosely bound hydroxo compound is regarded as a necessary preliminary to olation by the Stiasny school/....

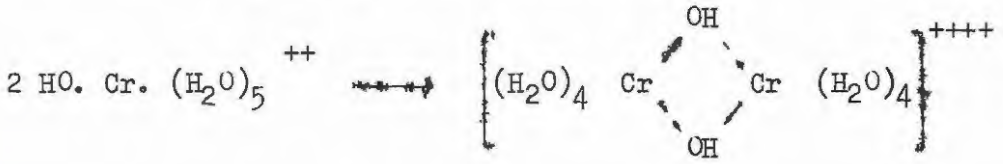
school (cf. page 5) so that rapid olation of the chromium species in fresh solutions is favoured after addition of ligand.

The conclusions reached in the preceeding sections indicate that the coordination reaction proceeds by the following mechanisms:-

Fresh solutions:

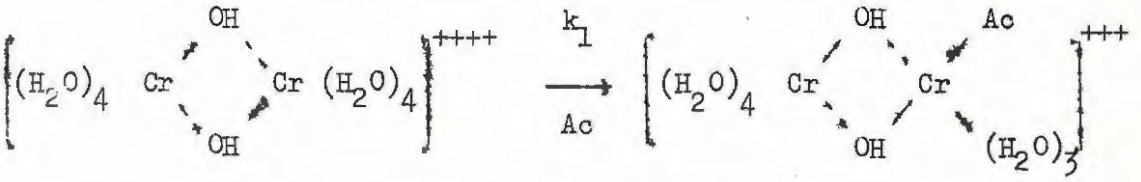


(I)

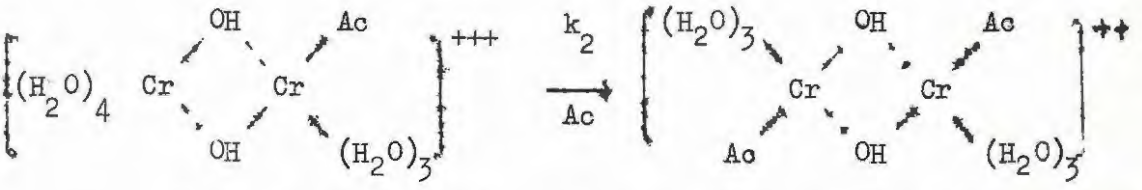


(II)

Fresh and aged solutions:

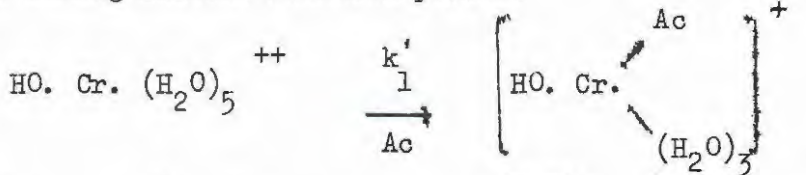


(III)

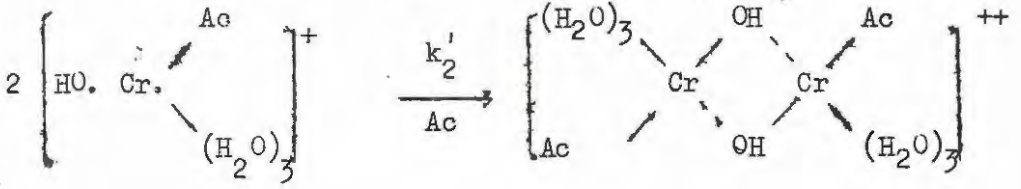


(IV)

In the case of fresh reactant solutions, a certain amount of mono-ol reaction with acetate ions with subsequent olation may be envisaged during initial reaction period:



(V)



(VI)

COORDINATION OF CARBOXYL GROUPS OF HIDE COLLAGEN TO TRIVALENT CHROMIUM ION UNDER AQUEOUS ACID CONDITIONS

(a) Comparative Kinetics.

Reference has been made previously to the importance of the acid dissociation constants of monodentate ligands in determining complex stability and carboxyl group availability (page 44) and to the close correspondence of the acid dissociation constant in the case of the acetate ion to the average value of that in the case of hide collagen acid residues. These considerations make it reasonable to expect similarity in reaction course when the fixation of chromium by hide collagen is compared with the coordination of acetate carboxyl groups under similar conditions, provided coordination of carboxyl groups of collagen is the chief mode of chromium fixation in animal hide. Any differences in reaction course might then be attributed to the limiting effects of the rate of penetration of chromium ions to reactive centres on the rate of reaction.

In order to compare the rate data of tannage systems with those of pure chemical systems, the acetate coordination studies were extended by means of a series of miniature tanning experiments on hide substance in the form of:-

(a) hide powder, and

(b) prepared pelt pieces.

In the case of the hide powder studies, general similarity in reaction course was apparent when the rate data (Figs. 4.1., 4.2. and 4.3.) was compared with that of the pure chemical system (Figs. 3.1., 3.2. and 3.3.). The actual correlation between the rate data has been demonstrated in Fig. 5.6. in which chromium fixation in fresh reactant solutions

at/.....

at various mole ratios is compared with acetate coordination in the pure chemical system at the same mole ratios and pH levels. Difficulty experienced in pH control at low levels in the pH adjusted miniature tannages due to the high degree of buffering of the hide substance, prevented direct comparison of the rate data by means of the correlation plot. The high degree of correlation revealed at various reactant ratios is remarkable in view of the widely differing physical characteristics of the two systems and serves to emphasize the importance of the coordination of collagen carboxyl groups and the essential similarity of reaction mechanism.

Correlation between the rate data in the case of hide powder and acetate studies indicates that diffusion effects are small due to the high degree of surface development. It is evident that a kinetic equation of a form similar to that of the classical second order expression applicable to the pure chemical system, would suffice to describe the initial reaction course in the case of hide powder tannage, so that a second order mechanism may be assigned to the tannage reaction. The insertion of the tannage rate data directly into the second order expression is prevented since there is some doubt as to the accuracy with which chromium fixation accurately reflects the extent of coordination, due to olation effects in fresh solution. This aspect of the reaction is discussed in the following section.

Correlation between the rate data obtained in the case of pelt tannage in fresh solutions at various mole ratios (Figs. 4.4. and 4.5.) and the rate data obtained in the case of the corresponding hide powder studies, is shown in Fig. 5.7. A much lower degree of correlation is

evident/.....

evident demonstrating the limiting effects of the rate of diffusion of chromium when the fibrous weave pattern of the tannage substrate is retained. Deviations from the ideal plot for exact correlation (represented by the dotted red line of slope, + 1.) lie on the side of greater chromium fixation by the hide powder and reach a maximum during the initial reaction stages after which there is a tendency to revert back towards the ideal correlation plot. The deviations from ideality are most pronounced in the case of the faster reactions and thus demonstrate clearly the diffusion-limited nature of the reaction in the case of pelt piece tannage. The effect of diffusion on the initial shape of the reaction curves obtained in the case of pelt tannage (Figs. 4.4., 4.5. and 4.6.) is evident when these are compared visually with those obtained in the case of the acetate studies (Figs. 3.1., 3.2. and 3.3.) and hide powder tannage (Figs. 4.1., 4.2. and 4.3.). Clearly any theoretical expression governing the course of the reaction in the case of diffusion-limited pelt tannage will be of a form fundamentally different to that of the second order kinetic expression applicable to the acetate and hide powder studies.

(b) The Importance of Olation.

In order to assess the importance of olation of chromium ions in solution, particularly with regard to the effect on the rate of tannage, a parallel series of miniature tannages was carried out using boiled and aged chromium nitrate solutions as in the case of the acetate studies. Initial pH adjustment in the olated tannage series was carried out to the same level as in the case of the corresponding solutions of the fresh reactant series for comparison purposes.

Examination/.....

Examination of the curves obtained in the case of both the hide powder (Figs. 4.1., 4.2. and 4.3.) and pelt piece (Figs. 4.4., 4.5. and 4.6.) tannages, reveals that the immediate effect of olation is to increase the rate of chromium fixation, the effect being more pronounced at the higher pH levels. After the initial reaction period (24 hours) there is a tendency for the fresh and olated series to converge as observed in the case of the acetate coordination studies, although convergence is not as complete in the hide powder series and less pronounced in the pelt tannage series.

The above observations may be explained on the basis that fixation of chromium by hide substance may be envisaged in two ways:-

(a) Directly, by coordination of a chromium atom to a side chain carboxyl group of the hide collagen.

(b) Indirectly, by attachment of a chromium atom by olation bonds to a previously coordinated chromium atom.

It is clear that the coordination of a diol species in boiled solutions to carboxyl groups results in a faster rate of chromium fixation than in the case of attachment of single bodies at the same rate of coordination. Estimation of "fixed" chrome in tannage with olated solutions might thus be expected to reflect a spurious reaction rate double that of the coordination rate, in the case of a diol species in which two chromium atoms are "fixed" per carboxyl group during the initial reaction stages. Strictly, it follows that the extent of chromium fixation by hide substance in solutions containing olated species does not reflect the extent of reaction; in practise, however, no ready method exists for the

determination/.....

determination of carboxyl groups coordinated which would be expected to provide a more accurate criterion for the extent of reaction.

As in the case of the corresponding curves in the acetate coordination studies, the tendency for the corresponding curves of the fresh and olated tannage series to converge, is attributed to rapid olation of the fresh solutions at the reaction pH levels. The convergence is not as rapid in the tannage systems where olation of chromium atoms after coordination is difficult since such "fixed" chromium atoms are no longer free to migrate through the aqueous phase. In the case of the pelt tannage systems, diffusion constitutes an additonal factor reducing the rate of convergence.

