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The reaction of iodine with starch and the Schardinger dextrins

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NOTE TO USERS

THE REACTION OF IODINE WITH STARCH AND THE SCHARDINGER DEXTRINS

by

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I. INTRODUCTION

Recent advances in the study of the starch-iodine reaction have been due to the development of efficient methods of fractionation of starch. It has been shown that starch can be separated into a straight-chain fraction and a branched-chain fraction and that the straight-chain fraction is responsible for the formation of the blue complex with iodine. As a result, the helical theory of starch has been revised and given additional significance.

The interpretation of the type of bonding between iodine and the straight-chain fraction of starch has been made by employing the helical structure. The iodine is held in a position along the axis of the helix by the interaction of dipole-induced dipole forces. A knowledge of the binding energy of the complex is important as an experimental verification of the helical theory, since it is possible to calculate, at least approximately, the theoretical value of the binding energy of a dipole-induced dipole bond.

Measurement of the binding energy of the starch-iodine complex has been attempted in the present work by the use of the iodine electrode. The activity of the iodine and the amount of iodine bound by the amylose have been determined from the potential of the iodine electrode in the presence

of an amylose solution.

This study of the amylose-iodine reaction has been aided by a study of the complexes produced by the reaction of iodine and the Schardinger dextrins. The ring structure of these dextrins makes it likely that the reaction-mechanism for the formation of iodine complexes is very similar to that proposed for the starch-iodine complex. The results obtained with the Schardinger dextrins can be applied to the interpretation of the reaction between amylose and iodine.

II. HISTORICAL

A. Starch-Iodine Complex

The first mention of the starch-iodine complex was made by Colin and de Claubry in 1814 (1). They reported the formation of a violet to blue-black material produced by the action of iodine on starch. The substance was soluble in water and gave an intensely blue solution which was rapidly decolorized by boiling. This was confirmed by Stromeyer in 1815 (2).

The starch-iodine reaction received some attention during the period from 1840 to 1860. The conditions necessary for the formation of the complex and the effect of heat on the complex were the main points of interest.

In 1861 Schoenheim (3) stated that the starch-iodine complex was a definite chemical compound. This idea was disputed by Duclaux (4) who argued that the formation of the starch-iodine complex was due merely to a type of molecular adhesion between the iodine and the starch, since the material did not have a constant composition. The ideas of chemical binding were still very vague at that time, and it is questionable that there was any real difference between their views. The criterion of compound formation during this

period appears to have been constant composition. On the basis of this criterion, Duclaux's view was the more correct interpretation of the experimental results. Undoubtedly, Schoenheim was basing his views on speculative thinking. Nevertheless each received considerable support.

Since all the work previous to 1935 was done with whole starch, whose amylose content varied with the source, the amount of iodine bound by starch varied over a very wide range. The interference of iodide ions and other electrolytes only added to the difficulty of interpreting the experimental results gathered previous to this date.

Few papers which can be considered important in view of present knowledge of the starch-iodine reaction appeared during this period. In 1885 Dafert reported finding a starch which colored red-brown upon reaction with iodine solution and one which colored pure red (5,6). In 1889 Shimoyama (7) prepared a starch from glutinous rice which gave a red color upon treatment with iodine. These were important forerunners to the later development of the waxy strains of various plants. In 1895 Meyer listed several plants which produced this red-staining starch (8).

The contention that starch-iodine is an adsorption compound gained favor in the period from 1900 to 1920 with the strong support of Lottermoser (9) and Biltz (10). Lottermoser based his arguments on the results of his potentiometric

titration of starch with iodine. He was able to interpret his results on the basis of a typical Freundlich adsorption isotherm.

In 1925 Murray (11) performed essentially the same set of experiments as Lottermoser but with greater accuracy. He interpreted his results as indicating definite compound formation between iodine and starch.

Recent work on the starch-iodine complex has been aided by the development of the two-component theory and efficient methods of separating the straight-chain fraction from the branched-chain fraction of starch.

B. Fractionation of Starch

The early methods of fractionation of starch produced fractions which were mixtures of branched- and straight-chain molecules. The results were not reproducible largely because of a lack of methods capable of determining the efficiency of separation and of characterizing the fractions obtained. This work previous to 1927 is summarized by Samec (12).

The application of methylation techniques to the problem of characterizing the starch components was successfully made by Meyer and his co-workers (13, 14, 15). The method they used to fractionate the starch consisted essentially of a hot water extraction of the starch followed by retrogradation[1] of the soluble fraction. They were able to show

[1] A slow aggregation of starch particles to form an insoluble microcrystalline precipitate.

that the soluble fraction consisted of straight-chain molecules, since the number of end groups obtained by methylation studies corresponded to the molecular weight determined by osmotic pressure measurements on the acetylated material. This method of fractionation was inefficient in respect to the amount of straight-chain fraction (amylose) removed from the starch, but the degree of purity of the amylose obtained appears to have been high.

A more satisfactory method of fractionation was later reported by Schoch (16). His method consisted of autoclaving a dilute suspension of starch and precipitating the amylose fraction with butanol. The amylose obtained consisted of small, strongly birefringent spherocrystals. Schoch's method produced a nearly quantitative separation of the amylose and amylopectin.

By a combination of Meyer's hot water extraction and precipitation of the extracted amylose with butanol, Kerr (17) obtained very regular crystals which have been shown to consist of shorter chains of amylose remarkably free from amylopectin (18).

Recently Whistler and Hilbert (19) have replaced the butanol in Schoch's procedure with mononitro derivatives of ethane and propane. The fractions obtained were characterized by the potentiometric iodine titration. The amylose fraction was reported to be as pure as that obtained with butanol.

Quantitative work was reported for only the above compounds, but the authors reveal that several compounds are capable of selectively precipitating the amylose fraction of starch. The following compounds were mentioned specifically: nitrobenzene, amyl acetate, methyl ethyl ketone, butyric acid, butyl mercaptan, and pyridine. In an earlier publication Bear (20) has shown that several such compounds are capable of producing the "V" modification.

Bates (21) succeeded in showing that phenol and aniline are also capable of selectively precipitating the amylose fraction of starch. His results indicate that phenol is as efficient as butanol and that aniline is about one-fourth as efficient as butanol in regard to the purity of amylose obtained.

Currently, mixed solvents are being used as fractionating agents with considerable success. The development of the potentiometric method of analysis has greatly aided the evaluation of new fractionating methods.

C. Electrometric Method

The quantitative relation between iodine and starch has been the object of numerous investigations. Walton (22) gives a comprehensive bibliography of the work up to 1928. With the development of Schoch's fractionation procedure (16),

the study has been concentrated on the butanol-precipitated or amylose fraction. By spectrophotometric titrations, Baldwin (23) has been able to show that the amount of iodine taken up by amylose is dependent upon the concentration of the iodide ion and decreases with increasing iodide concentration. By extrapolating the experimental values to zero iodide concentration, he obtained a ratio of six glucose residues per molecule of iodine at zero iodide concentration.

The iodine electrode has been used by several workers to study the iodine reaction. In 1921 Lottermoser (9) used the iodine electrode in conjunction with studies on the distribution of iodine between aqueous solutions of starch and carbon tetrachloride. He concluded from his measurements that the amount of iodine taken up by the starch obeys the Freundlich adsorption isotherm. He corrected for the formation of triiodide ion and assumed that the iodide ion was not absorbed by the starch, an assumption not in agreement with the conclusions he attempted to reach for the starch-iodine complex.

In 1925 Murray (11) repeated Lottermoser's work with greater accuracy, taking into account the formation of triiodide ion as well as the formation of iodide ion by the hydrolysis of iodine and by reduction of iodine by starch. His experiments were performed on solutions of corn starch obtained by boiling starch in one-tenth normal sulfuric

acid for one minute. He interpreted his results in terms of definite compound formation between starch and iodine and obtained the following formula for the complex:

$$\left[(C_6H_{10}O_5)_{15}I_5^-\right]^-$$

This is roughly two atoms of iodine for every six glucose residues, in excellent agreement with Baldwin's results.

The iodine electrode was used by Bates (21) to study the reaction of the amylose and amylopectin fractions. In his experiments, a solution of the starch fractions was titrated with iodine solution, and the potential of the iodine electrode against the normal calomel electrode was measured after each addition of iodine. The concentration of iodide ion was kept constant during the addition of iodine. He showed that the titration of amylose occurs in three steps. The initial addition of iodine increases the activity of the iodine in solution up to a certain activity. At this point the iodine reacts with the amylose, and the activity remains fairly constant until sufficient iodine has been added to react with the amylose. The activity then rises and approaches the value obtained if the titration is carried out in the absence of the amylose. In the titration of amylopectin, the activity increases uniformly and rapidly to a much higher activity than is obtained during the

titration of amylose. Bates did not attempt a quantitative explanation of the reaction but developed the iodine titration as a method of analysis for the per cent of amylose present in whole starch and for purity of amylose preparations.

The potential at the midpoint of the titration, which Bates called the characteristic potential, depends upon the chain length of amylose used. The characteristic potential decreases with increasing chain length of amylose. Foster (24) has been able to show that if the iodine molecules are considered as linear harmonic oscillators, the characteristic potential can be related to chain length by an expression of the type:

$$E = A + B\frac{1}{\sqrt{n}}$$

where n is the number of glucose residues and A and B are constants.

The characteristic potential increases with decreasing iodide concentration and with decreasing concentration of amylose. No further quantitative interpretation of the starch-iodine reaction has been attempted; however, the development of the helical theory has been a great aid in the study of the starch-iodine reaction.

D. Development of the Helical Theory

In 1937 Hanes (25) pointed out that dextrins containing less than six glucose residues are incapable of producing

the characteristic color when treated with iodine. This fact together with certain peculiarities in the action of alpha amylase on starch led him to postulate a helical structure for the starch molecule, with a periodicity of six glucose residues along the length of the helix.

Freudenberg and his co-workers (26) developed this idea and, by constructing a space model of a straight-chain molecule consisting of α-1,4 glucosidic units, showed that it was sterically possible to form such a helix without excessive strain. The model showed that the inside of the helix contains only C-H groupings and is large enough to accommodate the iodine molecule. They postulated that the iodine enters the helix and acquires the characteristic blue color because of the hydrocarbon-like surroundings. This color change, they believed, is similar to the color change which occurs in the transition of iodine from an aqueous solution to a non-polar solvent.

In 1941 Meyer (27) disputed Freudenberg's assumption on the grounds that it did not account for the reaction of iodine with certain acetals, methyl cellulose, and polyvinyl alcohols. These compounds are colored by the action of iodine, and it is generally considered that these compounds do not form helices. Since these compounds form colloidal micelles in solution, Meyer suggested that the starch molecules are also present as micelles in solution and are

essentially linear. The iodine molecule fits into the interstitial space between these starch molecules, and the color is due to action of secondary forces on the iodine molecule producing a shift in the adsorption spectra of the iodine.

In 1943 Rundle and Baldwin (28) reported studies on the dichroism of flow of starch pastes stained with iodine. They showed that it was possible to obtain dichroism of flow with the amylose or butanol-precipitated fraction obtained in Schoch's procedure but not with the amylopectin fraction. Dichroism of flow of the amylose-iodine complex indicates that the iodine molecules are aligned parallel to the flow lines in the flowing liquid. The iodine molecules themselves are not large enough to become appreciably oriented under the shearing forces experimentally available. If amylose molecules are considered as ellipsoids of revolution, with one axis considerably larger than the other two, the amylose molecule itself is oriented with the larger axis parallel to the flow lines, and the iodine molecules are oriented along the larger axis. In contrast, little or no orientation is observed with the amylopectin molecule. The orientation of the iodine molecules along the length of the amylose molecule can take place whether the amylose is considered as a straight-chain molecule or as a helical molecule.

In a later paper Rundle and French (29) reported the

optical properties of crystalline amylose prepared according to the directions given by Kerr (17). They showed that the light with its electric vector parallel to the surface of the platelet of the crystal was more strongly absorbed than light with its electric vector normal to the surface. The crystals absorbed iodine vapor without changing the crystal structure, and the complex so formed absorbed light with its electric vector prependicular to the surface of the platelet more strongly than the light with its electric vector parallel to the surface of the platelet. These results are incompatible with a straight-chain structure. The iodine molecules must be aligned along the greatest length of the amylose molecule, but the greatest polarizability of the amylose molecule is perpendicular to this direction. This is true if the amylose is coiled around the iodine molecules.

Further evidence to substantiate the helical hypothesis was given by Rundle and Edwards (30). From x-ray diffraction patterns, they concluded that the amylose-butanol complex precipitated in an orthorhombic cell with symmetry characteristics represented by the space group, $P2_12_12_1$. The symmetry requirements for this space group and the unit cell dimensions are met by close-packed helices alternating in direction, as suggested by Bear (20). The diagrams obtained were very similar to those obtained by Katz (31) and designated as the "V" modification.

The structure of the "B" modification has been determined by Rundle, Daasch and French (32). This modification is present in native granules and consists of linearly extended chains of glucose residues. They suggest that the relative positions of the primary alcohol group are characteristic of the different modifications. In the "B" modification, these groups are trans to each other, and in the "V" modification, they are cis.

As Rundle and his co-workers point out (33), the helical or "V" modification is not present in solution but is formed by the addition of a precipitating agent such as butanol or iodine.

The nature of the interaction between iodine and amylose has been discussed by Rundle, Foster and Baldwin (33). They postulate a dipole-induced dipole force holding the iodine molecules within the helix. The iodine molecules reinforce one another through the interaction of their induced dipoles. In this manner the longer chains of iodine molecules are more strongly bound; as a result, the absorption spectra of the complex shifts toward the red with increasing chain length of the amylose molecule (23), and the escaping tendency of the iodine decreases with increasing chain length (18).

The similarity of the colored products obtained by the action of iodine on polyvinyl alcohol and similar compounds

can be explained without recourse to a helical structure but by employing the dipole-induced dipole interaction used to explain the stability of the starch-iodine complex (34). Amylose differs from these compounds in that the iodine addition product is formed in solution, and in solution the orientation of dipoles required to produce the necessary dipole field is accomplished by the formation of a helix.

The helical theory can explain the experimental behavior of amylose with certain organic complexing agents as well as the formation of the amylose-iodine complex. The development of the helical theory has brought about a more rapid interpretation of the nature of the amylose complexes.

E. Schardinger Dextrins

The present work on the starch-iodine reaction has led to the consideration of the interaction of iodine and the Schardinger dextrins. Since these molecules have a cyclic structure, it is conceivable that their reaction with iodine is similar to the reaction of amylose with iodine. The molecular weights of the Schardinger dextrins are known, and the reaction with iodine is more easily interpreted than the reaction of iodine and amylose. The results obtained with these materials can be applied to the interpretation of the nature of the starch-iodine reaction.

In 1909 F. Schardinger reported the preparation of crystalline dextrins by the action of B. macerans on a starch suspension (35-a, 35-b).[1] Schardinger succeeded in isolating three fractions from his fermentation mixture: a soluble fraction, which he called alpha-dextrin; a slightly soluble fraction, which he called beta-dextrin; and an insoluble residue, which he called "Schlamm". He was able to show that the alpha- and the beta-dextrins do not reduce Fehling's solution and are not fermentable by yeast.

The fact that Schardinger's alpha-dextrin is capable of existing in several different crystalline modifications (37), in conjunction with unsatisfactory separation procedures, resulted in a great deal of confusion and conflicting reports as to the exact nature of these materials. In 1935 Freudenberg and Jacobi (38) organized the chemistry of the Schardinger dextrins by developing a satisfactory procedure for separating the dextrins through a fractional crystallization of the dextrins and their acetates. They were able to separate the enzymolysis mixture into five fractions: the alpha-dextrin and the beta-dextrin, corresponding to the compounds originally identified by Schardinger, and three new fractions,

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[1] It is interesting to note that in 1893 F. Villiers (36) reported isolating, from the product of the action of butyric ferment on starch, a material which was undoubtedly the Schardinger dextrin. The preparation of the Schardinger dextrins had also previously been reported by Schardinger in 1903 (35-c).

which they designated as gamma, delta and epsilon dextrins. They succeeded in characterizing these five dextrins and obtained the molecular weights of the alpha- and the beta-dextrins, from the freezing point depressions of the acetates in camphor, corresponding to five and six glucose residues respectively. The molecular weight of alpha-dextrin was substantiated by Kratky and Schneidmesser (39) who determined the molecular weight by x-ray diffraction studies; however, their results were later shown to be in error (40).

In 1938 Freudenberg (41) obtained 2,3,6-trimethyl glucose as the sole product from the hydrolysis of completely methylated dextrins and suggested a cyclic structure of five and six glucose residues connected by α-1,4 glucosidic bonds, for alpha-dextrin and beta-dextrin respectively.

Using x-ray diffraction methods, French and Rundle (40) were able to show that the molecular weights of alpha- and beta-dextrins correspond to six and seven glucose residues respectively. On the basis of the cyclic structure, the symmetry requirements of the space group assigned to the crystal structure by Kratky are not possible with five-membered rings. French and Rundle proposed the name cyclohexaamylose for alpha-dextrin and cycloheptaamylose for the beta-dextrin as being more descriptive of the structures.

French (42) prepared five crystalline modifications of cyclohexaamylose. From one of these modifications he concluded that the cyclohexaamylose ring has a molecular

packing diameter of 13.84 Å and a packing thickness of 8.3 Å.

The iodine-potassium iodide addition products of cyclohexaamylose were also studied by French (42). He obtained three distinct modifications by varying the concentrations of iodine and potassium iodide in the solution from which they were precipitated. The modifications differed in potassium iodide content while the ratio of iodine to cyclohexaamylose remained constant.

In the present work the potentiometric titration used to study the starch-iodine complex was applied to the study of the iodine-iodide complexes of alpha- and beta-dextrins in solution.

III. EXPERIMENTAL DETAILS

A. Development of the Method

A modification of the titration procedure of Bates, French and Rundle (18) was used in this investigation. In place of the calomel electrode, a second iodine electrode was used as the reference electrode. The cell is represented thus:

$$(Pt),\ I_2(c_1),\ I^-(m_1),\ \underline{A}\ :\ I^-(m_2),\ I_2(c_2),\ (Pt).$$

This is essentially a concentration cell without transference, and the electromotive force is related to the activity of iodine and iodide by the following expression:

$$E = \frac{RT}{2F} \ln \frac{[I_2]_1 [I^-]_2^2}{[I^-]_1^2 [I_2]_2} .$$

The theory of concentration cells has been reviewed by MacInnes (43).

The titrations were performed in two three-neck flasks, equipped with stirrers and connected by a salt bridge of saturated potassium chloride solution in 3% agar. The iodine electrodes consisted of bright platinum wire fused into soft glass tubing. The flasks were submerged in a constant-temperature water bath to a point just below the

openings of the flasks.

The potential of the cell was measured with a Leeds and Northrup Type K potentiometer in conjunction with a galvanometer capable of showing differences of 0.1 millivolt.

B. Preparation of Materials

The Schardinger dextrins were prepared by M. Levine of this laboratory by the action of the enzyme of B. macerans, prepared according to the directions given by Tilden and Hudson (44), on a suspension of potato starch. The cyclohexaamylose and the cycloheptaamylose were separated according to the directions of Freudenberg and Jacobi (38). The Schardinger dextrins thus prepared were substantially free from carbohydrate impurities. No attempt was made to dry the samples thoroughly. The dextrins were air-dried and the samples were weighed. The amount of the dextrins present in the samples was determined from the rotation values in distilled water. The values of the specific rotation were taken from McClenahan (45), who obtained specific rotations, on carefully purified dextrins, of $+150.5 \pm 0.5^{\circ}$ for cyclohexaamylose and $+ 162.5 \pm 0.5^{\circ}$ for the cycloheptaamylose. These results were duplicated on carefully dried samples of the dextrins used.

The amylose used was supplied by Corn Products Refining

Company and was prepared by them according to the directions of Schoch (16). The material was recrystallized three times, and upon analysis by the method of Bates, French and Rundle (13), was found to contain an immeasurably small amount of branched molecules.

C. Titration of Cyclohexaamylose

The initial titrations of cyclohexaamylose were carried out at a constant iodide level. A weighed amount of dextrin was dissolved in a small amount of distilled water, and enough potassium iodide solution was added to bring the concentration of potassium iodide in the final solution to the desired value. The solution was diluted to 200.0 milliliters and was placed in one of the three-neck flasks. An equal volume of potassium iodide solution of the same concentration was placed in the other flask. Small, equal, measured volumes of a solution of iodine of known iodine concentration were added to each half-cell, and the potential of the system was measured after each addition. The addition of iodine was continued until the amount of iodine bound reached a constant value. In order to maintain a constant iodide level, the concentration of iodide ion in the iodine solution was the same as the concentration of iodide ion in the half-cells. During the titration, the potential of the system reached a

constant value within one minute after the addition of iodine solution.

The titrations were carried out at iodide ion concentrations of 0.01, 0.10 and 1.00 molar, and at cyclohexaamylose concentrations of 0.873 and 1.75 milligrams per milliliter. The results are given in Tables 1, 2, 3, and 4. The weights of cyclohexaamylose given in the tables have been corrected to dry weight. The method of calculating the amount of iodine bound by the cyclohexaamylose will be given in the following section.

The effect of iodide ion was determined on a solution obtained by dissolving 174.6 milligrams of cyclohexaamylose in a small amount of water containing 9.564×10^{-2} millimols of iodine and 0.20 millimols of potassium iodide and by diluting the resulting solution to 200.0 milliliters. This solution was placed in one of the half-cells, and the same volume of a solution containing the same amount of iodine and potassium iodide was placed in the other half-cell. Equal volumes of a solution of potassium iodide were added to each half-cell, and the potential was measured after each addition. During the first half of the titration, dilute solutions of potassium iodide were added; however, toward the end of the titration, it became necessary to add more concentrated solutions. This was done to keep the volumes of iodide added small but large enough to be measured with

the accuracy desired. The results are shown in Table 5.

The effect of temperature on the titration of cyclohexaamylose was studied. The potential of a half-cell, containing 174.1 milligrams of cyclohexaamylose, 2.20 millimols of potassium iodide and 9.564×10^{-2} millimols of iodine, dissolved in 220.0 milliliters of solution, was measured at various temperatures. The results are given in Table 6.

D. Titration of Cycloheptaamylose

The titrations of cycloheptaamylose with iodine were carried out in the same manner as the titrations of cyclohexaamylose. The titrations were carried out at 0.010, 0.100 and 1.00 molar potassium iodide. The results are given in Tables 7, 8 and 9. The weights given have been corrected to dry weight. In the titration carried out at 1.00 molar potassium iodide, a dark brown precipitate was formed.

The effect of potassium iodide on the formation of the complex was studied by the titration of a solution of cycloheptaamylose with potassium iodide performed in the same manner as the titration of cyclohexaamylose. The results are given in Table 10.

E. Titration of Amylose

An accurately weighed amount of amylose was dissolved in several milliliters of normal potassium hydroxide solution. When the solution was complete, the potassium hydroxide was neutralized with iodine-free hydriodic acid and diluted to one liter. An aliquot fraction of this solution was removed, a known amount of potassium iodide solution was added, and the resulting solution was diluted to 200.0 milliliters. The amount of potassium iodide solution and amylose solution used depended upon the concentrations desired for the titration. This solution was placed in one half-cell. The other half-cell was filled with 200.0 milliliters of a potassium iodide solution of the same concentration as the solution containing the amylose. The titrations were then carried out in the same manner as the titrations of cyclohexaamylose. The time allowed between the addition of the iodine solution and the measurement of the electromotive force depended upon the temperature. Five minutes was sufficient at room temperature, but fifteen to twenty minutes was required at zero degrees before the potential became constant.

The titrations were carried out at potassium iodide concentrations of 0.100, 0.050 and 0.025 molar and at several amylose concentrations. The results obtained at 25° C. are

given in Tables 11 through 19; at 0° C., in Tables 20 through 29; at 50° C., in Tables 30 through 39.

The effect of iodide ion was determined by titrating, with KI, a solution of amylose containing half the theoretical amount of iodine necessary to form the complex. The titration was carried out in the same manner as the titration of cyclohexaamylose. The solution of amylose used for this titration was prepared in the same manner as the solutions used for the titrations with iodine. The solution placed in the half-cell contained 100.0 milligrams of amylose, 5.11×10^{-2} millimols of iodine and 1.53 millimols of potassium iodide. The results are given in Table 40.

The effect of temperature on the reaction was determined by measuring, at different temperatures, the potential of a system containing amylose and approximately one-third of the theoretical amount of iodine necessary to form the complex.

The solution used contained 100.0 milligrams of corn amylose in 200.0 milliliters of solution 0.05 molar with respect to potassium iodide. This was placed in one half-cell, and 200.0 milliliters of 0.05 molar potassium iodide solution were placed in the other half-cell. 5.00 milliliters of a solution of 0.00500 molar iodine in 0.050 molar potassium iodide were added to each half-cell. The temperature of the system was varied in ten-degree intervals, and the potential was measured at each temperature. The potential was measured

after sufficient time had elapsed for the system to reach equilibrium as indicated by a constant E. M. F. over a period of five minutes. The results are given in Table 41. The complex started to decolorize visibly at 76° C. and became completely colorless at 81° C. The color did not return upon cooling.

