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The properties of starch with relation to time of formation of starch gels

Oliver Wendell Chapman
Iowa State College

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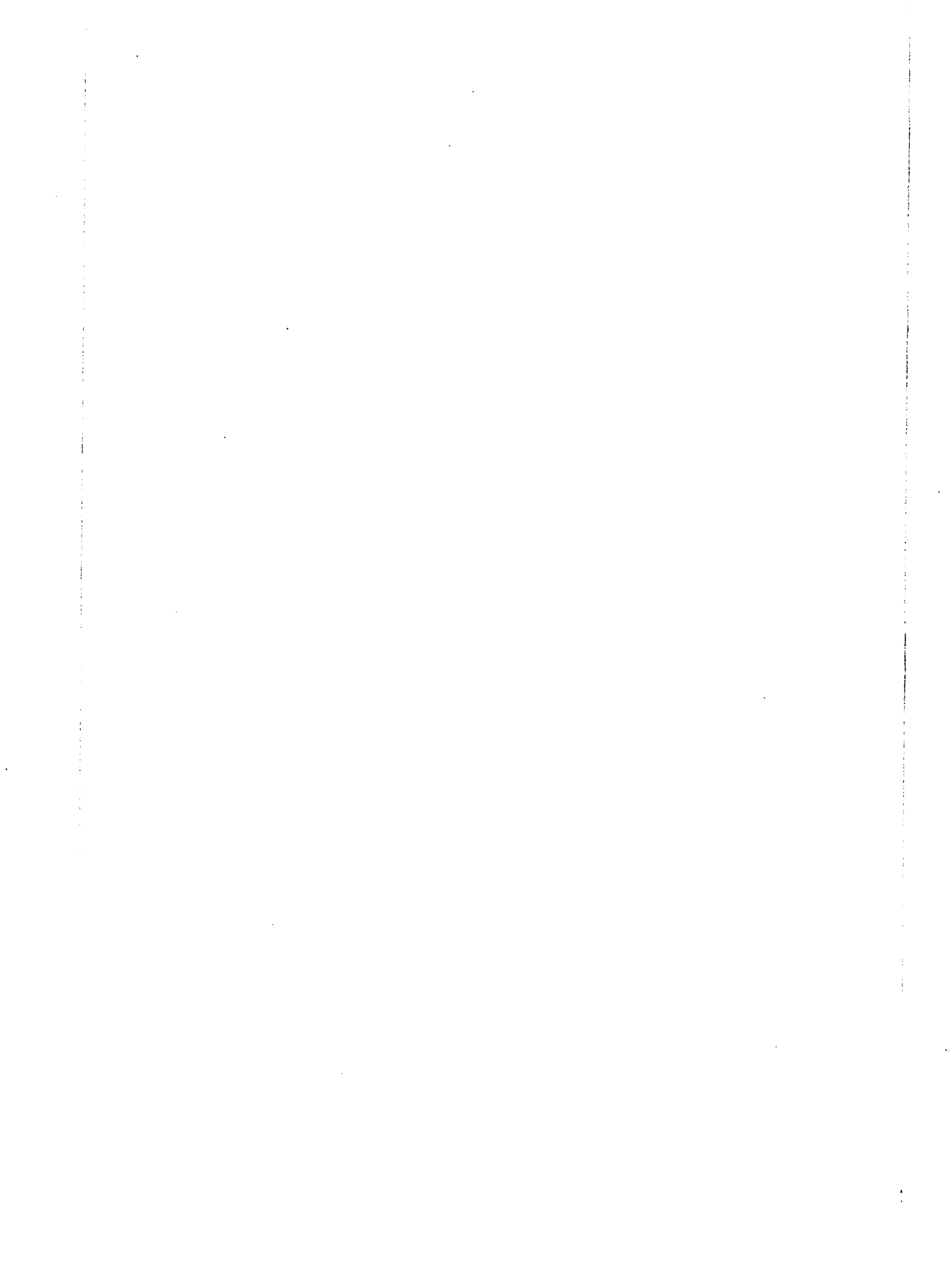
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THE PROPERTIES OF STARCH WITH RELATION
TO TIME OF FORMATION OF STARCH GELS

By

Oliver Wendell Chapman

A Thesis Submitted to the Graduate Faculty
for the Degree of
DOCTOR OF PHILOSOPHY
Major Subject - Food Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1927

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I. INTRODUCTION

A. The Role of Starch in Investigations of Starch Bearing Foods.

Because starch is an important constituent of foods, it has long been the subject of many investigations. The nature of its formation, its function in the plant, its structure, and the changes which it undergoes in various circumstances, such as in the preparation of the starch containing material as a food, have all entered into these researches. However, in some fields the role of starch has been either overlooked or relegated to a position of minor importance by many investigators. Such has been largely the case in the study of wheat flour. Although starch is a major constituent of flour, it has been studied less than the protein and mineral matter. Likewise in studies upon bread and breadmaking, starch has been considered more as an inert material. Other foods have been less widely studied than flour, and consequently the importance of starch in such materials has received even less attention than in the case of wheat.

B. Statement of the Problem.

The purpose of this work is to study starch, some of its properties and changes in the various phases of the

transformations which it may undergo in the treatment which it receives in the course of manufacture of different food products. The study has been chiefly on the starch derived from corn. Other starches have also been used; often for the sake of comparison, or as an aid in determining the cause of the behavior of the starch under certain conditions.

In the work with corn starch, interest has chiefly been directed toward the formation of gels, and the peculiar property that certain gels possess of expressing a portion of their water content, so that there results a rigid, or semi-rigid, body in contact with a layer of clear liquid. This phenomenon, known as "syneresis", may be observed in gels prepared from silicic acid, soap, and proteins, as well as in those made from starch. It is often observed upon opening canned sweet corn. Here may often be found a considerable layer of clear liquid on the surface of the solid material. This is objectionable because of the preference for a product of uniform consistency. Syneresis may also account in part for the staling of bread.

Since the formation of starch gels involves heating in the presence of water, it is not unlikely that the changes which occur during the heating are intimately connected with the behavior of the gel which is formed. Thus there is in-

volved in this investigation, a study of those changes which take place. In these are included the swelling of the granules of starch with the imbibition of water, and the gelatinization of the starch. Accompanying these changes, there is an enormous change in the viscosity of the starch in water suspension. Because of this an attempt has been made to correlate viscosity measurements with other changes in the starch paste and gel.

II. HISTORICAL

A. The Determination of Gelatinization Temperatures by Microscopic Methods, and Factors which Influence the Results Obtained.

Wolfgang Ostwald, (59) in his studies on colloidal substances, was led to believe that viscosity measurements might be advantageously used in the study of starch. Previous studies had been confined largely to microscopic observations. By such methods, detailed studies were made of a great variety of starches. These studies included a determination of the so-called "gelatinization point," which has been determined by a great number of investigators. The nature of this type of work, with the most generally accepted results, is recorded by Reichert (64).

The temperature of gelatinization for the starches with which this work is concerned are given the following values by Lippmann as reported by Reichert (64). Corn, 62.5°; potato, 62.5°; rice, 61.25°; and wheat, 67.5°. With these are also recorded the values as determined by Linter: Corn, 75°; potato, 65°; rice, 80°; and wheat, 75-80°. Whympfer (80) gives 65° as the temperature of complete gelatinization of wheat starch. Other values are given by Stocks (74) as follows: Corn, 70°; potato, 63°; rice, 74°, and wheat, 65°.

The gelatinization temperatures given above, and as ordinarily determined by other investigators, were obtained by microscopic examination. The method consists of heating the sample of starch, suspended in water, to different temperatures, and then examining the appearance of the granules under the microscope. With such treatment, the starch is seen to swell, the granules lose their form, and finally appear to burst. The temperature at which this takes place is considered to be the gelatinization temperature.

This method has been somewhat modified by different investigators. Dox and Roark (19) employed an electrically heated chamber on the microscope stage. Francis and Smith (25) also used a slide by which the temperature could be controlled while on the stage. They claimed that the gelatinization temperature could be determined within one tenth of a degree, provided that the temperature be raised rapidly enough. Nyman (57) devised a method for distinguishing different starches by the gelatinization of the grains as determined under the microscope by the use of polarized light.

Many of the investigators have stated that the gelatinization temperature can be determined accurately by the methods outlined above, yet a study of the results obtained reveals discrepancies. Alsberg and Rask (5) have pointed out that the method of preparation of the starches may in-

fluence the results obtained, because of effect of acids or alkalies which are often used in the course of the separation of the starch. They believe this to be especially true where alkalies have been used, since they have found (63) that the hydrogen-ion concentration of wheat starch paste is on the acid side of neutrality. Wolff and Fernbach (82) state that the paste made from potato starch is acid to phenolphthalein and alkaline to methylorange, and that alkalies affect the results obtained upon heating starch.

That alkalies affect the swelling of starch has also been observed by Symons (76). Similar observations were made by Samec (66). Lepeschkin (44) states that the action between starch and water is accelerated by the presence of acids.

Substances other than acids and alkalies may also affect the swelling of starch granules. Samec (66) found that salts and organic crystalloids affect the temperature of gelatinization. Wolff and Fernbach (82) found that different results were obtained if tap water were used instead of distilled water for washing the starch. This was also observed by Lloyd (45).

Nyman (57) observed that the gelatinization temperature

is different for large grains than for small ones. This was also found by Meyer (53). Whympers (81) noted that small grains are not as readily attacked by heat as are large grains, and that values obtained for the gelatinization temperature also vary with the state of maturity of the grains. Naudain (56) found that the larger grains gelatinize more readily than small grains. Alsberg and Perry (4) show that starch granules when injured by grinding in a pebble mill will swell instantaneously when they come in contact with cold water. Gerngross (26) states that as natural colloids age, their ability to swell decreases. Reichert (64) reports that the gelatinization temperatures are different for starches freshly taken from the grain than for those which have been dried. Samec (66) found another factor to be the time which the starch has been wet.

Still another factor which may influence the temperature of gelatinization is the rate of heating, as shown by Nyman (57), Dox and Roark (19), Francis and Smith (25) and others.

Alsberg and Rask (5) point out that different investigators use different means of judging the temperature where gelatinization occurs; for example, Reichert (64) and others took the point at which anisotropy disappears from the majority of grains. Francis and Smith (25) took the point

at which anisotropy disappears from all of the grains, while Dox and Roark (19) took the temperature at which it disappears from all of the grains large enough to show characteristic shape and markings. Hence Alsberg and Rask (5) believe that the microscopic method leaves too much room for personal judgment to give reliable results.

B. Measurement of Gelatinization Temperatures by the Change in Translucency.

In an attempt to find a method more satisfactory than the use of the microscope for the determination of gelatinization temperature, Samec (66) devised a method whereby a sudden change in translucency of the paste was observed. A light was placed so that it could be seen through the suspension, and the temperature was taken when there occurred a change in translucency.

While this method appears to have an advantage in that the starch need not be transferred to the microscope, it can not be considered of any great value because many starches do not show any marked changes in translucency.

This review of the work of many investigators shows that the methods used in the determination of the gelatinization temperatures of starches are not reliable and lead to results which can not be considered accurate. It also

shows that there is doubt of the existence of any definite point of gelatinization, but leads rather to the conclusion of Alsberg and Rask (5) that this should be considered as a gelatinization range.

G. Viscometric Methods.

In addition to the microscopic and change of translucency methods used in the study of starches, viscometric methods have also been employed.

Ostwald (59) in 1913 suggested the possibility of the use of viscosity measurements for this purpose. He believed that this method would prove to be of value because of the extreme sensitiveness of viscosity to changes in the nature of a colloid, and because of the ease with which the measurements may be made. Ostwald found that the viscosity of a starch suspension decreases with increasing temperature up to 57°, when the granules begin to swell. From this point upwards to a temperature of 95° he found the viscosity increased. At 120° soluble starch is formed, and the viscosity becomes less than at 90°.

Viscometric methods have been applied with varying results by many investigators since the use of the method was suggested by Ostwald. Different types of instruments have

been used, and the conditions under which they have been used have been modified from time to time. A review of this work will serve to indicate the value of this type of measurements.

The Ostwald capillary type of viscometer has been employed by a number of investigators, while others have preferred the torsion type. Others have designed special instruments, usually some modification of one of the above types.

Yoshimo (84) employed the Ostwald viscometer on rice starch. He found that when the concentration becomes high enough that the viscosity becomes infinite.

Samec (70) using an Ostwald viscometer found that the viscosity varied with the kind of starch. Harvey (29) also used the Ostwald type for starches which had been boiled by live steam. He found that the viscosity of potato starch decreased with time. Harrison (28) concluded that the Ostwald viscometer gave results which were not accurate, because when a certain concentration was reached, the suspended particles interfered with one another in passing through the capillary. He also found that the viscosity increased with time of heating up to a maximum, after which there was a decrease. Potato starch gave a very viscous solution, but its viscosity became less upon repetition of

the determinations, due to the breaking up of the swollen granules by flow down the capillary tube.