At the lower pH levels, differences between the fresh and olated series are less pronounced (Figs. 4.1. and 4.4.). This appears to indicate that the rate of olation is rapid in comparison with the rate of coordination which is found to be slow at these pH levels. Reaction in the case of both the fresh and aged series is then essentially similar, involving coordination of carboxyl groups to an olated species.

Reference has been made earlier to the trend exhibited in Fig. 5.6. where it was pointed out that initial deviations from the theoretical line tended to fall on the side of increased chromium fixation by the hide powder, apparently indicating an initial reaction factor in the case of tannage with fresh chromium solutions than that of the acetate coordination. This trend is also attributed to the effect of rapid olation in the fresh solutions with resultant enhancement of the rate of chromium fixation.

Theory/.....

(c) Theory of Tannage.

The various historical theories and modern concepts of tannage have been briefly reviewed in Chapter I. Accumulated experimental evidence has led to increased emphasis being placed on the coordination of carboxyl groups to chromium as a fundamental process of tannage and this viewpoint is supported by the experimental observations of the present study.

The findings of the previous two sections have led to the conclusion that:-

(a) the tannage reaction is essentially similar to that occurring in the coordination of acetate ions to chromium which has been found to be a second order reaction proceeding in two steps. The tannage rate data in the case of fresh solution approximates closely to that of the pure chemical system when the degree of surface development of the substrate is large. In normal tannage systems the rate of tannage is limited by diffusion effects so that the rate data show trends characteristic of a diffusion limited reaction, in which the rate is governed by physical factors.

(b) the effect of olation is to increase the rate of reaction, the effect being a spurious one since the "fixed" chrome content is theoretically ~~four times~~ twice that of the acetate coordination in the case of initial attachment of a diol species.

A further/.....

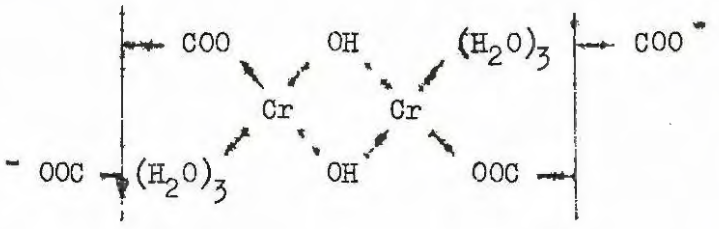
A further aspect of tannage, mentioned in Chapter I, is the high degree of thermal stability imparted by chrome fixation. This characteristic is regarded as indicative of the formation of cross-links between adjacent side chains of the collagen molecules, conferring rigidity to the structure so that dimensional stability is retained, even at fairly high temperatives ($\pm$ 100°C).

The studies carried out on acetate coordination in pure chemical systems indicated that the reaction consisted of the successive coordination of two acetate groups to a diol complex which constituted the chief chromium aggregate present in the solution. The operation of a similar mechanism in the tannage systems studied as indicated by similarities in the rate data, renders possible the formation of "bridges" between the carboxyl groups of adjacent protein side chains since the question of dimensional compatibility is resolved.

Some confusion exists over the average magnitude of the inter-carboxyl group distances of neighbouring side chains in hide substance, but it seems clear that a single chromium atom would not be able to achieve a bridging effect. In the case of a diol complex, such bridging becomes feasible since the initial single point attachment of one of the chromium atoms to a side chain acid residue can then be followed by similar coordination attachment of the second chromium atom to an acid residue in a neighbouring side chain. The bridging effect is then achieved through the olation bonds between the chromium atoms.

Structurally/.....

Structurally,



Comparison of the extents of chromium fixation and acetate co-ordination at the end of the 144 hour reaction period, reveals less reaction in the case of the hide powder and pelt tannages. Reduction in fixation may be attributed to:

(a) Steric hindrance at ionised carboxyl groups due to the variety of functional groups present,

(b) Macro-blockage of access to carboxyl groups within the collagen fibrils due to superficial fixation.

It should be emphasized that the studies carried out in the present investigation cannot in any way be regarded as exhaustive and the conclusions reached are subject to further confirmation. The possibility of further changes in the mode of chromium fixation as a result of subsequent treatments such as the drying of the tanned material, must be entertained. The observations made in the present study are considered significant, however, and serve to emphasize the need for further investigation along similar lines.

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APPENDIX A.

Figs. A.1. - A.14. reflect the modifications to the absorption spectra of freshly-prepared and aged chromium nitrate solutions as a result of the coordination of acetate radical at various reactant mole ratios, optical density measurements being carried out in the vicinity of the 420 mμ and 570 mμ absorption maxima.

The absorption spectra of chromium nitrate solutions at the same concentration levels, but without added ligand are included for reference (dotted graphs).

Fig. A.I. Changes in the absorption spectrum of fresh 0.02 M chromium nitrate solution in the vicinity of the 420 mμ and 570 mμ peaks as a result of the coordination of acetate ion.

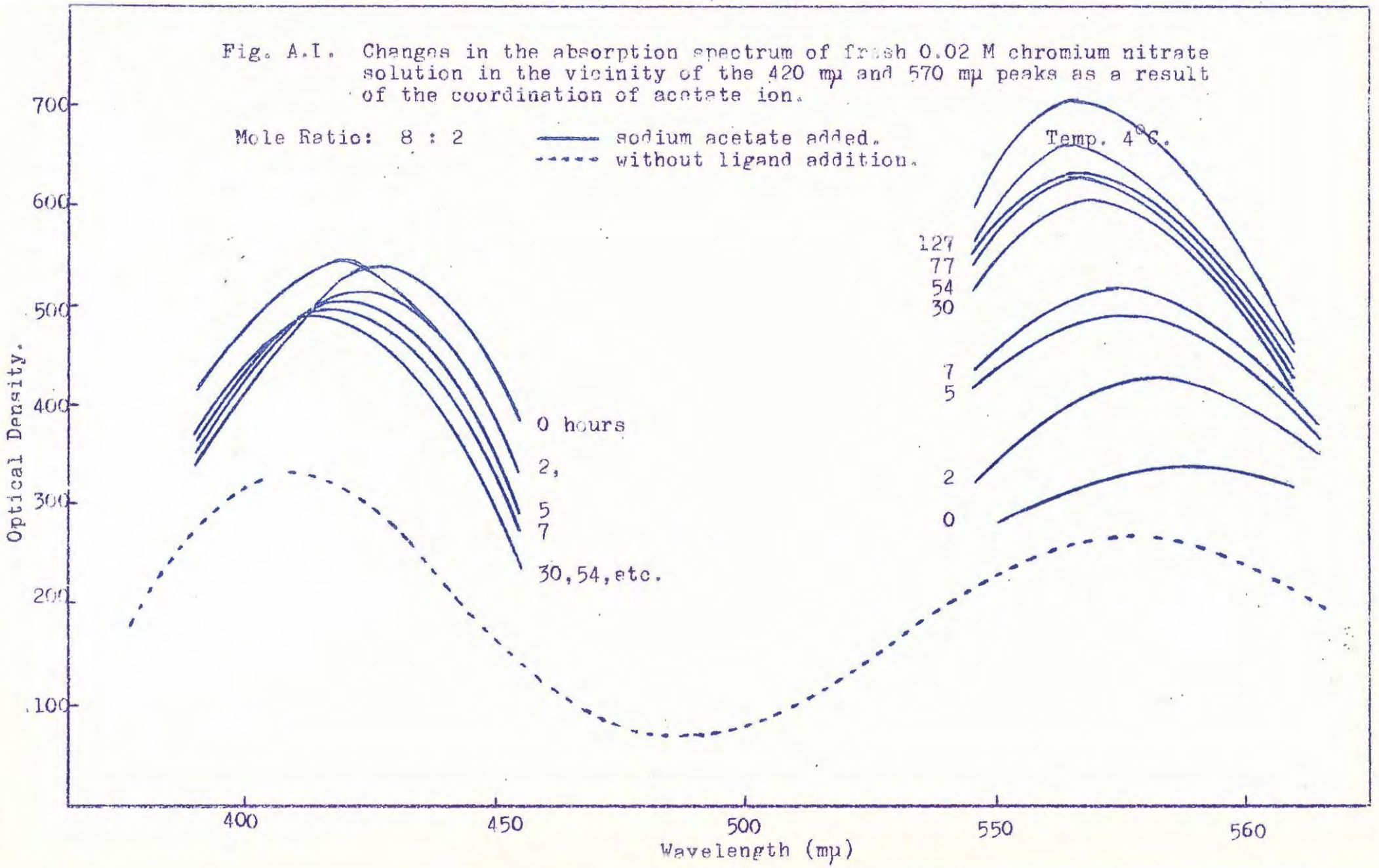


Fig. A.2. Changes in the absorption spectrum of aged 0.02 M chromium nitrate solution in the vicinity of the 420 mμ and 570 mμ peaks as a result of the coordination of acetate ion.