F. Reaction of Cyclohexaamylose and Iodine

The distribution of iodine between toluene and a solution of cyclohexaamylose in water was determined in order to obtain the equilibrium constant for the reaction

$$\alpha + I_2 \rightarrow \alpha I_2.$$

50.0 milliliters of a solution of iodine in toluene were placed in a glass-stoppered flask, and 50.0 milliliters of a solution containing cyclohexaamylose were added. The flask was shaken and allowed to stand for from forty-eight to sixty hours with occasional shaking. The concentration of free iodine in the water layer is fixed by the distribution coefficient of iodine between the water and toluene. This was determined by using the same volumes of solution, the same concentration of iodine as above and by allowing the system to stand for the same length of time. At the end of this time, a 10.0-milliliter sample of the water layer was

withdrawn and titrated with a standard sodium thiosulfate solution. The difference in the amount of iodine present in the solution of cyclohexaamylose and in the water was the amount bound by the cyclohexaamylose. The amount of iodine withdrawn from the toluene layer by the cyclohexaamylose solution was small and did not change the concentration of iodine in the toluene to any appreciable extent. The results are shown in Table 42.

G. Analysis of the Precipitated Complex of Cycloheptaamylose

The complex precipitated during the titration of cycloheptaamylose at 1.0 molar potassium iodide concentration was filtered, dried and analyzed.

The iodine was determined by weighing approximately 100.0 milligrams of the complex, adding an excess of standard sodium thiosulfate to the sample, and by allowing the sample to stand until completely dissolved and decolorized. The excess sodium thiosulfate was then titrated with standard iodine solution.

The amount of cycloheptaamylose was determined by weighing approximately 500 milligrams of sample, dissolving in 10.0 milliliters of distilled water, and by adding a crystal or two of sodium thiosulfate until the sample was completely

decolorized. The solution was then diluted to 25.0 milliliters, placed in a 4-decimeter tube and the rotation was read with a Schmidt and Haensch polarimeter. The amount of cycloheptaamylose was then calculated from the value of the specific rotation of 162.5°, given by McClenahan (45).

The amount of potassium iodide was determined by weighing approximately 0.2 gram of the sample into a weighed porcelain crucible and by ashing the sample at 550° C. in a muffle furnace for two hours. The weight of the remaining ash was taken as the weight of the potassium iodide in the sample.

The results of the analysis of the sample obtained during the titration at 1.0 molar potassium iodide concentration are given in columns 1 and 2 of Table 43.

Samples of the complex were prepared by adding a concentrated solution of iodine in potassium iodide to a solution of cycloheptaamylose. These samples were analyzed, and the results are given in columns 3 and 4 of Table 43. One of the samples prepared in this manner was recrystallized three times from distilled water, and the material was reanalyzed. The analysis before recrystallization is given in column 4 of Table 43, and the analysis after recrystallization is given in column 5 of Table 43.

IV. RESULTS AND DISCUSSION

A. Cyclohexaamylose-Iodine Complex

The activity of iodine in the left half-cell of the system

(Pt), $I_2(c_1)$, $I^-(m_1)$, alpha-dextrin: $I_2(c_2)$, $I^-(m_2)$, (Pt)

depends upon the amount of iodine bound by the cyclohexaamylose; therefore, by measuring the electromotive force of the system at increasing concentrations of iodine, it is possible to follow the course of the reaction between iodine and cyclohexaamylose.

The initial titrations were carried out at constant iodide levels. The results are indicated in Tables 1, 2, 3, and 4. Since the iodide concentrations in these titrations were large compared to the concentration of iodine, the amount of iodide bound as triiodide is negligible, and the concentration of the iodine can be calculated from the expression

$$E = \frac{RT}{2F} \ln \frac{[I_2]_1}{[I_2]_2} .$$

The concentration of iodine in the right half-cell can be calculated from the amount of iodine introduced and the volume of the system.

Some of the iodine is bound in the form of triiodide ion; however, it can be shown that the total iodine concentration ($I_2 \neq I_3^-$) can be substituted for the concentration of free iodine in the expression for the electromotive force of the system. The amount of iodine bound by the cyclohexaamylose, either as iodine or as triiodide ion, can be calculated from the concentration of total iodine in the right half-cell, and from the potential of the cell. The amount of iodine bound is the difference between the amount of iodine introduced into the left half-cell and the amount free in the left half-cell at equilibrium.

It is apparent from Table 1 that the amount of iodine bound by the cyclohexaamylose increases to a constant value corresponding to a 1:1 mol ratio of iodine and cyclohexaamylose. A plot of the log of the concentration of free iodine against the amount of iodine bound has the same characteristics as the function $(\frac{x}{1+x})$, Figure 1. The relation between the amount of iodine bound and the concentration of free iodine appears to be

$$K[I_2 \neq I_3^-] = \frac{(I_2 \neq I_3^-) \text{ bound}}{\alpha_o - (I_2 \neq I_3^-) \text{ bound}}$$

corresponding to the equation

$$I_2^* \neq \alpha \rightarrow \alpha I_2^*$$

where the asterisk indicates that no distinction is made

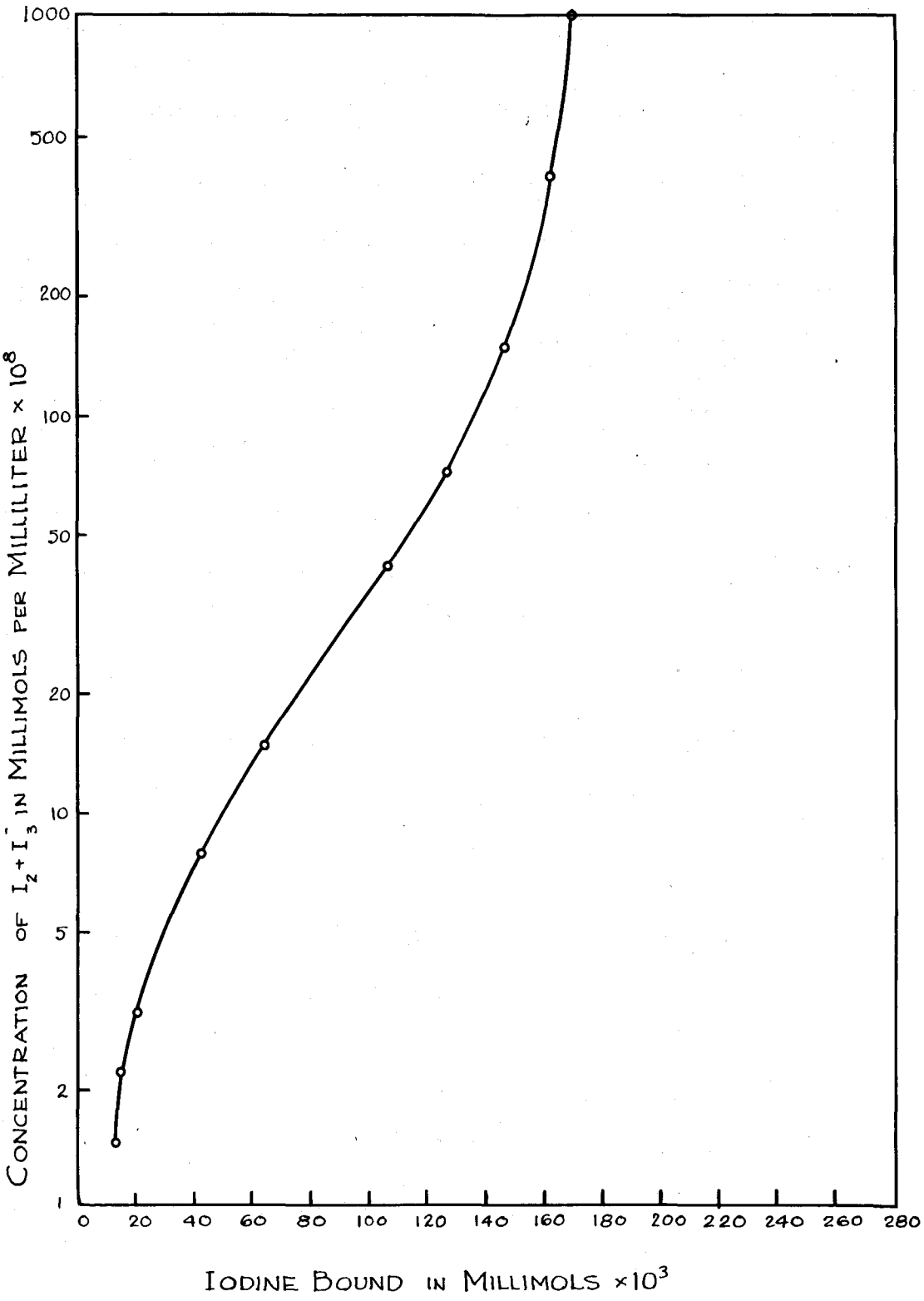

Fig. 1. Titration of Cyclohexaamylose with Iodine

between I_2 and I_3^-. If this is true, a plot of the log $[I_2 \nearrow I_3^-]$ as a function of

$$\frac{(I_2 \nearrow I_3^-)\text{bound}}{\alpha_o - (I_2 \nearrow I_3^-)\text{ bound}}$$

(which will be referred to as "extent of reaction") should give a straight line with a slope equal to unity. Such a plot is shown in Figure 2 which agrees with the proposed equation for the reaction.

In order to rule out the possibility of dimer or trimer formation, it is well to examine the following type of equation:

$$n\alpha \nearrow \; nI_2^* \longrightarrow (\alpha I_2^*)_n$$

where n = 2 or 3. The equilibrium constant for this reaction is

$$K = \frac{\left[(\alpha I_2^*)_n\right]}{\left[I_2^*\right]^n \left[\alpha\right]^n}$$

In terms of the amount of $(I_2 \nearrow I_3^-)$ bound, which will be designated by Q, the equation becomes

$$K\left[I_2^*\right]^n = \frac{\left[\frac{Q}{n}\right]}{\left[\alpha_o - Q\right]^n}$$

which can be rearranged to

$$\log K - \log V^{n-1} \nearrow \; n \log\left[I_2^*\right] = \log \frac{Q}{n(\alpha_o - Q)} .$$

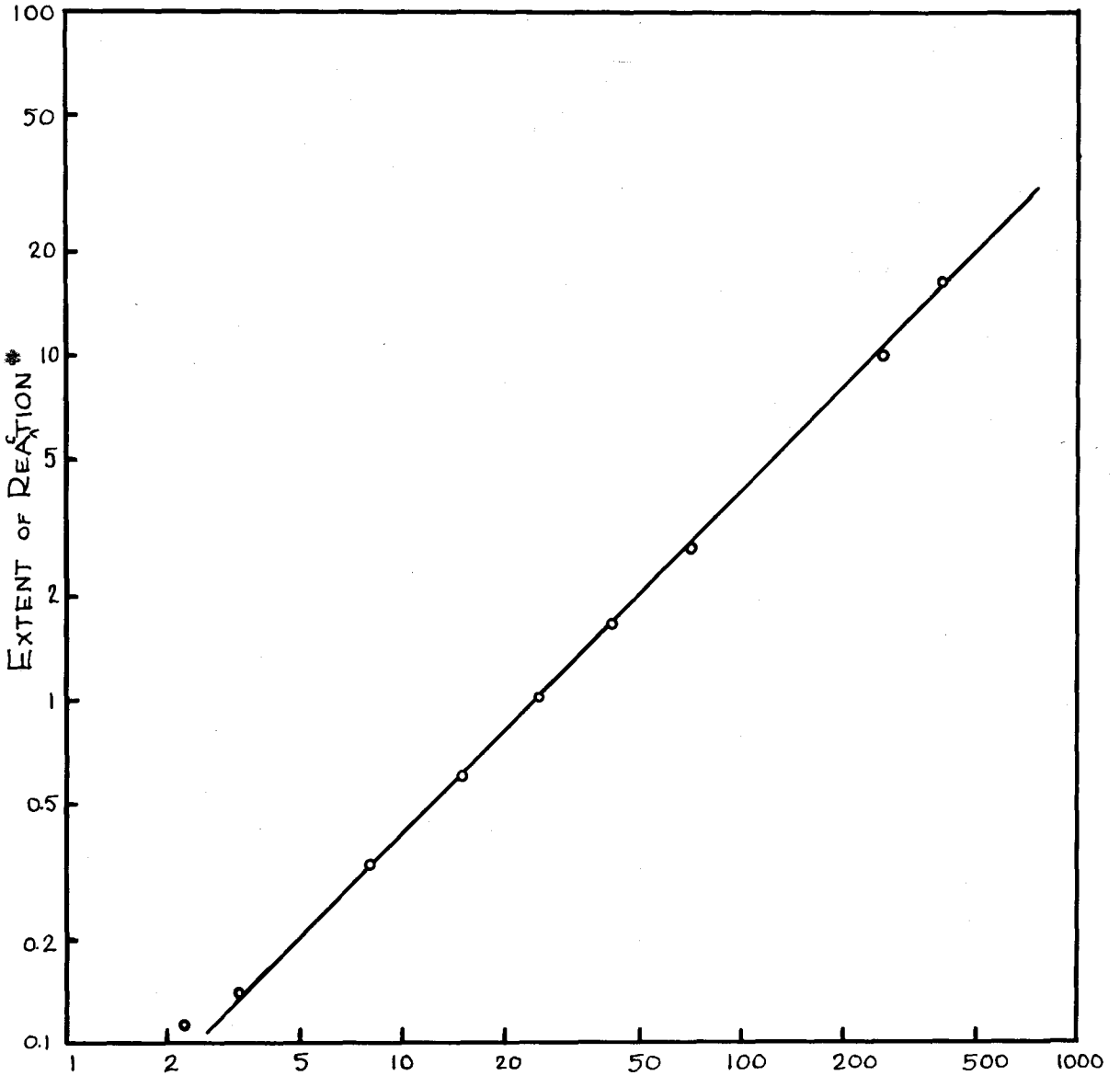

Fig. 2. Titration of Cyclohexaamylose with Iodine

*As defined in text

A plot of the function $\log \frac{Q}{n(\alpha_o - Q)}$ against the $\log [I_2^*]$ should give a straight line of slope equal to n. The slopes obtained were not those required by the above equation, thus eliminating the dimer and trimer as possible mechanisms.

The effect of varying the iodide concentration on the formation of the cyclohexaamylose-iodine complex was studied by performing the titrations at 0.10 and 1.00 molar potassium iodide concentrations and at concentrations of cyclohexaamylose of 1.0 and 2.0 milligrams per milliliter. The results are presented in Tables 2, 3 and 4, and Figure 3. The slopes of the graphs of $\frac{Q}{\alpha_o - Q}$ against iodine concentration are all indicative of a reaction of the type

$$I_2^* + \alpha \longrightarrow \alpha I_2^* ,$$

but a shift in the position of the lines indicates that the iodide concentration enters into the reaction.

In order to determine the role of the iodide ion in the formation of the complex, the E. M. F. of the previously mentioned cell was measured using half the theoretical amount of iodine required for the formation of the cyclohexaamylose-iodine complex and varying the concentration of the iodide ion. The results are given in Table 5.

If the function $\frac{Q}{(\alpha_o - Q)[I_2]}$ is plotted against the iodide concentration, the curve shown in Figure 4 is obtained.

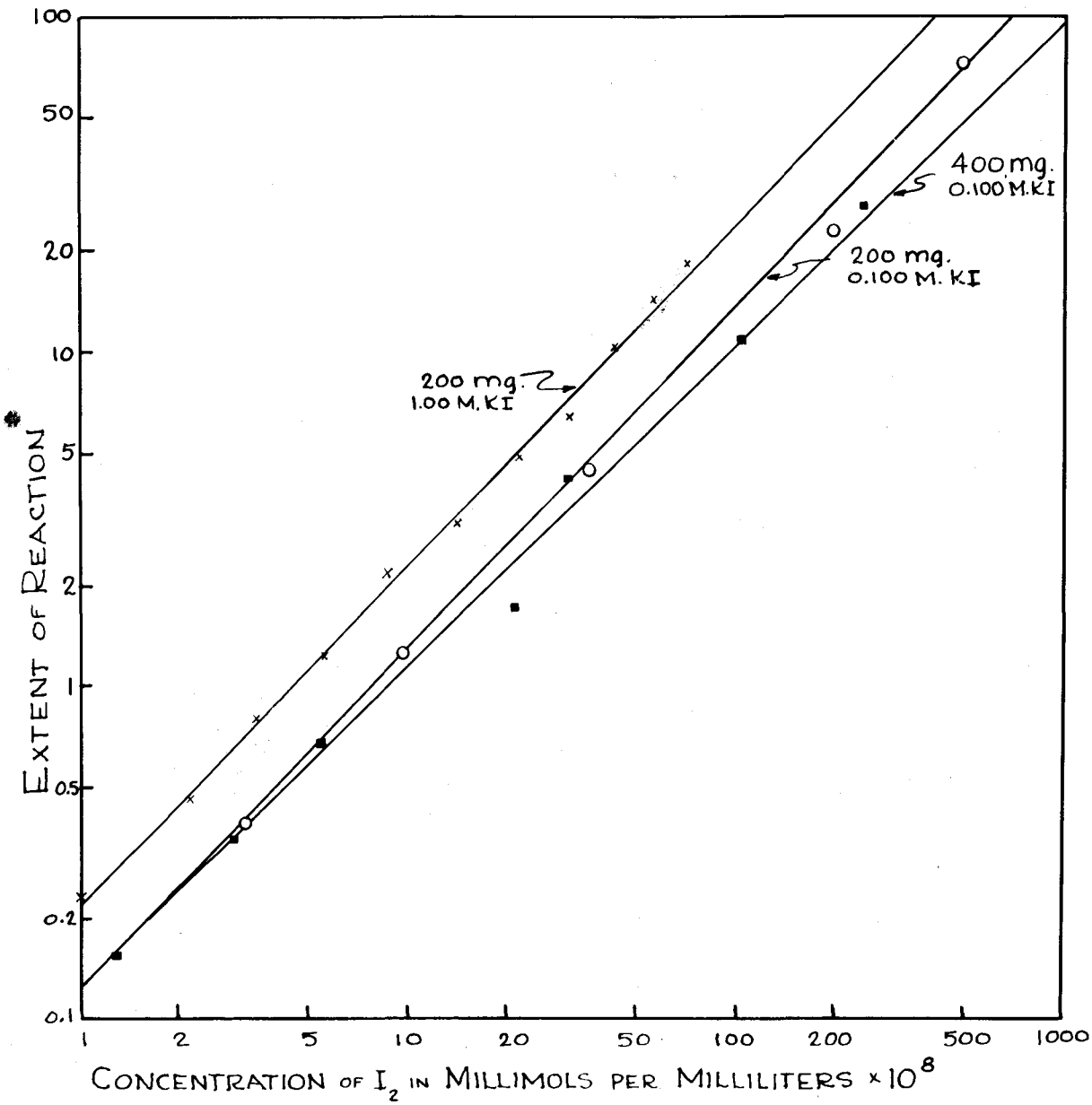

Fig. 3. Titration of Cyclohexaamylose with Iodine

* As defined in text

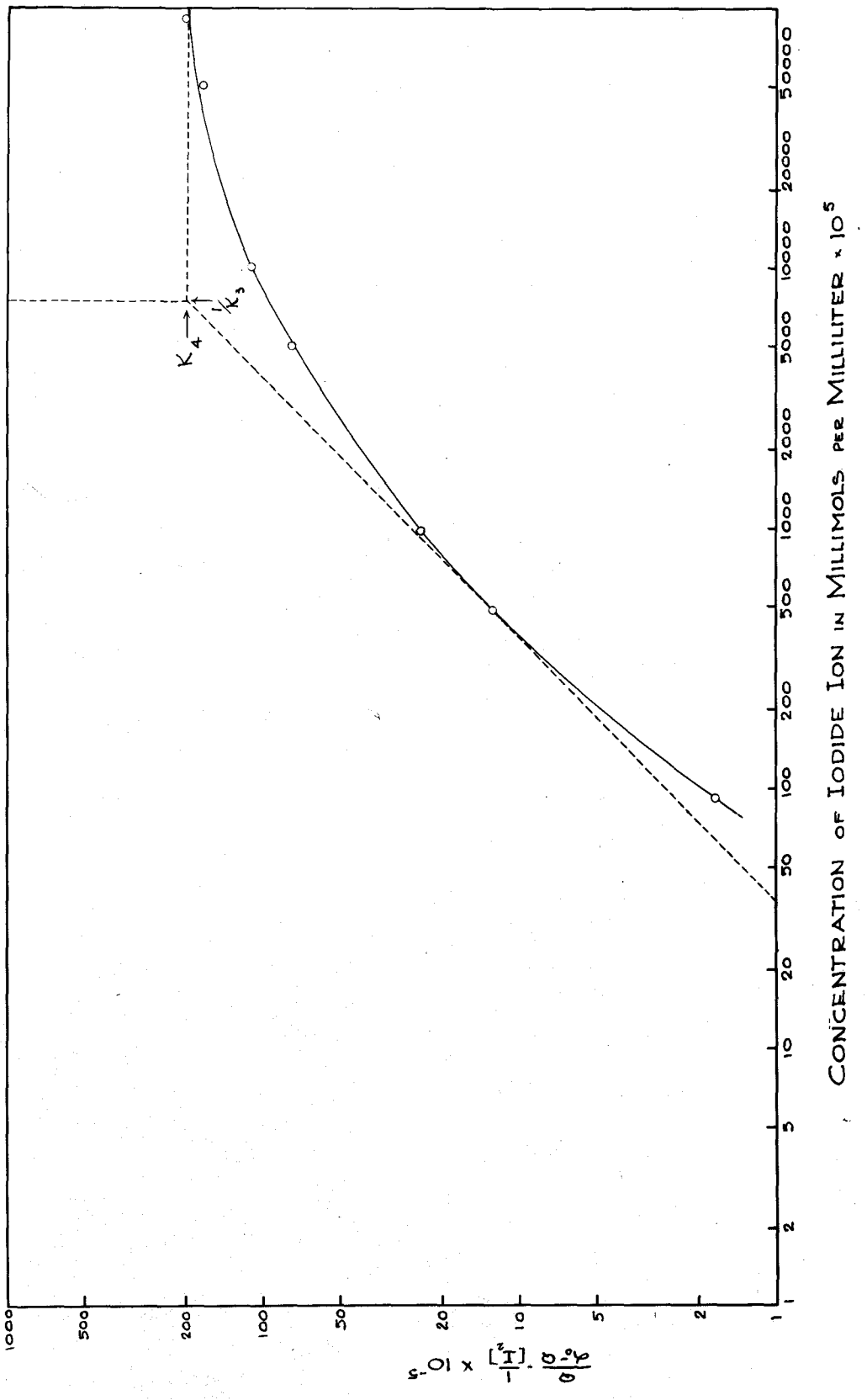

Fig. 4. Titration of Cyclohexaamylose-Iodine Complex with Potassium Iodide.

It is noted that the function appears to be approaching asymptotically a value of 2.5×10^{17} as the iodide concentration becomes greater than one molar and that, at lower iodide concentrations, the function is linear with a slope of nearly unity. Such a function suggests that the iodide ion enters into the reaction in two distinct steps.