Hatschek (30) pointed out that a comparison of viscosities by the Ostwald viscometer is valid only in cases where the rate of flow is approximately the same, since viscosity varies with the rate of flow. However, he recommends (31) the use of correctly designed capillary viscometers instead of the "grossly incorrect types used in industry." He further stated that viscosity measurements indicate changes in colloidal solutions but do not tell what the changes are.

Farrow and Lowe (22) found that good results were obtained with an Ostwald viscometer, provided that the same instrument be used for the different determinations.

Denham, Blair, and Watts (17) used the Ostwald type for flour suspensions, and found the results to be satisfactory and comparable, provided that the instrument be designed so as to give stream line flow.

The Ostwald viscometer has been modified by other investigators. One modification has been an arrangement whereby pressure could be used. Such viscometers were used by Ostwald (61) and by Herschel and Bulkley (35). Hess (36) used reduced pressure. Rothlin (65) employed

the Hess modification.

MacNider (49) used a Scott viscometer. Ermen (21) employed a Redwood instrument, while Rask and Alsberg (63) used a Stormer viscometer. Seaton, Probeck, and Sawyer (72) recommend the Doolittle instrument because it can be used for plasticity measurements. Buel (13) found the Doolittle to be unsatisfactory because of a gradual weakening of the wire.

Much of the work on the viscosity of flour suspensions has been done with the MacMichael, or other types of torsion viscometers. Henderson, Fenn, and Cohn (33), Blish and Sandstedt (11), Gortner and Sharp (27), and others used this type.

Other methods of measuring viscosity are described by Moness and Giesy (55) who designed an instrument in which the pressure could be kept constant. Brown and Herron (12) measured the weight required to sink a thin glass disc into the paste. Buel (13) measured the time of flow through a funnel. Cappenburg (14) measured the force required to draw a spherical weight upwards through the paste.

Mardles (52) used three types of viscometers in the study of the sol to gel transition. He found that a change of the size of the capillary in the Ostwald caused a change

in the results obtained. Revolving cylinder types were also found to give irregular results. The method of a falling sphere was found to give irregular results as the viscosity became high.

The principal objection to the measurements of starch suspensions by the methods described, is that the suspensions may be plastic rather than viscous. Bergquist (9) has pointed out that in order to measure the viscosity of starch suspensions, the concentration of the starch must be small, whereas in commerce, higher concentrations are ordinarily used. He recommends the use of the Bingham plastometer where measurements are to be made at temperatures lower than 70°. Above this temperature the flow of starch paste is viscous. Sharp (73) found flour suspensions to be plastic when the concentration is above nine per cent. Dunn (20) considered dough made from wheat flour to be essentially a plastic system.

Herschel and Bergquist (34) found the Bingham plastometer to be advantageous in the study of starch pastes, as they found it to be a more satisfactory indication of consistency than viscosity measurements. Herschel and Bulkley (35) described a method in which the Ostwald viscometer can be used to measure consistency by the employment of different rates

of flow.

Thus we find that there is a considerable difference of opinion, both as to the preferable type of instrument, and as to the value of the results obtained. Although true viscosity may not be measured, yet such measurements may prove of value in the attempt to gain some explanation of the changes which starch suspensions undergo.

D. Factors Which Affect the Viscosity of Starch Paste.

Ostwald (59) cites ten factors which influence the viscosity of colloidal systems: (1) concentration, (2) temperature, (3) degree of dispersion, (4) solvation, (5) electrical charge, (6) preliminary thermal treatment, (7) preliminary mechanical treatment, (8) inoculation with small amounts of viscous colloids, (9) age, and (10) electrolytes and non electrolytes. In connection with the effect of temperature, Ostwald noted an increase in viscosity with rise in temperature up to a certain point. This was followed by a decrease in viscosity. He further observed (60) a relationship between the degree of hydration and the viscosity.

Other investigators have noted the effect of the factors listed by Ostwald, as well as the influence of certain other conditions.

The effect of the age of the suspension was noted by

Stocks (74) who found that freshly prepared potato starch solution gave a higher viscosity than that obtained from a solution which had been allowed to stand. Denham, Blair, and Watts (17) report a similar "fall back" in viscosity that results upon the ageing of flour suspensions, and attribute the cause to syneresis of the paste. However, they believe that the gluten is chiefly responsible for this change. Harrison (28) found that there was a gradual increase in viscosity with heating, up to a maximum. This was followed by a decrease which he thought to be due to a breaking down of the swollen grains. He further observed that the rate of heating affected the results. Harvey (29) noted a similar decrease in viscosity with time for potato and cassava starches, but failed to find any decrease for corn starch.

Samec (66, 67, 68) found that a decrease in viscosity resulted when starch suspensions were heated at 120°. At the same time, he found that there was a decrease in the phosphorus content of the starch, and an increase in conductivity. Hence he concludes that the change which takes place upon ageing is one of gradual hydrolysis of amylophosphoric acid, one of the constituents of starch. He also noted that the viscosity decrease is hastened by

agitation. Tiebackx (79) believes that the viscosity of a starch solution is proportional to its content of amylopectin, a phosphoric acid ester. He agrees with Samee that heating or long standing causes a hydrolysis of the amylopectin, which is accompanied by a decrease in viscosity. Zwikker (85) failed to find any such relationship between amylopectin and viscosity. That there is an increase in viscosity after mixing flour in water was observed by Luers and Ostwald (46). This increase was attributed to the slow swelling of starch. Dhar (18) believes that the decrease in viscosity is connected with dehydration, because the greater the hydration, the more viscous the solution. Mardles (52) attributes such changes to progressive gelation. Gerngross (26) states that as colloids age, their water content and ability to swell decreases. Maquenne (50, 51) found that starch paste tends to return to the form of the crude starch. Herschel and Bergquist (34) believe the decrease in viscosity to be due to the breaking down of the structure upon passing through the capillary. Buel (13) and Farrow and Lowe (22) have also reported upon the change in viscosity with age.

The effect of added substances upon the viscosity of starch pastes has been considered by various writers. Wolff and Fernbach (23, 82, 83) found a considerable increase upon

the addition of CaCO_3 , the effect being greater with increased concentration of the salt, while the viscosity can be reduced by a reduction of the calcium content. They found that the addition of other basic substances, such as Al_2O_3 , MgCO_3 , NH_4OH , $\text{Ca}(\text{OH})_2$ and Na_2CO_3 , also increases the viscosity while the addition of salts neutral to methyl orange has no effect. MacNider (48) observed that small amounts of borax or of NaOH lower the viscosity, while larger amounts increase it. Forst and Moskowitz (62) found that the addition of alkali increased the firmness of the paste at first, but with increasing alkalinity the paste became weaker. Samec (69) found that NaOH or KOH react with starch. This is accompanied by a decrease in the P_2O_5 content and an increase in viscosity. Large amounts of the alkalies peptize the starch. Mohs (54) states that the addition of salts and acids up to 0.0085 N produces no change in the viscosity of flour suspensions. Henderson, Fenn, and Cohn (33) found that the addition of small amounts of salts diminishes the viscosity at first, but that this is followed by an increase. Na_2SO_4 and MgSO_4 cause the most marked effects. Clark and Mann (15) state that electrolytes increase the viscosity at small concentrations. The adsorption of NaOH by starch is

reported by Lloyd (45) to be much greater than for HCl or NaCl. Backhuyzen (7) states that the hydration of amylose may be increased by heating in water, or by the addition of KI, $\text{Ca}(\text{NO}_3)_2$, ZnCl_2 , KOH, or Na_2CO_3 . Hydration may be decreased by lowering the temperature, concentration of the solution, or the addition of alcohol or chloroform.

Other factors influencing viscosity determinations are reported. Among these may be considered the source of the starch. Rask and Alsberg (63) report that different results are obtained with starches from different varieties of wheat. They believe the viscosity to be affected by the degree of dispersion or the size of the individual particles, their water imbibing capacities, densities, shapes, and elasticities or plasticities.

Ermen (21) found that viscosity measurements are influenced by the temperature, size of flame, and size of beaker. deJong (41) found that errors are likely to result from a defective method of setting the viscometer.

That the method of preparation of the starch influences its behavior is pointed out by Rask and Alsberg (63). The alkali used in the process of the separation is especially likely to affect the properties of the starch. Alsberg and Griffing (3) show that the degree of grinding is not without

effect. Johnson (40) notes that the temperature employed in the extraction of the starch, and the time that it is allowed to stand in contact with water affect the viscosity. Brown and Herron (12) found that if alkalies and acids were used in the preparation of starch, a paste of lower viscosity resulted. They also found that starch which has been dried slowly yields more viscous solutions than that dried quickly.

Thus it is evident that the treatment involved in the preparation of starch affects the viscosity. There is also the effect of the mechanical treatment of the paste. This has been shown by Hatschek (32) who believes that there are layers of solvent formed about each particle. This layer is destroyed by agitation; hence a decrease in viscosity. That agitation by stirring, or that resulting in successive determinations, produces a change in viscosity is also indicated by Ostwald (59), Buel (13), Bergquist (9), Herschel and Bergquist (34), Rothlin (65), and Hess (37).

Tadokoro and Sato (77) have made the interesting observation that the viscosity of rice starch is lowered by the action of ultraviolet rays. This may explain in part the difference in viscosity of starch from wheat from different localities.

Other theories regarding viscosity and causes of changes

in viscosity include that of Swanson (75) who believes that the viscosity of dough is due to the surface tension forces in the films of water adsorbed on the starch and protein particles, and depends directly upon the thickness of the film of water surrounding the particles.

Alexander (1) believes that colloidal properties, such as viscosity, depend largely upon the size of the dispersed particles.

Blair, Watts, and Denham (10) believe that the increase in viscosity may be due to strong repulsive forces between similarly charged nuclei within one water envelope. This condition represents an early stage in the formation of a gel in which the viscosity is enormous in spite of a low colloid concentration.

Clark and Mann (15) state that agglomeration with increase in concentration into homogeneous larger particles can not account for an increase in viscosity, for such a process should result in a decrease in viscosity, because of the decrease in surface and the amount of bound water. Agglomeration may, however, be accomplished by an increase in viscosity if there is enclosure of water between the masses, and not an increase in the size of the particles by coalescence of smaller ones. This is believed to be what

happens in the case of starch.

Alsberg (2) believes that the viscosity of starch suspensions does not depend upon any colloiddally dissolved substance. The swelling he believes to be due to three factors: rigidity, inherent swelling power of the granule substance, and the relation of the mass of the swelling substance to the surface area of the granule.

Katz (42) is of the opinion that the swelling and stiffening of starch in water is an equilibrium process, the limiting condition thus depending on the temperature and the relative amount of water present.

This review of the work of many investigators indicates that viscosity measurements are indeed sensitive to slight changes in the system. While this confirms the opinion that viscosity measurements are of value in the study of the colloidal state, it also indicates the need of choosing methods and conditions such that comparable results can be obtained.

E. Structure and Syneresis of Gels.

A review of some of the theories of the structure and properties of gels will serve to aid the solution of the part

of the problem which deals with gel formation and syneresis.

Taylor (78) presents some views regarding the structure of gels. He states that since gels are obtained by the cooling or evaporation of emulsoid sols, it is natural to conclude that gels possess the same structure, that is, two liquids persist from the sol stage. The structure then is cellular, the walls being a highly viscous solution enclosing a more dilute solution.

The nature of the structure of the cell walls is discussed by Taylor, showing the disagreement among many investigators. The honeycomb, open and closed network, rayed and piled shot structures have been proposed. Taylor concludes: "A gel comprises two phases: an ultra-microscopic solid phase, bathed in a liquid dispersion medium, which it retains partly by molecular and partly by capillary forces. The ultimate solid particles of gels are probably spherites. This generally accepted view is a return to the earliest theories of gels, put forward by Frankenheim in 1835, and by vonNageli in 1858."

Arsem (6) also reviews the theories of gel structure. He notes that while some writers view a gel as a homogenous system, others consider a gel as a heterogeneous system

composed of two mingled phases, either liquid-liquid, or solid-liquid. From the two phase solid-liquid theory have been derived the theories of the solid phase honeycomb, network, sponge, and fibrillar structure. Ultramicroscopic study has convinced Arsem that many gels are apparently without structure, but in some cases where structure is seen, the solid phase is not a honey comb, but a mass of straight fibrils joined at their points of intersection. Others appear to consist of minute portions joined in an irregular manner.

Arsem holds the view that a normal gel consists of an associated phase and a free phase. The associated phase is a single large molecule held in combination by the residual valences of the molecular units. The associated phase differs from a normal crystal lattice in that the molecular units are irregularly oriented, and the lattice is expanded and contains a large number of voids. The free phase permeates the associated phase and fills the voids in it.