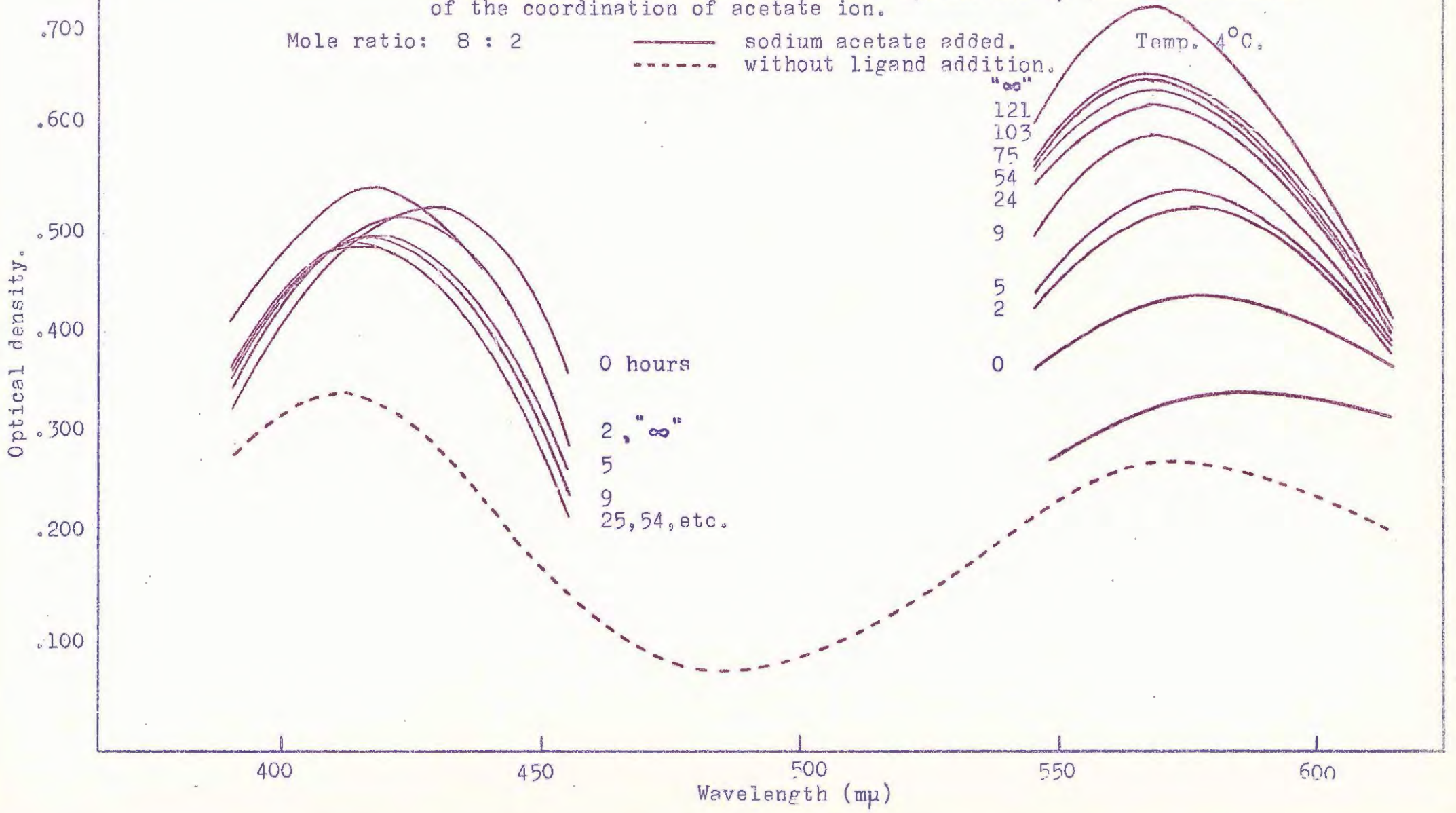
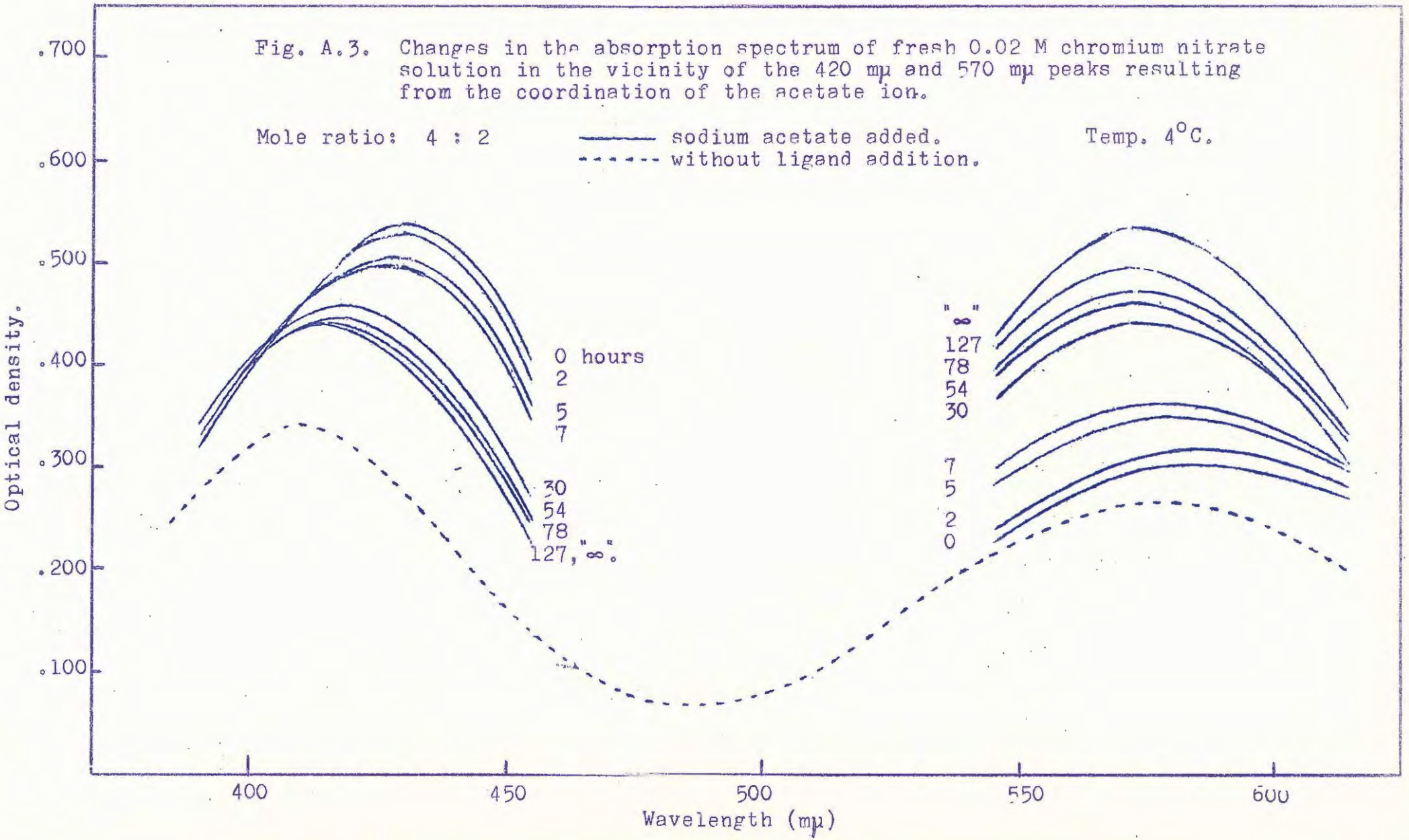


Fig. A.3. Changes in the absorption spectrum of fresh 0.02 M chromium nitrate solution in the vicinity of the 420 mμ and 570 mμ peaks resulting from the coordination of the acetate ion.

Mole ratio: 4 : 2 ——— sodium acetate added. Temp. 4°C.
------ without ligand addition.



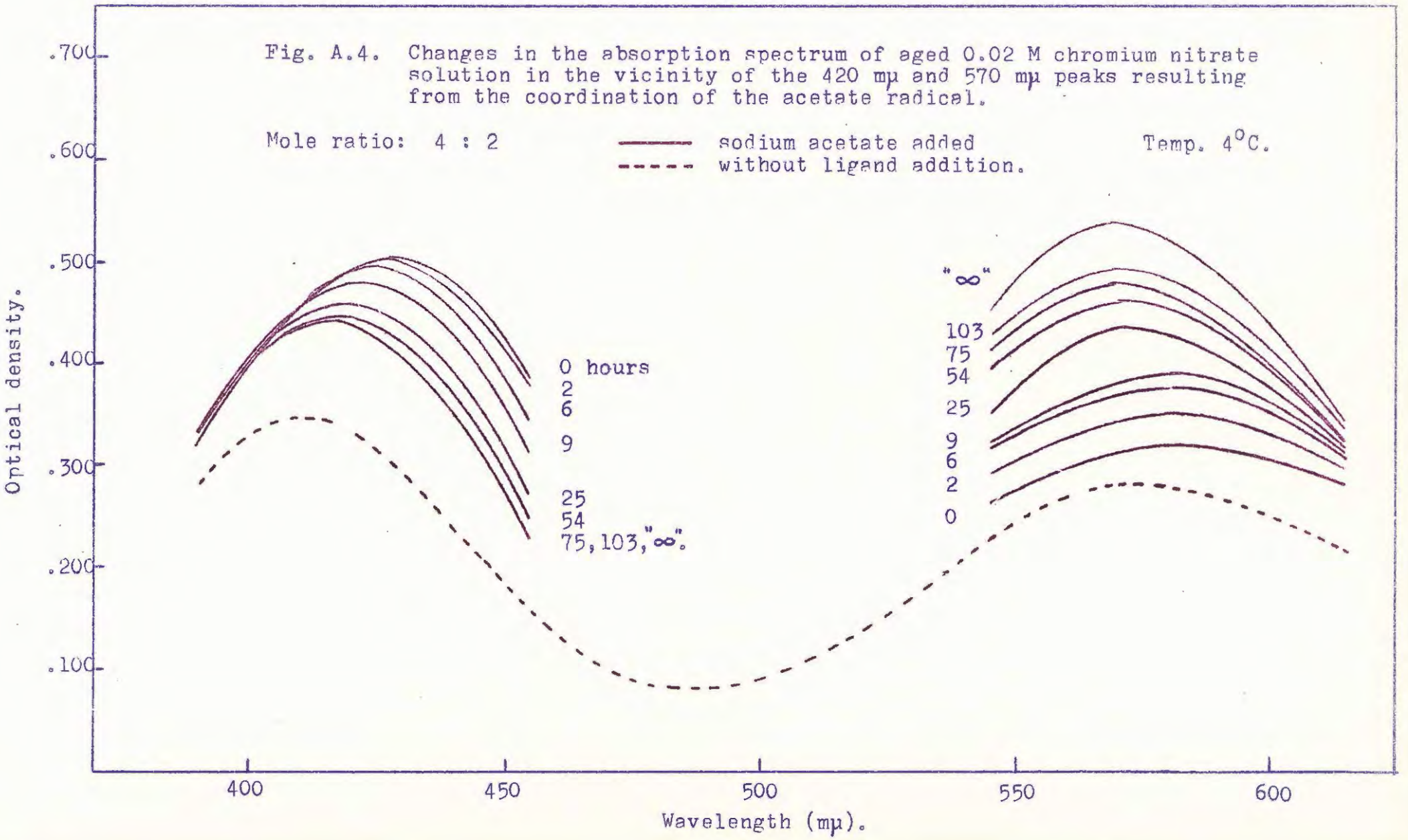


Fig. A.4. Changes in the absorption spectrum of aged 0.02 M chromium nitrate solution in the vicinity of the 420 mμ and 570 mμ peaks resulting from the coordination of the acetate radical.

