

THE MAGNETIC SUSCEPTIBILITY OF  
STARCH AND STARCH PRODUCTS

by

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## INTRODUCTION

From the earliest studies of its behavior and uses, starch has presented especially puzzling problems which have retarded the attainment of any very complete understanding of the diverse phenomena that it presents. Notwithstanding these difficulties, recent years have finally been marked by great advances in our knowledge of its nature. In 1937 Hanes stated that

...the constitutional studies on starch are proceeding from finer to grosser structures....from the individual glucose unit and its mode of union, to the chain molecule, and finally to the still obscure question of the manner in which these larger units are bound together to form highly colloidal structures. The point has not yet been reached where this line of investigation throws light on the chemical organization of the native starch granule.

This statement is essentially true today although it cannot be denied that research on starch has, in the past, increased at a rapid pace with the result that many important and interesting facts have been learned. Because the various proposed structures of the starch molecule and granule are, at best, highly controversial, the ultimate elucidation of the constitution of starch will depend to a large extent upon man's ability to recognize, interpret, and coordinate the important contributions.

Starch always has been recognized as one of the most abundant and important staples of nature. It has in the past seen considerable application to various industries, such as those producing food, paper, and textiles. Outside of the food applications, however, most of these industries employ only certain of the physical properties of starch which make it suitable for sizing, filling, binding, or other operations that might in

general be termed colloidal applications. Many of these uses owe their existence to the complexity of starch, and yet this very complexity limits its utilization.

Only mild chemical alterations of the starch molecule have been ordinarily achieved; however, the future looks to the employment of more drastic chemical modifications which apparently will be designed to alter the chemical structure of the repeating units without allowing degradation of the starch polymers. The high polymeric nature of the resulting compounds would suggest the preparation of plastics and other important products. At present, the studies of chlorination reactions of starch by Barham and Thomson (5) seem to be the most promising key to the starch granule. Certain phases of this chlorination and other seemingly anomalous results, obtained by this and other laboratories, seem to indicate a certain incidence of free radicals present in the starch granule and especially in the modified granule. Magnetic susceptibility was chosen as the tool for the evaluation of this hypothesis, for if a starch were paramagnetic it would be unambiguous evidence that free radicals exist in the starch granule.

## REVIEW OF LITERATURE

### Evidence of Free Radicals in Starch and Starch Products

The alkali lability of a starch often is taken as an indication of its source, past treatment, and of its desirability for various uses, although the significance of the alkali lability is not clearly understood. In general, it is believed

that the focal points for reaction with alkali are reducing groups which exist in raw starch or which are produced as a result of some form of chemical or physical alteration. At first it was believed that the aldehydic end groups of the starch molecules were the focal points for attack by alkali. However after considering that the molecular weight of starch is on the order of 300,000 and that there is only one aldehydic end group per molecule, it was obvious that the aldehydic end groups per se could not account for the large consumption of alkali.

In response to this, Taylor (16) suggested that the alkaline decomposition of starch proceeds from an initial attack of the terminal aldehyde group, which is followed by a progressive destruction of the glucose residues. On the other hand, Taylor and Keresztesy (17) found that the alkali lability was increased if the starch was ball-milled. They contended that, in addition to producing more aldehydic end groups by disrupting chains at the glucosidic linkages, ball-milling made existing end groups more available. The latter would be accomplished by breaking certain hydrogen bonds that shielded aldehyde groups which otherwise would be chemically free. However, if this hypothesis were correct, it would be logical to assume that the more available water is to a given starch the higher is its alkali lability. Barham and Wagoner (7), while studying the effects of cure on sweet potato starches, found the opposite to be true. They observed that if a starch was solvent extracted a reduced rate of availability of water for

swelling was accompanied by increased alkali lability. Their results indicated that some kind of structural change was caused by solvent extraction. It would seem that obstruction to the free flow of alkali through the starch micelles upsets the existing configuration to the extent that an alkali consuming component is created in starch. The nature of this component is indefinite but it is becoming increasingly evident that it could be in the form of a free radical.