Upon analysis it was found that the following set of equations can best explain the type of interaction between iodine, iodide and cyclohexaamylose.

$$\alpha + I_2 \longrightarrow \alpha I_2; \ (K_1) \qquad (1)$$

$$\alpha I_2 + I^- \longrightarrow \alpha I_3^-; \ (K_2) \qquad (2)$$

$$\alpha + I^- \longrightarrow \alpha I^-; \ (K_3) \qquad (3)$$

$$\alpha I^- + I_2 \longrightarrow \alpha I_3^-; \ (K_4) \qquad (4)$$

K_1, K_2, K_3 and K_4 are the equilibrium constants corresponding to the above reactions. It is logical to assume that the cyclohexaamylose iodide complex is formed only at high iodide concentrations and that the amount of cyclohexaamylose-iodine complex present in solution is very small at these concentrations. If the equilibrium expressions for reactions (3) and (4)

$$K_3 = \frac{[\alpha I^-]}{[\alpha]\,[I^-]} \qquad (5)$$

$$K_4 = \frac{[\alpha I_3^-]}{[\alpha I^-]\,[I_2]} \qquad (6)$$

are combined by eliminating $[\alpha I^-]$.

$$K_3K_4[I^-] = \frac{[\alpha I_3^-]}{[I_2]\,[\alpha]} \qquad (7)$$

is obtained. Since Q is the total amount of iodine bound either as αI_2 or αI_3^-, and it is assumed that the amount of αI_2 present is negligible at high concentrations of iodide ion,

$$[Q] = [\alpha I_3^-] \qquad (8)$$

Let α_o be the original concentration of cyclohexaamylose before the reaction. Then

$$(\alpha) = (\alpha_o) - (\alpha I_2) - (\alpha I_3^-) - (\alpha I^-)$$

or

$$[\alpha] = [\alpha_o] - [Q] - [\alpha I^-] . \qquad (9)$$

Substituting equations (8) and (9) into equation (7)

$$K_3K_4[I^-] = \frac{[Q]}{[\alpha_o - Q - \alpha I^-]\,[I_2]} \qquad (10)$$

or

$$\frac{[\alpha_o - Q - \alpha I^-]}{[Q]} K_3K_4[I_2] = \frac{1}{[I^-]} \qquad (11)$$

Separating fractions,

$$\left| \frac{[\alpha_o - Q]\,[I_2]}{[Q]} - \frac{[\alpha I^-]\,[I_2]}{[Q]} \right| K_3K_4 = \frac{1}{[I^-]} \qquad (12)$$

Since $[Q] = [\alpha I_3^-]$, equation (6) can be substituted into equation (12) and setting

$$\frac{[\alpha_o - Q]\,[I_2]}{[Q]} = \frac{1}{s} \qquad (13)$$

and rearranging, the following is obtained:

$$S = K_3K_4 \frac{[I^-]}{1 + K_3[I^-]} . \qquad (14)$$

Taking the log of both sides and differentiating with respect to log $[I^-]$

$$\frac{d \log S}{d \log [I^-]} = 1 - \frac{K_3[I^-]}{1 + K_3[I^-]}$$

or

$$\frac{d \log S}{d \log [I^-]} = \frac{1}{1 + K_3[I^-]} . \qquad (15)$$

At low iodide concentrations, the slope approaches unity, and at high iodide concentrations, the slope approaches zero. When the slope is equal to one-half,

$$K_3 = \frac{1}{[I^-]} . \qquad (16)$$

Rearranging equation (14), the following expression is obtained:

$$S = \frac{K_3K_4}{\frac{1}{[I^-]} + K_3} \qquad (17)$$

From this it can be shown that as the iodide concentration approaches infinity, the value of S approaches K_4.

Similarly for the reaction at low iodide concentrations where the formation of cyclohexaamylose-iodide is negligible,

$$K_1 = \frac{[\alpha I_2]}{[\alpha] \cdot [I_2]} \qquad (18) \qquad K_2 = \frac{[\alpha I_3^-]}{[\alpha I_2][I^-]} \qquad (19)$$

Eliminating $[\alpha I_2]$ between the two equations,

$$K_1K_2[I_2] = \frac{[\alpha I_3^-]}{[\alpha]\,[I^-]}. \qquad (20)$$

Assuming that $[\alpha I^-]$ is negligible (which will be shown to be true later),

$$[\alpha] = [\alpha_o] - [\alpha I_2] - [\alpha I_3^-] \qquad (21)$$

$$[Q] = [\alpha I_2] + [\alpha I_3^-] \qquad (22)$$

or

$$[\alpha] = [\alpha_o] - [Q]. \qquad (23)$$

Substituting (22) and (23) into equation (20),

$$K_1K_2[I^-] = \frac{[Q - \alpha I_2]}{[\alpha_o - Q][I_2]}. \qquad (24)$$

Separating fractions and substituting equation (18),

$$K_1K_2[I^-] = \frac{[Q]}{[\alpha_o - Q][I_2]} - K_1 \qquad (25)$$

or

$$S = K_1K_2[I^-] + K_1. \qquad (26)$$

Taking the log of both sides and differentiating with respect to log $[I^-]$

$$\frac{d \log S}{d \log [I^-]} = \frac{K_2[I^-]}{K_2[I^-] + 1}. \qquad (27)$$

The slope becomes zero as the concentration of iodide ion approaches zero, and approaches one as the concentration

of iodide ion becomes large. It is also apparent that when the slope is equal to one-half, $K_2 = \frac{1}{[I^-]}$. From equation (26) $S = K_1$ at zero iodide concentration.

The straight line connecting the intersection of the line $S = K_1$ and $[I_2] = \frac{1}{K_2}$ and the intersection of $S = K_4$ and $[I_2] = \frac{1}{K_3}$ has a slope of unity and is tangent to the titration curve at the midpoint. Once the values of K_3 and K_4 have been determined, the values of K_1 and K_2 are limited by the above relationship to K_3 and K_4.

On the basis of the equations just developed, a plot of the log of the function S against the log of the concentration of iodide ion should have the characteristics of the curve in Figure 5. The relative positions of the upper and the lower level portions of the curve depend upon the difference in the values of log K_1 and log K_4.

An examination of the experimental curve in Figure 4 shows that the curve does not become level at low iodide concentrations as is expected from the equations. As will be shown when the constants are evaluated, the concentration at which this leveling occurs is too low to allow accurate measurement of the iodine concentration by the electrometric method used in this study.

The values of the equilibrium constants of the four reactions are best determined graphically according to the analysis given above. In order to fit the theoretical curve

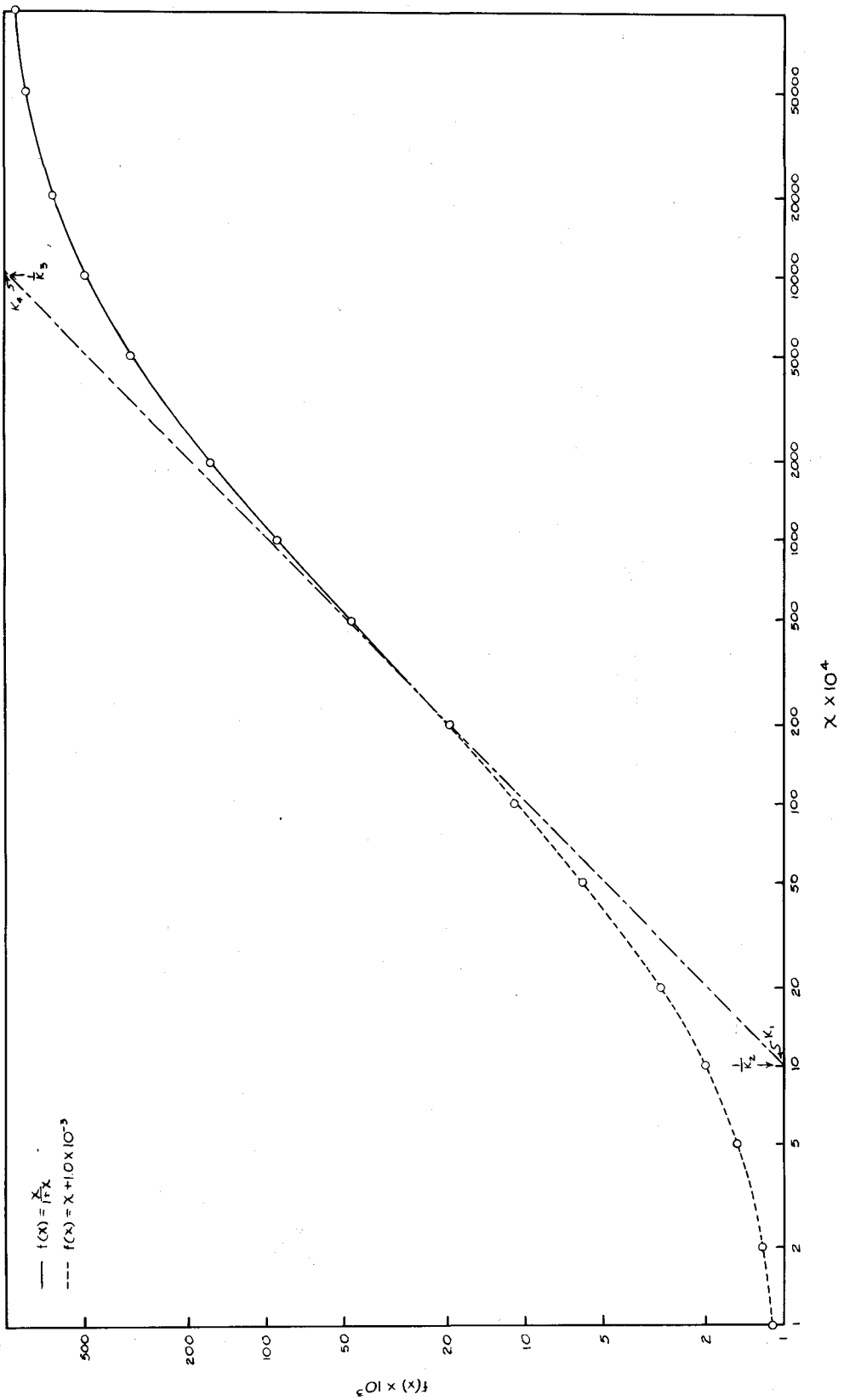

Fig. 5. Theoretical Curve of the Iodide Titration

to the experimental points as accurately as possible, the log of the function $\frac{x}{1+x}$ (corresponding to values of K_3 and K_4 equal to unity) was plotted against the log of x on the same scale as the experimental data (Figure 5). The theoretical curve was then superimposed upon the experimental points. The equilibrium constants K_3 and K_4 are then fixed by equations (15) and (16). The values obtained are:

$$K_3 = 13.5$$

$$K_4 = 2.00 \times 10^{+7}.$$

These values were then applied to the experimental data at the lowest iodide concentrations, and by a series of approximations, it was possible to estimate the values of K_1 and K_2 as $1.4 \times 10^{+4}$ and $1.9 \times 10^{+4}$ respectively.

The values of the four equilibrium constants were applied to the remaining experimental points. It was possible to show that these values are compatible with these experimental points within experimental error. At iodide ion concentrations above 5.0×10^{-3} molar, the concentration of cyclohexaamylose-iodine complex obtained from these constants is low; therefore the assumption that K_1 and K_2 do not effect the experimental points at higher iodide concentrations is justifiable.

The values of K_1 and K_2 are doubtful. The experimental errors at low iodide concentrations are large enough to cause an appreciable error in the values of these constants; consequently, an independent method of determining these constants

was sought. It is necessary to determine only one of these constants, since the other is fixed by the expression

$$K_1K_2 = K_3K_4 ,$$

and the values of K_3 and K_4 are fairly accurate. The reaction which is most favorable for study is the formation of cyclohexaamylose-iodine complex in the absence of iodide ion. The distribution of iodine between a water solution of cyclohexaamylose and a non-miscible solvent, in which iodine is soluble, was selected as the system most likely to give the information required. The concentration of iodine in the water solution is fixed by the distribution coefficient of iodine between water and the non-miscible solvent. The concentration of iodine, cyclohexaamylose and the complex in the water layer can be determined as described in the experimental section. The non-miscible solvent selected must not react with the cyclohexaamylose. Toluene does not precipitate cyclohexaamylose from dilute solutions of cyclohexaamylose and appears to meet the other requirements of a non-miscible solvent.

The values obtained for the equilibrium constant were 5.2×10^{-3}, 2.0×10^{-3}, and 1.3×10^{-3}. These are lower than the values obtained from E. M. F. measurements and do not agree very well among themselves. The value 2.0×10^{-3} was selected, since the first experimental value is doubtful. The equilibrium constant for reaction (2) on this basis is 1.35×10^{-5}. These values do not fit the experimental points

at the lowest iodide concentrations, but this is undoubtedly due to the large experimental error present at these iodide concentrations.

The standard free energies of formation for the complexes in solution are:

$\alpha + I_2 \rightarrow \alpha I_2$ $\quad \Delta F^\circ_{298} = -4{,}500$ cals./mole

$\alpha + I^- \rightarrow \alpha I^-$ $\quad \Delta F^\circ_{298} = -1{,}550$ cals./mole

$\alpha + I_2 + I^- \rightarrow \alpha I_3^-$ $\quad \Delta F^\circ_{298} = -11{,}500$ cals./mole

The entropy change of the first reaction can be calculated as follows:

$$\Delta F^\circ_{298} = -RT \ln K \qquad (28)$$

or

$$\Delta F^\circ_{298} = -2.33\ RT \ln \frac{[\alpha I_2]}{[I_2][\alpha]} . \qquad (29)$$

Taking the partial derivative with respect to temperature,

$$\left(\frac{\partial \Delta F^\circ}{\partial T}\right)_p = -2.33\ R \log \frac{[\alpha I_2]}{[\alpha][I_2]} - 2.33\ RT \frac{\partial \log \frac{[\alpha I_2]}{[\alpha]}}{\partial T}$$

$$+ 2.33\ RT \frac{\partial \log [I_2]}{\partial T} \quad ; \qquad (30)$$

however,

$$\left(\frac{\partial \Delta F^\circ}{\partial T}\right)_p = -\Delta S^\circ . \qquad (31)$$

At concentrations of iodide sufficiently high compared to the concentration of free iodine,

$$[I_2] = [I_2 + I_3^-] \frac{K'}{K' + [I^-]} \qquad (32)$$

where K' is the dissociation constant of the triiodide ion. Let $[I_2 + I_3^-] = C$; then from the equation (32),

$$\frac{\partial \log [I_2]}{\partial T} = \frac{\partial \log C}{\partial T} + \frac{\partial \log K'}{\partial T} - \frac{1}{K' + [I^-]} \frac{\partial K'}{\partial T} \qquad (33)$$

or

$$\frac{\partial \log [I_2]}{\partial T} = \frac{\partial \log C}{\partial T} + \frac{\partial \log K'}{\partial T} \cdot \frac{[I^-]}{K' + [I^-]} . \qquad (34)$$

A plot of log C against the temperature, using the values of Table 6 (obtained with 174.1 milligrams of cyclohexaamylose in 0.01 M KI as described in the experimental section), is shown in Figure 6. The plot is a straight line of slope equal to 2.83×10^{-3}. A plot of the log of the dissociation constant of triiodide ion (46, 47) against the reciprocal of absolute temperature is a straight line with a slope of $-9.6 \times 10^{+2}$ (Figure 7); therefore,

$$\frac{\partial \log K'}{\partial T} = \frac{9.6 \times 10^{+2}}{T^2} . \qquad (35)$$

Substituting in equation (34)

$$\frac{\partial \log [I_2]}{\partial T} = 2.83 \times 10^{-3} + \frac{9.6 \times 10^{+2}}{2.98} \cdot \frac{0.010}{1.40 \times 10^{-3} + 0.010} \qquad (36)$$

$$\frac{\partial \log [I_2]}{\partial T} = 3.11 \times 10^{-2} . \qquad (37)$$

The ratio $\frac{[\alpha I_2]}{[\alpha]}$ as a function of temperature is also given in

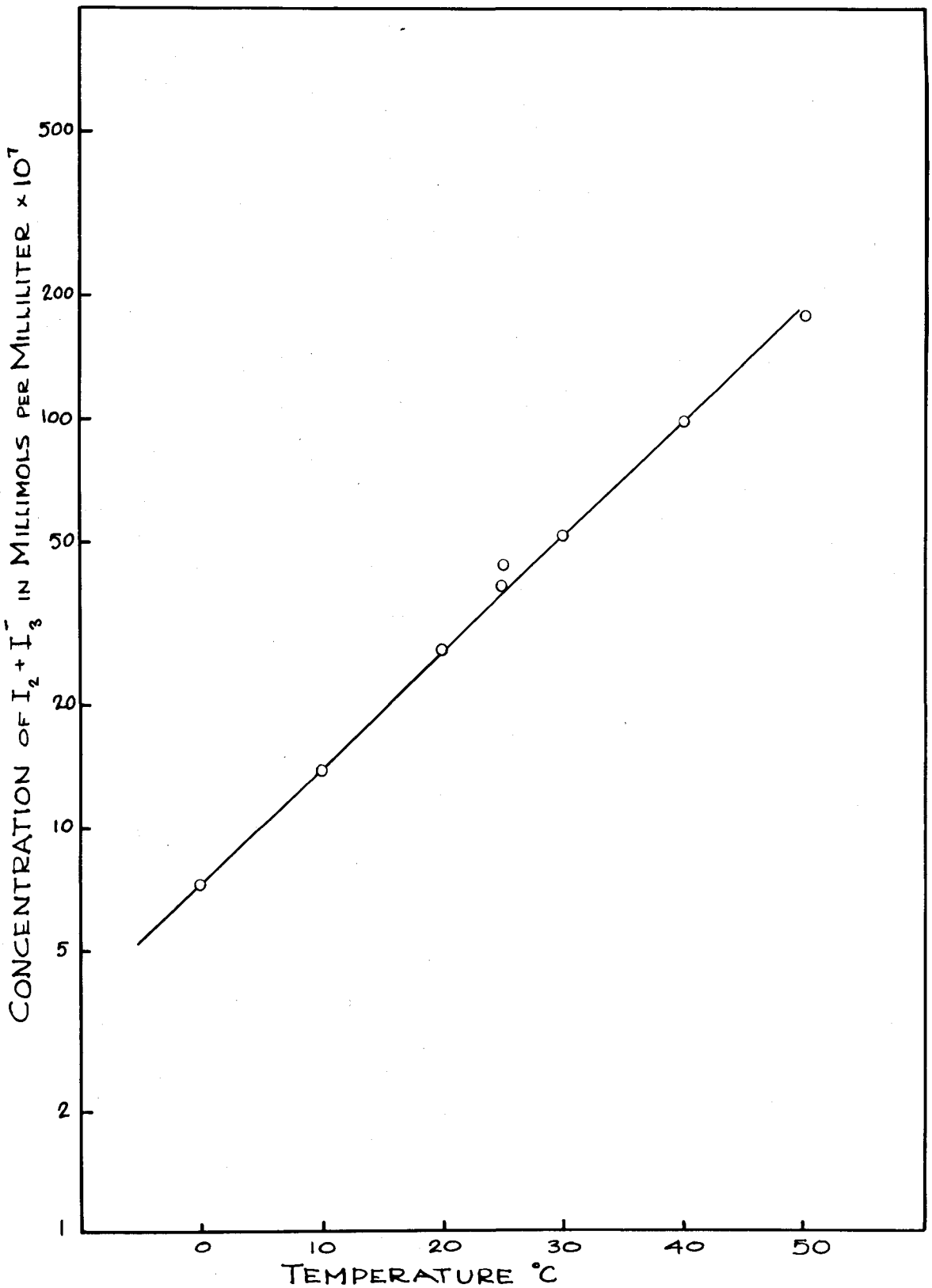

Fig. 6. Effect of temperature on the concentration of Iodine in the presence of cyclohexaamylose

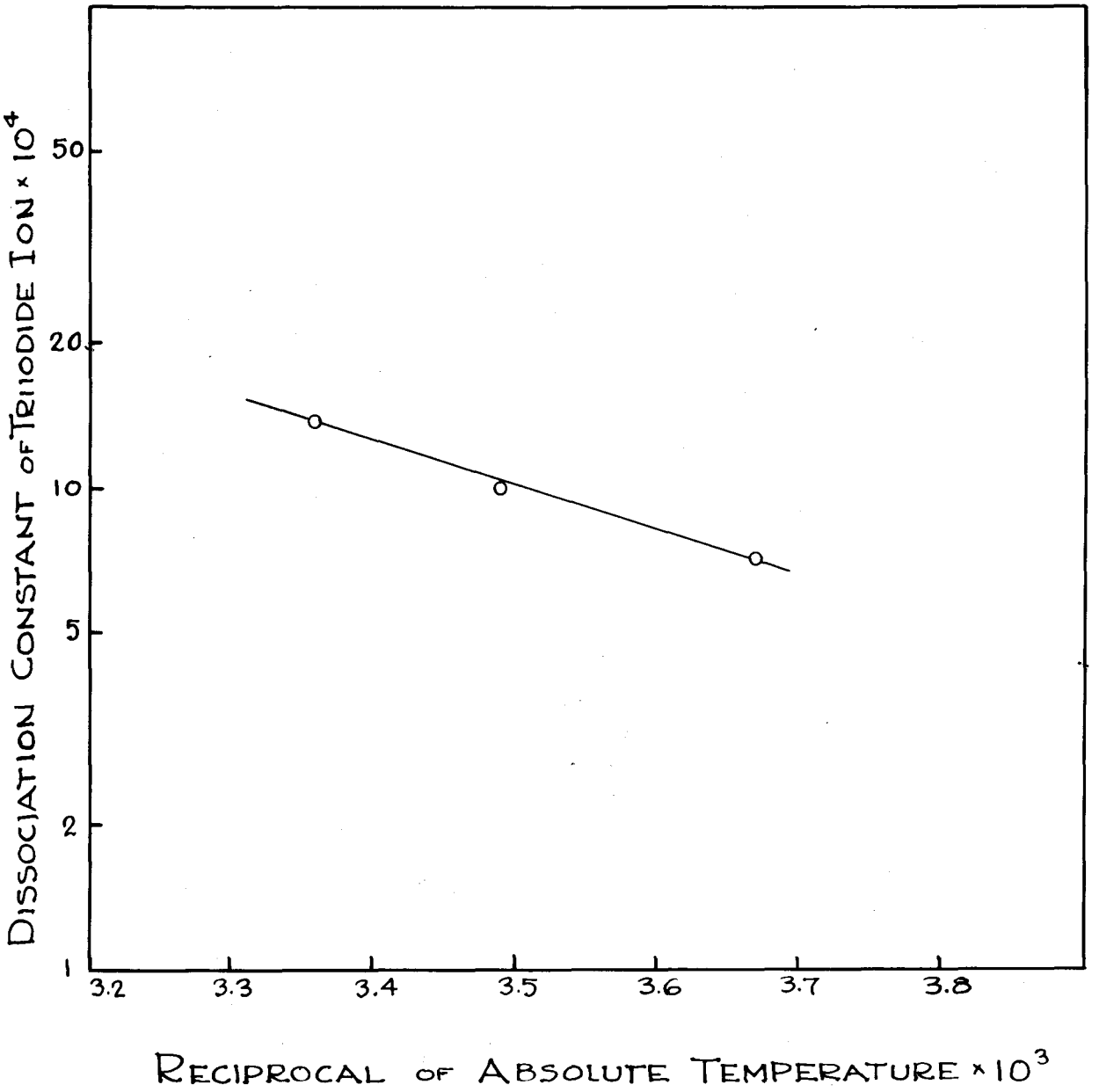

Fig. 7. Effect of temperature on the Dissociation Constant of Triiodide Ion

Table 6. The term $[\alpha I_2]$ includes the cyclohexaamylose-triiodide complex. The effect of this term in calculation of the change in entropy is small, so that the error introduced by considering that all the complex is in the form αI_2 is small. A plot of the log $\frac{[\alpha I_2]}{[\alpha]}$ against temperature is given in Figure 8. The slope at 25° C. is -2.64×10^{-4}, or

$$\frac{\partial \log \frac{[\alpha I_2]}{[\alpha]}}{\partial T} = -2.64 \times 10^{-4}. \qquad (38)$$

Substituting the numerical values into equation (30),

$$\Delta S^{\circ}_{298} = 2.33 \times 1.98 \log K_{298} + 298 \times 2.64 \times 10^{-4} - 298 \times 3.11 \times 10^{-2}. \qquad (39)$$

$$K_{298} = 2.0 \times 10^{3};$$

therefore,

$$\Delta S^{\circ}_{298} = -27.2 \text{ e.u.} \qquad (40)$$

and

$$\Delta H^{\circ}_{298} = -12,600 \text{ cals. per mole.} \qquad (41)$$

The existence of a complex of cyclohexaamylose and iodine in the absence of iodide ion has been shown previously. The complex of cyclohexaamylose and iodide ion has been prepared from a solution of cyclohexaamylose and potassium iodide. Upon slow evaporation of the solution, small, five-sided, strongly birefringent platelets were obtained. An analysis of the crystals showed that the cyclohexaamylose and the iodide are present in nearly equimolecular proportions as required by the formula assigned to the complex.