Mole ratio: 4 : 2 ——— sodium acetate added ----- without ligand addition. Temp. 4°C.

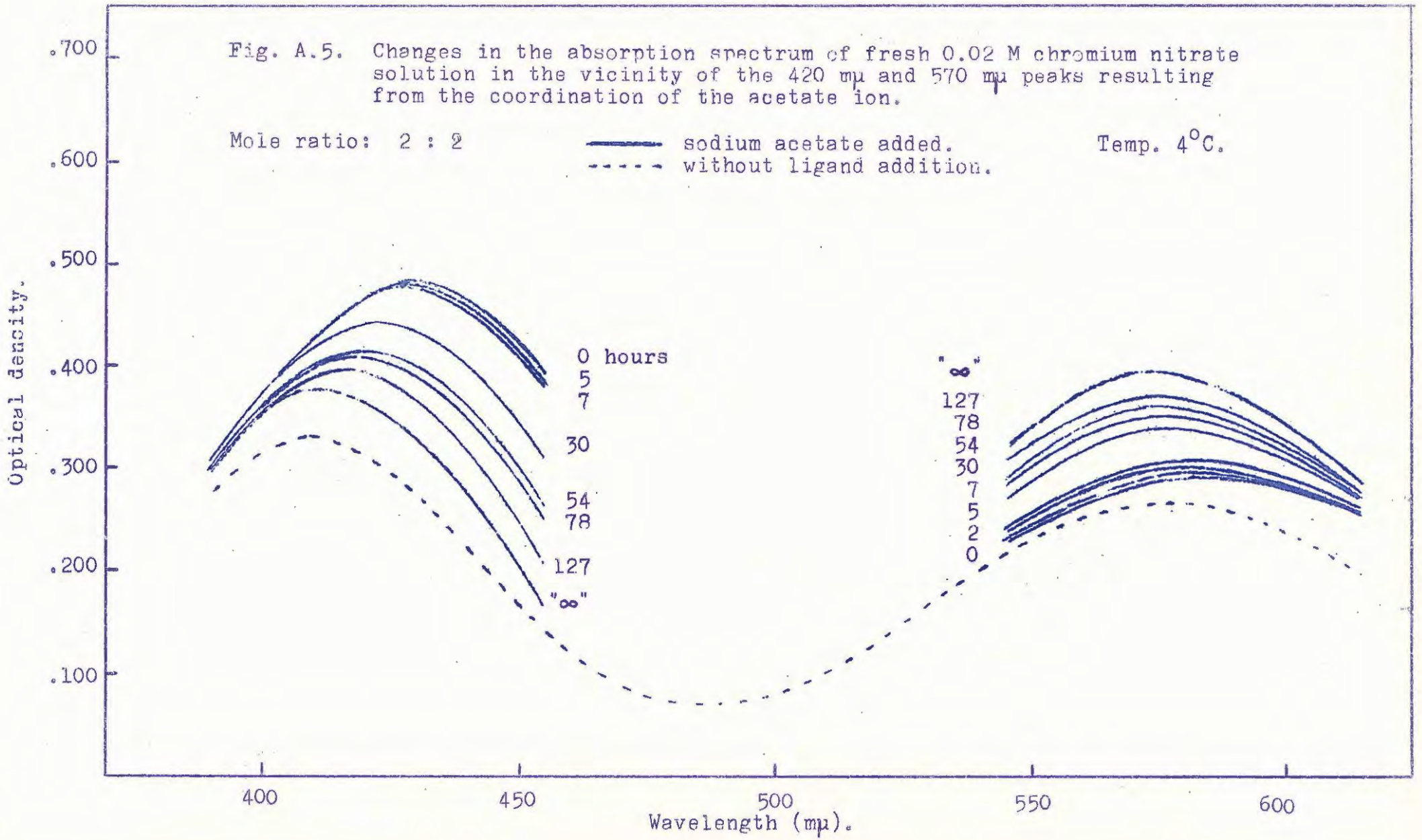
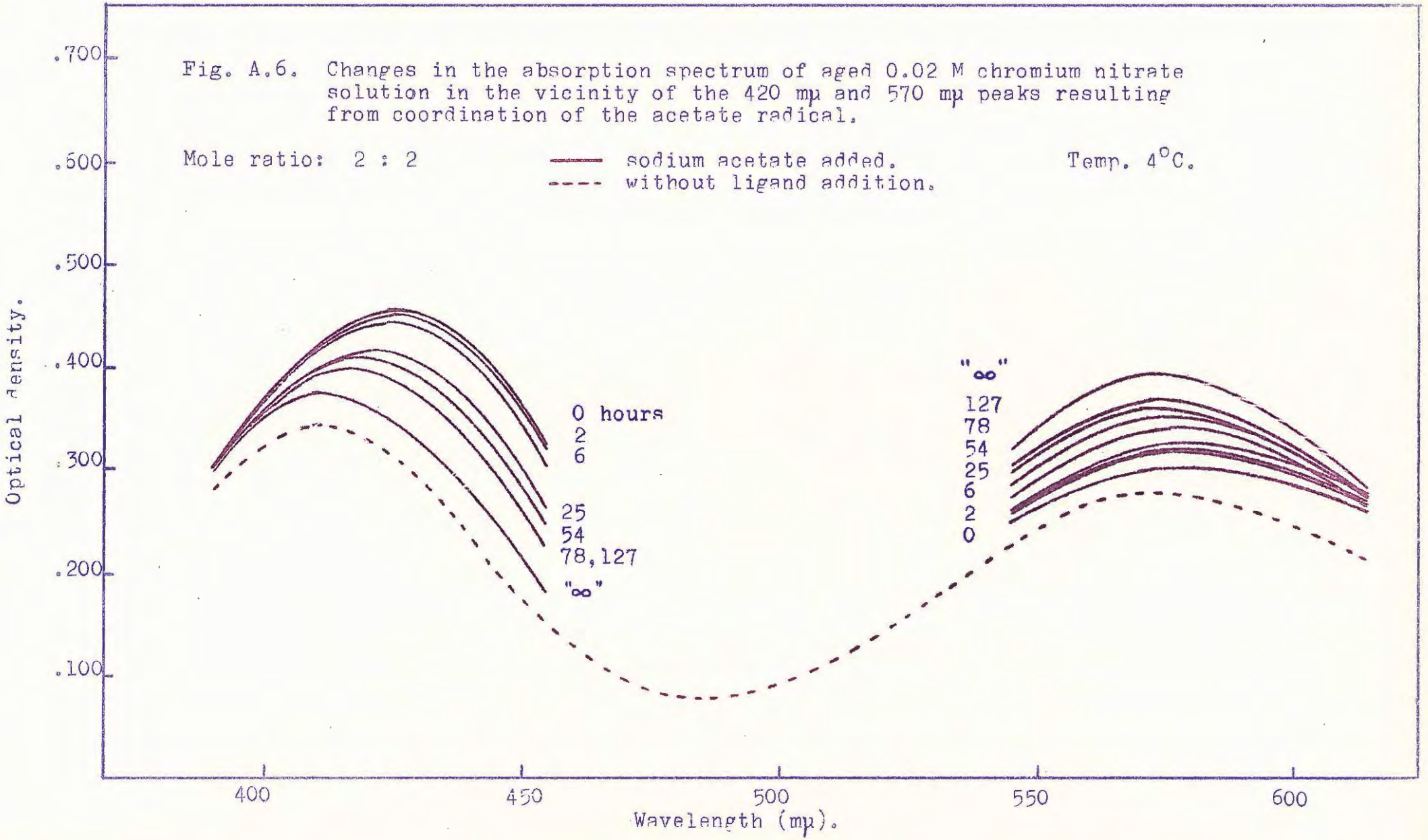


Fig. A.5. Changes in the absorption spectrum of fresh 0.02 M chromium nitrate solution in the vicinity of the 420 mμ and 570 mμ peaks resulting from the coordination of the acetate ion.

Mole ratio: 2 : 2 ——— sodium acetate added. Temp. 4°C.
----- without ligand addition.

Fig. A.6. Changes in the absorption spectrum of aged 0.02 M chromium nitrate solution in the vicinity of the 420 mμ and 570 mμ peaks resulting from coordination of the acetate radical.

Mole ratio: 2 : 2 — sodium acetate added. ---- without ligand addition. Temp. 4°C.