Levene (11), in seeking to account for the activity of glucose, also made use of a free radical theory. In order to explain the results obtained by various workers in the fields of biology and chemistry, he assumed the existence of an "active glucose." To this he attributed a free radical structure obtained from the severing of the oxygen bridge of the lactal forms of glucose, as shown in Fig. 1. Levene stated that in a

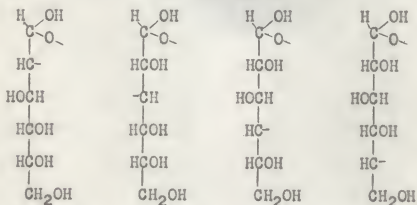


Fig. 1. Lactal forms of glucose showing free radical character.

given process, the reaction was dependent on the maintenance of the proper conditions conducive to the existence of one of the forms shown in Fig. 1. In the case of starch, it seems



that sufficient strain set up within the granule could weaken or even break these lactone bonds.

In support of the idea that strain exists in the highly complex starch granule, Campbell (8) used palmitic acid, progressively adsorbed in and desorbed from a starch of known history, as a means of controlling the factors which influence granule behavior. She found that changes in density and specific surface accompanying the adsorption-desorption process formed closed cycles, and that the adsorption-desorption isotherms and changes in the rate of hydration, alkali number, low temperature maximum viscosity, and gel strength indicated a close approach to reversibility. Pronounced increases in specific surface during the cycle suggested the development of strain within the granule.

Nef, in an attempt to explain the reducing power of carbohydrates, suggested that the equilibrium shown in Fig. 2

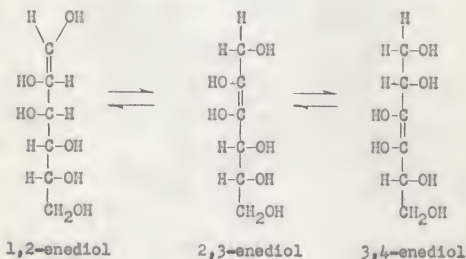


Fig. 2. Enediol equilibrium of glucose in alkaline solution.

existed in alkaline solution. Nef assumed that in the presence of alkali, hexoses form 1,2-, 2,3-, and 3,4-enediols, and that besides giving a mixture of six sugars, these enediols split at the double linkage into a mixture of various carbohydrate-like compounds containing 1, 2, 3, 4, and 5 carbon atoms, the rupture at the double bond yielding radicals which contain divalent carbon. For example, the 1,2-enediol would produce the components shown in Fig. 3. The great reactivity

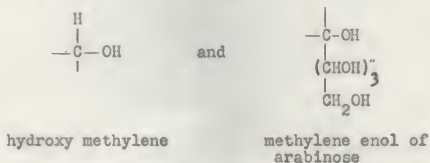


Fig. 3. Products of 1,2-enediol splitting.

of the divalent carbon would enable it to absorb oxygen quite readily, yielding formic acid from the hydroxy methylene and d-arabonic acid together with d-ribonic acid from the methylene enol of arabinose. If this enediolic formation is used in explaining the alkali lability of starch it falls far short of accounting for the amount of alkali consumed, unless it is accompanied by glucosidic scission, occurring at the same rate. However, this glucosidic scission was shown to be very unlikely by the work of Evans and Benoy (9). In their experiments with the alkaline oxidation of maltose they found that of the two kinds of decomposition open to the maltose molecule, enediolic splitting is rapid while hydrolysis is very slow.



In the chlorination of starch by liquid chlorine, Barham and Thomson (6) observed a black induction product which possessed properties characteristic of free radicals. They suggested that this could be a condition in which the incidence of active glucose residues is very high, resulting from the effect of hydrogen chloride on the lactal interconversion.

Thomson (18) postulated a mechanism for the direct chlorination of starch involving the presence of free radicals. The dichloride was reported as having colors which ranged from orange-red to blue, but which faded soon after it had been removed from the autoclave. A tetrachloride product gave a reversible color change between yellow and blue, depending on whether water or benzene was added to the product. All of these suggest free radicals although it is not positive evidence of their existence.

As further evidence that free radicals exist in starch and starch products, Barham, Stickley, and Thomson (4) successfully carried out the addition of chlorine to benzene without the presence of light. This was accomplished by catalyzing the reaction with starch and its chlorine derivatives. The fact that the black induction product catalyzed the addition reaction more effectively than starch itself, agrees with the belief expressed above that a higher incidence of free radicals may exist in the induction product which could possibly account for its high absorption of light.