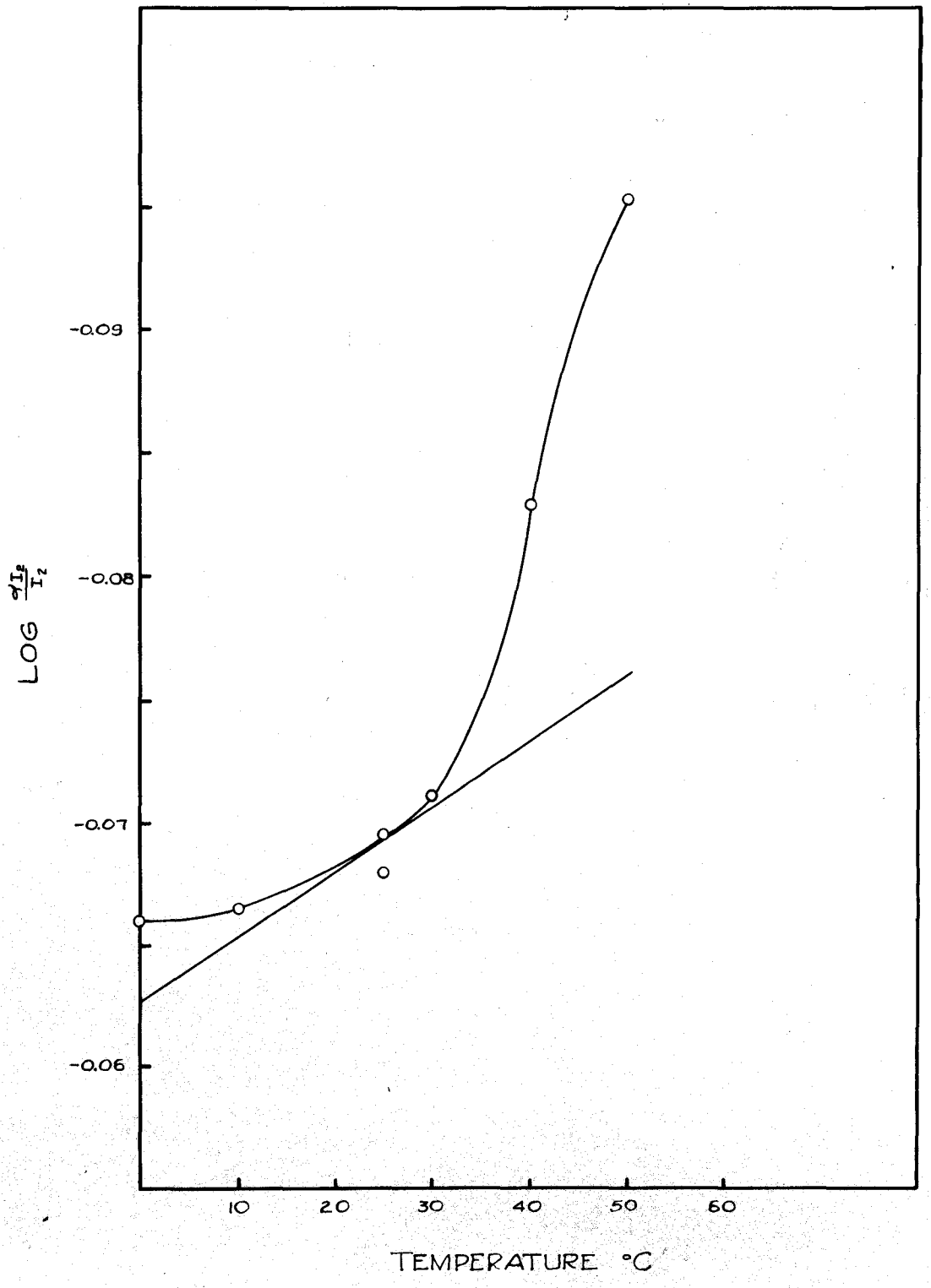

Fig. 8. Effect of temperature on the cyclohexaamylose-Iodine Complex

The equations proposed for the reactions between iodine, iodide and cyclohexaamylose agree with the molecular proportions of the three precipitated complexes prepared by French. He reported that one modification has a molecular formula $(C_6H_{10}O_5)_6 \cdot I_2 \cdot KI$. This corresponds to the formula proposed for one of the complexes in solution. The second modification reported has a molecular formula $\left[(C_6H_{10}O_5)_6 \cdot I_2\right]_2 \cdot KI$. This can be explained in terms of the proposed equations for the reactions in solution. The solid is formed by the precipitation of equimolecular proportions of αI_3^- and αI_2. The third modification reported $(C_6H_{10}O_5)_6 \cdot I_2$ is identical with the formula proposed for one of the complexes formed in solution.

The system of equations proposed for the reaction of cyclohexaamylose, iodine and iodide ion explains the experimental results completely.

B. Cycloheptaamylose-Iodine Complex

The application of the electrometric titration to the study of the complexes of cycloheptaamylose and iodine is a logical extension of the work on cyclohexaamylose. In this case, however, the results are not as harmonious as those of the cyclohexaamylose.

The molecular weight of cycloheptaamylose was determined by French and Rundle (40). The molecule consists of a ring

of seven glucose residues bound by α-1,4 glucosidic bonds. The number of molecules in the unit cell is two, but the position of these molecules in the unit-cell is not known.

The reaction of cycloheptaamylose and iodine at concentrations of potassium iodide below 1.0 molar did not appear to go to completion. It was not experimentally possible to introduce enough iodine into the system to raise the concentration of free iodine high enough to increase the extent of the reaction over 95%, based on a 1:1 mole ratio of iodine and cycloheptaamylose (Figure 9). During the titrations carried out at 1.0 molar KI, the complex precipitated (Tables 7, 8 and 9).

The shape of the titration curves in which no precipitation occurred indicates that the complex formed has a 1:1 mole ratio of iodine and cycloheptaamylose. The analysis used for cyclohexaamylose applies to cycloheptaamylose. A plot of the function $\log \frac{Q}{(\beta_o - Q)}$ against the log of the concentration of free iodine is a straight line with a slope of unity (Figure 10).

The effect of iodide ion concentration on the formation of cycloheptaamylose-iodine complex was determined in the same manner as was the effect of iodide ion concentration on the formation of cyclohexaamylose-iodine complex. A plot of the function

$$\frac{Q}{(\beta_o - Q)} \cdot \frac{1}{[I_2]}$$

against the iodide ion concentration is given in Figure 11.

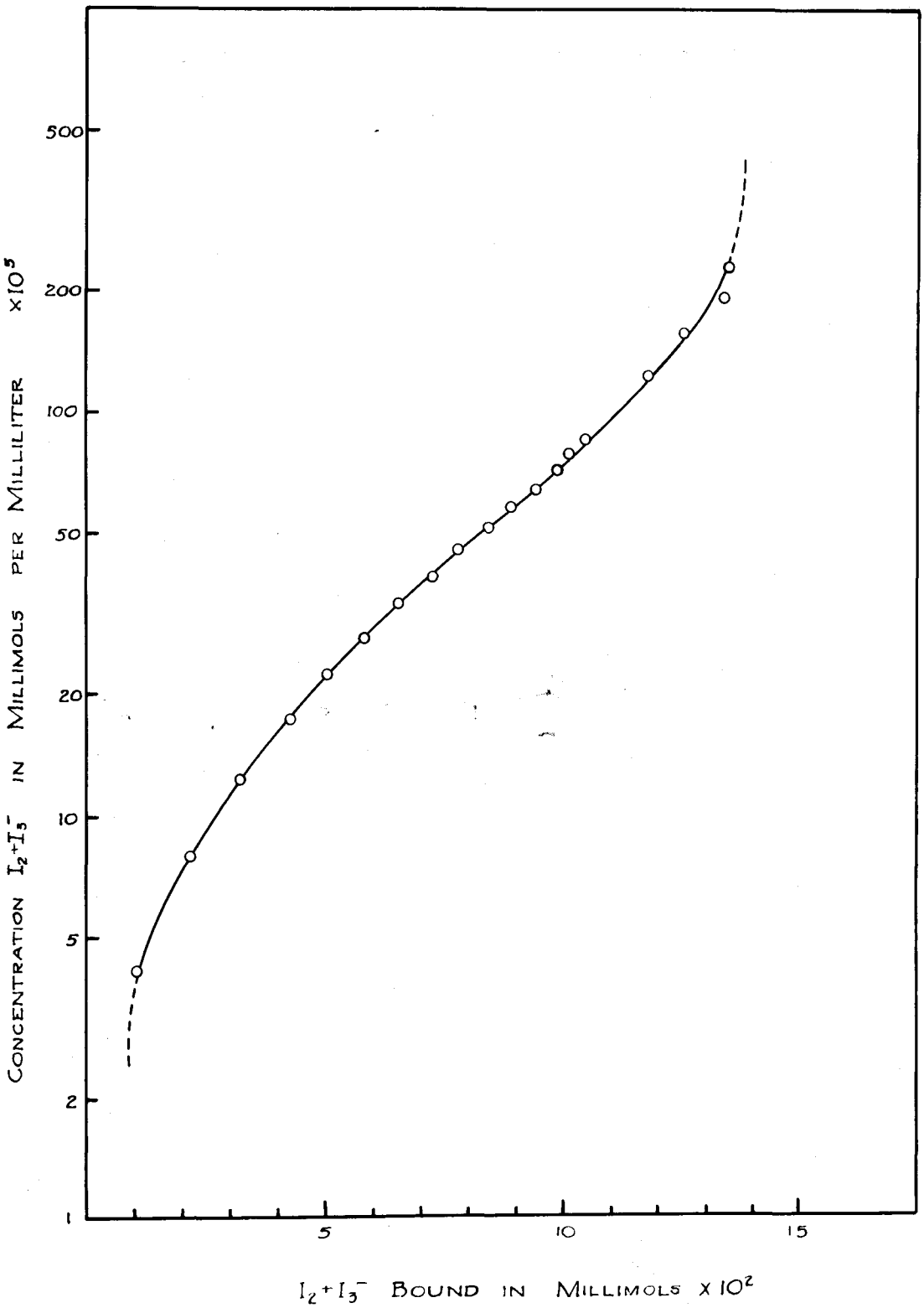

Fig. 9. Titration of Cycloheptaamylose with Iodine

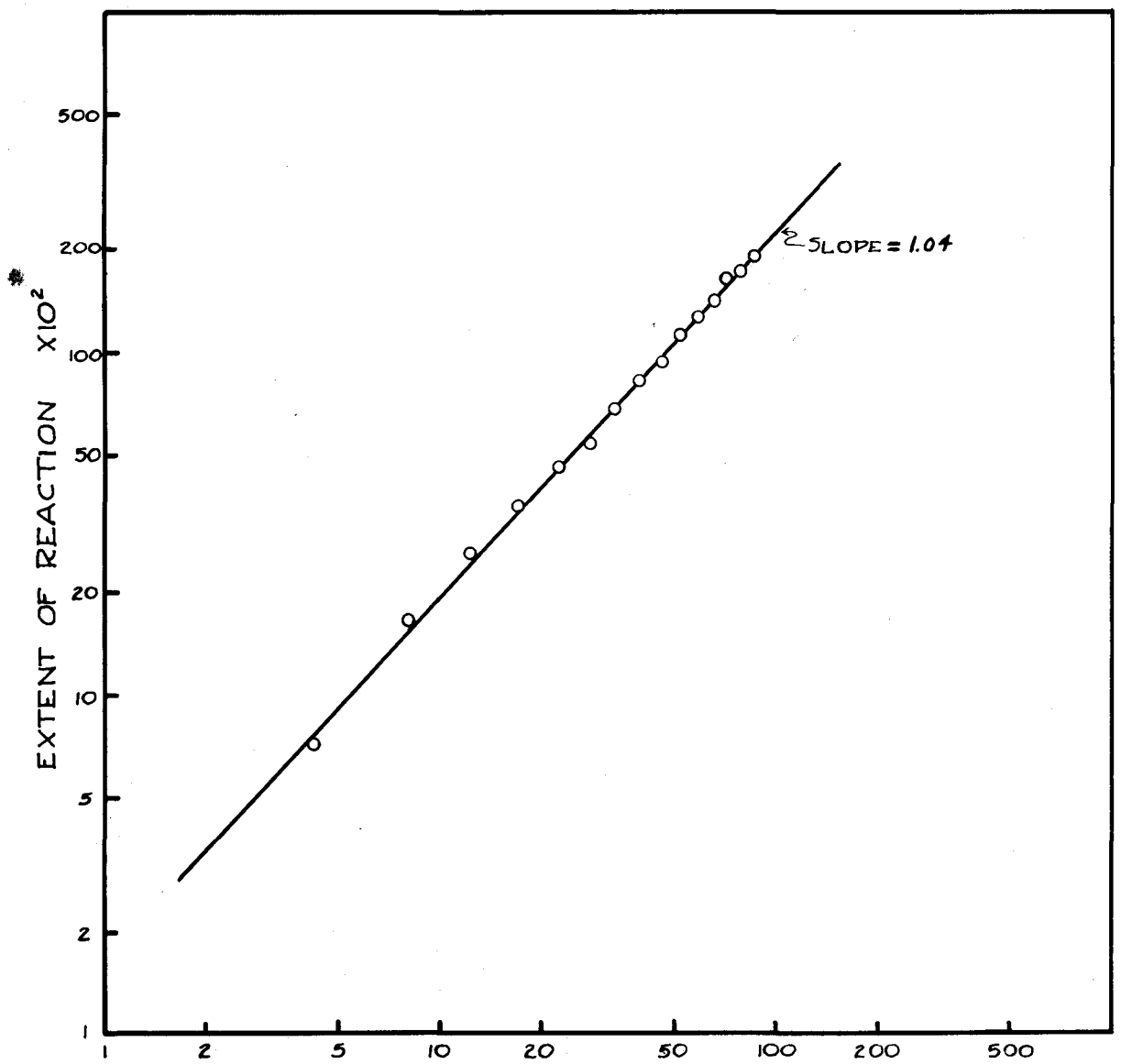

Fig. 10. Titration of Cycloheptaamylose with Iodine

* As defined in text

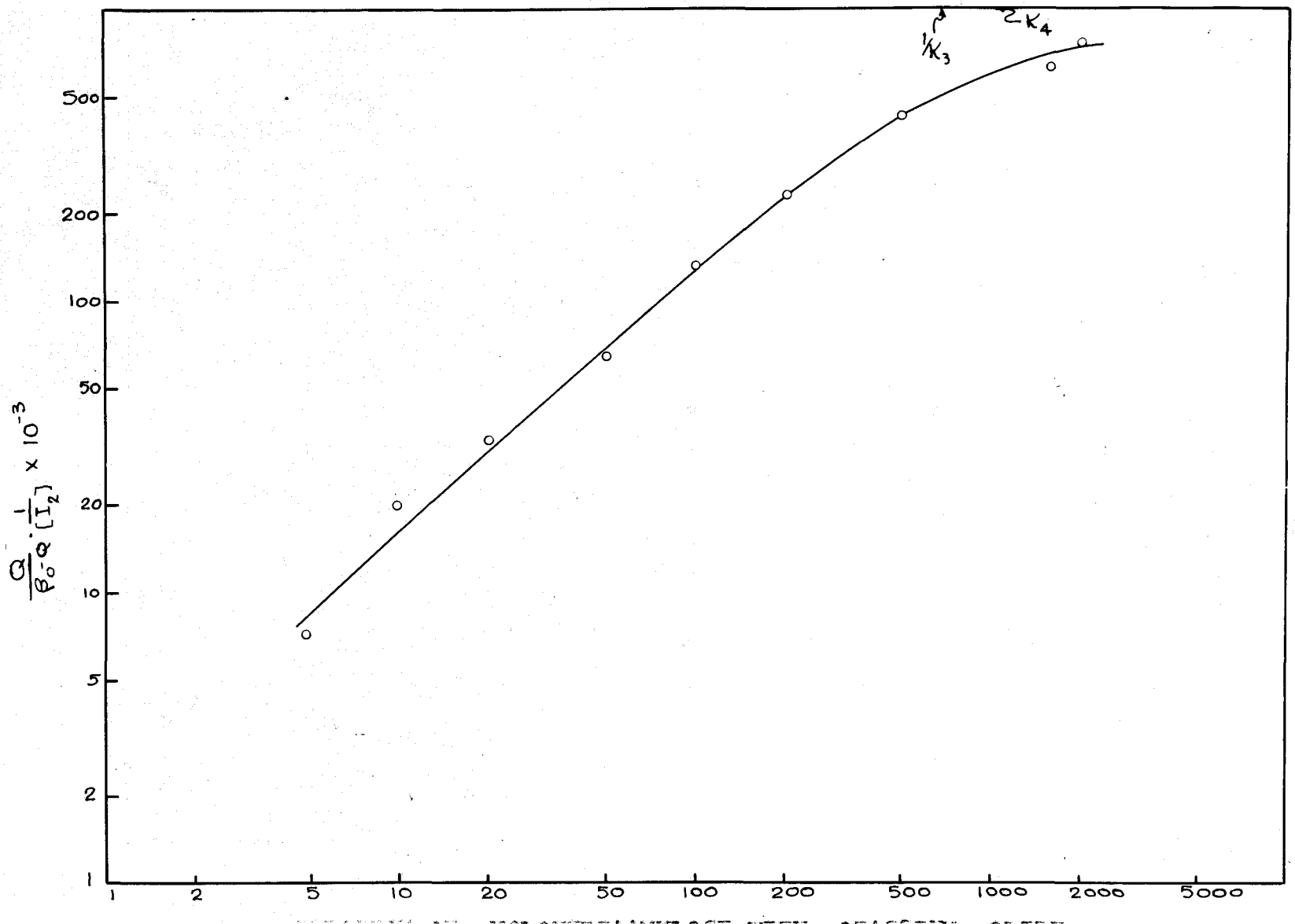

Fig. 11. Titration of Cycloheptaamylose with Potassium Iodide

The curve is similar to the one obtained with cyclohexaamylose, and a similar set of equations can be used to interpret the results. In the case of cycloheptaamylose, the curve does not become level until a high iodide ion concentration is reached; however, fairly accurate values for the equilibrium constant can be obtained by fitting the theoretical curve to the experimental points as was done with cyclohexaamylose.

The system of equations proposed for the formation of the complex between cycloheptaamylose and iodine in solution is

$$\beta \neq I_2 \longrightarrow \beta I_2 ; \quad (K_1)$$

$$\beta I_2 \neq I^- \longrightarrow \beta I_3^- ; \quad (K_2)$$

$$\beta \neq I^- \longrightarrow \beta I^- ; \quad (K_3)$$

$$\beta I^- \neq I_2 \longrightarrow \beta I_3^- ; \quad (K_4).$$

The values obtained graphically for the equilibrium constants K_3 and K_4 are 1.45 and 1.00 x 10^{-6} respectively. The values of K_1 and K_2 cannot be determined from the experimental data, and the method used in the study of cyclohexaamylose cannot be applied to cycloheptaamylose because the latter precipitates readily with immiscible solvents (53).

The standard free energy of formation of cycloheptaamylose-iodide calculated from the equilibrium constant is -220 cals. per mole.

The problem of the nature of the precipitated complex is considerably more involved. The complex of cyclohepta-

amylose-iodine, precipitated at high iodide concentrations, contains five moles of iodine and one mole of iodide ion to every four moles of dextrin. The analyses of the complex are not consistent in regard to the exact ratio of iodine and cycloheptaamylose. This ratio appears to be determined by the method of preparation.

Whatever the nature of the precipitated complex of iodine, iodide, and cycloheptaamylose, the nature of the reaction in solution appears to be consistent and correct.

C. Amylose-Iodine Complex

1. Phase relationship

The results obtained with cyclohexaamylose can be applied to the interpretation of the reaction between iodine and amylose; however, there is an additional factor which has to be considered. The decrease in the characteristic potential with an increase in amylose concentration must be explained. This can be done by studying the effect of the presence of solid phases on the titration curves of the amylose-iodine reaction.

The iodine is in the aqueous phase, but the amylose and the amylose-iodine complex can be in solution or can be present as solids finely dispersed in the water. By a combination of these conditions it is possible to write four

equations for the reaction.

$$Am(aq) + NI_2(aq) \longrightarrow Am(I_2)_N(aq) \qquad (1)$$

$$Am(s) + NI_2(aq) \longrightarrow Am(I_2)_N(aq) \qquad (2)$$

$$Am(s) + NI_2(aq) \longrightarrow Am(I_2)_N(s) \qquad (3)$$

$$Am(aq) + NI_2(aq) \longrightarrow Am(I_2)_N(s) \qquad (4)$$

The equilibrium constant for each reaction can be related to the potential of the iodine electrode. The potential of the iodine electrode against the normal calomel electrode is given by the following expression:

$$E = E^{o} - \frac{RT}{2F} \ln \frac{[I^-]^2}{[I_2]} \qquad (5)$$

where E^{o} is the sum of the standard potential of the iodine electrode and the potential of the normal calomel electrode.

The equilibrium constant for reaction (1) is

$$K = \frac{[Am(I_2)_N]}{[Am][I_2]^N} . \qquad (6)$$

Eliminating the concentration of iodine between equations (5) and (6) and, rearranging, the expression

$$E + \frac{1}{N}\frac{RT}{2F} \ln K = E^{o} - \frac{RT}{2F} \ln[I^-]^2 + \frac{1}{N}\frac{RT}{2F} \ln \frac{[Am(I_2)_N]}{[Am]} \qquad (7)$$

is obtained. The ratio of concentration of complex to amylose is unity at the midpoint of the titration, and the potential at this point is independent of the amylose concentration.

The equilibrium constant for reaction (2) is given by the expression

$$K = \frac{[Am(I_2)_N]}{[I_2]^N} \quad . \tag{8}$$

Eliminating the concentration of iodine between equations (5) and (8), the expression

$$E \neq \frac{1}{N}\frac{RT}{2F} \ln K = E^o - \frac{RT}{2F} \ln [I^-]^2 \neq \frac{1}{N}\frac{RT}{2F} \ln [Am(I_2)_N] \tag{9}$$

is obtained. An increase in the concentration of amylose at the midpoint of the titration results in an increase in the concentration of complex and an increase in the characteristic potential.

The equilibrium constant for reaction (3) is given by the expression

$$K = \frac{1}{[I_2]^N} \quad . \tag{10}$$

Eliminating the concentration of iodine between equations (5) and (10),

$$E \neq \frac{1}{N}\frac{RT}{2F} \ln K = E^o - \frac{RT}{2F} \ln [I^-]^2 \quad . \tag{11}$$

The potential is independent of the amylose concentration and the degree of reaction.

The equilibrium constant for reaction (4) is given by the expression

$$K = \frac{1}{[Am][I_2]^N} \quad . \tag{12}$$

Eliminating the concentration of iodine between equations (5) and (12), the expression

$$E \neq \frac{1}{N}\frac{RT}{2F} \ln K = E^{o} - \frac{RT}{2F} \ln [I]^2 - \frac{1}{N}\frac{RT}{2F} \ln [Am] \quad (13)$$

is obtained. The characteristic potential decreases with increasing concentration of amylose.

Bates (21) has shown that the characteristic potential decreases with increasing amylose concentration; therefore, equation (4) is the only one which agrees qualitatively with the experimental results. Bates found that an increase in the concentration of iodide ion decreases the potential at the midpoint of the titration which is also predicted by equation (13).

2. Reversibility

In writing an expression for the reaction between iodine and amylose and formulating an equilibrium constant for the reaction, it is assumed that the reaction is reversible. This assumption was shown to be correct by a study of the effect of change in temperature on a system containing amylose and sufficient iodine to react with one-half of the amylose present, as described in the experimental section. The results are given in Table 41, and the plot of the potential as a function of temperature is given in Figure 12. The

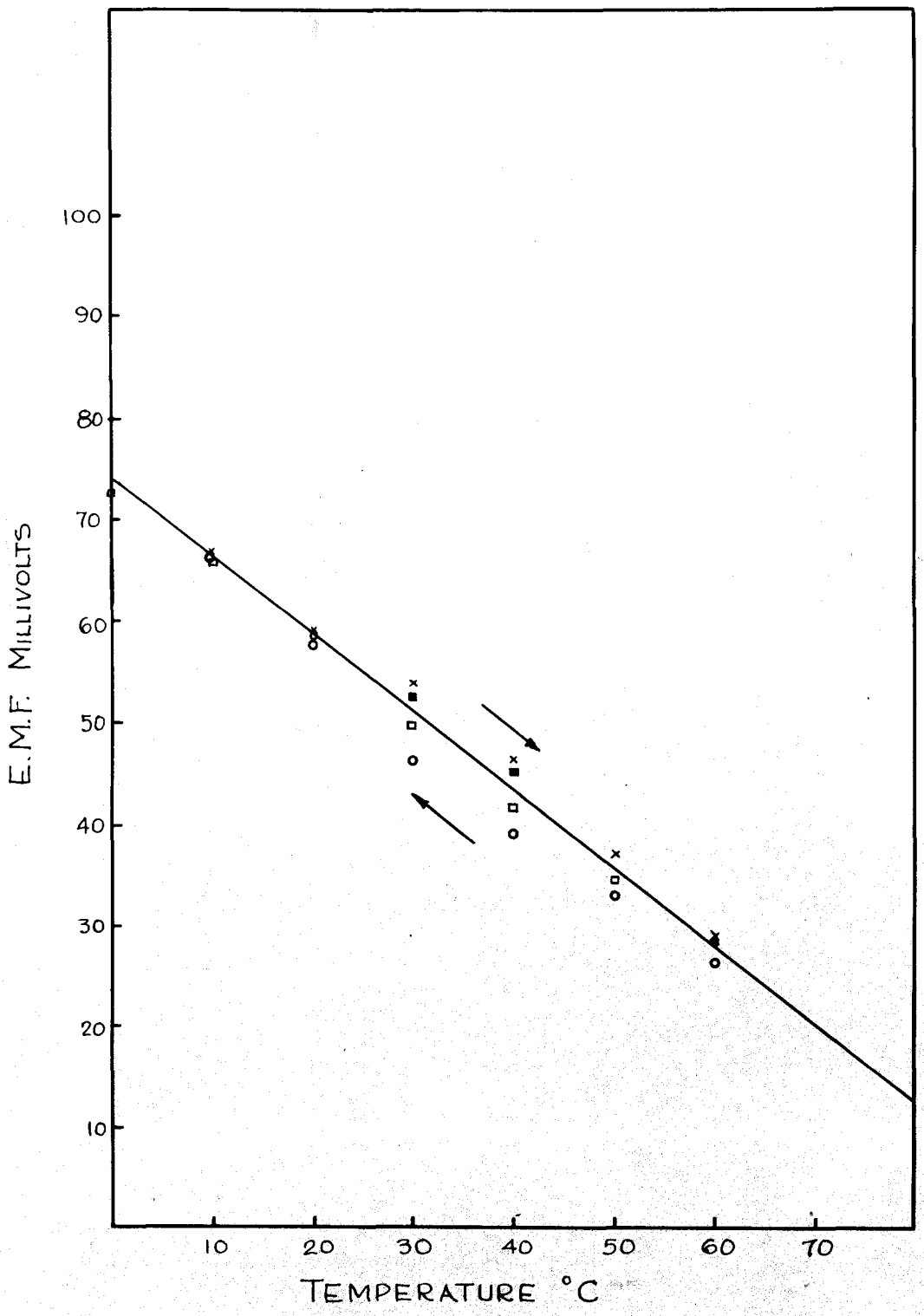

Fig. 12. Reversibility of the Amylose-Iodine Reaction

points above the straight line were obtained on decreasing the temperature, and the points below, on increasing the temperature.