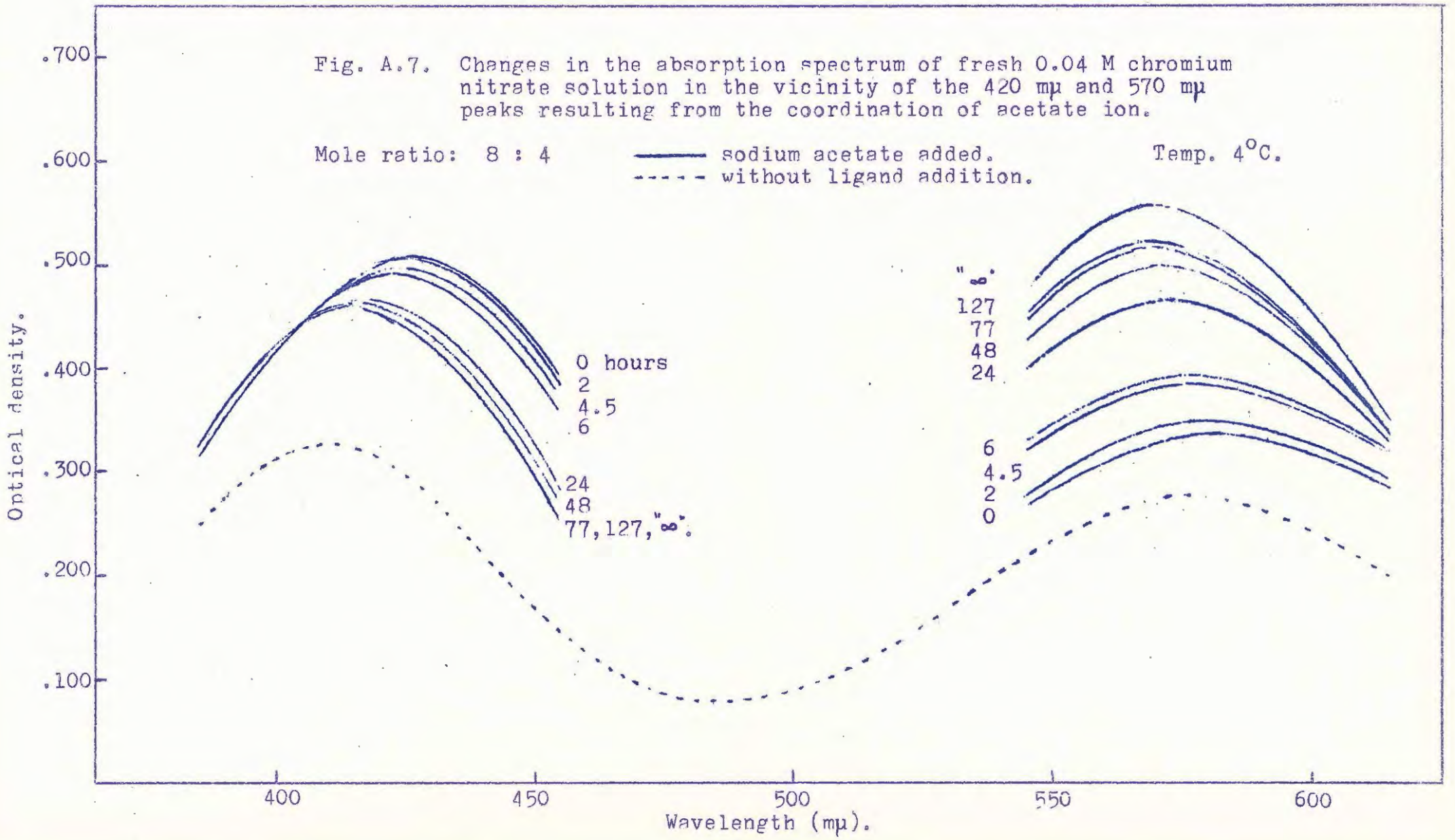


Fig. A.7. Changes in the absorption spectrum of fresh 0.04 M chromium nitrate solution in the vicinity of the 420 mμ and 570 mμ peaks resulting from the coordination of acetate ion.

Mole ratio: 8 : 4 ——— sodium acetate added. Temp. 4°C.
----- without ligand addition.

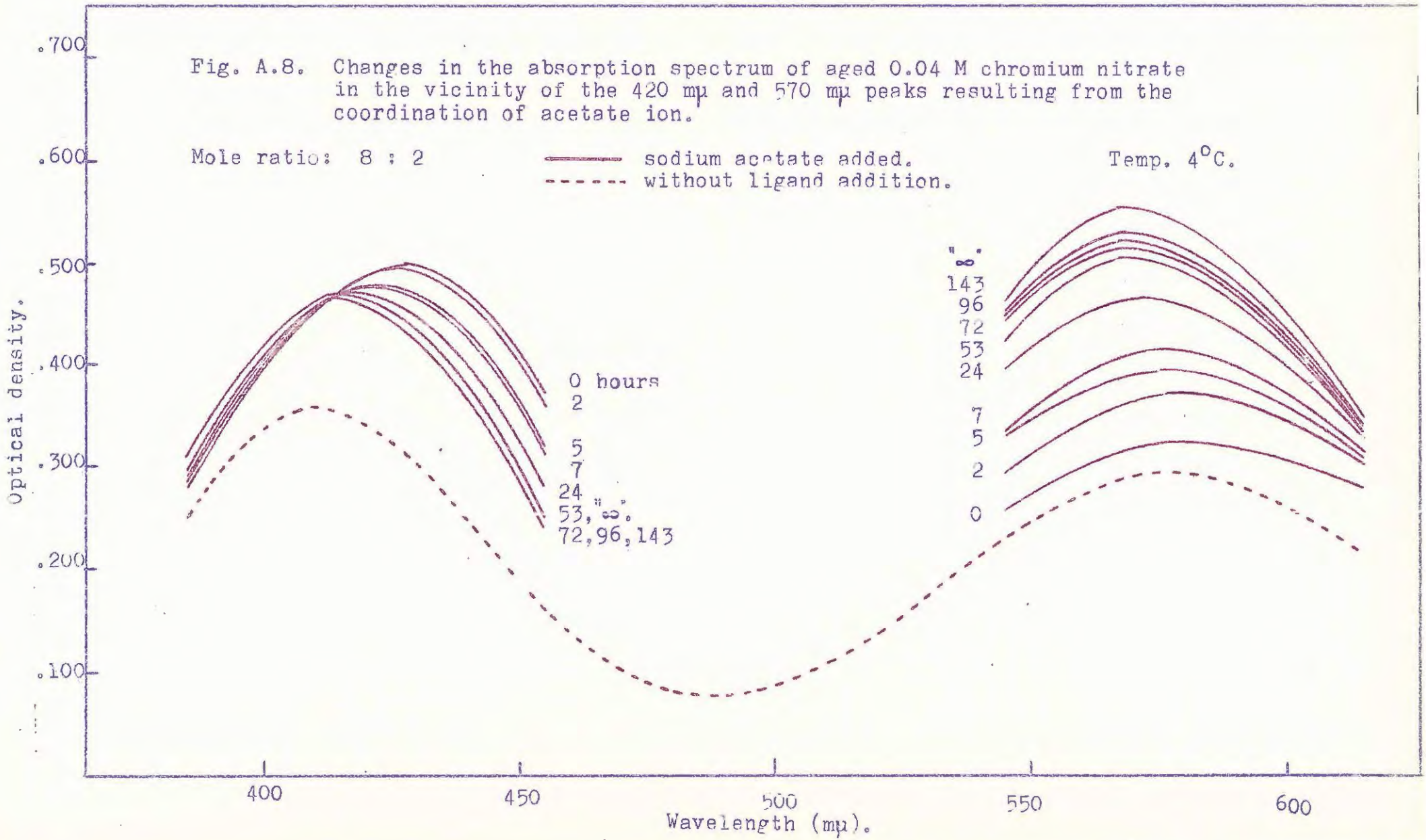
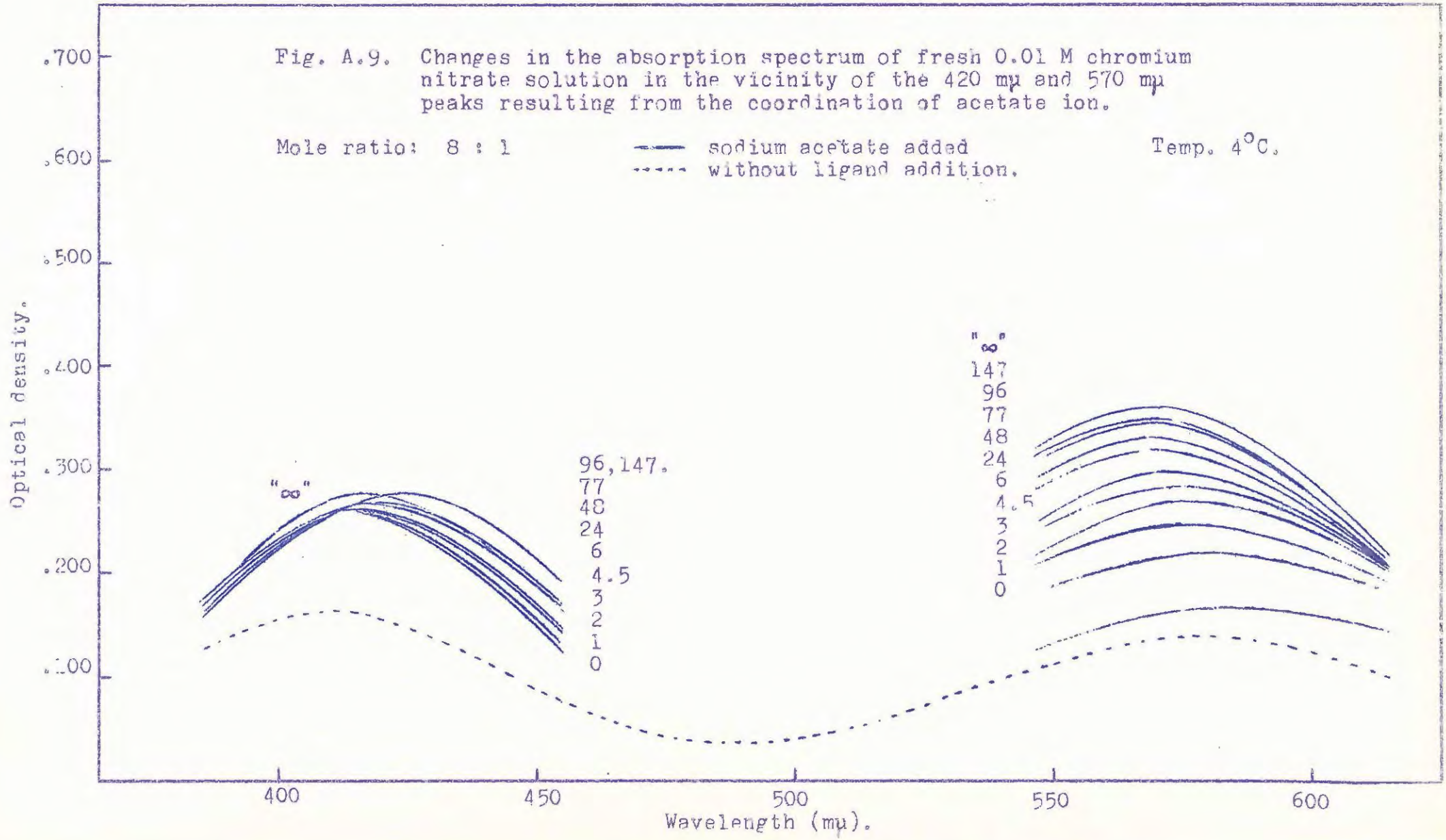