Two types of gels are distinguished by Arsem: (1) Normal gels, which have a uniform space distribution of the molecular units of the associated phase, with voids of approximately molecular dimensions. (2) Segregated gels, which have a non-uniform distribution of the units of the associated phase,

which consequently has a relatively coarse structural framework in which the voids are large.

The mechanism of the formation of gels is discussed by Arsem. In many cases when a substance separates from solution, conditions do not favor the building of a regular crystalline lattice. This is especially true when the substance has a high molecular weight. Many proteins and carbohydrates form gels readily because their large and unsymmetrical molecular units do not orient themselves regularly upon separation from solution, so that an expanded lattice is built up with its units irregularly arranged.

Syneresis is classified by Arsem as an irreversible change of the solid phase. He believes that the structural arrangements of units in a gel is inherently unstable, so that a further condensation of the associated phase is possible through the re-orientation of units, the release of loosely combined molecules of the liquid phase, and the union of previously non functioning residual valences. Syneresis then is defined by Arsem as a shrinkage of the solid phase caused by progressive association and re-orientation of molecular units.

Holmes (38) believes that gels are formed by molecules or other aggregates uniting to form long filaments which

interlace in a sort of a "brush heap" structure. Water may be held in the capillary spaces between fibers, by hydration of the aggregates, or by dissolving in the aggregates.

Barratt (8) points out that certain gels which do not show fibril formation at first may do so with the lapse of time. Gels in which the fibrils are coarse will exhibit syneresis.

Kraemer (43) states that a sol must immediately precede the gel state, although the sol state may be brief. The gel structure proposed by Nageli is believed by Kraemer to be the only one consistent with the general behavior of gels.

McBain (47) points out the resemblances between sols and gels, the chief differences being rigidity and elasticity. He believes that the linking together of colloid particles to form larger structures is caused by bonds of union as definite as those acting in adsorption or secondary valency. Gelation is due to the splitting off of some substances so that interlocking bonds between small particles may form.

That gels of rice starch show a compact network structure under the ultramicroscope was observed by Tadokoro and Sato (77).

Swanson (75) favors the theory of a network structure of gels of dough, but believes that in starch gels the net-

work structure is not as pronounced as in proteins.

Lepeschkin (44) does not regard the formation of starch gel as a particular case of swelling. He believes that the swelling of starch in hot water involves two processes: (1) a chemical reaction between the starch and water with the formation of hydrates; and (2) a swelling in water of the products thus formed. The reaction between starch and water is accelerated by acids, except H_2SO_4 , but the acceleration is not due to the hydrogen-ion concentration.

Courtonne (16) found that concentrated solutions of certain chlorides, as those of calcium, barium, and magnesium, cause the formation of gels from starch at room temperature. This is also reported by Stocks (74) who believes that the addition of certain substances lower the surface tension of the starch granules so that the thickening point is more or less depressed. Stocks found this to be especially the case with caustic soda, zinc chloride, and hydrochloric acid, which in concentrated solutions form a tenacious white translucent gel with starch even at ordinary temperatures. Other metallic chlorides behave similarly, although less marked in their action, but the chlorides of the alkalis appear to be without effect.

The syneresis of gels has been observed by other investi-

gators, as Holmes (39) who defines it as the separation of water solutions from highly hydrated substances, such as silicic acid gels. He observed syneresis to be greater in vaselined tubes where the gel is free to contract, and that the amount of syneresis varies directly as the free surface.

Fischer (24) states that when the solid phase of a gel is no longer adequate to enclose all the solution of colloid in the solvent, the system tends to "sweat," or the gel shows syneresis. The gel still exists, but is no longer dry.

Stocks (74) observed that starch gels on standing separate into two phases, a more solid gel and a liquid phase, the latter containing very little starch. The phenomenon he believes to be due to the aggregation of the molecular complexes, the colloid becoming less dispersed.

In his studies on starch gels, Meyer (53) observed that the dispersing agent is separated from starch gels without the application of outside pressure. He found that the separation was greater for gels of rather low concentration and which had stood for some time. The separation was found to be hastened and increased by gentle shaking of the tubes containing the gel. Since the separation appears to occur with the pressure of the gel itself, Meyer believes that it

is probable that the gel has a continuous net structure. Gels of lower concentration show the greater separation, probably because such gels have a lighter and looser connecting net work. The separated liquid was found to contain small amounts of suspended particles of amylose water solution in water.

Mardles (52) also found that mechanical agitation destroys gel structure by breaking the connection between clots.

Osborne (58) believes that the weaker gels hold part of the liquid phase by capillarity in the lattice of the solid phase, whereas in the stronger gels the water exists in solid solution in the substance of the frame work. This view is held because the weaker gels extrude water more readily.

Maquenne (50) noted a change in the translucency of a homogeneous starch gel, gradually becoming opaque, and finally depositing flocks. This Maquenne believed to be due to a change in the starch, tending toward a form of amylocellulose.

This review indicates that starch gels may be considered as consisting of two phases which may be termed the associated phase and the free phase. The solid phase

probably exists in some kind of an irregular fibrial structure. Syneresis may be regarded as a separation of the free phase, and its cause is probably the segregation of the associated phase.

III. EXPERIMENTAL PART

A. Microscopic Examination of Starch.

While no attempt was made to determine the gelatinization temperature of starch by microscopic methods, suspensions of starch in water were examined after having been heated at different temperatures for different periods of time. This was done in order to study the nature of the swelling of the granules, and to determine whether or not the reaction was the same for large and small granules.

Several suspensions of starch in water were prepared, and each heated to different temperatures. A portion of each sample thus treated was examined under the microscope. The length of the time of heating at the different temperatures was also varied from a few minutes to two hours.

When the starches are heated in water as described, the granules appear to swell. As the temperature is increased, the degree of swelling is increased. As the heating is continued, the granules become distorted, and finally appear to burst.

The larger granules of starch appear to begin swelling at a lower temperature than do the smaller ones. When heated to 60°, the larger grains of wheat starch were observed to have increased somewhat in size and to be distorted, while

none of the smaller grains appeared to have increased in size. As the temperature was increased, it was evident that the swelling of the small grains was a much slower process, for while it soon became difficult to identify the large granules as individuals, a large proportion of the small granules still remained intact. Even when heated as high as 95° for five minutes, it was still possible to distinguish some of the small grains.

The effect of the time of heating was studied by holding a suspension of starch in water at 70°. Samples were withdrawn at the end of every five minutes and examined. At the end of five minutes none of the granules were broken. After thirty minutes none of the smaller grains appeared to be broken, while but a few of the larger grains remained unbroken. At the end of two hours many of the small granules were still unbroken, while nearly all of the large granules had burst.

From the microscopic observations it is evident that gelatinization is a progressive process, and that the gelatinization temperature is dependent upon the size of the individual granules and the time of heating the suspensions.

B. Gelation Temperature.

The changes which take place when starch is heated in

water are believed by Alsberg and Rask (5) to involve an imbibition of water and consequent swelling to a point where the grains burst. The final result is a conversion of the starch suspension into a sol which gels on cooling. This conversion may be defined as gelatinization.

Since the gelatinization of starch leads to the formation of gels, the temperature to which the starch suspension must be heated so that a gel is formed should be a measure of the gelatinization temperature. Accordingly, such measurements were attempted.

A series of suspensions of six grams of starch in 100 c.c. of water was prepared. Each was heated to a different temperature and held at that temperature for fifteen minutes. Each was then cooled and examined to determine whether or not a rigid gel had been formed. It was found necessary to heat corn starch to approximately a temperature of 90° in order to obtain a firm gel, while wheat starch required a temperature of about 92°.

Since this method determines the temperature to which the starch must be heated so that a gel results, it may be called the "gelation" temperature. The method can only give approximate results, because of the difficulty in determining the point where the gel may be considered to be rigid. Such

determinations will also be influenced by the concentration of starch employed, and the time that the suspension is heated.

The gelation temperatures thus obtained do not differ greatly from the temperatures of maximum viscosity as given by Alsberg and Rask (5). This temperature for corn starch is given as 91°, while that for wheat starch is 95°, as compared to 90° for corn starch and 92° for wheat starch, the values obtained by measuring the temperature necessary for gel formation.

This comparison indicates that there is a close relationship between the viscosity and gelation of starch suspensions.

C. Viscometric Methods.

1. Types of Viscometers Employed.

A Scott's viscometer was first selected for the viscosity studies, but was found unsuitable. The difficulty in the use of this instrument was due chiefly to the settling out of the starch, so that in making determinations, especially at low temperatures, it was found that a considerable portion of the starch remained behind. At higher temperatures some difficulty was experienced with the formation of clots, which oftentimes prevented the free flow through the delivery tube. Further difficulty was experienced in loss by evaporation and

the formation of films on the surface of the pastes.

The determinations were next made with a "Doolittle's Improved Torsion Viscosimeter." While this instrument proved much more satisfactory than the Scott viscometer, difficulties were encountered in its use. Chief among these were again the formation of surface films, which would cling to the rod suspending the cylinder, so that, if not broken by continual stirring, when determinations were made there was a sheet of film rotating with the cylinder. While this film could be prevented from forming, it is not unlikely that the agitation necessary caused a difference in the results. Some loss was also experienced by evaporation, necessitating the frequent addition of water to keep the volume constant. It was also difficult to control the temperature, especially at higher temperatures.

Finally viscometers of the Ostwald capillary type were used. This type of instrument appears to offer the most satisfactory method of making the desired determinations. Difficulties were anticipated from the clogging of the capillary tube, but only in a few instances did this occur. The starch particles were readily kept in suspension by agitation obtained by applying gentle suction to the tubes. The exposed surfaces of the liquid are so small, that practically no difficulty was encountered either by the

formation of films or by loss by evaporation. The temperature is easily and accurately controlled, and if desired, several instruments may be placed in the same bath so that a number of determinations may be carried on side by side.

The viscosity determinations which are discussed in the following pages were made either by the Doolittle or the Ostwald instrument, as indicated in the discussion.

2. The Effect of Concentration and Temperature upon the Viscosity of Starch Suspensions.

The effect of the concentration of starch in water on the change in viscosity with increasing temperature was determined by measurements on suspensions of different concentrations at increasing temperatures.

For the measurements in which the Doolittle viscometer was used, the suspensions were made by adding from two to sixteen grams of corn starch to 200 c.c. of distilled water. The suspensions were transferred to the viscometer cup and readings taken at different temperatures. Care was taken to prevent the formation of film, and the volume was kept constant by replacing the water lost by evaporation.

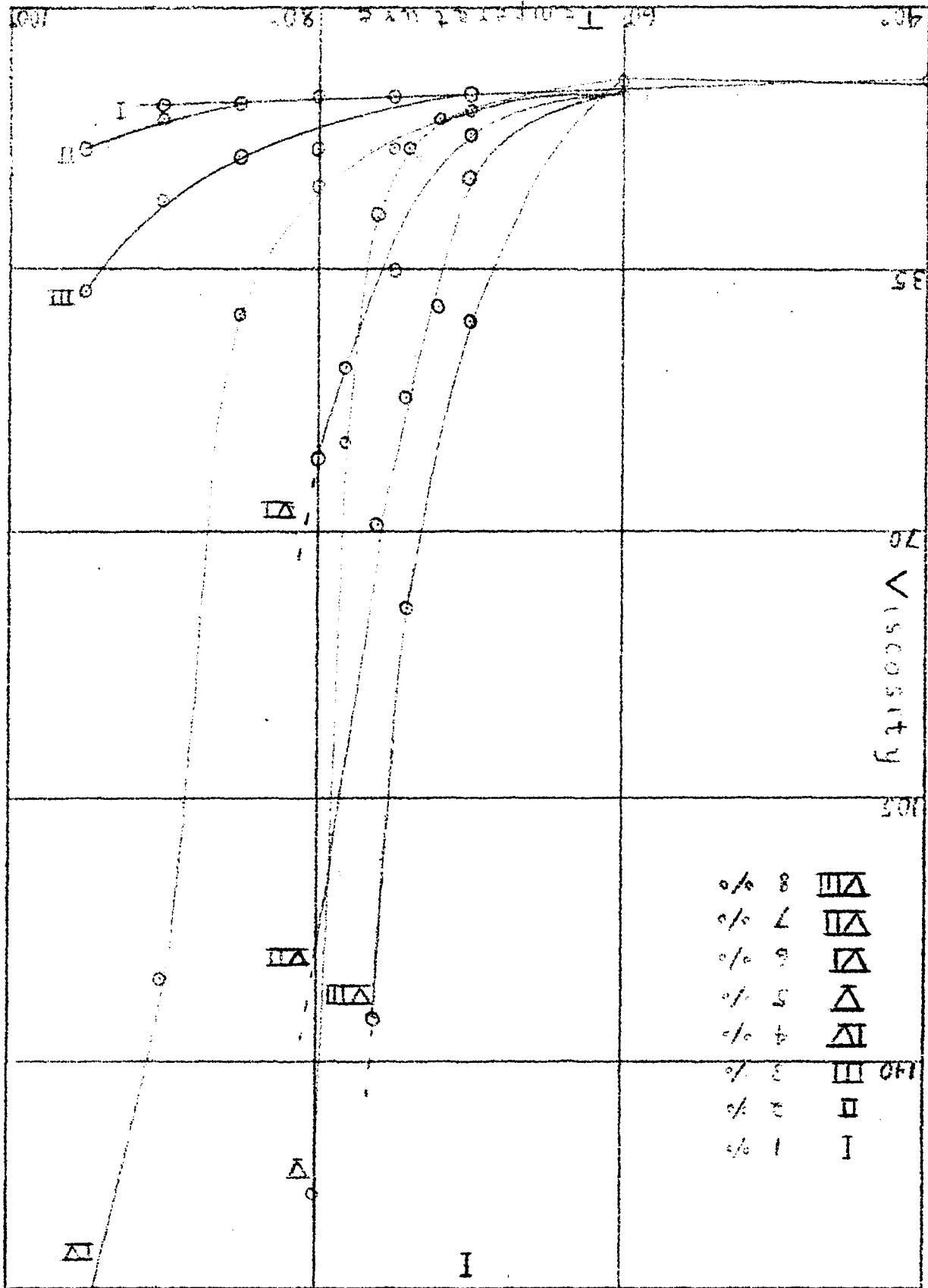
The results are recorded in Table I, and represented graphically on Chart I.