The system is slow in reaching equilibrium; however, the points on any one temperature are sufficiently close together to show that concentration of iodine is a function of temperature. Iodine leaves the complex when the temperature is raised and re-enters when the temperature is lowered. The reaction is reversible.

3. Effect of iodide ion

The effect of change in the concentration of iodide ion is not completely explained by equation (13). The effect of a change in the concentration of iodide ion was studied by titrating a solution of amylose containing half the theoretical amount of iodine, with potassium iodide (Table 40). A plot of the concentration of iodine against the concentration of iodide ion is given in Figure 13. At low iodide concentrations the curve has a slope of -1, and at an iodide concentration of unity the slope suddenly levels to zero or nearly so. This can be explained by employing equations similar to those used to explain the reaction between cyclohexaamylose and iodine. Previous considerations require that the triiodide complex precipitate; therefore the following set of equations is proposed:

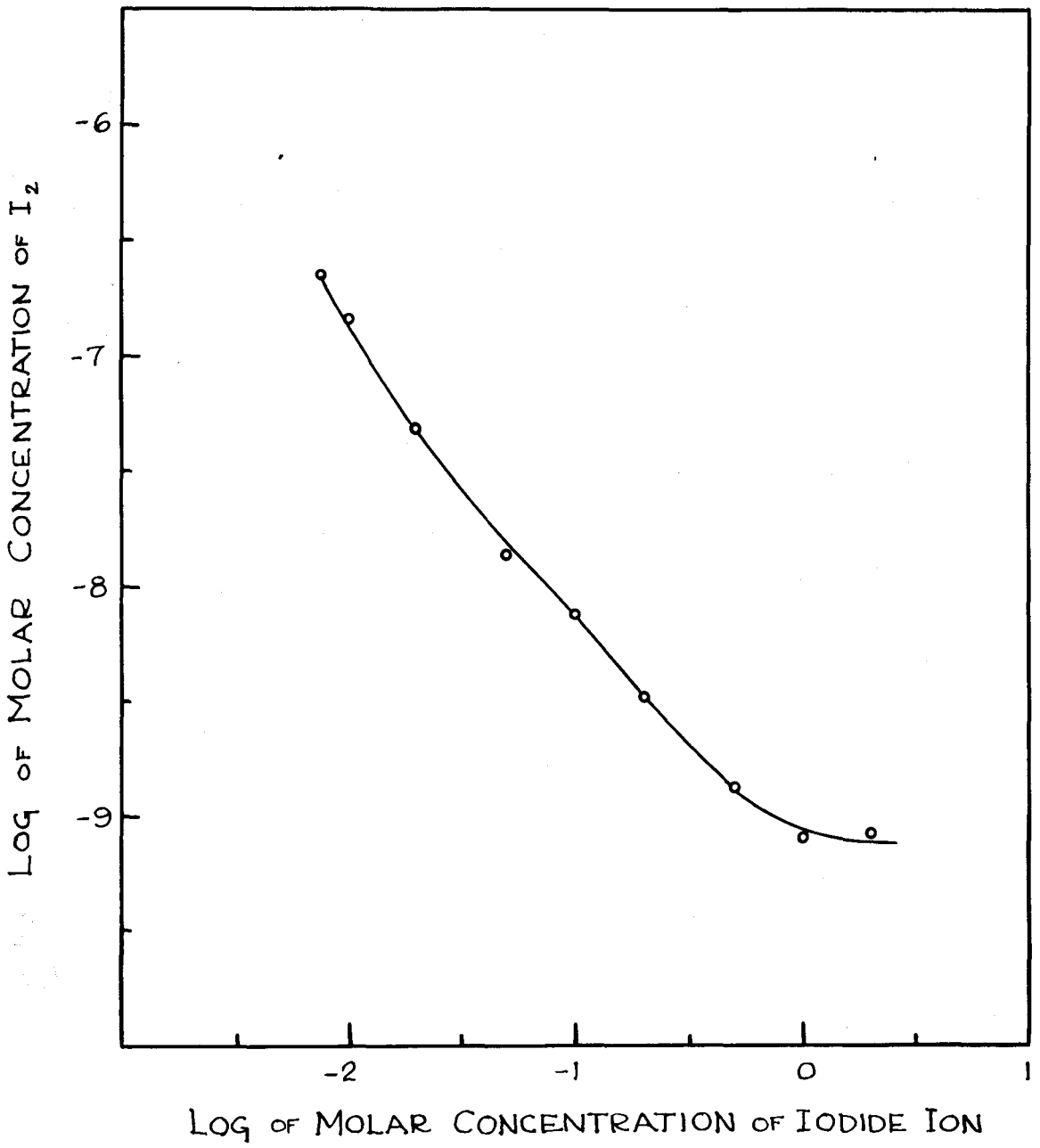

Fig. 13. Titration of Amylose with Potassium Iodide

$$Am(aq) \quad + \quad NI_2(aq) \longrightarrow Am(I_2)_N(aq) \qquad (14)$$

$$Am(I_2)_N(aq) \quad + \quad NI^-(aq) \longrightarrow Am(I_3^-)_N(s) \qquad (15)$$

$$Am(aq) \quad + \quad NI^-(aq) \longrightarrow Am(I^-)_N(aq) \qquad (16)$$

$$Am(I^-)_N(aq) \quad + \quad NI_2(aq) \longrightarrow Am(I_3^-)_N(s). \qquad (17)$$

At high iodide concentrations the last two reactions are the controlling ones, and at low iodide concentrations, the first two reactions are the controlling ones.

The equilibrium constants for reactions (16) and (17) are

$$K_3 = \frac{[Am(I^-)_N]}{[Am][I^-]^N} \qquad (18)$$

$$K_4 = \frac{1}{[Am(I^-)_N][I_2]^N} . \qquad (19)$$

Eliminating $[Am(I^-)_N]$ between these two reactions, the following equation is obtained:

$$K_3[Am]\,[I^-]^N = \frac{1}{K_4[I_2]^N} . \qquad (20)$$

The concentration of amylose can be expressed in terms of the initial concentration of amylose A_o, the amount of iodine bound Q, and the amount of amylose-iodide complex $Am(I^-)_N$.

$$K_3\left[A_o - \frac{Q}{N} - Am(I^-)_N\right][I_2]^N = \frac{1}{K_4[I^-]^N} . \qquad (21)$$

Substituting equation (19) into equation (21),

$$K_3\left[A_o - \frac{Q}{N}\right][I_2]^N - \frac{K_3}{K_4} = \frac{1}{K_4[I^-]^N}, \qquad (22)$$

Rearranging

$$\left[A_o - \frac{Q}{N}\right][I_2]^N = \frac{1}{K_4}\left|\frac{1}{K_3[I^-]^N} \pm 1\right| \qquad (23)$$

In the experiment, the amount of iodine bound remained essentially constant; therefore the term $\left[A_o - \frac{Q}{N}\right]$ can be considered constant. Taking the logarithm of both sides, rearranging and dividing through by N,

(24)

$$\log[I_2] = \frac{1}{N}\log\left|\frac{1}{K_3[I^-]^N} \pm 1\right| - \frac{1}{N}\log K_4 - \frac{1}{N}\log\left[A_o - \frac{Q}{N}\right].$$

Differentiating with respect to log $[I^-]$

$$\frac{\partial \log[I_2]}{\partial \log[I^-]} = -\frac{1}{1 \pm K_3[I^-]^N}. \qquad (25)$$

This is the expression for the slope of the graph of log $[I_2]$ against log $[I^-]$. Since N is large, at low iodide concentrations $K_3[I^-]^N \rightarrow 0$ and the slope $\rightarrow -1$. At high iodide concentrations $K_3[I^-]^N \rightarrow \infty$ and the slope $\rightarrow 0$.

The equilibrium constants for reactions (14) and (15) are given by the following expressions:

$$K_1 = \frac{[Am\ (I_2)_N]}{[Am][I_2]^N} \qquad (26)$$

$$K_2 = \frac{1}{\left[Am(I_2)_N\right]\left[I^-\right]^N} \quad . \qquad (27)$$

Eliminating $\left[Am(I_2)_N\right]$

$$K_1\left[Am\right]\left[I_2\right]^N = \frac{1}{K_2\left[I^-\right]^N} \qquad (28)$$

or

$$\log\left[Am\right] + N \log\left[I_2\right] = -N \log\left[I^-\right] - \log K_1 K_2. \qquad (29)$$

Since $\left[Am\right]$ is essentially constant

$$\frac{\partial \log\left[I_2\right]}{\partial \log\left[I^-\right]} = -1 \qquad (30)$$

for all values of the concentration of iodide ion.

The above equations require that the curve relating the logarithm of the concentration of iodine to the logarithm of the concentration of iodide ion be a straight line with a slope of negative one at low iodide concentrations changing rapidly to a straight line with a slope of zero at higher iodide concentrations. This agrees with a plot of the experimental values as shown in Figure 13.

The value of $(K_4)^{\frac{1}{N}}$ can be determined from equation (23) and Figure 13. Since

$$\left[A_o - \frac{Q}{N}\right]\left[I_2\right]^N = \frac{1}{K_4}\left|\frac{1}{K_3\left[I^-\right]^N} + 1\right| \qquad (31)$$

As $\left[I^-\right]^N \rightarrow \infty$

$$\left[I_2\right]^N = \frac{1}{K_4\left[A_o - \frac{Q}{N}\right]} \qquad (32)$$

or

$$(K_4)^{\frac{1}{N}} = \frac{1}{\left[I_2\right]} \cdot \frac{1}{\left[A_o - \frac{Q}{N}\right]^{\frac{1}{N}}} . \qquad (33)$$

The concentration of iodine as $\left[I^-\right]^N \rightarrow \infty$ obtained from Figure 13 is 8.0×10^{-10}. The term $\left[A_o - \frac{Q}{N}\right]^{\frac{1}{N}}$ approaches unity as N becomes larger; therefore

$$(K_4)^{\frac{1}{N}} = 1.25 \times 10^{19} \qquad (34)$$

and

$$\Delta F^o_{298} = -12{,}500 \text{ cals. per mole of iodine.} \qquad (35)$$

The value of $(K_3)^{\frac{1}{N}}$ can be determined from the expression

$$\left[A_o - \frac{Q}{N}\right]\left[I_2\right]^N = \left|\frac{1}{K_4} \frac{1}{K_3\left[I^-\right]^N} \neq 1\right| \qquad (36)$$

At $\left[I^-\right] = 1$, $\left[I_2\right] = 8.37 \times 10^{-10}$ and $K_4 = 1.25 \times 10^{19}$.

Substituting these values into equation (36),

$$\frac{(K_3 \neq 1)^{\frac{1}{N}}}{K_3} = 1.045\left[A_o - \frac{Q}{N}\right]^{\frac{1}{N}} \qquad (37)$$

Since $\left[A_o - \frac{Q}{N}\right]^{\frac{1}{N}}$ approaches unity for large values of N,

$$\frac{1}{K_3} \neq 1 = (1.045)^N \qquad (38)$$

or
$$(K_3)^{\frac{1}{N}} = \frac{1}{\left[(1.045)^N - 1\right]^{\frac{1}{N}}} \quad (39)$$

As N becomes larger the value of the numerator approaches 1.045; therefore

$$(K_3)^{\frac{1}{N}} = 0.96 \quad (40)$$

and

$$\Delta F^{\circ}_{298} = - 24.7 \text{ cals. per mole of iodine.} \quad (41)$$

It is evident that the important reactions are

$$Am(aq) + NI_2(aq) \rightarrow Am(I_2)_N(aq) \quad (14)$$

$$Am(I_2)_N(aq) + NI^-(aq) \rightarrow Am(I_3^-)_N(s). \quad (15)$$

The equilibrium constants for these reactions cannot be determined from the data on hand; but the pseudo-equilibrium constant of the overall reaction,

$$Am + NI_2 + NI^- \rightarrow Am(I_3^-)_N(s), \quad (42)$$

is equal to the product of $(K_3)^{\frac{1}{N}}$ and $(K_4)^{\frac{1}{N}}$ or $1.20 \times 10^{+9}$.

4. Value of N

The equilibrium constant for reaction (42) is given by the expression

$$K = \frac{1}{[Am][I_2]^N[I^-]^N} . \quad (43)$$

This requires that

$$[Am]_1 [I_2]_1^N [I^-]_1^N = [Am]_2 [I_2]_2^N [I^-]_2^N \qquad (44)$$

where the subscripts indicate different equilibrium conditions. Rearranging, the expression becomes

$$\log \frac{[Am]_1}{[Am]_2} = N \log \frac{[I^-]_2 [I_2]_2}{[I^-]_1 [I_2]_1} . \qquad (45)$$

It should be possible to calculate the value of N from titrations performed at different amylose concentrations. The ratio of the weights of amylose used is equal to the ratio of the concentrations. The concentration of iodine, at which the amylose bound one-half of the final amount of iodine, was used to determine the value of N. The values obtained are low and vary over a wide range. The difference in the concentration of iodine should be small in order to obtain large values of N. This fact, adsorption, and the inhomogeneity of the sample prevent any accurate determination of N using this equation.

5. Distribution of chain length

If the amylose were homogeneous in regard to chain length, the concentration of iodine would remain constant during the titration. The concentration of iodine is given by the following expression:

$$[I_2] = \frac{1}{K^{\frac{1}{N}}} \quad \frac{1}{[Am]^{\frac{1}{N}}} \quad \frac{1}{[I^-]^{\frac{1}{N}}} \cdot \qquad (46)$$

For large values of N the quantity $[Am]^{\frac{1}{N}}$ does not change measurably with the degree of reaction. At constant iodide concentration, the concentration of iodine is a function of the equilibrium constant K, which is constant for a single chain length.

A plot of the concentration of iodine against the amount of iodine bound for a typical titration (Figure 14) shows that the concentration of iodine increases during the course of the reaction.

Bates (21) has shown that the characteristic potential of the iodine titration varies with the chain length of the amylose. The longer chains bind iodine at a lower iodine activity. Rundle, Baldwin and Foster (33) have shown that the iodine enters a partly filled helix more readily than an unfilled helix; the iodine completely fills a helix before starting to fill another. In a system of amylose molecules of different chain lengths, the iodine will react completely with the longer chains first and then with successively shorter chains.

Considering the chain of iodine molecules in a helix as a linear harmonic oscillator, Foster (24) was able to show that the characteristic potential is related to the chain

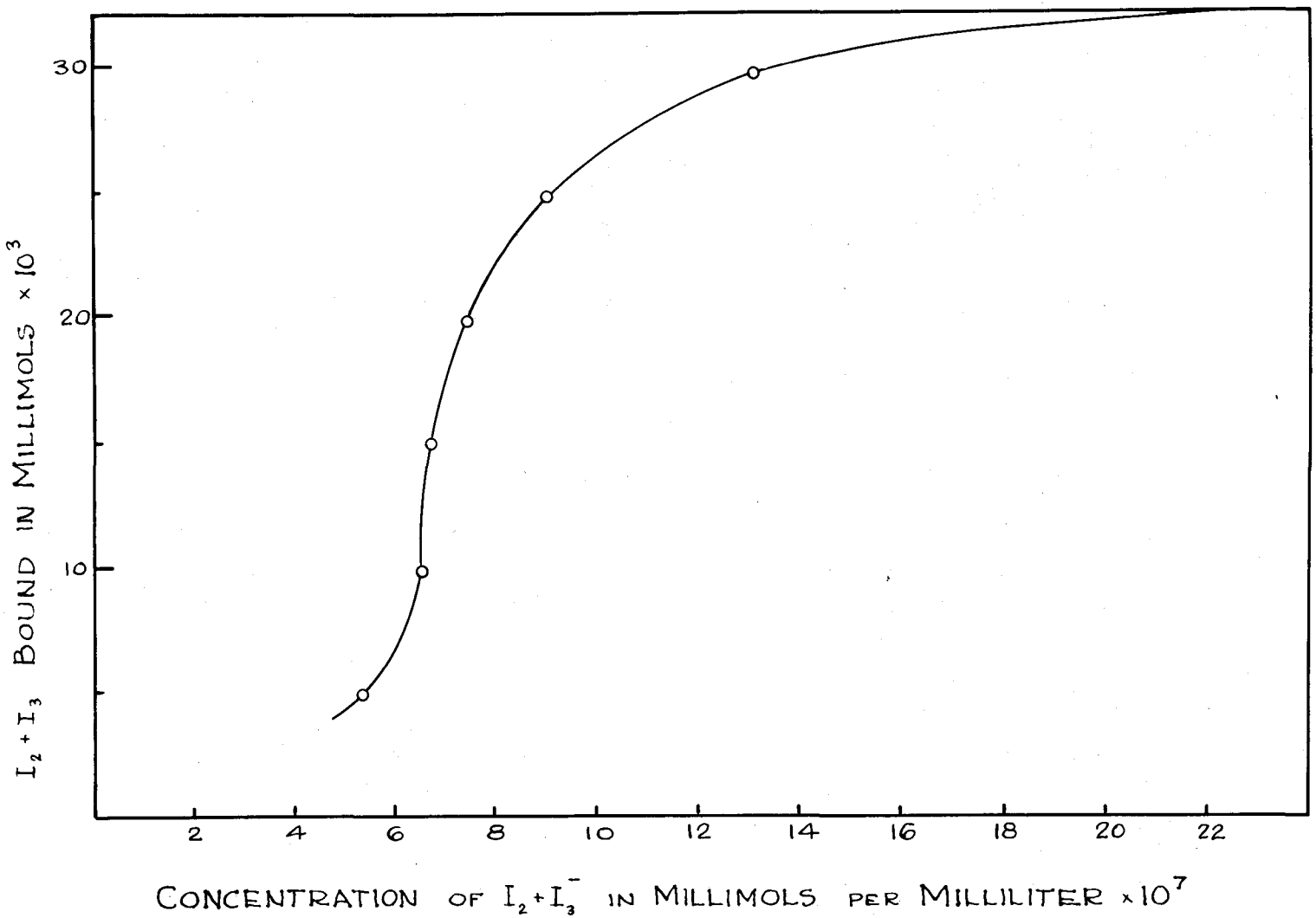

Fig. 14. **Amount of Iodine Bound by Amylose as a Function of Iodine Concentration**

length of amylose by an expression of the type

$$E = A + B \frac{1}{\sqrt{n}} \qquad (47)$$

where A and B are constants and n is the number of glucose residues in the chain. Since the potential of the iodine electrode is related to the activity of the iodine in solution, the activity of the iodine can be expressed as a function of the chain length of the amylose molecule by an expression of the type

$$\log [I_2] = A' + B' \frac{1}{\sqrt{n}} \qquad (48)$$

where A' is a function of the concentration of amylose and the concentration of iodide ion, and B' is a function of universal constants.

Since the concentration of amylose and the concentration of iodide ion enter only into the intercept term A', differences in experimental conditions can be corrected by shifting the scale of the logarithm of the concentration of iodine in a plot of the logarithm of the concentration of iodine against the reciprocal of the square root of n. Such a plot is shown in Figure 15, obtained by using the numerical values of A and B given by Foster (24).

This equation can be applied to the determination of the chain length distribution of amylose. The iodine concentration at which the greatest increase in the amount of

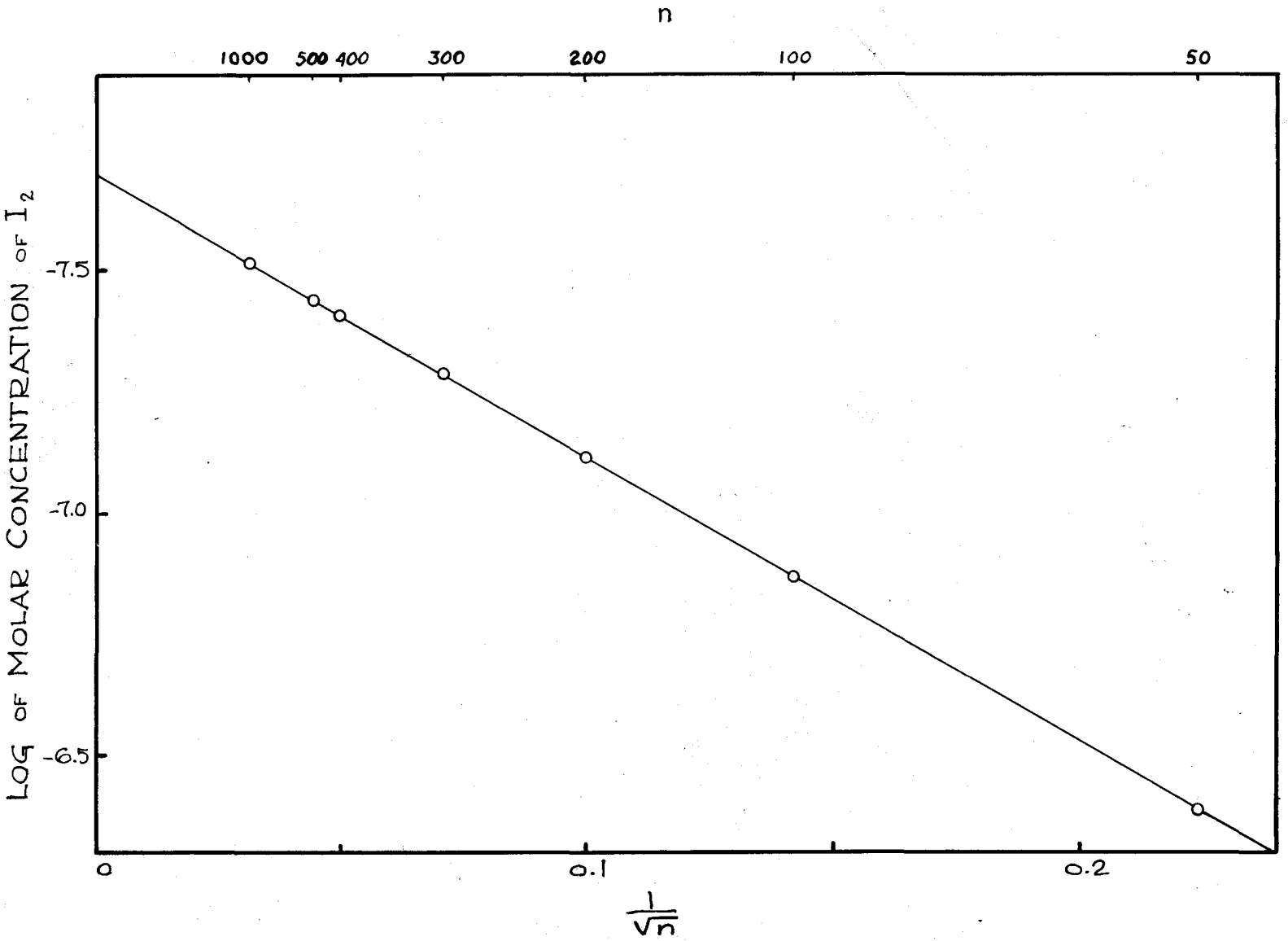

Fig. 15. Characteristic Iodine Concentration as a Function of Chain Length of Amylose

iodine bound occurs is estimated from a plot of the amount of iodine bound against the concentration of iodine. The scale of the logarithm of the concentration of iodine in Figure 15 is shifted until this concentration of iodine corresponds to the average chain length of the amylose being studied. The logarithm of the concentrations of iodine corresponding to various chain lengths are read from the graph. Increments of one hundred glucose residues were taken. The amount of iodine bound corresponding to these chain lengths is determined from the plot of the amount of iodine bound against the concentration of iodine in solution, and the fraction of the total iodine bound at each increment is computed. A plot of the results obtained when this method is applied to the titration of 50.0 milligrams of corn amylose in 0.05 molar KI is shown in Figure 16. The average chain length was taken as 250 glucose residues. Such a plot gives the fraction of the amylose having chain lengths greater than the corresponding value of n. The increase in the fraction of iodine bound within the range of chain length is a measure of the fraction of amylose having chain lengths within these limits; therefore the slope of the curve in Figure 16 represents the chain length distribution of amylose used (Figure 17).