Fig. A.8. Changes in the absorption spectrum of aged 0.04 M chromium nitrate in the vicinity of the 420 mμ and 570 mμ peaks resulting from the coordination of acetate ion.
Mole ratio: 8 : 2
sodium acetate added.
without ligand addition.
Temp. 4°C.
Optical density.
.700
.600
.500
.400
.300
.200
.100
0 hours
2
5
7
24
53, "∞".
72, 96, 143
"∞".
143
96
72
53
24
7
5
2
0
400
450
500
550
600
Wavelength (mμ).

Fig. A.9. Changes in the absorption spectrum of fresh 0.01 M chromium nitrate solution in the vicinity of the 420 mμ and 570 mμ peaks resulting from the coordination of acetate ion.

Mole ratio: 8 : 1 — sodium acetate added ----- without ligand addition. Temp. 4°C.



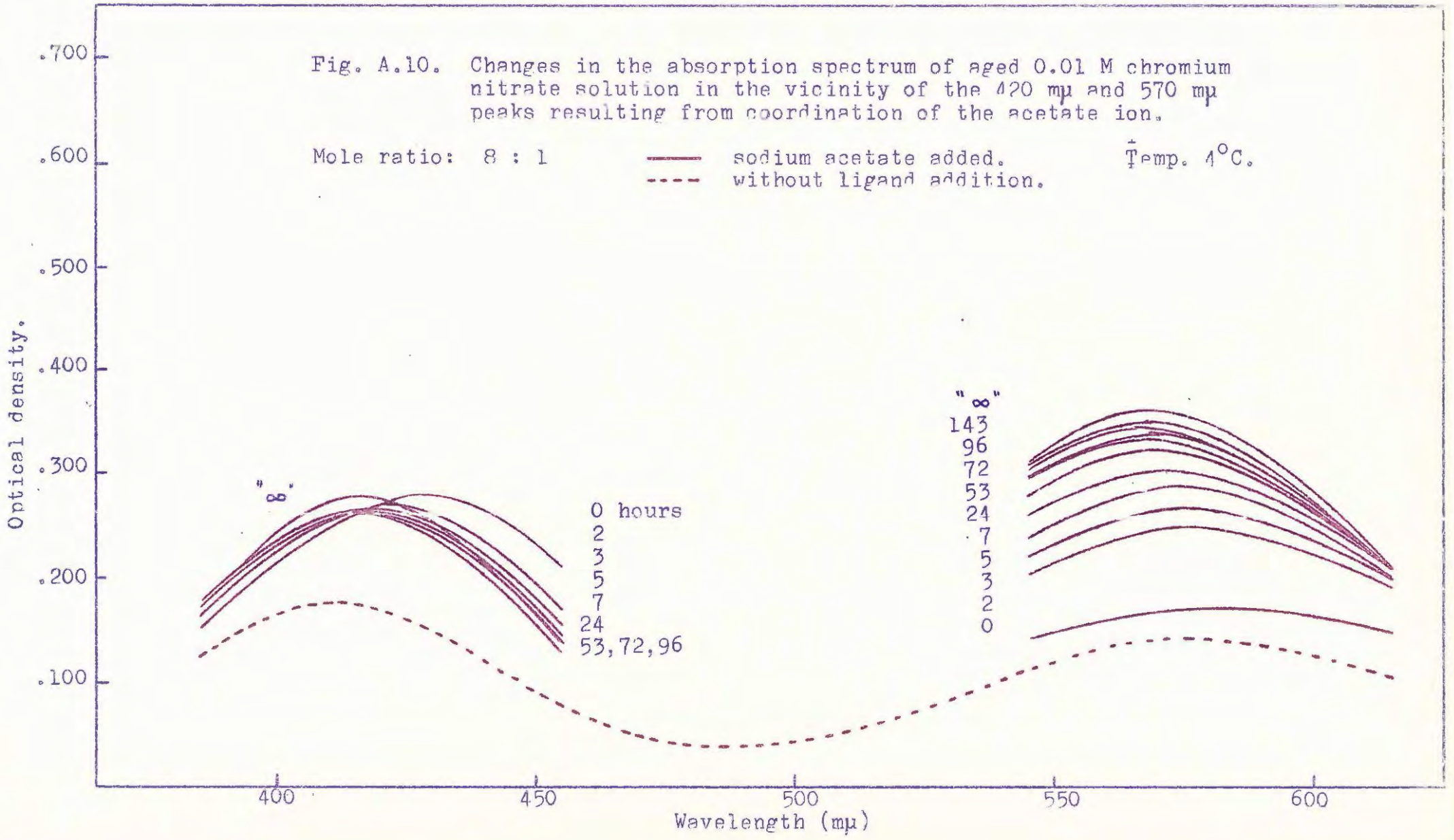


Fig. A.10. Changes in the absorption spectrum of aged 0.01 M chromium nitrate solution in the vicinity of the 420 mμ and 570 mμ peaks resulting from coordination of the acetate ion.
Mole ratio: 8 : 1
sodium acetate added.
without ligand addition.
Temp. 4°C.
Optical density.
.700
.600
.500
.400
.300
.200
.100
"∞"
0 hours
2
3
5
7
24
53,72,96
"∞"
143
96
72
53
24
7
5
3
2
0
400
450
500
550
600
Wavelength (mμ)