TABLE I

THE VISCOSITY IN DEGREES RETARDATION OF DIFFERENT
CONCENTRATIONS OF CORN STARCH WITH INCREASING
TEMPERATURE AS MEASURED BY THE DOOLITTLE VISCOMETER

Grams: of Starch: in 100 g. g.:	Degrees Retardation at a Temperature of											
	40	60	70	72	74	75	76	78	80	85	90	95
1	10	12	12			12			12		13	
2	11	10	12			12			12	13	15	19
3	11	11	12						19	20	26	38
4		10	14			19			24	41	129	175
5		12	12	15	19		28	58	157	*	*	*
6		13	17			35		48	60	*	*	*
7		12	23	40	52		69		126	*	*	*
8		10	42		80		134	*	*	*	*	*

*Too viscous to read.



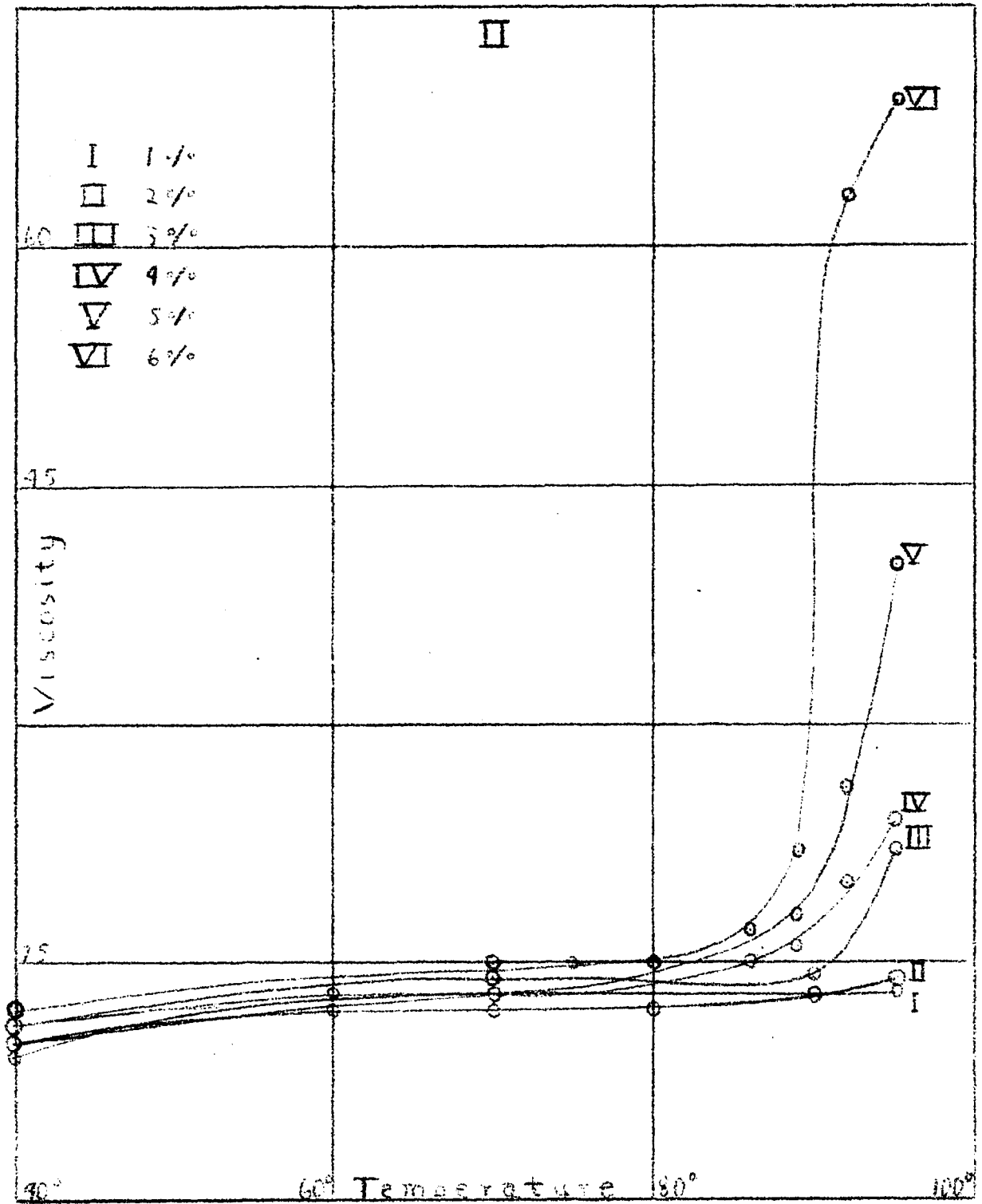
The results of a similar series of determinations made in the same way, except that the corn starch was replaced by wheat starch, are recorded in Table II, and represented graphically on Chart II.

TABLE II.

THE VISCOSITY IN DEGREES RETARDATION OF DIFFERENT CONCENTRATIONS OF WHEAT STARCH WITH INCREASING TEMPERATURE AS MEASURED BY THE DOOLITTLE VISCOMETER

Grams: of : Starch: in : 100 : c.c.:	Degrees Retardation at a Temperature of										
	40	60	70	75	80	86	89	90	92	95	
1	9	12	13		12			13	13	13	
2	10	12	12		12			11	13	14	
3	11	12	14		14			14		22	
4	11	13	13		12	15	16		20	24	
5	10	12	13	14	15	15	18		26	40	
6	12	13	15	15	15	17	22		63	69	
12	12	13	15	*	*	*	*	*	*	*	*

*Too viscous to read.

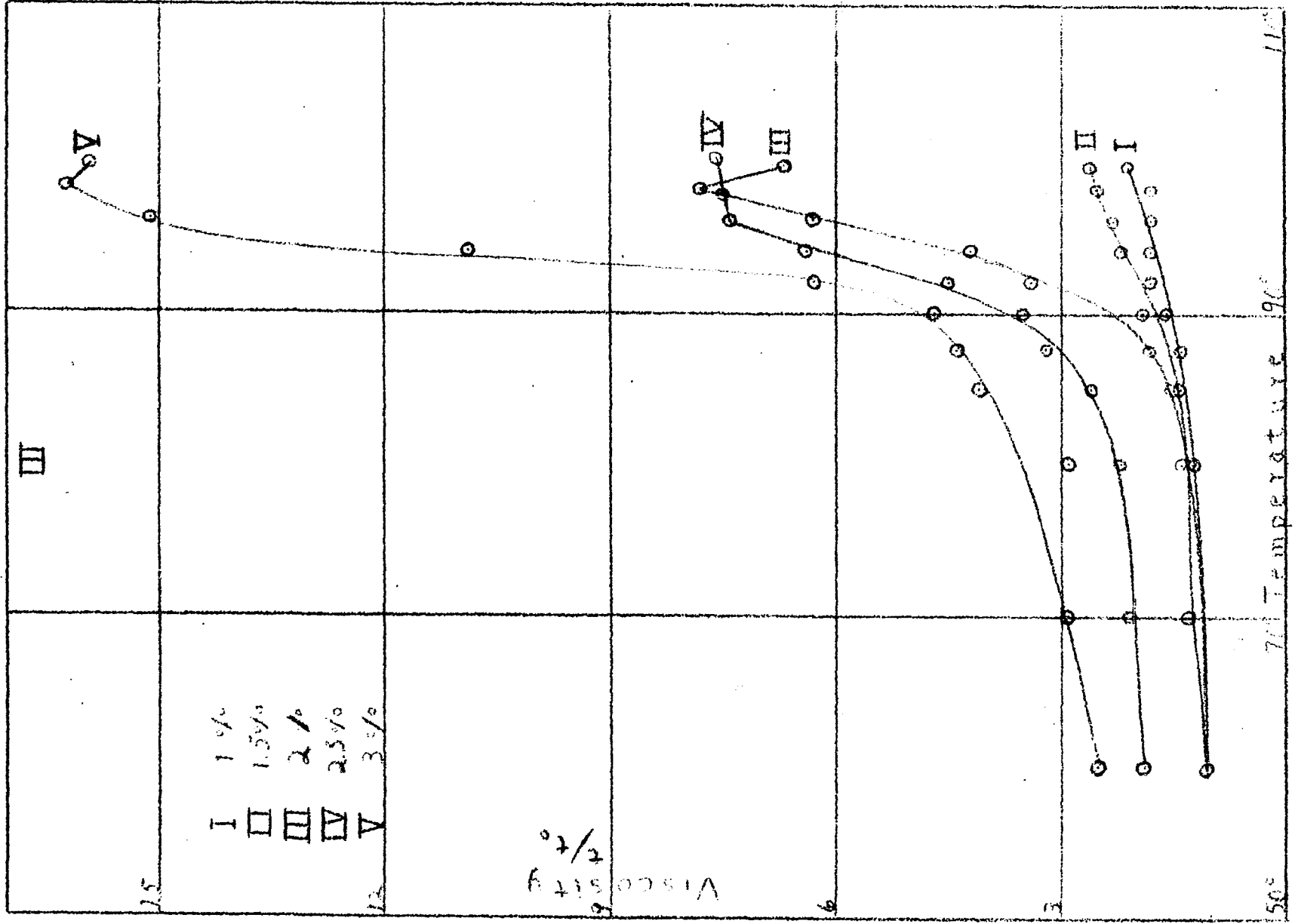


Similar experiments were carried out for corn starch, using the Ostwald viscometer in place of the Doolittle. The results are recorded in Table III, in which the viscosity is expressed by $\frac{t}{t_0}$, obtained by dividing the time of flow for the starch paste by the time of flow for water. The results are shown graphically on Chart III.

TABLE III.