The region of short chain lengths is not reliable. The amount of iodine bound is increased by an unknown amount because of the adsorption of iodine toward the end of the

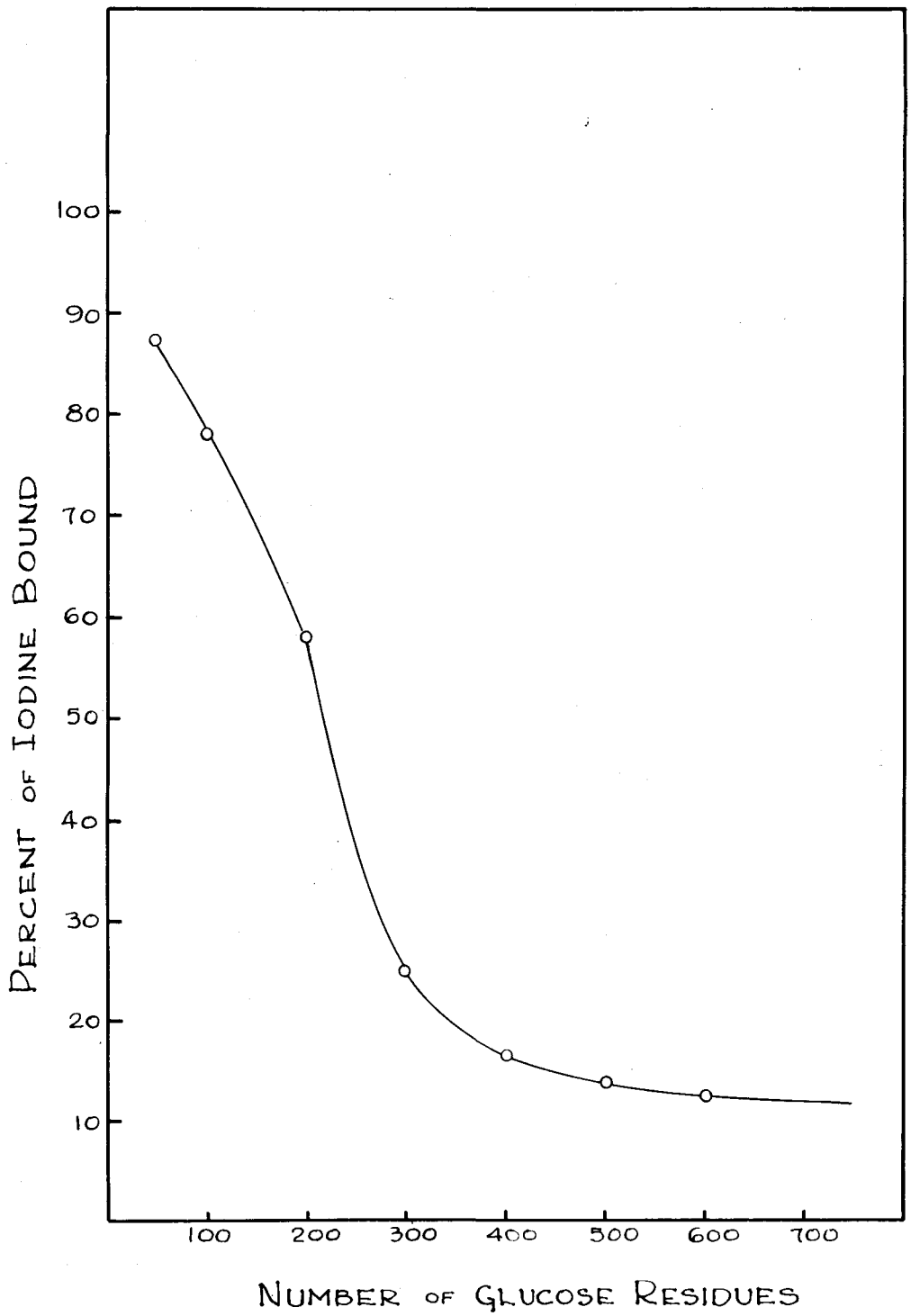

Fig. 16. Fraction of Amylose Having Chain Lengths Greater Than n

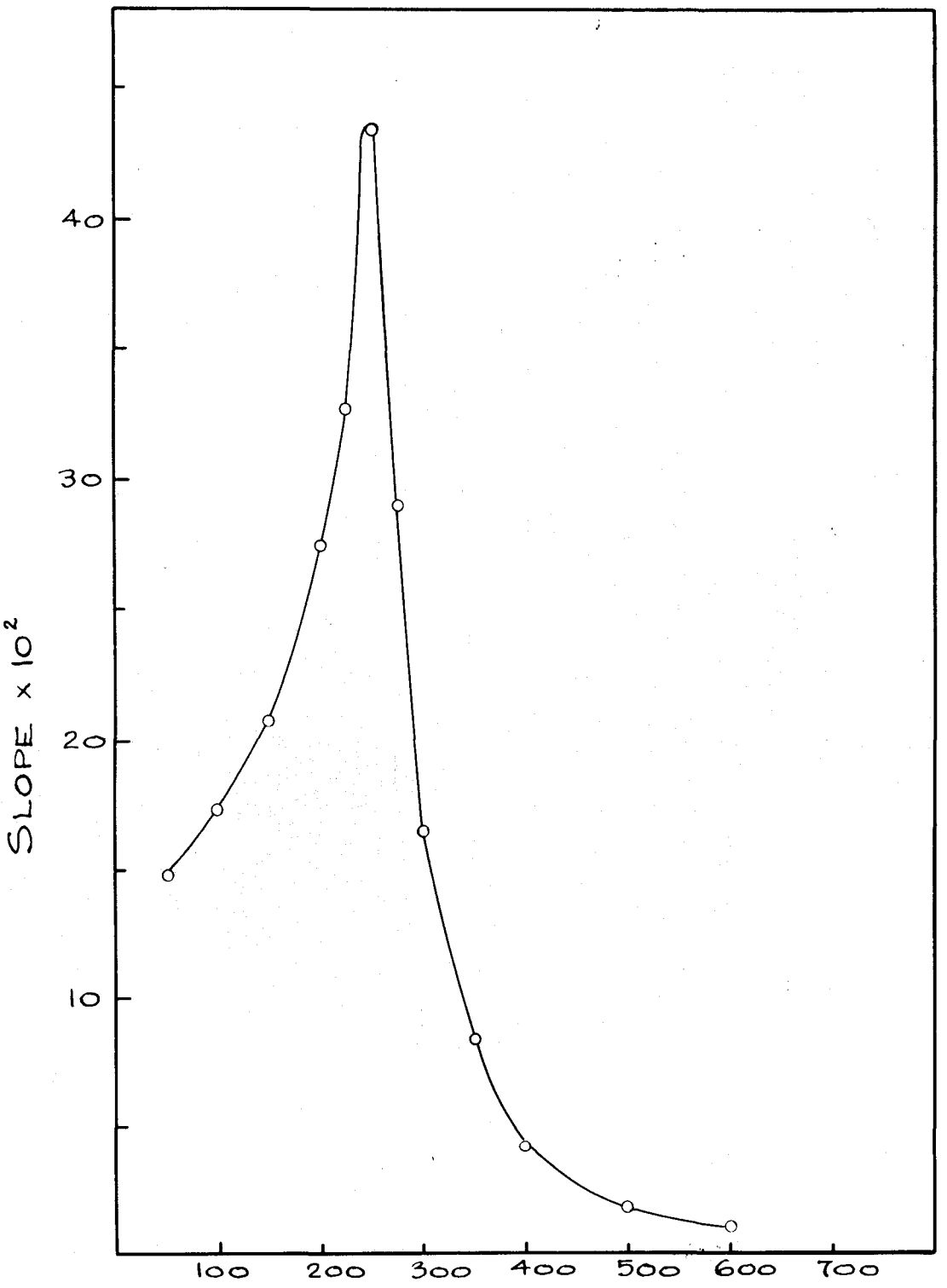

Fig. 17. Chain length distribution of Corn Amylose

titration. The method is not applicable to chain lengths of less than fifty glucose residues.

The results obtained indicate that twenty to twenty-five per cent by weight of corn amylose consists of molecules having chain lengths greater than five hundred glucose residues. It must be realized that Figure 16 represents the weight average distribution of chain length.

The values of the average chain length used by Foster in determining the constants of his equation are based on viscosity and osmotic pressure measurements; consequently the above method of determining chain length distribution is dependent upon the accuracy of these measurements. In spite of these limitations, the method is useful in that it is a simple means of determining chain length distribution and can be used to study the efficiency of fractionation procedures.

6. Calculation of thermodynamic constants

The distribution curve can be used to calculate the equilibrium constant of the starch-iodine reaction more accurately. The concentration of iodine corresponding to a particular chain length can be selected more reasonably from the distribution curve.

Consider the reaction

$$Am(aq) + NI^{-}(aq) + NI_2(aq) \rightarrow Am(I_3^{-})_N(s). \quad (49)$$

It is possible to formulate a pseudo-equilibrium constant

$$K^{\frac{1}{N}} = \frac{1}{[Am]^{\frac{1}{N}} [I_2] [I^-]} \qquad (50)$$

which applies to the reaction per mole of iodine. For large values of N, the term $[Am]^{\frac{1}{N}}$ is essentially unity and, within experimental error, is constant for values of the degree of reaction from 0.01 to 0.99. Selecting the concentration of iodine at which the greatest increase in the amount of iodine bound occurs, the values of the pseudo-equilibrium constant have been calculated at various concentrations of iodide ion and amylose and are given in Table 44.

The low value of the pseudo-equilibrium constant at 0.025 molar iodide concentration is not readily explained. The titrations performed at this iodide concentration are also irregular in another respect as will be shown in the next section. The values of the pseudo-equilibrium constant are in good agreement at the higher iodide concentrations. The value appears to be 1.0×10^{19}. The standard free energy of formation corresponding to this value is -12,000 cals. per mole of iodine. This value agrees with the value determined in the preceding section from the effect of iodide ion.

The equilibrium constant at 0° C. was determined in the same manner and was found to be 7.2×10^{19}.

The entropy change for the reaction at 25° C. has been determined in the same manner as was the entropy change for the formation of the cyclohexaamylose-iodine complex. Since $[Am]^{\frac{1}{N}}$ is nearly unity and constant within experimental error, the pseudo-equilibrium constant for the reaction can be written as

$$K^{\frac{1}{N}} = \frac{1}{[I_2][I^-]} \qquad (51)$$

The standard free energy change is

$$\Delta F^o = 2.33\ RT \log [I_2][I^-] \qquad (52)$$

and

$$\frac{\partial \Delta F^o}{\partial T} = -\Delta S = 2.33\ RT \frac{\partial \log [I_2]}{\partial T} + 2.33\ R \log [I_2][I^-] \qquad (53)$$

From the previous section

$$\frac{\partial \log [I_2]}{\partial T} = \frac{\partial \log C}{\partial T} + \frac{\partial \log K'}{\partial T} \cdot \frac{[I^-]}{K' + [I^-]} \qquad (54)$$

and

$$\frac{\partial \log K'}{\partial T} = 9.6 \times 10^{+2} \frac{1}{T^2} .$$

A plot of log C against the temperature for 100.0 milligrams of corn amylose in 0.05 molar KI is given in Figure 18. The slope at 25° C. is 3.15×10^{-2}. Substituting these values and the values $[I^-] = 5.0 \times 10^{-2}$, $K' = 1.40 \times 10^{-3}$ and $T = 298°$ A. into equation (54),

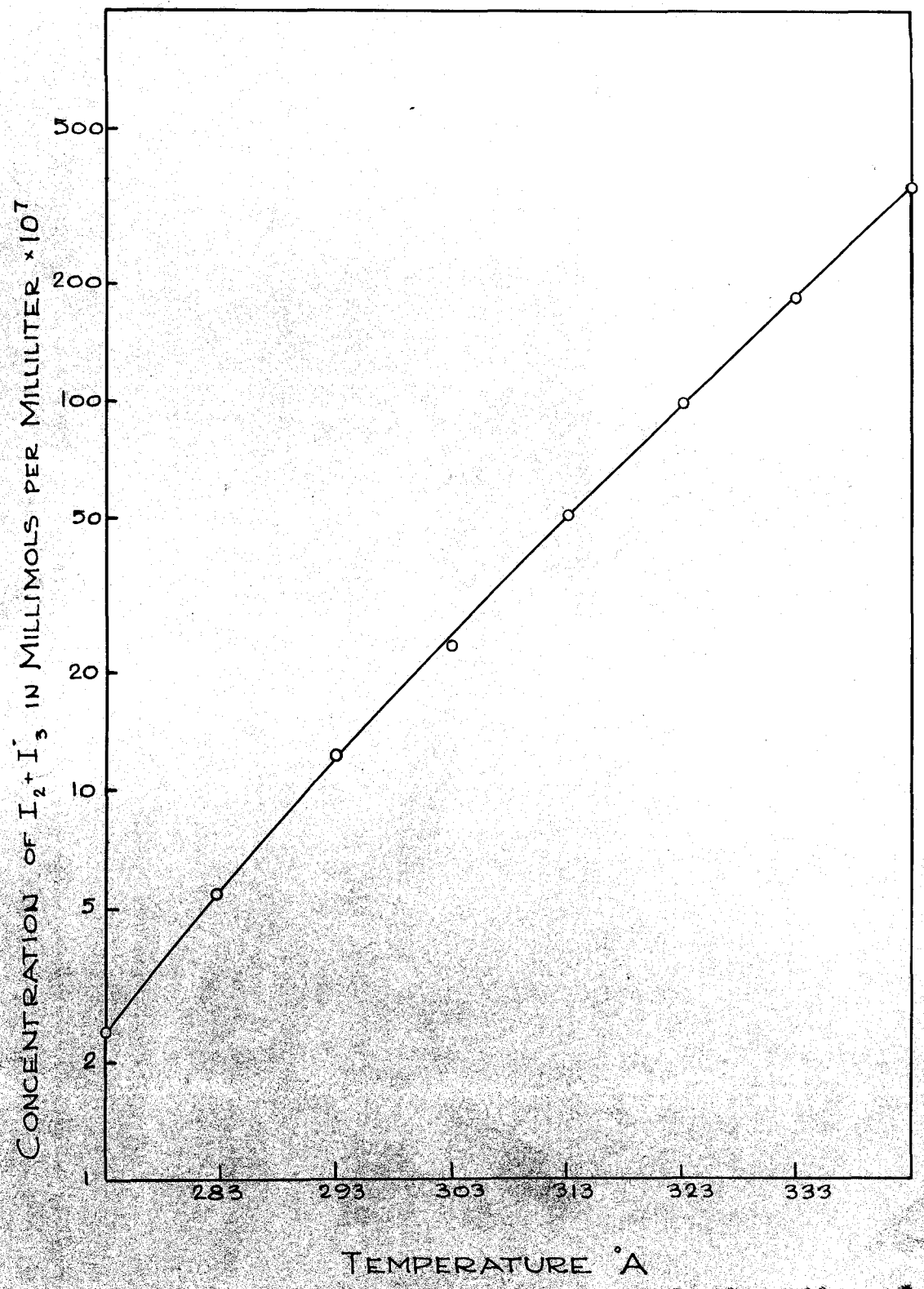

Fig. 18. Effect of temperature on the formation of Amylose-iodine complex

$$\frac{\partial \log [I_2]}{\partial T} = 4.20 \times 10^{+2} \qquad (55)$$

and

$$-\Delta S = 2.33\ RT \times 4.20 \times 10^{-2} + 2.33\ R \log \frac{[I_2 + I_3^-]K'}{K' + [I^-]} \cdot [I^-] \qquad (56)$$

Substituting the proper numerical values

$$\Delta S^{\circ}_{298} = -25.6 \text{ e.u. per mole of iodine.} \qquad (57)$$

The standard heat of reaction is

$$\Delta H^{\circ}_{298} = -19,600 \text{ cals. per mole of iodine.} \qquad (58)$$

7. Amount of iodine bound

The amount of iodine bound by the amylose has been determined from the results of the titrations of amylose with iodine. It is not possible to distinguish between the amount of iodine bound as I_2 and the amount bound as I_3^- ion. Table 45 gives the number of glucose residues per molecule of iodine bound at the different iodide concentrations used, at several different amylose concentrations and at the three temperatures studied.

The amount of iodine bound was determined by extrapolating the level portion of the plot of iodine bound against the concentration of total iodine as shown in Figure 19. The level portion of the curve is nearly flat for the experiments performed at 25° C. and at 50° C.; however, for the experiments performed at 0° C. the curves do not become level but

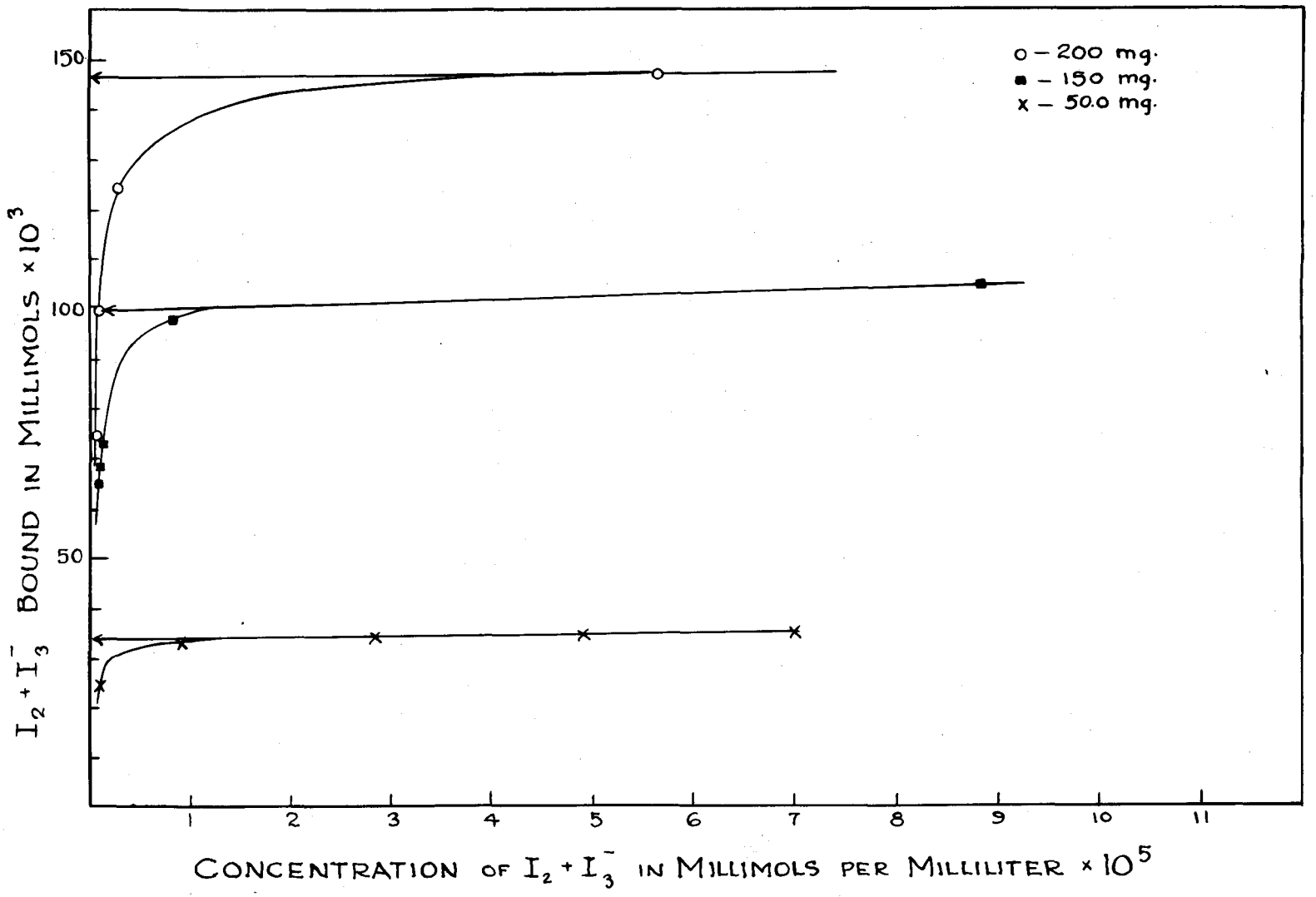

Fig. 19. Amount of Iodine bound by Corn Amylose (0.05 Molar KI)

have a definite and decreasing slope. The amount of iodine bound for these titrations was estimated from the point on the curve at which the change in slope appears to become constant.

The amount of iodine bound at 0.05 molar KI and at 0.100 molar KI concentrations is essentially the same, and a change in the temperature does not greatly alter the amount of iodine bound. There appears to be an abnormally large amount of iodine bound at 0.025 molar KI concentration. This agrees with the abnormalties observed for the iodine concentration at the midpoint of the titration, at this iodide level. This effect has not been satisfactorily explained.

The values at 0.100 and 0.05 molar KI concentrations agree with those obtained by Bates (21).

V. SUMMARY AND CONCLUSIONS

1. An extensive investigation of the reactions of iodine and cyclohexaamylose, iodine and cycloheptaamylose, and iodine and amylose in solution was made. The reactions were followed by a potentiometric titration employing concentration cells.

2. The following set of equations is proposed for the reactions between iodine, iodide ion and cyclohexaamylose (α) in solution:

$$\alpha + I_2 \longrightarrow \alpha I_2 \qquad (1)$$

$$\alpha I_2 + I^- \longrightarrow \alpha I_3^- \qquad (2)$$

$$\alpha + I^- \longrightarrow \alpha I^- \qquad (3)$$

$$\alpha I^- + I_2 \longrightarrow \alpha I_3^- \qquad (4)$$

3. The equilibrium constants for the reactions at 25° C. were determined. The values are: $K_1 = 2.0 \times 10^{+3}$, $K_2 = 1.35 \times 10^{+5}$, $K_3 = 13.5$ and $K_4 = 2.00 \times 10^{+7}$. The subscripts designate the reaction.

4. The following thermodynamic quantities for the reaction

$$\alpha + I_2 \longrightarrow \alpha I_2$$

at 25° were calculated.

$$\Delta F^\circ_{298} = -4,500 \text{ cals. per mole}$$

$$\Delta S^{\circ}_{298} = -27.2 \text{ e. u. per mole}$$

$$\Delta H^{\circ}_{298} = -12,600 \text{ cals. per mole}$$

5. A crytalline complex between cyclohexaamylose and potassium iodide was prepared.

6. The following set of equations is proposed for the reaction of iodine, iodide ion and cycloheptaamylose in solution:

$$\beta \not\parallel I_2 \longrightarrow \beta I_2 \qquad (1)$$

$$\beta I_2 \not\parallel I^- \longrightarrow \beta I_3^- \qquad (2)$$

$$\beta \not\parallel I^- \longrightarrow \beta I^- \qquad (3)$$

$$\beta I^- \not\parallel I_2 \longrightarrow \beta I_3^- \qquad (4)$$

7. The equilibrium constants for the last two reactions were determined. The values are: $K_3 = 1.45$ and $K_4 = 1.00 \times 10^{+6}$.

8. The phase relationship of the amylose iodine reaction was studied and it was concluded that the triiodide complex is in the solid phase. The following set of equations is proposed for the reaction of iodine, iodide ion and amylose:

$$Am\ (aq) \not\parallel NI_2(aq) \longrightarrow Am(I_2)_N\ (aq)$$

$$Am(I_2)_N\ (aq) \not\parallel NI^-\ (aq) \longrightarrow Am(I_3^-)_N\ (s)$$

$$Am\ (aq) \not\parallel NI^-\ (aq) \longrightarrow Am(I^-)_N\ (aq)$$

$$Am(I^-)_N\ (aq) \not\parallel NI_2\ (aq) \longrightarrow Am(I_3^-)_N\ (s)$$

9. The pseudo-equilibrium constant per mole of iodine was calculated for the reaction

$$Am\ (aq) \neq NI_2 \neq NI^- \longrightarrow Am(I_3^-)_N\ (s).$$

The value obtained is $(K)^{\frac{1}{N}} = 1.0 \times 10^{19}$.

10. The thermodynamic quantities per mole of iodine were calculated for the above reaction. The values are:

F°_{298} = -12,000 cals. per mole of iodine

S°_{298} = -25.6 e.u. per mole of iodine

H°_{298} = -19,600 cals. per mole of iodine.

11. Foster's equation relating chain length of amylose and the characteristic potential was applied to the study of the chain length distribution of amylose. It was shown that the chain length distribution of amylose can be determined from a single iodine titration.