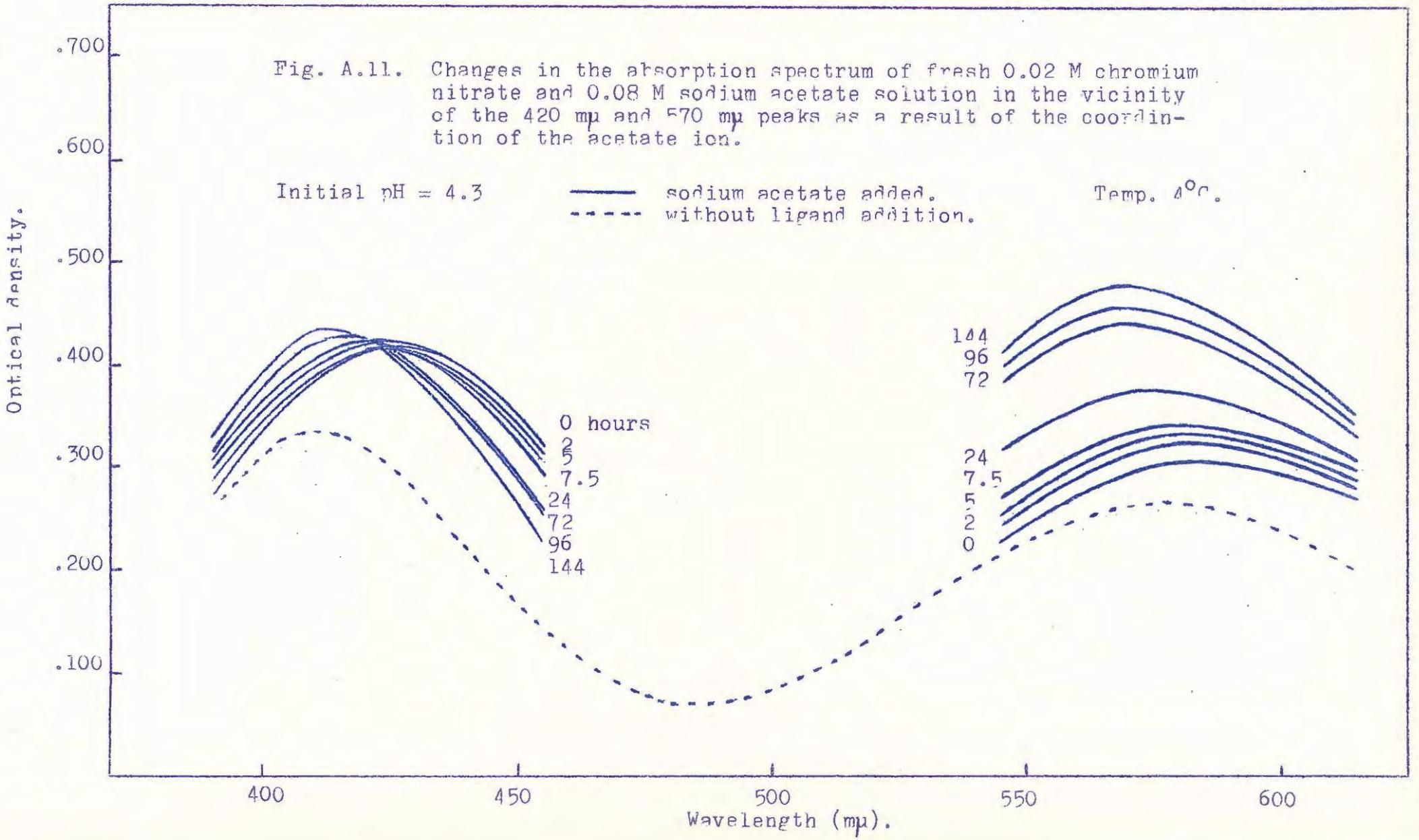
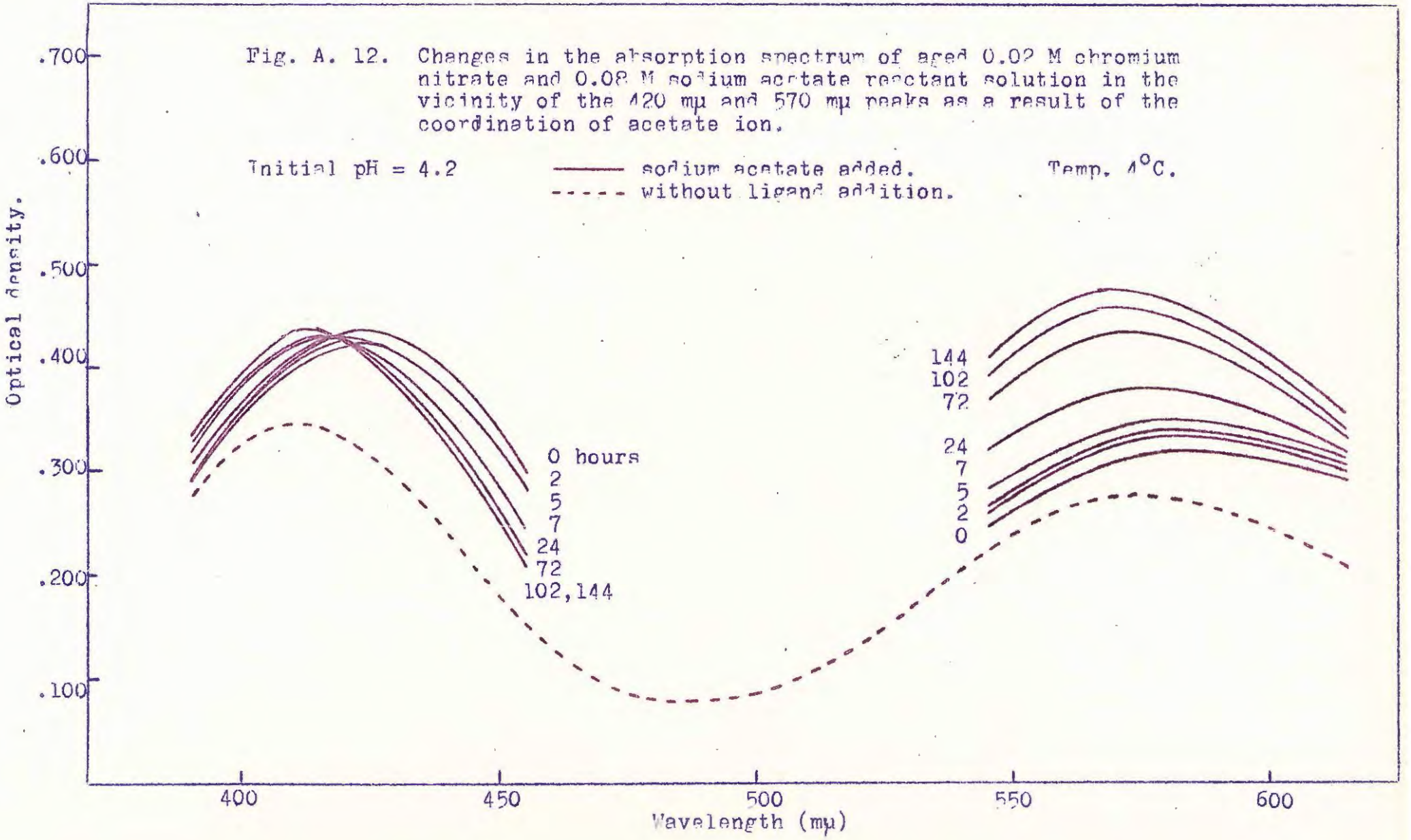


Fig. A.11. Changes in the absorption spectrum of fresh 0.02 M chromium nitrate and 0.08 M sodium acetate solution in the vicinity of the 420 mμ and 570 mμ peaks as a result of the coordination of the acetate ion.

Fig. A. 12. Changes in the absorption spectrum of aged 0.02 M chromium nitrate and 0.08 M sodium acetate reactant solution in the vicinity of the 420 mμ and 570 mμ peaks as a result of the coordination of acetate ion.

Initial pH = 4.2 —— sodium acetate added. Temp. 4°C.
----- without ligand addition.



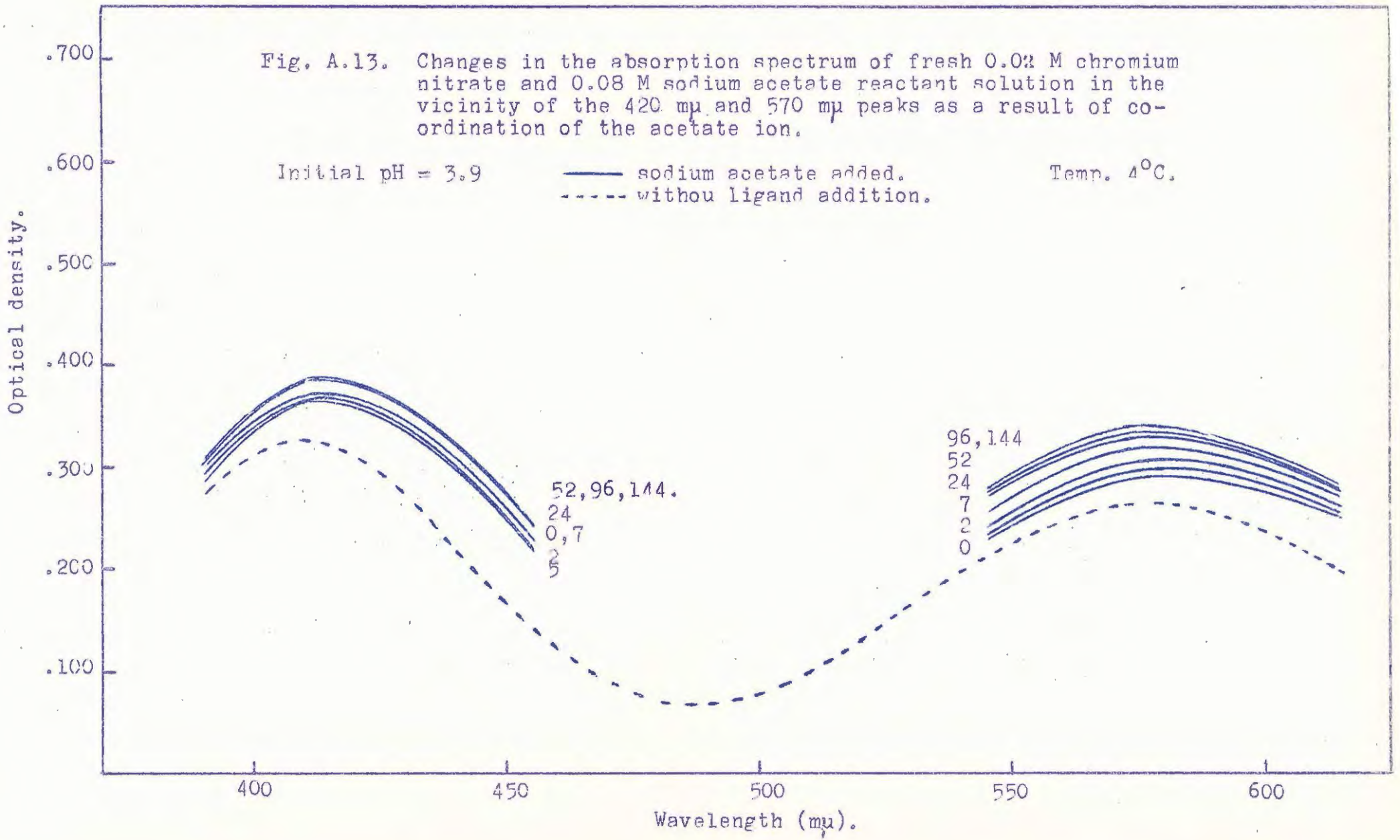
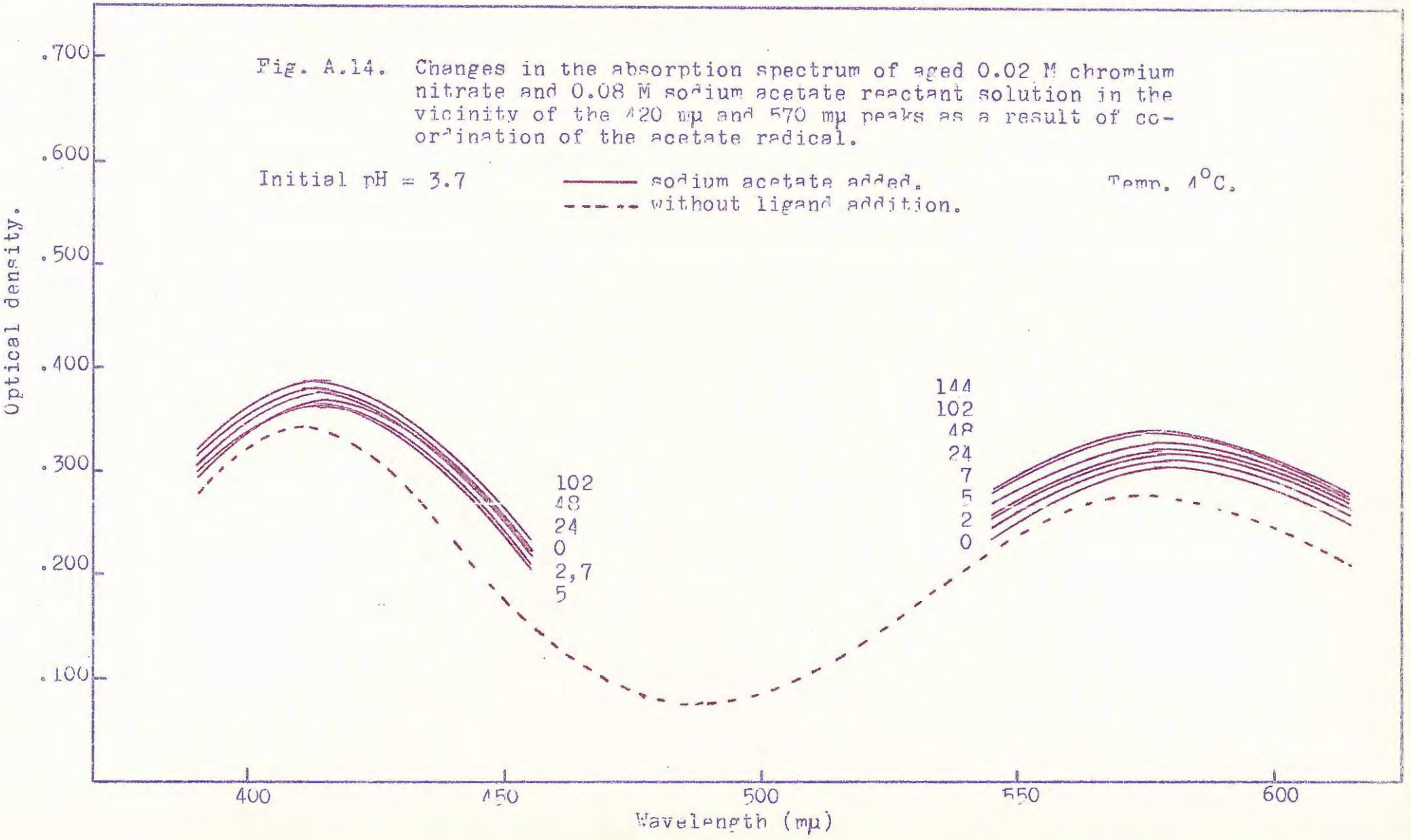