THE VISCOSITY OF DIFFERENT CONCENTRATIONS OF CORN STARCH WITH INCREASING TEMPERATURE AS MEASURED BY THE OSTWALD VISCOMETER

Grams: of Starch in 100 c. c.:	$\frac{t}{t_0}$ at a Temperature of											
	60	70	80	85	87.5	90	92	94	96	98	99.5	
1.	1.0		1.2	1.4	1.4	1.6	1.8	1.8	1.8	1.8	2.1	
1.5	1.0	1.3	1.4	1.4	1.5	1.6	1.9	2.2	2.3	2.5	2.6	
2.	1.1	1.2	1.3	1.5	1.8	1.9	3.4	4.2	6.3	7.8	6.7	
2.5	1.9	2.1	2.2	2.6	3.2	3.5	4.5	6.4	7.4	7.5	7.6	
3.	2.5	2.9	2.9	4.1	4.4	4.7	6.3	10.9	15.1	16.2	15.9	



III

V

I 1%
II 1.5%
III 2%
IV 2.5%
V 3%

Viscosity
2/2
9

IV
III

II
I

Temperature 90°

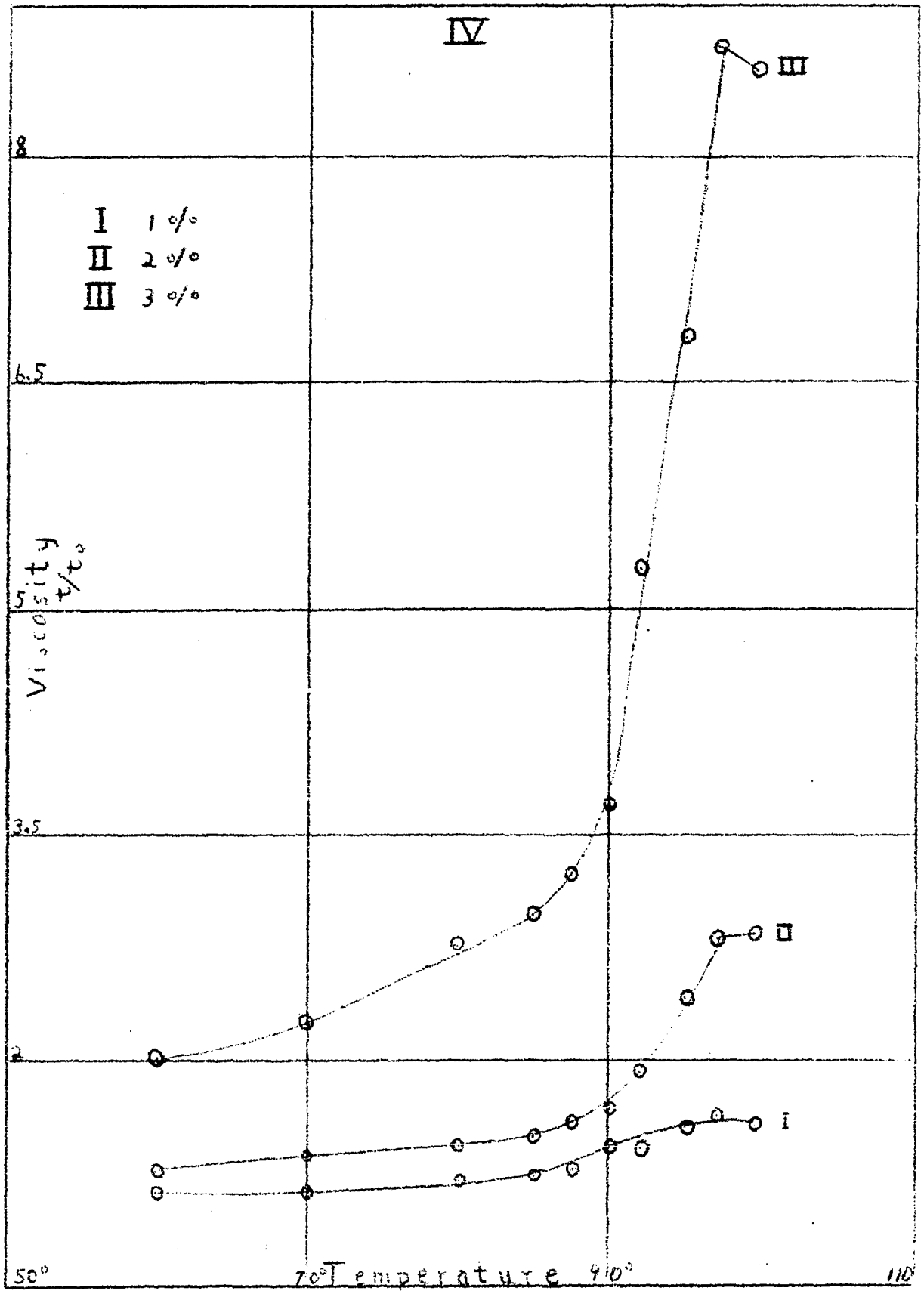
50°

The effect of concentration of wheat starch on viscosity was also measured with the Ostwald viscometer. The results are recorded in Table IV, and shown graphically on Chart IV.

TABLE IV.

THE VISCOSITY OF DIFFERENT CONCENTRATIONS OF WHEAT STARCH WITH INCREASING TEMPERATURE AS MEASURED BY THE OSTWALD VISCOMETER

Grams of Starch in 100 c.c.	$\frac{t}{t_0}$ at a Temperature of									
	60	70	80	85	87.5	90	92	95	97	99.5
1.	1.1	1.1	1.2	1.2	1.3	1.4	1.4	1.6	1.6	1.6
2.	1.3	1.4	1.4	1.5	1.6	1.7	1.9	2.4	2.8	2.9
3.	2.0	2.3	2.8	3.0	3.2	3.7	5.3	6.8	8.7	8.6



A comparison of the results obtained by the different instruments is somewhat difficult, since the most characteristic results are obtained by using different concentrations. The concentration which is most favorable for use in both types is about three per cent. Lower concentrations do not appreciably affect the readings on the Doolittle instrument, while higher concentrations become too viscous to be determined by the Ostwald. A comparison of results must then be more qualitative than quantitative in nature, and for that reason there is no advantage in converting the readings to absolute viscosity. The results obtained with the Doolittle viscometer are accordingly reported as degrees retardation as read directly, while those obtained with the Ostwald viscometer are reported as relative viscosity, obtained by dividing the time of flow for the starch suspension by the time of flow for water at the same temperature.

An examination of the results recorded in the Tables I, II, III, and IV, shows that the maximum viscosity is attained at different temperatures, depending upon the concentration of starch used. The viscosity of suspensions of low concentrations at the temperature of boiling water is not greatly different than that at room temperature, while suspension of higher concentrations become too viscous to read as the

temperature is increased. It is also evident that the temperature at which the greatest increase occurs can not be readily determined when suspensions of low concentrations are used.

The temperature of maximum viscosity obtained upon heating suspensions of three grams of starch in 100 c.c. of water is different for different instruments. For corn starch, the Doolittle viscometer shows this maximum to be 95°. The maximum with the Ostwald is 98°. For wheat starch of the same concentration, the maximum viscosity is at 95° with the Doolittle instrument, and at 97° with the Ostwald. This difference may be because higher temperatures can be reached more rapidly when the Ostwald viscometer is used. This probably also accounts for the failure of the readings obtained by the use of the Doolittle viscometer to show the "fall back" in viscosity, that is, the decrease in viscosity after the maximum is reached. However, the decrease is shown by measurements made by the latter instrument after the paste has been allowed to stand a short time.

In addition to the determinations made using corn and wheat starch, rice and potato starches were also used. These different starches were used in order to determine whether or not the differences in viscosity are due to the relative size

of the starch granules.

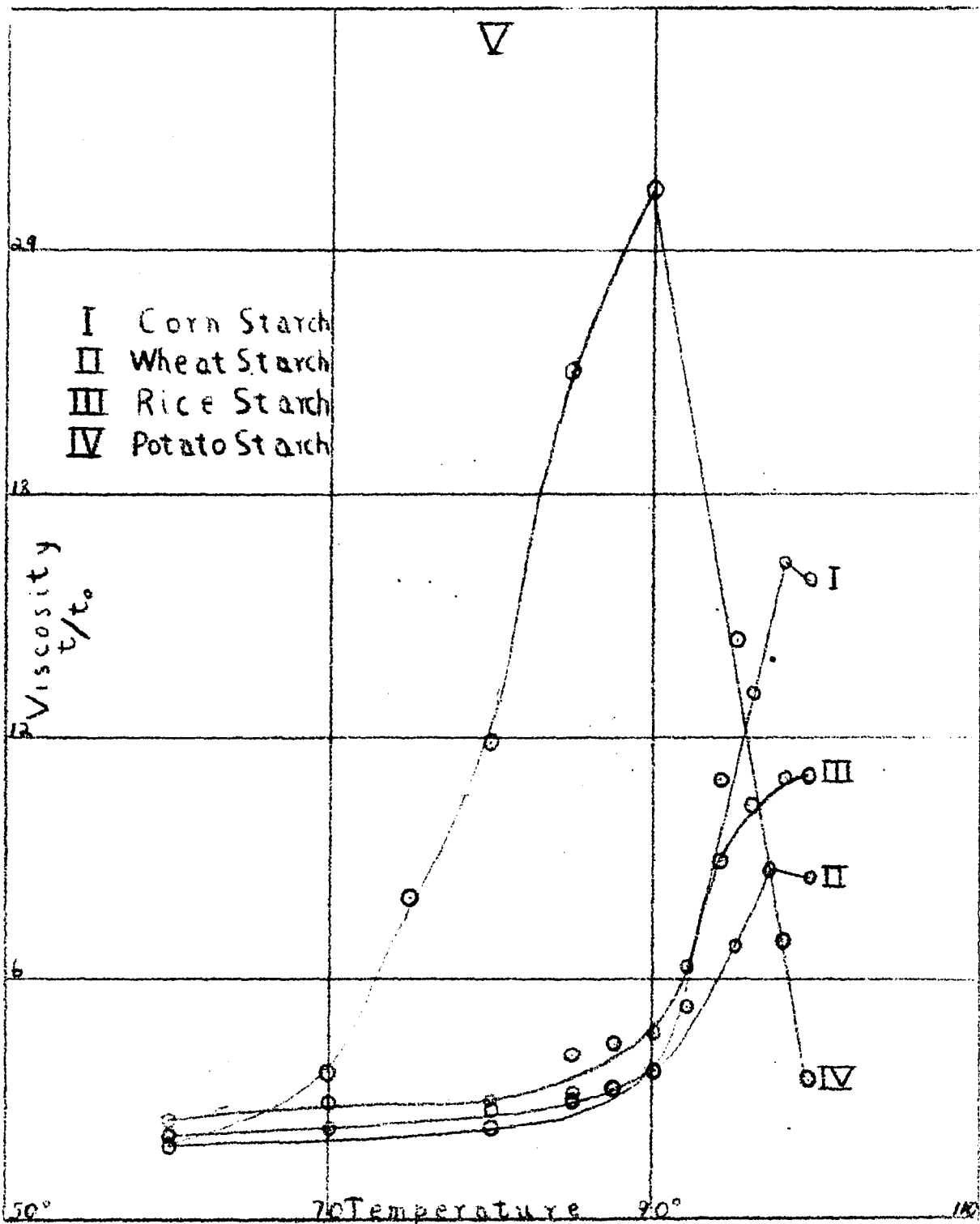
A comparison of the viscosities of the different starches is made in Table V. Three grams of each starch were suspended in 100 c.c. of water, and the determinations made at increasing temperatures with the Ostwald viscometer. The results are shown graphically on Chart V.

TABLE V

A COMPARISON OF THE VISCOSITIES OF DIFFERENT STARCHES OF THE SAME CONCENTRATION AS MEASURED BY THE OSTWALD VISCOMETER

Kind of Starch:	$\frac{t}{t_0}$ at a Temperature of												
	60	70	80	85	87.5	90	92	94	95	96	98	99.5	
Corn	2.5	2.9	2.9	4.1	4.4	4.7	6.3	10.9		15.1	16.2	15.9	
Wheat	2.0	2.3	2.8	3.0	3.2	3.7	5.3		6.8		8.7	8.6	*
Rice	1.9	2.3	2.3	3.1	3.1	3.7	5.3	9.0		10.2	10.98	11.0	
Potato	2.0	3.7	11.9	21.0		25.4			14.4		6.9	3.5	

* Reading at 97°.



In Table V it is shown that the point of maximum viscosity is reached at a much lower temperature for potato starch than for the others, while rice starch requires the highest temperature. A comparison of the temperature of maximum viscosity with the average diameter of the granules is made in Table VI.

TABLE VI.

COMPARISON OF THE TEMPERATURE OF
MAXIMUM VISCOSITY WITH AVERAGE DIAMETER OF STARCH GRANULES

Variety of Starch	Temperature of Maximum Viscosity	Average Diameter of Granules
Rice	99.5	0.022 m. m.
Corn	98	0.03 m. m.
Wheat	97	0.05 m. m.
Potato	90	0.14 m. m.

The comparison made in Table VI. indicates that the temperature of maximum viscosity varies with the size of the granules. However, if this were the only factor, the temperatures of maximum viscosity for the starches of rice and corn might be expected to fall closer to the same value.

That a very considerable decrease in viscosity occurs for potato starch after having reached the maximum value, is evident from Chart V. Rice shows the least decrease, while

there is but little difference shown by wheat and corn starch. Here again is indicated a relationship to the relative size of the grains.

3. The Decrease in Viscosity of Starch Suspensions with Continued Heating.

Attention has been called to the decrease in the viscosity of starch suspensions after the maximum value has been reached. This decrease has been found to become more evident as the heating is continued, and to vary with the rate at which the suspension has been brought to the desired temperature.

Corn starch suspensions of different concentrations were heated quickly to the boiling point, transferred to the Ostwald viscometer, and the first measurement made without delay. The time which elapsed from the beginning of the heating to the start of the first determination was about three minutes. This could not be controlled exactly, hence the values obtained were not always identical. However, the curves obtained are of the same general type.

Table VII and Chart VI show how the viscosities of three different concentrations of corn starch decrease when held at the temperature of boiling water.