12. The reaction of iodine and amylose was studied potentiometrically at 0° C., 25° C., and 50° C. It was shown that the reaction at 0° C. is very slow and that there is considerable adsorption of iodine in addition to that required to form the complex. It was shown that the amount of iodine bound appears to be independent of the temperature.

Table 1

Titration of 174.6 Milligrams of Cyclohexaamylose in 200 Milliliters of 0.01 M. KI with 0.004292 M. I_2

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
0.0935	1.00	201.0	4.29	0.00292	4.29	1.45
0.0847	2.00	202.0	8.58	0.01195	8.57	5.92
0.0779	3.00	203.0	12.88	0.02955	12.85	14.5
0.0762	4.00	204.0	17.17	0.0452	17.12	22.2
0.0745	5.00	205.0	21.46	0.0645	21.39	31.5
0.0712	10.00	210.0	42.92	0.167	42.76	79.6
0.0680	15.00	215.0	64.38	0.321	64.06	149.2
0.0647	20.00	220.0	85.84	0.556	85.28	253.
0.0609	25.00	225.0	107.3	0.942	106.4	418.
0.0558	30.00	230.0	128.8	1.65	127.1	718.
0.0483	35.00	235.0	150.2	3.49	146.7	1480.
0.0370	40.00	240.0	171.7	9.54	162.1	3970.
0.0265	45.00	245.0	193.1	24.8	168.3	10100.
0.0204	50.00	250.0	214.6	43.8	170.8	17500.
0.0167	55.00	255.0	236.0	64.3	171.7	25200.
0.0141	60.00	260.0	257.5	85.8	171.7	33000.
0.0124	65.00	265.0	279.0	106.	172.0	40000.
0.0108	70.00	270.0	300.4	129.	171.4	47800.
0.0098	75.00	275.0	321.9	150.	172.4	54400.
0.0082	85.00	285.0	364.8	192.	172.8	67400.

Column headings:

(1) Electromotive force in volts
(2) Volume of iodine solution added, in milliliters
(3) Total volume of solution, in milliliters
(4) Total iodine added, in millimols x 10^3
(5) $I_2 + I_3^-$ in the reaction cell, in millimols x 10^3
(6) $I_2 + I_3^-$ bound by cyclohexaamylose, in millimols x 10^3
(7) Concentration of $I_2 + I_3^-$ in reaction cell, in millimols per milliliter x 10^8

Table 2

Titration of 174.6 Milligrams of Cyclohexaamylose in 200.0 Milliliters of 0.100 M. KI with 0.04946 M. I_2

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
0.0606	1.00	201.0	4.95	0.0441	4.90	2.19
0.0546	2.00	202.0	9.89	0.1395	9.75	6.91
0.0432	3.00	203.0	14.84	0.514	14.3	25.3
0.0246	4.00	204.0	19.79	2.94	16.8	144.
0.0155	5.00	205.0	24.73	7.38	17.4	360.
0.0114	6.00	206.0	29.68	12.2	17.5	589.

Column headings:

(1) Electromotive force in volts

(2) Volume of iodine solution added, in milliliters

(3) Total volume of solution, in milliliters

(4) Total iodine added to cell, in millimols x 10^2

(5) $I_2 + I_3^-$ in reaction cell, in millimols x 10^2

(6) $I_2 + I_3^-$ bound by cyclohexaamylose, in millimols x 10^2

(7) Concentration of $I_2 + I_3^-$ in reaction cell, in millimols per milliliter x 10^6

Table 3

Titration of 349.3 Milligrams of Cyclohexaamylose in 200.0 Milliliters of 0.100 M. KI with 0.04946 M. I_2

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
0.0715	1.00	201.0	4.95	0.0187	4.93	9.31
0.0695	2.00	202.0	9.89	0.0434	9.85	21.4
0.0669	3.00	203.0	14.84	0.0811	14.76	40.0
0.0634	4.00	204.0	19.79	0.1421	19.64	69.7
0.0586	5.00	205.0	24.73	0.2548	24.48	124.2
0.0513	6.00	206.0	29.68	0.471	29.21	229.
0.0388	7.00	207.0	34.62	1.66	32.96	805.
0.0264	8.00	208.0	39.57	5.12	34.65	2460.
0.0198	9.00	209.0	44.52	9.54	34.98	4570.
0.0160	10.00	210.0	49.46	14.2	35.26	6760.
0.0136	11.00	211.0	54.41	18.8	35.59	8930.

Column headings:

(1) Electromotive force in volts

(2) Volume of iodine solution added, in milliliters

(3) Total volume of solution, in milliliters

(4) Total iodine added, in millimols x 10^2

(5) $I_2 \neq I_3^-$ in reaction cell, in millimols x 10^2

(6) $I_2 \neq I_3^-$ bound by cyclohexaamylose, in millimols x 10^2

(7) Concentration of $I_2 \neq I_3^-$ in reaction cell, in millimols per milliliter x 10^7

Table 4

Titration of 174.6 Milligrams of Cyclohexaamylose in 200.0 Milliliters of 1.00 M. KI with Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
			Titration with 0.002348 M. Iodine			
39.1	1.00	201.0	2.35	0.110	2.24	7.68
41.0	3.00	203.0	7.04	0.292	6.75	20.2
41.2	5.00	205.0	11.74	0.477	11.26	32.4
41.1	7.00	207.0	16.44	0.674	15.76	45.6
40.8	9.00	209.0	21.14	0.884	20.25	59.2
40.3	11.00	211.0	25.83	1.123	24.71	74.7
40.0	13.00	213.0	30.53	1.36	29.17	89.2
39.7	15.00	215.0	35.23	1.58	33.65	103.
			Titration with 0.02473 M. Iodine			
37.7	1.00	216.0	59.96	3.15	56.81	204.
35.3	2.00	217.0	84.69	5.39	79.30	348.
32.5	3.00	218.0	109.42	8.69	100.73	558.
29.2	4.00	219.0	134.15	14.	120.15	894.
25.4	5.00	220.0	158.88	22.	136.63	1432.
21.7	6.00	221.0	183.61	34.	149.6	2158.
18.4	7.00	222.0	208.34	49.7	158.6	3130.
15.6	8.00	223.0	233.07	69.1	164.0	4340.
13.5	9.00	224.0	257.80	89.7	168.1	5600.
11.8	10.00	225.0	282.53	112.1	170.4	6970.
10.6	11.00	226.0	307.26	133.5	173.8	8270.
9.5	12.00	227.0	331.99	158.	174.0	9750.

Column headings:

(1) Electromotive force, in millivolts

(2) Volume of iodine solution added, in milliliters

(3) Total volume of solution, in milliliters

(4) Total iodine added, in millimols x 10^3

(5) $I_2 \neq I_3^-$ in reaction cell, in millimols x 10^3

(6) $I_2 \neq I_3^-$ bound by cyclohexaamylose, in millimols x 10^3

(7) Concentration of I_2, in millimols per milliliter x 10^{10}

Table 5

Titration of 174.6 Milligrams of Cyclohexaamylose in 200.0 Milliliters of 0.0004782 Molar Iodine with Potassium Iodide Solution

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)
27.4	200.0	0.00050	5.64	4.14	2.08
40.6	201.0	0.00100	2.00	4.50	0.581
52.5	209.4	0.00500	0.79	4.62	0.0824
52.7	221.2	0.0100	0.78	4.62	0.0431
48.3	223.0	0.0500	1.09	4.59	0.0133
44.2	225.4	0.100	1.50	4.55	0.00924
30.2	246.1	0.500	4.51	4.25	0.00512
24.3	280.7	0.902	7.14	3.98	0.00394

Column headings:

(1) Electromotive force, in millivolts

(2) Volume of solution, in milliliters

(3) Concentration of potassium iodide, in mols per liter

(4) $I_2 + I_3^-$ in reaction cell, in millimols x 10^3

(5) $I_2 + I_3^-$ bound by the cyclohexaamylose, in millimols x 10^2

(6) Concentration of I_2, in mols per liter x 10^5

Table 6

Effect of Temperature on the Titration of Cyclohexaamylose

(174.1 milligrams in 220.0 milliliters of solution 0.010 molar with respect to KI and containing 0.09564 millimols of iodine)

(1)	(2)	(3)	(4)	(5)	(6)
25.0	60.6	8.52	9.48	4.26	0.855
0.0	75.0	1.62	9.54	0.81	0.859
10.0	70.0	3.08	9.53	1.54	0.858
20.0	64.1	5.98	9.50	2.99	0.855
30.0	57.9	11.4	9.45	5.70	0.849
40.0	51.0	21.8	9.34	10.9	0.826
50.0	44.2	39.8	9.16	19.9	0.803
25.0	58.9	9.76	9.46	4.88	0.852
8.0	68.0	3.46	9.53	1.73	0.858
25.0	59.0	9.76	9.46	4.88	0.852

Column headings:

(1) Temperature, in degrees centigrade

(2) E. M. F., in millivolts

(3) $I_2 \neq I_3^-$ in reaction cell, in millimols x 10^4

(4) $I_2 \neq I_3^-$ bound by cyclohexaamylose, in millimols x 10^2

(5) Concentration of $I_2 \neq I_3^-$ in reaction cell, in millimols per milliliter x 10^6

(6) Ratio of $\frac{\alpha I_2}{\alpha}$

Table 7

Titration of 2.712 Grams of Cycloheptaamylose in 250.0 Milliliters of 1.00 Molar KI with 0.4292 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
23.9	1.00	251.0	0.429	0.067	0.362	0.268
21.5	2.00	252.0	0.858	0.161	0.697	0.641
19.1	3.00	253.0	1.29	0.290	0.998	1.14
16.9	4.00	254.0	1.72	0.458	1.26	1.80
14.7	5.00	255.0	2.15	0.682	1.46	2.68
8.0	10.0	260.0	4.29	2.29	2.00	8.82
5.5	15.0	265.0	6.44	4.20	2.24	15.8
4.6	20.0	270.0	8.58	5.96	2.62	22.0
3.8	25.0	275.0	10.7	7.94	2.79	28.8
3.2	30.0	280.0	12.9	10.0	2.82	35.8
2.8	35.0	285.0	15.0	12.0	3.01	42.2
2.4	40.0	290.0	17.2	14.2	2.98	48.9

Column headings:

(1) Electromotive force, in millivolts
(2) Volume of iodine solution added, in milliliters
(3) Total volume of solution, in milliliters
(4) Total iodine added, in millimols
(5) $I_2 \neq I_3^-$ in reaction cell, in millimols
(6) $I_2 \neq I_3^-$ bound by cycloheptaamylose, in millimols
(7) Concentration of $I_2 \neq I_3^-$ in reaction cell, in millimols per milliliter x 10^3

Table 8

Titration of 1.2010 Grams of Cycloheptaamylose
in 200.0 Milliliters of 0.01 Molar KI
with 0.004792 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
33.4	1.00	201.0	4.29	0.32	3.97	1.58
32.9	2.00	202.0	8.58	0.66	7.92	3.29
32.9	3.00	203.0	12.9	1.00	11.9	4.91
32.8	4.00	204.0	17.2	1.34	15.9	6.56
32.7	5.00	205.0	22.4	1.76	20.6	8.58
32.4	6.00	206.0	25.7	2.07	23.6	10.0
32.3	7.00	207.0	30.0	2.44	27.6	11.8
32.2	8.00	208.0	34.3	2.80	31.5	13.5
31.9	9.00	209.0	38.6	3.24	35.4	15.5
31.8	10.00	210.0	42.9	3.63	39.3	17.3
31.7	11.00	211.0	47.2	4.00	43.2	18.9
31.6	12.00	212.0	51.5	4.40	47.1	20.8
31.4	13.00	213.0	56.8	4.93	51.8	23.1
31.3	14.00	214.0	60.1	5.27	54.8	24.6
31.0	15.00	215.0	64.4	5.74	58.7	26.7
30.8	16.00	216.0	68.7	6.24	62.5	28.9
30.6	17.00	217.0	72.9	6.80	66.1	31.3
30.3	18.00	218.0	77.2	7.34	69.9	33.7
30.2	19.00	219.0	81.5	7.83	73.7	35.7
30.0	20.00	220.0	85.8	8.34	77.5	37.9

Column headings:

(1) Electromotive force, in millivolts
(2) Total volume of iodine added, in milliliters
(3) Total volume of solution, in milliliters
(4) Total iodine added, in millimols x 10^3
(5) $I_2 \neq I_3^-$ in reaction cell, in millimols x 10^3
(6) $I_2 \neq I_3^-$ bound by cycloheptaamylose, in millimols x 10^3
(7) Concentration of $I_2 \neq I_3^-$ in reaction cell, in
in millimols per milliliter x 10^6

Table 9

Titration of 180.8 Milligrams of Cycloheptaamylose in 200.0 Milliliters of 0.100 Molar KI with 0.0194 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
10.7	1.00	201.0	1.94	0.847	1.09	4.21
11.1	2.00	202.0	3.87	1.62	2.25	8.05
10.5	3.00	203.0	5.80	2.54	3.26	12.5
10.0	4.00	204.0	7.74	3.53	4.21	17.4
9.5	5.00	205.0	9.68	4.61	5.07	22.5
9.0	6.00	206.0	11.61	5.75	5.86	27.9
8.5	7.00	207.0	13.54	6.98	6.56	33.8
8.1	8.00	208.0	15.48	8.23	7.25	39.8
7.6	9.00	209.0	17.42	9.63	7.79	46.0
7.3	10.00	210.0	19.4	10.9	8.5	52.1
6.9	11.00	211.0	21.3	12.4	8.9	58.7
6.6	12.00	212.0	23.2	13.8	9.4	65.4
6.3	13.00	213.0	25.2	15.3	9.9	71.8
6.0	14.00	214.0	27.1	16.9	10.2	79.3
5.8	15.00	215.0	29.0	18.5	10.5	86.0
4.7	20.00	220.0	38.7	26.8	11.9	122.
3.9	25.00	225.0	48.4	35.8	12.6	159.
3.4	30.00	230.0	58.0	44.7	13.3	194.
2.9	35.00	235.0	67.7	54.2	13.5	230.

Column headings:

(1) Electromotive force, in millivolts

(2) Volume of iodine solution added, in milliliters

(3) Total volume of solution, in milliliters

(4) Total iodine added, in millimols x 10^2

(5) $I_2 \neq I_3^-$ in reaction cell, in millimols x 10^2

(6) $I_2 \neq I_3^-$ bound by cycloheptaamylose, in millimols x 10^2

(7) Concentration of $I_2 \neq I_3^-$ in reaction cell, in millimols per milliliter x 10^5

Table 10

Titration of Cycloheptaamylose with Potassium Iodide

(90.4 milligrams of cycloheptaamylose in 200.0 milliliters of 0.00117 molar KI containing 0.0445 millimols of iodine)

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)
5.2	208.0	0.00500	2.95	1.50	1.42
6.2	219.5	0.0100	2.74	1.71	1.25
5.7	246.7	0.0200	2.85	1.60	1.15
4.9	248.2	0.0502	3.02	1.43	1.22
5.0	250.7	0.100	3.01	1.44	1.20
4.5	255.9	0.200	3.13	1.32	1.22
3.1	272.9	0.500	3.50	0.95	1.28
1.4	356.8	1.56	3.97	0.48	1.11
1.2	408.0	2.00	4.04	0.41	0.99

Column headings:

(1) Electromotive force, in millivolts
(2) Total volume of solution, in milliliters
(3) Concentration of potassium iodide, in millimols per milliliter
(4) $I_2 + I_3^-$ in reaction cell, in millimols x 10^3
(5) $I_2 + I_3^-$ bound by cycloheptaamylose, in millimols x 10^2
(6) Concentration of $I_2 + I_3^-$ in reaction cell, in millimols per milliliter x 10^4

Table 11

Titration of 10.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.025 Molar KI
with 0.00250 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
19.3	1.00	201.0	2.50	0.556	1.94	2.76
28.0	2.00	202.0	5.00	0.573	4.43	2.84
31.2	3.00	203.0	7.50	0.662	6.84	3.26
34.2	4.00	204.0	10.0	0.694	9.3	2.40
34.2	5.00	205.0	12.5	0.868	11.6	4.23
34.2	6.00	206.0	15.0	1.04	14.0	5.05
31.2	7.00	207.0	17.5	1.55	15.9	7.50
25.8	8.00	208.0	20.0	2.71	17.3	13.0
20.1	9.00	209.0	22.5	4.66	17.8	22.3
16.2	10.00	210.0	25.0	7.07	18.0	33.6

Column headings:

(1) Electromotive force, in millivolts
(2) Total volume of iodine added, in milliliters
(3) Total volume of solution, in milliliters
(4) Total iodine added, in millimols x 10^3
(5) $I_2 + I_3^-$ in reaction cell, in millimols x 10^3
(6) $I_2 + I_3^-$ bound by amylose, in millimols x 10^3
(7) Concentration of $I_2 + I_3^-$ in reaction cell, in millimols per milliliter x 10^6

Table 12

Titration of 30.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.025 Molar KI
with 0.00250 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
40.4	5.00	205.0	12.5	0.536	12.0	2.62
47.0	10.00	210.0	25.0	0.644	24.4	3.07
32.8	15.00	215.0	37.5	2.93	34.6	13.6
16.0	20.00	220.0	50.0	14.4	35.6	65.4

Column headings are the same as in Table 11.

Table 13

Titration of 50.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.025 Molar KI
with 0.00250 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
44.4	5.00	205.0	12.5	0.396	12.1	1.93
51.8	10.00	210.0	25.0	0.441	24.6	2.10
55.2	15.00	215.0	37.5	0.507	37.0	2.36
58.0	20.00	220.0	50.0	0.539	49.5	2.45
59.2	25.00	225.0	62.5	0.635	61.9	2.78
58.8	30.00	230.0	75.0	0.757	74.2	3.29
52.7	35.00	235.0	87.5	1.44	86.1	6.12
34.1	40.00	240.0	100.0	7.04	93.0	29.3
24.4	45.00	245.0	112.5	17.0	95.5	69.3

Column headings are the same as in Table 11.

Table 14

Titration of 100.0 Milligrams of Corn Amylose in 200.0 Milliliters of 0.025 Molar KI with 0.00250 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
45.5	5.00	205.0	12.5	0.362	12.1	1.76
54.4	10.0	210.0	25.0	0.360	24.6	1.71
58.0	15.0	215.0	37.5	0.404	37.1	1.88
61.0	20.0	220.0	50.0	0.431	49.6	1.96
62.6	25.0	225.0	62.5	0.473	62.0	2.10
65.6	30.0	230.0	75.0	0.454	74.6	1.98
66.4	35.0	235.0	87.5	0.497	87.0	2.11
67.4	40.0	240.0	100.0	0.523	99.5	2.18
67.5	45.0	245.0	112.5	0.582	111.9	2.38
66.1	50.0	250.0	125.0	0.726	124.3	2.90
66.4	55.0	255.0	137.5	0.780	136.7	3.06
66.4	60.0	260.0	150.0	0.851	149.2	3.27
64.0	65.0	265.0	162.5	1.112	161.4	4.20
59.5	70.0	270.0	175.0	1.70	173.3	6.30
46.8	75.0	275.0	187.5	4.90	182.6	17.8
35.4	80.0	280.0	200.0	12.96	187.4	45.1
29.4	85.0	285.0	212.5	21.9	190.6	76.8
24.0	90.0	290.0	225.0	35.0	190.0	121.

Column headings are the same as in Table 11.

Table 15

Titration of 50.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.05 Molar KI
with 0.0050 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
49.3	1.00	201.0	5.00	0.107	4.89	0.536
55.5	2.00	202.0	10.0	0.132	9.87	0.653
60.3	3.00	203.0	15.0	0.137	14.9	0.675
62.6	4.00	204.0	20.0	0.152	19.8	0.745
62.9	5.00	205.0	25.0	0.186	24.8	0.907
60.4	6.00	206.0	30.0	0.270	29.7	1.31
37.5	7.00	207.0	35.0	1.87	33.1	9.04
24.8	8.00	208.0	40.0	5.86	34.1	28.2
19.0	9.00	209.0	45.0	10.2	34.8	49.1
15.6	10.0	210.0	50.0	14.7	35.3	70.0
8.4	15.0	215.0	75.0	38.9	36.1	181.
5.8	20.0	220.0	100.	63.6	36.4	289.
4.3	25.0	225.0	125.	89.2	35.8	396.

Column headings are the same as in Table 11.

Table 16

Titration of 150.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.05 Molar KI
with 0.00500 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
49.6	1.00	201.0	5.00	0.118	4.88	0.588
58.4	2.00	202.0	10.0	0.104	9.90	0.514
62.8	3.00	203.0	15.0	0.113	14.9	0.556
65.0	4.00	204.0	20.0	0.127	19.9	0.622
67.3	5.00	205.0	25.0	0.132	24.9	0.644
70.4	6.00	206.0	30.0	0.124	29.9	0.603
72.2	7.00	207.0	35.0	0.126	34.9	0.608
73.1	8.00	208.0	40.0	0.134	39.9	0.644
73.9	9.00	209.0	45.0	0.141	44.9	0.674
75.0	10.0	210.0	50.0	0.144	49.9	0.685
75.7	15.0	215.0	75.0	0.205	74.8	0.958
51.8	20.0	220.0	100.	1.77	98.2	8.04
23.7	25.0	225.0	125.	19.9	105.	88.4

Column headings are the same as in Table 11.

Table 17

Titration of 200.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.05 Molar KI
with 0.0050 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
49.7	1.00	201.0	5.00	0.104	4.89	0.546
57.0	2.00	202.0	10.0	0.117	9.88	0.579
61.9	3.00	203.0	15.0	0.121	14.9	0.595
66.1	4.00	204.0	20.0	0.116	19.9	0.567
67.6	5.00	205.0	25.0	0.130	24.9	0.634
76.8	10.0	210.0	50.0	0.127	49.9	0.604
78.7	15.0	215.0	75.0	0.164	74.8	0.763
79.1	20.0	220.0	100.	0.212	99.8	0.963
68.1	25.0	225.0	125.	0.625	124.	2.78
31.4	30.0	230.0	150.	13.0	147.	56.5
21.1	35.0	235.0	175.	33.8	142.	144.

Column headings are the same as in Table 11.

Table 18

Titration of 50.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.100 Molar KI
with 0.0187 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
63.2	1.00	201.0	18.7	0.136	18.6	0.677
33.6	2.00	202.0	37.4	2.73	34.7	13.5
13.6	3.00	203.0	56.1	19.4	36.7	95.5
8.9	4.00	204.0	74.8	37.6	37.2	184.
6.7	5.00	205.0	93.5	55.6	37.9	271.

Column headings are the same as in Table 11.

Table 19

Titration of 200.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.100 Molar KI
with 0.0187 Molar Iodine

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
66.7	1.00	201.0	18.7	0.143	18.6	0.711
74.3	2.00	202.0	37.4	0.114	37.3	0.564
78.2	3.00	203.0	56.1	0.126	56.0	0.616
80.7	4.00	204.0	74.7	0.139	74.7	0.682
81.8	5.00	205.0	93.4	0.160	93.4	0.780
81.2	6.00	206.0	112.	0.200	112.	0.970
74.4	7.00	207.0	131.	0.396	131.	1.91
43.0	8.00	208.0	150.	5.27	145.	25.3
28.0	9.00	209.0	168.	19.3	149.	92.3

Column headings are the same as in Table 11.

Table 20

Titration of 10.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.025 Molar KI
with 0.00250 Molar Iodine

Temperature 0° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
49.5	1.00	201.0	2.50	0.0373	2.46	0.186
55.7	2.00	202.0	5.00	0.0435	4.96	0.215
61.0	3.00	203.0	7.50	0.0449	7.46	0.221
60.0	4.00	204.0	10.0	0.0610	9.94	0.299
59.5	5.00	205.0	12.5	0.0796	12.4	0.388
53.8	6.00	206.0	15.0	0.156	14.8	0.757
45.7	7.00	207.0	17.5	0.359	17.1	1.73
31.5	8.00	208.0	20.0	1.37	18.6	6.58
23.5	9.00	209.0	22.5	3.06	19.4	14.60
19.0	10.0	210.0	25.0	4.99	20.0	23.8

Column headings are the same as in Table 11.

Table 21

Titration of 50.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.025 Molar KI
with 0.00250 Molar Iodine

Temperature 0° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
66.0	5.00	205.0	12.5	0.0464	12.5	0.226
73.0	10.0	210.0	25.0	0.0520	24.9	0.248
77.0	15.0	215.0	37.5	0.0548	37.4	0.255
78.2	20.0	220.0	50.0	0.0649	49.9	0.295
79.0	25.0	225.0	62.5	0.0759	62.4	0.337
77.0	30.0	230.0	75.0	0.110	74.9	0.478
67.4	35.0	235.0	87.5	0.289	87.2	1.23

Column headings are the same as in Table 11.