Fig. A.13. Changes in the absorption spectrum of fresh 0.02 M chromium nitrate and 0.08 M sodium acetate reactant solution in the vicinity of the 420 mμ and 570 mμ peaks as a result of co-ordination of the acetate ion.

Initial pH = 3.9 —— sodium acetate added. Temp. 4°C.
----- withou ligand addition.

Fig. A.14. Changes in the absorption spectrum of aged 0.02 M chromium nitrate and 0.08 M sodium acetate reactant solution in the vicinity of the 420 mμ and 570 mμ peaks as a result of co-ordination of the acetate radical.

Initial pH = 3.7 ——— sodium acetate added. Temp. 4°C.
- - - - - without ligand addition.



APPENDIX B.

Analysis Figures for the various Chromium Nitrate Solutions used in the Study.

Moisture Content of prepared Pelt as determined by the Official Method of the International Society of Leather Trades' Chemists [58].

(a) Solvent Extraction Studies:-

Mole Ratio Cr : Ac	Molarity	
	Fresh	Aged
2 : 8	0.0195	0.0196
2 : 4	0.0199	0.0199
2 : 2	0.0193	0.0198
1 : 8	0.00970	0.00976
4 : 8	0.0379	0.0379
2 : 8($\frac{1}{2}$)	0.0189	0.0190
2 : 8($\frac{3}{4}$)	0.0196	0.0195

(b) Spectrophotometric Studies:-

Mole Ratio Cr : Ac	Molarity	
	Fresh	Aged
2 : 8	0.0199	0.0199
2 : 4	0.0199	0.0199
2 : 2	0.0199	0.0199
1 : 8	0.0112	0.0113
4 : 8	0.0408	0.0408
2 : 8($\frac{1}{2}$)	0.0192	0.0194
2 : 8($\frac{3}{4}$)	0.0193	0.0194

(c) Hide Powder Studies:-

Mole Ratio Cr : Ac	Molarity	
	Fresh	Aged
2 : 8	0.0193	0.0193
2 : 4	0.0195	0.0192
2 : 2	0.0194	0.0193
1 : 8	0.00970	0.00962
4 : 8	0.0384	0.0384
2 : 8($\frac{1}{2}$)	0.0190	0.0190
2 : 8($\frac{3}{4}$)	0.0190	0.0191

(d) Pelt Piece Studies:-

Mole Ratio Cr : Ac	Molarity	
	Fresh	Aged
2 : 8	0.0195	0.0195
2 : 4	0.0196	0.0193
2 : 2	0.0196	0.0195
1 : 8	0.00994	0.00970
4 : 8	0.0391	0.0390
2 : 8($\frac{1}{2}$)	0.0188	0.0186
2 : 8($\frac{3}{4}$)	0.0204	0.0201

Figures in brackets above refer to ecuivalent amounts of acid added.

Moisture Content of prepared Pelt as Determined by the Official Method of the Society of Leather Trades' Chemists.(58)

Moisture Content	Mean
21.4 %	
21.2 %	21.1 %
20.7 %	

APPENDIX C.

Derivation of the classical first and second order rate expressions and the modified equations resulting in special cases of bimolecular reactions where:-

(a) both reactants are at the same concentration, and

(b) one reactant is present in excess.

FIRST ORDER REACTIONS.

This class of reaction is comprised of those processes whose rates are determined by the concentration of a single reactant species. The rate of removal of the reactant species at any instant is proportional to the concentration of the unreacted species at the same instant.

Mathematically,

$$-\frac{d(a - x)}{dt} = k(a - x)$$

where a = initial concentration
x = moles reacted
k = rate constant
t = time in hours

$$\therefore \quad \frac{dx}{dt} = k(a - x)$$

$$\therefore \quad \int \frac{dx}{a - x} = \int k.dt$$

$$\therefore \quad -\ln(a - x) = kt + c$$

When $t = 0$, $x = 0$; hence $c = -\ln a$.

$$\text{Thus } kt = \ln\frac{a}{a - x}$$

$$\text{or} \quad t = \frac{2.303}{k}\log a - \frac{2.303}{k}\log(a - x) \qquad (1)$$

In the case of a first order reaction, a plot of $\log(a - x)$ against time, t, yields a linear plot according to the expression (1) above. The proportionality constant, k, is referred to as the first order rate constant for the reaction.

SECOND ORDER REACTIONS.

This class of reactions is comprised of bimolecular processes in which the concentration of each reactant species is an operative factor in determining the reaction rate.

Mathematically,

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

where a and b are initial reactant concentrations of the species respectively, and the other symbols have the same significance as before.

$$\therefore \quad \frac{dx}{(a - x)(b - x)} = k.dt$$

The above expression is integrated by the method of partial fractions.

Let $$\frac{dx}{(a - x)(b - x)} = \frac{Adx}{a - x} + \frac{Bdx}{b - x}$$

Then $$\frac{1}{(a - x)(b - x)} = \frac{A}{a - x} + \frac{B}{b - x}$$

$$= \frac{A(b - x) + B(a - x)}{(a - x)(b - x)}$$

Equating the coefficients of x in the numerators of the expressions above, we have:-

$$0 = -A - B$$

$$\text{and } A = -B$$

Equating terms independent of x, we have:-

$$1 = Ab + Ba$$

Hence,

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

and

$$B = \frac{+1}{a - b}$$

Thus,

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

$$= \frac{1}{a - b}\left[+\ln(a - x) - \ln(b - x)\right]$$

$$\therefore \frac{1}{a - b} \ln \frac{a - x}{b - x} = \int k.dt$$

$$= kt + c$$

When $t = 0$, $x = 0$.

$$c = \frac{1}{a - b} \ln \left(\frac{a}{b}\right)$$

Hence,

$$k = \frac{1}{t(a - b)} \ln \frac{b(a - x)}{a(b - x)}$$

or

$$t = \frac{2.303}{k(a - b)} \log \frac{b}{a}$$

$$+ \frac{2.303}{k(a - b)} \log \frac{(a - x)}{(b - x)} \quad (2)$$

Hence in the case of second order reactions, a plot of the logarithm of the mole ratio of reactants remaining against time, yields a linear plot. The proportionality constant, k, is referred to as the second order rate constant for the reaction.

Special cases:

(a) Two reactants at equivalent concentrations.

When the concentrations of the two reactants are the same, equation (2) above cannot be applied directly. In this case we have:-

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

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

Hence $$\frac{1}{(a - x)} = kt + c$$

When $t = 0$, $x = 0$.

$$c = \frac{1}{a}$$

$$\therefore kt = \frac{1}{a - x} - \frac{1}{a} \qquad (3)a$$

$$\therefore t = \frac{1}{ka} \cdot \frac{x}{a - x} \qquad (3)b$$

From equation (3)a above, a plot of $\frac{1}{a - x}$ against time yields a linear plot in the case of a second order reaction.

(b) <u>One reactant present in excess</u>.

When one reactant species participating in a bimolecular reaction, is present in large excess, the normal second order rate equation (2) can be shown to reduce to a form similar to that for first order reactions (1). The reaction is then described as pseudo-unimolecular.

Suppose b is large in comparison with a and x so that

$$a - b = -b \quad \text{(approximately)}$$

and $$b - x = b \quad \text{(approximately)}$$

Equation (2) then becomes:-

$$t = \frac{2.303}{kb} \log \frac{a}{a - x} \qquad (4)$$

Since b is a constant (initial reactant concentration), the expression (4) above is analogous to expression (1) for first order reaction.