TABLE VII

DECREASE IN VISCOSITY OF SUSPENSIONS
OF CORN STARCH WITH CONTINUED HEATING

Three minutes required to bring the suspensions to temperature and start the first determination. Readings taken at 99°.

Grams: of Starch: in 100 c.c.:	t/t ₀										
	Heating continued for										
	0	5	10	15	30	45	60	75	90	105	120
	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.
1.	3.3	2.8	2.5	2.4	2.2	2.0	1.8	1.6	1.6	1.6	1.5
2.	16.0	11.0	10.1	10.2	10.0	9.0	9.1	8.7	8.8	8.9	8.9
3.	52.4	33.3	22.9	17.8	10.2	6.4	4.9	4.5	4.1	3.9	3.5

To show that the decrease in viscosity is affected by the rate of heating the suspension, several suspensions of equal concentration of corn starch were prepared and brought to the desired temperature at different rates.

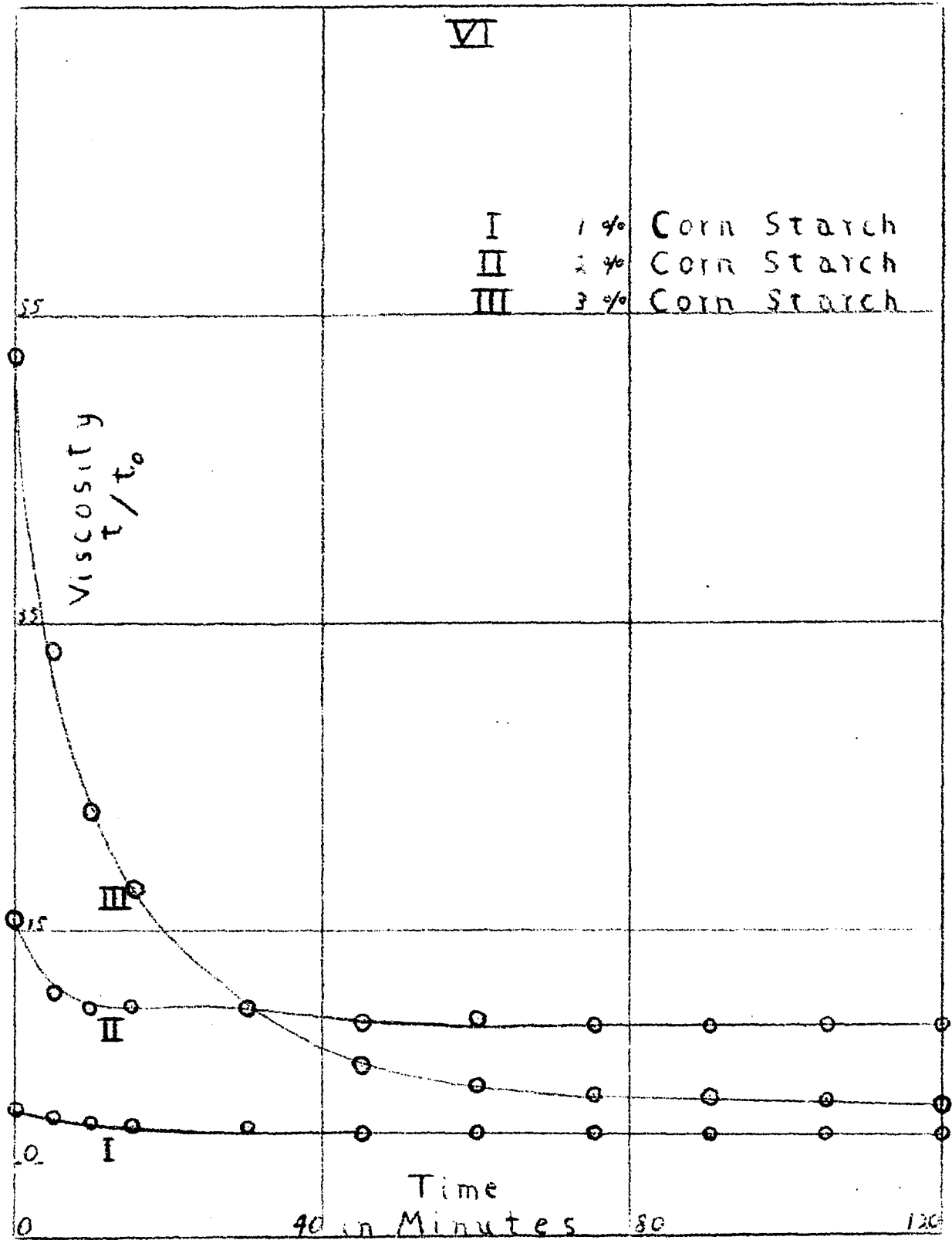


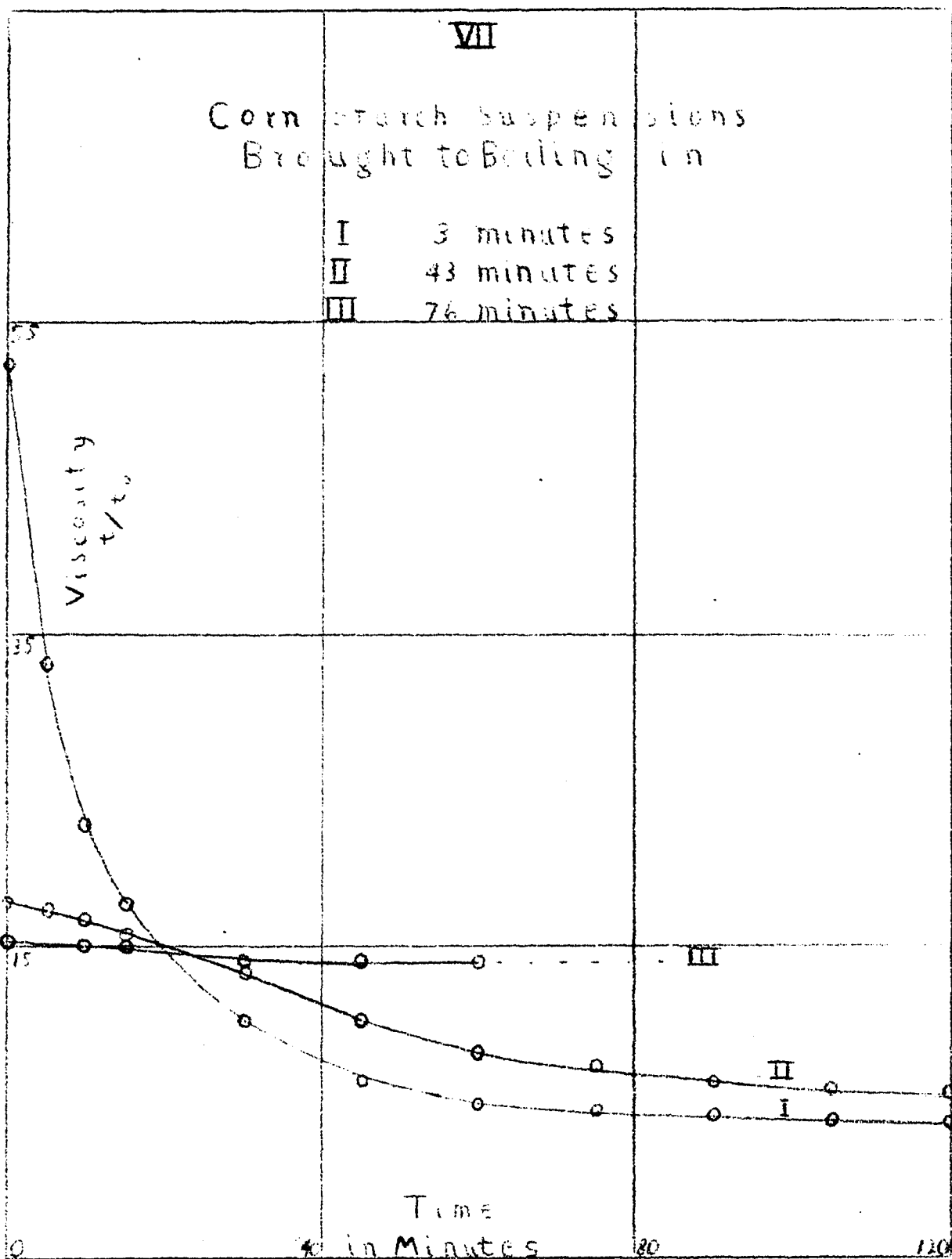
Table VIII and Chart VII show that the rate of decrease is greater for the suspensions which were heated quickly. The table also shows that the suspensions which were heated slowly fail to show as high a viscosity as those which were heated rapidly. Further, the viscosity of the rapidly heated suspensions decrease until less than the values obtained for those which were heated slowly.

TABLE VIII

EFFECT OF THE RATE OF HEATING ON THE DECREASE IN VISCOSITY OF CORN STARCH AS MEASURED WITH THE OSTWALD VISCOMETER

Readings taken at 99°.

Time re-: quired : to bring: to temp.:	t/t ₀										
	Heating continued for										
	0	5	10	15	30	45	60	75	90	105	120
	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.
3 min.	52.4	33.3	22.9	17.8	10.2	6.4	4.9	4.5	4.1	3.9	3.5
43 min.	17.8	17.3	16.7	15.7	13.3	10.2	8.0	7.1	6.1	5.7	5.5
76 min.	15.4	15.6	15.	15.	14.	14.	14.				



A comparison of the rates of decrease in the viscosity of different varieties of starch upon continued heating is made in Table IX. Three grams each of corn, wheat, rice, and potato starch were suspended in 100 c.c. of water, heated rapidly over a flame, and the viscosities determined at the temperature of boiling water. The potato starch was so viscous that readings could not be made during the first fifteen minutes. The results are represented graphically by Chart VIII.

TABLE IX

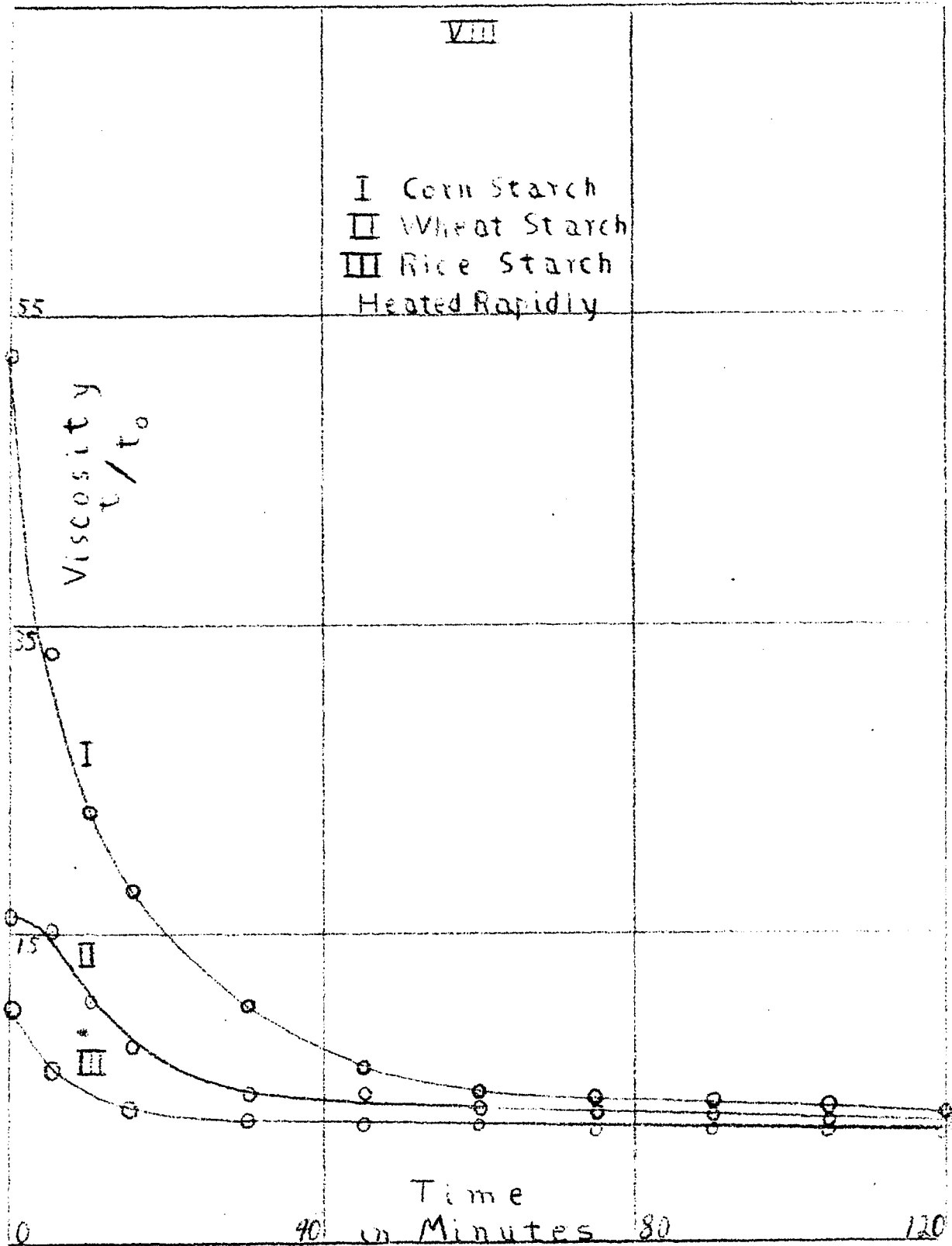
DECREASE IN VISCOSITY OF DIFFERENT STARCHES
OF THE SAME CONCENTRATION WITH CONTINUED HEATING

Suspensions brought to temperature in three minutes. Readings made at 99°.