Table 22

Titration of 100.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.025 Molar KI
with 0.00250 Molar Iodine

Temperature 0° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
57.9	5.00	205.0	12.5	0.0904	12.4	0.442
68.5	10.0	210.0	25.0	0.0742	24.9	0.353
72.5	15.0	215.0	37.5	0.0795	37.4	0.369
75.9	20.0	220.0	50.0	0.0800	49.9	0.363
80.9	25.0	225.0	62.5	0.0646	62.4	0.287
81.6	30.0	230.0	75.0	0.0727	74.9	0.316
84.6	35.0	235.0	87.5	0.0657	87.4	0.280
85.0	40.0	240.0	100.0	0.0730	99.9	0.304
87.0	45.0	245.0	112.5	0.0695	112.4	0.283
87.0	50.0	250.0	125.0	0.0748	124.9	0.299
85.0	55.0	255.0	137.5	0.100	137.4	0.392
83.5	60.0	260.0	150.0	0.124	149.9	0.477
82.0	65.0	265.0	162.5	0.153	162.3	0.577
36.0	80.0	280.0	200.0	9.34	190.7	3.33

Column headings are the same as in Table 11.

Table 23

Titration of 10.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.05 Molar KI
with 0.00125 Molar Iodine

Temperature 0° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
42.0	1.00	201.0	1.25	0.0194	1.23	0.0965
49.6	2.00	202.0	2.50	0.0369	2.46	0.183
50.0	3.00	203.0	3.75	0.0535	3.70	0.263
55.0	4.00	204.0	5.00	0.0463	4.95	0.227
49.5	5.00	205.0	6.75	0.100	6.65	0.491
26.4	6.00	206.0	7.50	0.797	6.70	0.387
18.2	7.00	207.0	8.75	1.82	6.93	0.880
13.9	8.00	208.0	10.0	3.08	6.92	1.48
11.6	9.00	209.0	11.2	4.22	7.03	2.02
9.7	10.0	210.0	12.5	5.48	7.02	2.61
8.5	11.0	211.0	13.8	6.67	7.08	3.16
7.7	12.0	212.0	15.0	7.77	7.23	3.67

Column headings are the same as in Table 11.

Table 24

Titration of 20.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.05 Molar KI
with 0.00125 Molar Iodine

Temperature 0° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
44.3	1.00	201.0	1.25	0.0290	1.22	0.144
55.4	2.00	202.0	2.50	0.0223	2.48	0.110
61.0	3.00	203.0	3.75	0.0210	3.73	0.104
61.6	4.00	204.0	5.00	0.0267	4.97	0.131
62.1	5.00	205.0	6.75	0.0346	6.72	0.169
65.0	6.00	206.0	7.50	0.0302	7.47	0.147
67.0	7.00	207.0	8.75	0.0299	8.72	0.144
68.0	8.00	208.0	10.0	0.0310	9.97	0.149
68.0	9.00	209.0	11.2	0.0348	11.2	0.167
62.3	10.0	210.0	12.5	0.0631	12.4	0.300
41.8	11.0	211.0	13.8	0.393	13.4	1.86
29.0	12.0	212.0	15.0	1.27	13.7	5.98
22.7	13.0	213.0	16.8	2.44	14.3	11.0
19.0	14.0	214.0	17.5	3.50	14.0	16.4

Column headings are the same as in Table 11.

Table 25

Titration of 50.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.05 Molar KI
with 0.00500 Molar Iodine

Temperature 0° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
60.6	1.00	201.0	5.00	0.0291	4.97	0.145
65.4	2.00	202.0	10.0	0.0390	9.96	0.193
72.0	3.00	203.0	15.0	0.0333	15.0	0.164
77.0	4.00	204.0	20.0	0.0292	20.0	0.143
72.0	5.00	205.0	25.0	0.0555	24.9	0.271
74.9	6.00	206.0	30.0	0.0522	30.0	0.253
39.4	7.00	207.0	35.0	1.23	33.8	5.95
24.2	8.00	208.0	40.0	5.13	34.9	24.6
19.4	9.00	209.0	45.0	9.43	35.6	45.1
15.0	10.0	210.0	50.0	14.2	35.8	67.6
12.6	11.0	211.0	55.0	18.8	36.2	89.1
11.2	12.0	212.0	60.0	23.3	36.7	110.
10.2	13.0	213.0	65.0	27.3	37.7	128.
9.1	14.0	214.0	70.0	32.4	37.6	151.
8.3	15.0	215.0	75.0	37.1	37.9	173.
7.8	16.0	216.0	80.0	41.3	38.7	191.

Column headings are the same as in Table 11.

Table 26

Titration of 100.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.05 Molar KI
with 0.00500 Molar Iodine

Temperature 0° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
59.0	1.00	201.0	5.00	0.0331	4.97	0.165
66.0	2.00	202.0	10.0	0.0371	9.96	0.184
69.0	3.00	203.0	15.0	0.0428	15.0	0.211
72.5	4.00	204.0	20.0	0.0425	20.0	0.208
76.0	5.00	205.0	25.0	0.0397	25.0	0.194
79.5	6.00	206.0	30.0	0.0312	30.0	0.151
83.0	7.00	207.0	35.0	0.0302	35.0	0.146
85.5	8.00	208.0	40.0	0.0280	40.0	0.135
75.5	9.00	209.0	45.0	0.0746	44.9	0.357
74.0	10.0	210.0	50.0	0.0938	49.9	0.446
77.6	11.0	211.0	55.0	0.0763	54.9	0.362
69.2	12.0	212.0	60.0	0.168	59.8	0.788
62.5	13.0	213.0	65.0	0.322	64.7	1.51
43.2	14.0	214.0	70.0	1.78	68.2	8.31
32.0	15.0	215.0	75.0	4.90	70.1	22.8
25.9	16.0	216.0	80.0	8.80	71.1	41.2
22.2	17.0	217.0	85.0	12.9	72.8	59.5
19.5	18.0	218.0	90.0	17.2	72.8	78.9
17.4	19.0	219.0	95.0	21.8	73.2	99.6
15.8	20.0	220.0	100.	26.2	73.8	119.

Column headings are the same as in Table 11.

Table 27

Titration of 25.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.100 Molar KI
with 0.00468 Molar Iodine

Temperature 0° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
65.5	1.00	201.0	4.68	0.0181	4.66	0.0903
73.4	2.00	202.0	9.36	0.0184	9.34	0.0910
54.6	3.00	203.0	14.0	0.134	13.9	0.660
22.6	4.00	204.0	18.7	2.76	15.9	1.35
14.8	5.00	205.0	23.4	6.67	16.7	3.25

Column headings are the same as in Table 11.

Table 28

Titration of 50.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.100 Molar KI
with 0.00468 Molar Iodine

Temperature 0° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
50.8	1.00	201.0	4.68	0.0624	4.62	0.311
55.0	2.00	202.0	9.36	0.0867	9.27	0.429
56.9	3.00	203.0	14.0	0.110	13.9	0.542
58.3	4.00	204.0	18.7	0.132	18.6	0.647
58.3	5.00	205.0	23.4	0.165	23.2	0.805
63.4	6.00	206.0	28.1	0.129	28.0	0.626
55.4	7.00	207.0	32.8	0.292	32.5	1.41
32.3	8.00	208.0	37.4	2.40	35.0	11.5
23.0	9.00	209.0	43.1	6.00	36.1	28.7
18.0	10.0	210.0	46.8	10.2	36.6	48.6

Column headings are the same as in Table 11.

Table 29

Titration of 100.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.100 Molar KI
with 0.00468 Molar Iodine

Temperature 0° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
65.2	1.00	201.0	4.68	0.0186	4.66	0.0926
77.7	2.00	202.0	9.35	0.0129	9.34	0.0638
81.0	3.00	203.0	14.0	0.0144	14.0	0.0710
82.7	4.00	204.0	18.7	0.0165	18.7	0.0808
84.8	5.00	205.0	23.4	0.0173	23.4	0.0844
86.8	6.00	206.0	28.0	0.0176	28.0	0.0854
86.0	7.00	207.0	32.7	0.0219	32.7	0.106
84.0	8.00	208.0	37.4	0.0297	37.4	0.143
80.9	9.00	209.0	42.1	0.0438	42.0	0.208
82.2	10.0	210.0	46.8	0.0433	46.7	0.206
81.2	11.0	211.0	51.4	0.0518	51.4	0.245
78.4	12.0	212.0	56.1	0.0717	56.0	0.338
62.5	13.0	213.0	60.8	0.301	60.5	1.41
43.5	14.0	214.0	65.4	1.62	63.8	7.58
33.2	15.0	215.0	70.1	4.17	66.0	19.4
26.8	16.0	216.0	74.8	7.52	67.3	34.8
23.2	17.0	217.0	79.5	11.1	68.4	51.2
20.7	18.0	218.0	84.2	14.5	69.7	66.5

Column headings are the same as in Table 11.

Table 30

Titration of 10.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.025 Molar KI
with 0.00250 Molar Iodine

Temperature 50° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
7.2	1.00	201.0	2.50	1.47	1.03	5.12
6.8	2.00	202.0	5.00	2.99	2.01	9.94
8.4	3.00	203.0	7.50	4.03	3.47	17.10
9.3	4.00	204.0	10.0	5.05	4.95	24.2
11.0	5.00	205.0	12.5	5.56	6.94	33.8
11.6	6.00	206.0	15.0	6.35	8.65	42.0
13.2	7.00	207.0	17.5	6.57	10.9	52.8
13.5	8.00	208.0	20.0	7.35	12.6	60.8
13.7	9.00	209.0	22.5	8.12	14.4	68.7
13.6	10.0	210.0	25.0	9.12	16.9	80.3
13.1	11.0	211.0	27.5	10.4	17.1	80.9
12.6	12.0	212.0	30.0	11.8	18.2	85.8
11.9	13.0	213.0	32.5	13.4	19.1	89.4
10.9	14.0	214.0	35.0	15.8	19.2	89.6
10.0	15.0	215.0	37.5	18.2	19.3	89.6
9.3	16.0	216.0	40.0	20.2	19.8	91.6

Column headings are the same as in Table 11.

Table 31

Titration of 50.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.025 Molar KI
with 0.00250 Molar Iodine

Temperature 50° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
19.6	5.00	205.0	12.5	0.306	9.4	14.9
28.3	10.0	210.0	25.0	3.28	21.7	15.6
32.1	15.0	215.0	37.5	3.75	33.7	17.4
34.4	20.0	220.0	50.0	4.23	45.8	19.3
35.9	25.0	225.0	62.5	4.73	57.8	21.0
36.1	30.0	230.0	75.0	5.59	69.4	24.3
34.0	35.0	235.0	87.5	7.61	79.9	32.4
31.0	40.0	240.0	100.0	10.8	89.2	45.0
25.5	45.0	245.0	112.5	18.0	94.5	73.4

Column headings are the same as in Table 11.

Table 32

Titration of 100.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.025 Molar KI
with 0.00250 Molar Iodine

Temperature 50° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
18.8	5.00	205.0	12.5	3.32	9.2	16.2
26.0	10.0	210.0	25.0	3.85	21.2	18.3
30.8	15.0	215.0	37.5	4.11	33.4	19.1
33.6	20.0	220.0	50.0	4.42	45.6	20.1
36.4	25.0	225.0	62.5	4.56	57.9	20.2
38.4	30.0	230.0	75.0	4.75	70.2	20.6
40.0	35.0	235.0	87.5	4.94	82.6	21.0
41.1	40.0	240.0	100.	5.21	94.8	21.7
41.6	45.0	245.0	112.	5.65	106.	23.0
42.9	50.0	250.0	125.	5.73	119.	22.9
42.6	55.0	255.0	138.	6.42	132.	25.2
42.6	60.0	260.0	150.	7.01	143.	27.0
41.4	65.0	265.0	162.	8.28	154.	31.3
40.1	70.0	270.0	175.	9.83	165.	36.4
38.4	75.0	275.0	188.	11.9	176.	43.3
36.6	80.0	280.0	200.	14.3	186.	51.1
32.4	85.0	285.0	212.	20.6	191.	72.3

Column headings are the same as in Table 11.

Table 33

Titration of 10.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.050 Molar KI
with 0.000500 Molar Iodine

Temperature 50° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
3.1	5.00	205.0	2.50	2.00	0.50	9.75
8.7	10.0	210.0	5.00	2.63	2.37	12.5
11.6	15.0	215.0	7.50	3.18	4.32	14.8
12.0	20.0	220.0	10.0	4.12	5.88	18.7
10.8	25.0	225.0	12.5	5.73	6.77	25.5
8.7	30.0	230.0	15.0	7.89	7.11	34.3
6.0	40.0	240.0	20.0	12.9	7.10	53.7

Column headings are the same as in Table 11.

Table 34

Titration of 20.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.050 Molar KI
with 0.000500 Molar Iodine

Temperature 50° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
11.4	5.00	205.0	2.50	1.06	0.144	5.17
16.7	10.0	210.0	5.00	1.50	0.350	7.14
20.6	15.0	215.0	7.50	1.71	0.574	7.95
22.4	20.0	220.0	10.0	2.00	0.800	9.08
22.6	25.0	225.0	12.5	2.46	1.00	10.9
21.6	30.0	230.0	15.0	3.18	1.18	13.8
19.6	35.0	235.0	17.5	4.30	1.32	18.3
16.7	40.0	240.0	20.0	6.02	1.40	25.2
13.5	45.0	245.0	22.5	8.56	1.39	34.9

Column headings are the same as in Table 11.

Table 35

Titration of 50.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.050 Molar KI
with 0.00500 Molar Iodine

Temperature 50° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
21.6	1.00	201.0	5.00	1.06	4.04	5.28
30.0	2.00	202.0	10.0	1.16	8.84	5.68
33.4	3.00	203.0	15.0	1.35	13.6	6.70
35.6	4.00	204.0	20.0	1.56	18.4	7.65
37.4	5.00	205.0	25.0	1.71	23.3	8.33
37.6	6.00	206.0	30.0	2.02	28.0	9.80
35.7	7.00	207.0	35.0	2.69	32.3	13.0
29.2	8.00	208.0	40.0	4.93	35.1	23.7
24.5	9.00	209.0	45.0	7.76	37.2	37.1
18.4	10.0	210.0	50.0	13.3	36.7	63.3
15.4	11.0	211.0	55.0	18.2	36.8	86.1
13.4	12.0	212.0	60.0	22.9	37.1	108.
11.9	13.0	213.0	65.0	27.8	37.2	130.
10.6	14.0	214.0	70.0	32.5	37.5	152.
9.6	15.0	215.0	75.0	36.9	38.1	172.

Column headings are the same as in Table 11.

Table 36

Titration of 100.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.050 Molar KI
with 0.00500 Molar Iodine

Temperature 50° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
23.8	1.00	201.0	5.00	0.960	4.04	4.78
32.4	2.00	202.0	10.0	0.961	9.04	4.76
36.5	3.00	203.0	15.0	1.09	13.9	5.40
39.9	4.00	204.0	20.0	1.13	18.9	5.54
42.7	5.00	205.0	25.0	1.16	23.8	5.65
45.0	6.00	206.0	30.0	1.18	28.8	5.73
46.4	7.00	207.0	35.0	1.24	33.8	5.99
47.0	8.00	208.0	40.0	1.37	38.6	6.59
47.2	9.00	209.0	45.0	1.51	43.5	7.22
48.5	10.0	210.0	50.0	1.53	48.5	7.29
48.0	11.0	211.0	55.0	1.75	53.2	8.30
45.0	12.0	212.0	60.0	2.37	57.6	11.2
42.1	13.0	213.0	65.0	3.16	61.8	14.8
37.5	14.0	214.0	70.0	4.73	65.3	22.1
31.8	15.0	215.0	75.0	7.63	67.4	35.5
27.0	16.0	216.0	80.0	11.5	68.5	53.2
23.7	17.0	217.0	85.0	15.5	69.5	71.3
18.8	18.0	218.0	90.0	23.3	66.7	107.
17.3	19.0	219.0	95.0	27.4	67.6	125.
16.0	20.0	220.0	100.0	31.7	68.3	144.

Column headings are the same as in Table 11.

Table 37

Titration of 25.0 Milligrams of Corn Amylose in 200.0 Milliliters of 0.100 Molar KI with 0.00468 Molar Iodine

Temperature 50° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
19.0	1.00	201.0	4.68	1.20	3.48	5.97
24.5	2.00	202.0	9.36	1.61	7.75	7.97
26.8	3.00	203.0	14.1	2.07	12.0	10.2
24.4	4.00	204.0	18.8	3.26	15.5	16.0
17.8	5.00	205.0	23.5	6.53	17.0	31.8
13.5	6.00	206.0	28.2	10.7	17.5	51.9
11.0	7.00	207.0	32.9	14.6	18.3	70.5

Column headings are the same as in Table 11.

Table 38

Titration of 50.0 Milligrams of Corn Amylose in 200.0 Milliliters of 0.100 Molar KI with 0.00468 Molar Iodine

Temperature 50° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
26.4	1.00	201.0	4.68	0.704	3.98	3.50
30.2	2.00	202.0	9.36	1.13	8.23	5.59
33.3	3.00	203.0	14.1	1.31	12.8	6.45
35.1	4.00	204.0	18.8	1.52	17.3	7.44
35.8	5.00	205.0	23.5	1.79	21.7	8.73
36.3	6.00	206.0	28.2	2.07	26.1	9.95
35.6	7.00	207.0	32.9	2.55	30.3	12.3
31.0	8.00	208.0	37.3	4.04	33.5	19.4
23.8	9.00	209.0	42.2	7.86	34.6	36.6
19.4	10.0	210.0	46.9	11.7	35.2	55.7
16.3	11.0	211.0	51.6	16.0	35.6	75.7

Column headings are the same as in Table 11.

Table 39

Titration of 200.0 Milligrams of Corn Amylose
in 200.0 Milliliters of 0.100 Molar KI
with 0.0187 Molar Iodine

Temperature 50° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
44.2	1.00	201.0	18.7	0.778	18.0	3.87
51.0	2.00	202.0	37.4	0.959	36.4	4.74
55.4	3.00	203.0	56.1	1.05	55.1	5.17
58.2	4.00	204.0	74.8	1.14	73.7	5.58
59.8	5.00	205.0	93.5	1.27	91.2	6.18
60.4	6.00	206.0	112.	1.46	111.	7.08
59.3	7.00	207.0	131.	1.87	129.	9.03
45.7	8.00	208.0	150.	5.60	144.	26.9
31.2	9.00	209.0	168.	18.1	150.	86.6
19.8	10.0	210.0	187.	45.2	142.	215.

Column headings are the same as in Table 11.

Table 40

Titration of Amylose with Potassium Iodide

(100.0 milligrams of amylose in 200.0 milliliters of 0.00765 molar KI containing 0.0511 millimols of iodine)

Temperature 25° C.

(1)	(2)	(3)	(4)	(5)	(6)
66.5	200.0	0.00765	3.89	5.08	2.24
68.6	210.0	0.00981	2.43	5.09	1.45
70.5	275.0	0.0200	2.10	5.09	0.499
74.6	276.6	0.0505	1.52	5.09	0.136
74.0	279.2	0.0993	1.59	5.09	0.0792
76.0	284.7	0.200	1.36	5.10	0.0333
75.3	302.7	0.500	1.44	5.10	0.0133
71.0	338.0	1.00	2.02	5.09	0.00837
58.2	438.0	1.98	5.42	5.06	0.00867

Column headings:

(1) Electromotive force, in millivolts
(2) Total volume of solution, in milliliters
(3) Concentration of KI, in millimols per milliliter
(4) $I_2 + I_3^-$ in reaction cell, in millimols x 10^4
(5) $I_2 + I_3^-$ bound by amylose, in millimols x 10^2
(6) Concentration of I_2 in reaction cell, in millimols per milliliter x 10^7

Table 41

Effect of Temperature

(100.0 milligrams of corn amylose in 205.0 milliliters of 0.0500 molar KI containing 0.0250 millimols of iodine)

(1)	(2)	(3)	(4)	(5)
26.2	60.0	42.4	2.08	20.7
33.0	50.0	23.4	2.27	11.4
39.4	40.0	13.4	2.37	6.49
46.6	30.0	5.18	2.45	2.53
57.6	20.0	2.61	2.47	1.27
66.0	10.0	1.31	2.49	0.639
73.6	0.0	0.475	2.50	0.232
67.0	10.0	1.02	2.49	0.498
59.2	20.0	2.31	2.48	1.13
54.0	30.0	3.99	2.46	1.95
46.4	40.0	7.98	2.42	3.90
37.3	50.0	17.1	2.33	8.35
29.0	60.0	35.2	2.15	17.2
34.5	50.0	20.8	2.29	10.2
41.9	40.0	11.2	2.39	5.56
49.3	30.0	5.73	2.44	2.84
56.4	20.0	2.77	2.47	1.38
66.0	10.0	1.02	2.49	0.507
72.5	0.0	0.525	2.50	0.261
52.4	30.0	4.54	2.46	2.26
45.1	40.0	8.83	2.42	4.38
28.6	60.0	36.1	2.14	17.9
19.0	70.0	72.1	1.78	35.8

Column headings:

(1) Electromotive force, in millivolts
(2) Temperature, in degrees centigrade
(3) $I_2 + I_3^-$ in reaction cell, in millimols x 10^4
(4) $I_2 + I_3^-$ bound by amylose, in millimols x 10^2
(5) Concentration of $I_2 + I_3^-$ in reaction cell, in millimols per milliliter x 10^6

Table 42

Distribution of Iodine Between Aqueous Cyclohexaamylose Solution and Toluene

Temperature 25° C.

Sample #	1	2	3	4	5	6
Original volume of toluene, milliliters	50.0	50.0	50.0	50.0	50.0	50.0
Original volume of water, milliliters	50.0	50.0	50.0	50.0	50.0	50.0
Weight of cyclohexaamylose in water layer, mg.	21.8	0	43.6	0	43.6	0
Volume of water withdrawn, milliliters	10.0	10.0	10.0	10.0	10.0	10.0
Volume of sodium thiosulfate solution used (average), milliliters	3.30	1.97	9.65	7.03	40.0	28.6
Normality of sodium thiosulfate	0.00475		0.00475		0.00123	
Molar conc. of total iodine x 10^4	7.84	4.67	22.9	16.7	24.6	17.6
Molar conc. of excess iodine x 10^4	3.17		6.22		7.00	
Molar conc. of αI_2 x 10^4	3.17		6.22		7.00	
Molar conc. of α-dextrin x 10^4	1.31		2.78		2.00	
Molar conc. of free iodine x 10^4	4.67		16.7		17.6	
K_1	5180		1340		1980	

Table 43

Analysis of Precipitated Complex of Cycloheptaamylose, Iodine, and Potassium Iodide

Sample #	1	2	3	4	5
Millimols of iodine	1.27	1.27	1.30	1.36	1.44
Millimols of cyclohepta-amylose	1.00	1.00	1.00	1.00	1.00
Millimols of potassium iodide	0.28	0.42	-	0.41	0.26

Table 44

Values of $K^{\frac{1}{M}}$ at Various Concentrations of Iodine and Amylose

(Values of $K^{\frac{1}{M}}$ have been multiplied by 10^{-9})

Molar concentration KI	Milligrams of amylose					
	10.0	20.0	50.0	100.0	150.0	200.0
0.025	0.22	0.26	0.31	0.34	-	-
0.050	0.63	0.87	1.0	-	1.0	1.0
0.100	-	-	1.1	-	-	1.1

Table 45

Glucose Residues per Molecule of Iodine Bound

Molar conc. KI	Milligrams of amylose							Average
	10.0	20.0	25.0	50.0	100.0	150.0	200.0	
			Temperature 0° C.					
0.025	3.4	-	-	4.2	3.3	-	-	3.6
0.050	8.8	8.8	-	8.6	8.8	-	-	8.8
0.100	-	-	9.1	8.6	9.2	-	-	9.0
			Temperature 25° C.					
0.025	3.4	3.4	-	3.2	3.2	-	-	3.3
0.050	8.6	9.1	-	8.4	-	9.2	8.4	8.6
0.100	-	-	-	8.3	-	-	8.4	8.4
			Temperature 50° C.					
0.025	3.2	-	-	3.3	3.2	-	-	3.2
0.050	8.7	8.8	-	8.1	9.1	-	-	8.7
0.100	-	-	8.4	8.8	-	-	8.5	8.6

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IX. VITA

Harvey Albert Dube was born in Chicopee, Massachusetts, April 19, 1918, the first child of Anna (Beausoleil) and Albert Jules Dube. His elementary education was obtained at Our Lady of Mount Carmel, Willamansett, Massachusetts, and his secondary education in the Niagara Falls High School, Niagara Falls, New York. He entered Niagara University in 1937 and received the degree of Bachelor of Science in Chemistry in 1941. He entered the University of Detroit in 1941 and received the degree of Master of Science with a major in physical chemistry in 1943. He entered Iowa State College in 1943. His study of the reactions of iodine and starch was under the direction of Dr. R. E. Rundle until 1945 when his place was taken by Dr. Dexter French. During his graduate work he held the Corn Industries Research Foundation Fellowship. In 1943 he married Helen Honor Slazyk of Niagara Falls, New York.