Variety: Of Starch :	t/t ₀ Heating continued for										
	0	5	10	15	30	45	60	75	90	105	120
	:Min.	:Min.	:Min.	:Min.	:Min.	:Min.	:Min.	:Min.	:Min.	:Min.	:Min.
Corn	:52.4	:33.3	:22.9	:17.8	:10.2	:6.4	:4.9	:4.5	:4.1	:3.9	:3.5
Wheat	:16.3	:15.3	:10.6	:7.6	:4.7	:4.7	:3.7	:3.5	:3.3	:2.7	:2.7
Rice	:10.2	:6.1	:4.1	:3.7	:3.1	:2.7	:2.7	:2.5	:2.5	:2.5	:2.5
Potato	:*	:*	:*	:260	:224	:208	:171	:159	:117	:111	:100

*Too viscous to read.

**71 after 400 minutes.



The data in Table IX show that the relative rate of decrease is in the order: potato, corn, wheat, rice. The order of the same starches according to the decreasing average size of the granules is: potato, wheat, corn, rice. The rate of decrease for corn and wheat starch is the reverse of that expected from a consideration of the size of the granules.

To obtain a further comparison of the rate of decrease in viscosity with continued heating, suspensions of the same starches of the same concentration were brought slowly to the temperature desired for the observations. The time required was forty-four minutes. The results of this series of determinations are shown in Table X and Chart IX.

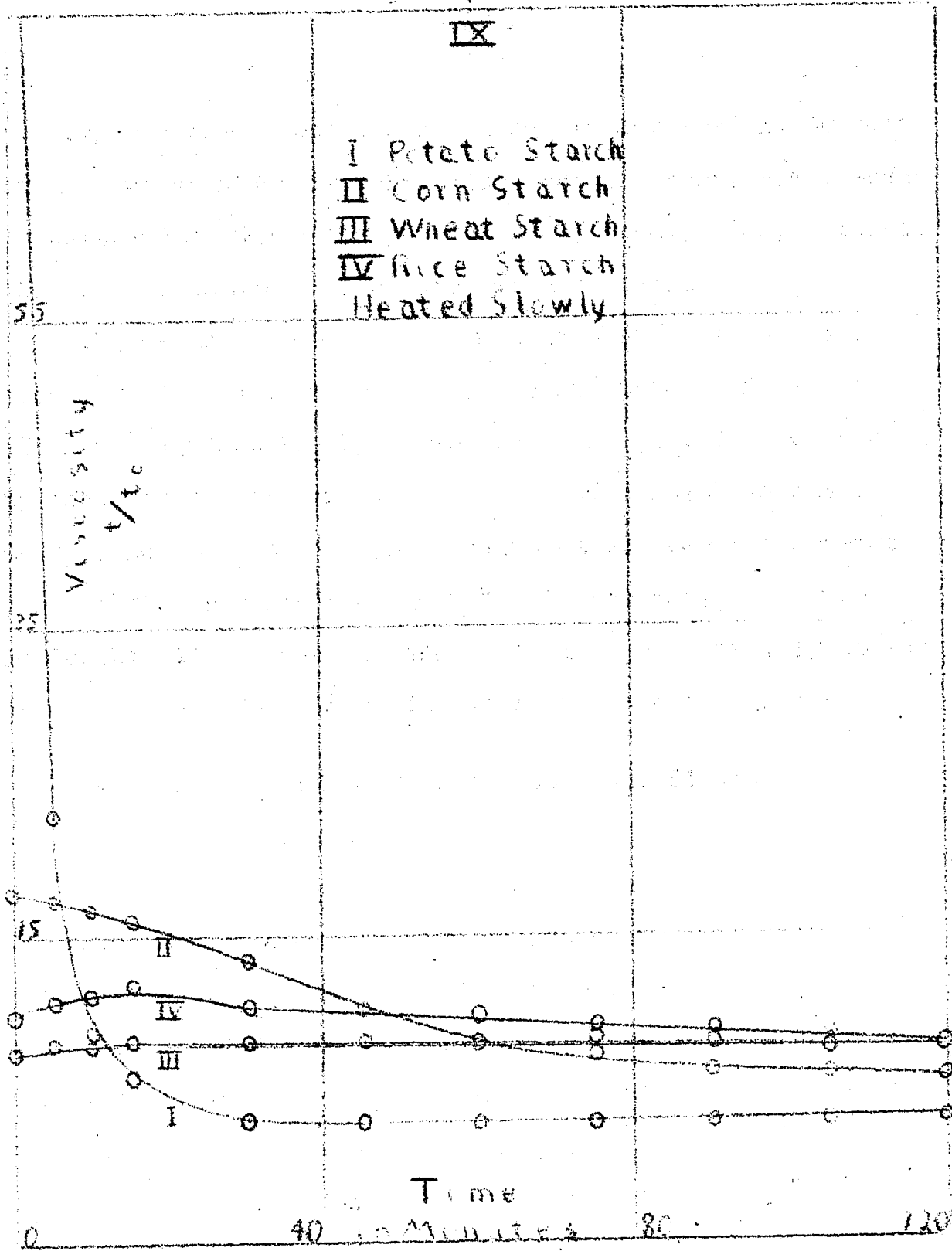
TABLE X

DECREASE IN VISCOSITY OF DIFFERENT STARCHES
OF THE SAME CONCENTRATION WITH CONTINUED HEATING

Suspensions brought to temperature in forty-four minutes.

Readings made at 99°.

Variety: of Starch :	t/t ₀										
	Heating continued for										
	0	5	10	15	30	45	60	75	90	105	120
	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.
Corn	17.8	17.3	16.7	15.7	13.3	10.2	8.0	7.1	6.1	5.7	5.5
Wheat	7.1	7.8	7.5	8.0	8.0	8.0	7.8	8.1	7.8	7.5	7.5
Rice	9.8	10.6	11.0	11.6	10.4	10.2	9.6	9.0	8.6	8.4	7.6
Potato	21.1	22.8	8.6	5.7	2.9	2.9	2.7	2.7	2.7	2.7	2.7



The order of decrease in viscosity for the slower rate of heating as shown by Table X is: potato, corn, rice, wheat, as compared to the order potato, corn, wheat, rice, obtained when the suspensions were more rapidly heated.

The experimental work shows that there occurs a considerable decrease in the viscosity of starch pastes soon after the maximum has been reached. The rate of decrease is shown to be greater when the rate of heating is rapid. There also appears to be some relation between the average size of the granules and the rate of decrease. This relationship is not marked, and is readily evident only in the case of a considerable variation in the average diameters.

4. Effect of Added Reagents upon the Viscosity of Starch Suspensions.

From the discussion of the results obtained in the determination of the viscosity of starch in water, it is evident that the determination of the effect of reagents would be attended with difficulties. This is true because the viscosity of starch in water is affected by the concentration, temperature, rate of heating, time of heating, and mechanical treatment during the determination. In spite of these difficulties, some knowledge of the effect of added

substances may be gained, provided that all determinations are made in the same manner.

The Doolittle viscometer was used in the study of the effect of added reagents, because of the greater convenience in adding material after the determination of the viscosity of the starch in water. The additions could be made without appreciable change in starch concentration, because the evaporation of water necessitated the addition of water or of some solution to keep the volume constant. This procedure was not found practical with the Ostwald, because of the use of smaller volumes, and because the loss by evaporation was small.

The effect of the addition of some acids and alkalies upon the decrease in viscosity is shown in Table XI. For each determination six grams of corn starch were added to 200 c.c. of water. The suspensions were then placed in a boiling water bath, held there for thirty minutes, then transferred to the viscometer cup, and the determinations made at once. 5 c.c. of the indicated reagents were then added, and the viscosity determined at the noted intervals of time.

TABLE XI

THE EFFECT OF ACIDS AND ALKALIES ON THE DECREASE IN VISCOSITY OF SUSPENSIONS OF CORN STARCH

Reagents added. 5 c.c. of: 0.1N.	Degrees Retardation after intervals of					
	0*	3	13	23	33	43
	Min.	Min.	Min.	Min.	Min.	Min.
Water		52	50	47		37
CH ₃ COOH	50	54	51	41	32	27
HCl	56	51	26	18	16	16
H ₂ SO ₄	61	51	22	18	16	16
H ₃ PO ₄	47	45	25	18	17	16
KOH	50	72	55	44	41	31

*Reading taken before the addition of any reagent.

The preceding table shows that the addition of acids causes a more rapid decrease in the viscosity of the starch suspensions than that shown for water alone. The rate is nearly the same for hydrochloric, sulphuric, and phosphoric acids, but is somewhat slower for acetic acid. The addition of potassium hydroxide causes a marked increase in the viscosity, which is followed by a decrease.

The effect of added salts upon the viscosity of corn starch is shown in Table XII. It was found from preliminary

determinations that the effect of salts added in as small amounts as were the acids and alkalies was not appreciable, hence the starch was suspended in salt solutions rather than in water. To 200 c.c. of water the weight of salt required to make the solution one-half molar was added. To this six grams of starch were added. The viscosity was then determined at increasing temperatures.

TABLE XII

THE CHANGE IN VISCOSITY WITH CHANGE IN TEMPERATURE OF SUSPENSIONS OF CORN STARCH IN SALT SOLUTIONS

Suspension of Starch in	Degrees Retardation at a Temperature of													
	40	50	52	54	56	58	60	65	70	75	80	85	95	
H ₂ O	13	14					14		16		18	23	29	
NaCl	13	13					12	13	13	15		15	24	
Na ₂ SO ₄	10	12					13			14	13	13	16	
Na ₃ PO ₄	12	19	43	101	138	157	154	120	70	49	36	29	17	

TABLE XIII

THE CHANGE IN VISCOSITY WITH CONTINUED HEATING OF SUSPENSIONS OF CORN STARCH IN SALT SOLUTIONS

Suspension: of Starch : in :	Degrees Retardation after heating for					
	30	45	55	65	75	85
	Min.	Min.	Min.	Min.	Min.	Min.
Na_2SO_4	39	83	102	109	115	114
Na_3PO_4	17	16	17	17		

The results shown in Table XII indicate that sodium chloride has no appreciable effect upon the viscosity change with an increase of temperature. Sodium sulphate appears to depress the viscosity, but an examination of Table XIII will show that the effect is rather one of retardation. Sodium phosphate causes a considerable increase in the viscosity, and the maximum is reached at a much lower temperature than with water alone. The maximum is followed by a regular decrease, the values soon becoming constant. The constant readings are reached in less than thirty minutes as shown in Table XIII, whereas with Na_2SO_4 , the maximum is not reached until after heating for seventy-five minutes.

These determinations have shown that the addition of acids to starch paste causes a rapid decrease in the viscosity of the paste. Preliminary experiments in which more concentrated

acids were used caused so rapid a decrease that the changes could not be followed. The addition of an alkali has been shown to cause an increase in viscosity. Other experiments have shown that the presence of alkalies lower the temperature of maximum viscosity.

The effect of the presence of salts upon the viscosity of starch suspensions may be due in part to hydrolysis to give an alkaline reaction, as it is evident from the tables that the order in increasing effect is NaCl, Na₂SO₄, and Na₃PO₄.

D. The Formation of Starch Gels and the Syneresis of the Gels.

When a suspension of starch in water is heated, water is taken up by the granules. This causes the granules to swell and to disintegrate, and a paste is formed. When the paste is allowed to cool, the whole mass sets to form a jelly-like body. The gel so formed, when allowed to stand, may separate into two phases; a clear layer of liquid is formed on the surface, leaving a more concentrated gel behind. The liquid, when filtered and evaporated, is found to contain some solid material. No doubt this is starch in true solution. The phenomenon of the separation of a clear liquid from a gel is known as syneresis.

The study of gel formation and syneresis involves the effect of concentration, rate of heating, amount of exposed surface, variety of starch, the time that the gels are allowed to stand, and the effect of certain added substances.

Various concentrations of starch suspensions were heated over a free flame to the desired temperature, and the resulting pastes transferred to test tubes. Two sizes of tubes were used so that the effect of exposed surface might be determined. The larger tubes averaged 2.2 cm. in diameter by 18 cm. in length, while the smaller tubes varied from 1.2 to 1.5 cm. in diameter by 17 cm. in length. The smaller tubes were graduated so that the volumes could be read directly. The larger tubes were not graduated, so it was necessary to remove the contents for measurement.

The tubes were used without any coating material, or with a coating of vaseline. Other substances, such as wax, paraffin and colloidion were found to be of no value as coating material. The use of vaseline was found to be but slightly beneficial, thus indicating that the starch gels do not cling firmly to the walls of the tubes.

Some difficulty was experienced with mold growth in the tubes. This growth was prevented by the addition of small amounts of toluene, and by storing the tubes at a temperature

of -2° . All tubes were tightly stoppered to prevent loss by evaporation.

As the proportion of starch to water is increased, more rigid gels are formed. When concentrations as low as one or two percent are used, the resulting gel is not continuous, but there appear to be formed separate clumps of gel. When concentrations of three percent or greater are used, a continuous gel is formed. The higher concentrations form gels more quickly when cooled than do the lower concentrations.

That the amount of syneresis decreases as the concentration of the starch increases is shown by the results recorded in Tables XIV and XV. This decrease is seen to be less marked for the gels made from potato starch than those made from other varieties.

TABLE XIV

THE SYNERESIS OF STARCH GELS

Variety of Starch	Grams of Starch in: 100 c. c.	Volume and percent of separated liquid			
		After 15 days c. c.	%	After 20 days c. c.	%
Corn	3	10	20	20.8	46
Corn	4	8	16.6	17.6	39
Corn	5			14.6	34
Corn	6	4.5	12.1	10.2	25
Wheat	3	11.	25.	8.3	18.4
Wheat	4	7	14.6	5.3	12.3
Wheat	5	10	21.7	3.6	8.4
Wheat	6	1.	2.6	1.3	3.3
Rice	3	5.	10.8	9.5	1.9
Rice	4	0	0	0	0
Rice	5	0	0	0	0
Rice	6	0	0	0	0
Potato	3	5	10.2	17.7	39.3
Potato	4			14.9	36
Potato	5	1.0	2.2	10.5	27
Potato	6	5.5	13.7	10.	26.

TABLE XV

THE SYNERESIS OF STARCH GELS

Variety of Starch	Grams of Starch in 100 c. c.	Volume and Percent of Separated Liquid							
		Tubes Vaseline'd				Tubes Not Vaseline'd			
		15 days		20 days		15 days		20 days	
	c. c.	%	c. c.	%	c. c.	%	c. c.	%	
Corn	3	0.2	1.3	2.9	15.2	1.0	6.0	2.0	10.5
Corn	4	0.4	2.4	3.0	15.4	1.2	6.5	3.0	15.8
Corn	5	0	0	2.4	13.3	0.2	1.2	2.5	13.5
Corn	6	0.3	2.1	2.5	13.5	1.0	4.6	2.7	15.
Wheat	3			0.1	0.5		0	0.2	1.0
Wheat	4	0	0	0.1	0.5	1.6	8.6	0.1	0.5
Wheat	5	0	0	0.1	0.5	1.5	8.2	0.7	4.0
Wheat	6	0	0	0.1	0.5	0	0	0.1	0.5
Rice	3	0	0	0	0	2.2	13.3	1.3	7.9
Rice	4	3.0	12.7	0	0	1.5	8.5	0.6	3.4
Rice	5	0	0	0	0	2.0	10.8	0	0
Rice	6	0	0	0	0	0	0	0	0
Potato	3	2.0	11.5	3.5	18	0	0	4.5	24.
Potato	4	1.2	6.3	1.5	8.0			3.0	13.9
Potato	5	2.0	12.1	2.5	11.3	0	0	1.5	8.6
Potato	6	2.0	13.3	2.0	14.8	3.0	12.1	2.5	15.0

The temperature to which the suspensions must be heated so that gels will be formed varies with the kind of starch. This was shown in the discussion of the gelation temperature. As the temperature necessary in all cases was not far below the boiling point of water, all of the starch suspensions were brought to this temperature.

Neither the rate of heating nor the time of heating appear to effect the rigidity of the gels formed, nor is there any appreciable effect upon the amount of syneresis. This was shown by heating different concentrations of the different varieties of starch to the temperature of boiling water at different rates, and holding them at this temperature for varying lengths of time.

That the surface area of the gel has an influence upon the amount of syneresis is shown by a comparison of Tables XIV and XV. When the larger tubes are used, the amount of syneresis is greater. That this is not due to the larger volume of the whole is shown by the percentage amount of syneresis. This value is obtained by dividing the volume of clear liquid by the whole volume.

The amount of syneresis is also shown to be different for different varieties of starch. A comparison of Tables XIV and XV shows that corn starch exhibits somewhat the

greatest amount of syneresis, then potato, wheat, and rice. Corn and potato starches show very nearly the same values, while wheat and rice starch have much the same values, both being much less than for the first two.

That syneresis is a progressive phenomenon is shown by a comparison of the amounts of liquid expressed by the gels after standing for fifteen days with the amounts expressed after twenty days. In all tubes in which any appreciable amount of syneresis was shown, some liquid was separated at the end of one day. The amount shown increases rapidly for a few days, and then the rate of increase becomes slow. Syneresis has been found to be practically complete, in most cases, at the end of fifteen or twenty days, although there is a slight increase after that time. Tubes allowed to stand one hundred twenty days gave values which in nearly every case were the same as those at the end of a fifty day period.

The addition of dilute acids to the suspensions of starch in water was found to prevent the formation of gels, and to convert the pastes into clear, non viscous liquids. The addition of alkalies in as small amounts as from 0.1 to 0.5 c.c. of 0.15 N to 50 c.c. of the paste was found to greatly reduce the rigidity of the gels formed. When larger

amounts were added, there resulted a very viscous fluid, but gels were not formed.

To study the effect of other added substances upon the syneresis of starch gels, a series of suspensions of corn starch was prepared by the addition of four grams of the starch to 100 c.c. of water, together with the weight of the salt used such as required to make the salt concentration one-half molar. These suspensions were heated to the boiling point over a free flame, transferred to large test tubes, which were stoppered and stored at -2° .

Table XVI shows the effect of the salts upon the syneresis of the gels.

TABLE XVI

THE SYNERESIS OF CORN STARCH GELS IN THE PRESENCE OF SALTS

Kind of Salt:	Volume and percent of separated liquid after 15 days			
	g. c.	%	c. c.	%
NaCl	1.3	3.1	1.0	2.4
NaNO ₃	0	0	0	0
NaI	0	0	0	0
NaC ₂ H ₃ O ₂	15.5	36.9	20.5	37.2
Na ₂ SO ₄	14.5	40.8	17.	41.4
Na ₂ C ₂ O ₄	12.5	29.	14.1	29.4
Na ₂ CO ₃	0	0	0	0
Na ₂ HPO ₄	0	0	1.1	2.4
Na ₃ PO ₄	0	0	0	0
KCl	0.3	0.6	0	0
NH ₄ Cl	0.8	1.8	2.2	4.1
M _g Cl ₂	0.2	0.4	0	0
CaCl ₂	0	0	0	0
SrCl ₂	0	0	0	0
BaCl ₂	0	0	0	0
ZnCl ₂	0	0	0	0
KGnS	0	0	0	0
(NH ₄) ₂ SO ₄	18.5	33.5	16.5	36.6
Ca(NO ₃) ₂	0	0	0	0
Control	8	16.5	8	16.

AlCl₃, FeCl₃, and SnCl₄ prevent the formation of gels.

Table XVI shows that the acetate, sulphate, and oxalate ions have caused a large increase in the amount of syneresis of the gels. That the effect is largely due to the anion is apparent, since sodium and ammonium sulphates produce nearly the same effect. The metals with the valence of three or four prevented the formation of gels. All of the other salts used, appear to either prevent or retard syneresis.

That the results obtained on the formation of starch gels and syneresis can not claim to be quantitative is obvious, since of the difficulty in controlling the factors, which have been pointed out, which influence the results. However, the results may be considered to be qualitative, since the observations made in different determinations point toward the same conclusions.

The experimental work has shown that the amount of syneresis is greater in gels of low concentrations; it is not appreciably affected by the rate or time of heating the starch suspension; it is directly proportional to the surface area of the gel; it is different for different varieties of starch; it is dependent upon the age of the gel; and it is increased or decreased by certain added substance. That there is no direct relationship between the average diameter of the

original starch granules and the amount of syneresis has also been shown.

That there is a relationship between the amount of syneresis and the viscosity of the starch pastes is evident, since the viscosity has been shown to increase greatly with but little increase in concentration. Syneresis has been shown to decrease with the increase in concentration, the decrease being considerable for slight increase in concentration.

III. DISCUSSION

Certain investigators believe that the flow of starch pastes is plastic rather than viscous, as has been shown in the literature review. Whether or not this is true, nearly all of the workers in this field agree that the viscometric measurements are of value since they indicate that certain changes are taking place in the system.

The nature of the changes which take place when starch is heated in water is not fully understood, although many explanations have been attempted. From the observations made during the course of this work, and from the study of other investigations, are derived the explanations attempted here.

The increase in viscosity with the rise in temperature may be considered as due to the imbibition of water by the starch granules, followed by the bursting of the grains and consequent dispersion of the material of which the granules are composed. The dispersed material presents a surface area which is greater than that of the original granules. The newly formed aggregates of starch molecules may be considered as each having a film of water about them. The aggregates then tend to coalesce, and thus may be formed

relatively small particles of gel, in which the surface film of water of each aggregate is included, as well as other enclosed water. These aggregates must be held together tightly, as they are not free to flow. Continuous gels are then formed by the gradual aggregation of these gel particles, until a continuous gel is formed, which is so viscous that there is no flow.

The decrease in viscosity after the maximum value is attained must then be considered to be due to the breaking of the bonds which hold the gel particles together. When the bonds are broken, the gel particles are free to move and enter into new combinations. This permits the enclosed water to escape, or the gel exhibits syneresis. The breaking of the bonds also lowers the viscosity, so the decrease in viscosity and syneresis may be considered to be due to the same cause. When the gel particles recombine, less water will be occluded; the result is that a more concentrated gel is formed, while the excess liquid separates from the gel.

The bonds which hold the starch aggregates together may be broken by mechanical agitation, such as results when the paste is stirred, or by the agitation that results upon repeated determinations of the viscosity.

It has been shown that starch granules which are large

give pastes of greater viscosity than do the smaller granules. The large surface area of the individual granules may permit a more ready imbibition of water, and thus lead to a greater degree of dispersion.

Pastes in which the starch concentration is low lead to the formation of gels in which the aggregates are but loosely bound, and in which a relatively large amounts of liquid are enclosed. The bonds are easily broken, and the aggregates tend to recombine in closer union to form more concentrated gels. This rearrangement results in the separation of considerable amounts of liquid, and explains why gels of low concentration show the greatest amount of syneresis.

IV. CONCLUSIONS

1. The temperature of maximum viscosity of starch pastes varies with the size of the granules.
2. The viscosity of starch pastes increases greatly with comparatively little increase in the concentration of the starch.
3. The amount of syneresis of starch gels becomes less as the concentration of the starch increases.
4. The more viscous a paste of any variety of starch, the less is the syneresis of the gel formed from that paste.
5. The rate of the syneresis of starch gels may be hastened or retarded by the addition of certain reagents.

V. SUMMARY

Microscopic examination has shown that the swelling of starch in water is affected by the size of the granules and the rate of heating. Gelatinization temperatures can not be satisfactorily measured by microscopic methods, nor can the temperature be accurately determined by the firmness of the gels formed from the pastes.

The Ostwald type of viscometer was found best suited for most of the viscometric work. The viscosity is shown to be dependent upon the temperature, rate of heating, time of heating, concentration, and variety of starch or the average diameter of the starch granules.

The decrease in viscosity which occurs after the maximum value is reached is shown to be influenced by the concentration of the starch, the variety of starch, and the rate of heating the suspension.

Acids were found to cause a rapid decrease in the viscosity of starch pastes. The addition of alkalies caused an increase, followed by a decrease. Salts that hydrolyze to give an alkaline reaction have much the same effect upon viscosity as the alkalies.

The syneresis of gels is shown to become less as the concentration of the starch increases, or as the paste from

which the gel is formed becomes more viscous. The amount of syneresis is shown to increase with increased surface and with the age of the gel. Certain salts are shown to either retard or hasten syneresis, the most marked effect being due to the presence of acetates, sulphates, and oxalates.

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