To further explore the possibility of the existence of

free radicals in starch, Rosenberg (13) found that certain starches and starch products had the ability to induce polymerization of acrylonitrile and styrene and also to decompose acrylonitrile. He found that upon treatment of starch with such procedures as vacuum-drying, solvent extraction, and ball-milling, a qualitative correlation was obtainable between trends in the aforementioned activities of starch and its alkali lability. According to his interpretation, these treatments affect the same component of starch which appeared to be related to the degree of strain existing in the granule. He also found that certain products of starch, namely, hydrogen chloride-treated starch, the induction product of a liquid phase chlorination reaction, and chlorinated starch, possessed the same ability to induce polymerization of acrylonitrile and styrene, as well as decomposition of acrylonitrile. In addition, he noted a reaction occurred between starch dichloride and styrene. Since only a few other substances of free radical character, such as benzoyl peroxide, are capable of polymerizing and decomposing acrylonitrile, the behavior of starch and starch products in this respect constitutes circumstantial evidence in favor of free radicals existing in starch.

#### Magnetic Susceptibility

If a substance is placed in a magnetic field whose intensity may be represented by a certain number of lines per square centimeter, the number of lines within the substance may be either less or greater than the number in the surrounding space. In the first case the substance moves in the direction of

decreasing field strength and Faraday termed it diamagnetic. In the second case, the opposite is true; the substance moves in the direction of increasing field strength. Faraday termed any substance which so behaves paramagnetic.

Ferromagnetism, as exhibited by substances such as iron and the lodestone, plays no role in organic chemistry and requires consideration only insofar as contamination with even slight traces of ferromagnetic impurities may cause appreciable error in the magnetic measurements of solid organic materials (19). Nevertheless ferromagnetism is of great technological importance even though it occurs in only a few elements, alloys, and compounds. Paramagnetism is fairly common in nature, while diamagnetism is a universal property of matter.

That magnitude which is directly accessible to measurement and correlated with the force of displacement of a substance in an inhomogeneous magnetic field is the magnetic susceptibility. If the magnetic susceptibility of a substance is positive, the substance is essentially paramagnetic. Conversely, if the magnetic susceptibility of a substance is negative, the substance is not paramagnetic and only the diamagnetic property is evident. From the susceptibility there is derived, by theoretical reasoning, the magnetic dipole moment. A paramagnetic substance has a permanent magnetic dipole moment. A diamagnetic substance has no magnetic dipole moment in the absence of a magnetic field, but acquires an induced magnetic moment when exposed to the field. The induced magnetic moment for any molecular species is always negative, and relatively weak. A

permanent magnetic dipole moment, if it exists at all, is always positive and comparatively strong. In this respect there is no analogy for the general behavior of magnetic and electric dipole moments.

The molecular susceptibility,  $\chi_M$ , then, has the significance of being the magnetic moment in the direction of the field produced in one gram-molecule of the substance by a field of one gauss (15). The volume susceptibility, designated by  $k$ , is the magnetic moment produced in one cubic centimeter of the substance. And, finally, the specific susceptibility,  $\chi$ , is the magnetic moment produced in one gram of the substance. The molecular susceptibility is probably the most useful of the three and is obtained by multiplying the specific susceptibility by the molecular weight of the substance. The specific susceptibility is determined by dividing the volume susceptibility by the density of the substance. And, in turn, the volume susceptibility can be determined by comparing the behavior of the substance in a magnetic field with the behavior of a compound of known susceptibility. Since nearly all magnetic measurements are made today on this relative basis, there is no need to calculate the absolute magnetic susceptibility of a substance. Originally, however, this was accomplished by measuring the magnetization,  $I$ , of a substance in a magnetic field of strength  $H$  gauss. The ratio, then,  $I/H$  is the volume susceptibility of the medium (1).

Diamagnetism arises through the interaction of the magnetic field with the completed electron groups of the atoms

of the medium, whereby the orbital motion of the electrons is caused to precess around the direction of the lines of force so as to give rise to a field opposed to the applied field. Thus all organic molecules with an even number of electrons, all of which are paired, or the "valence-saturated compounds," are diamagnetic. At first approximation, the diamagnetic susceptibility of a molecule is additively composed of the susceptibilities of its atoms. As a result of extensive systematic measurements of the magnetic susceptibilities of organic compounds, Pascal found that the molecular susceptibility was an additive function, and that in general  $\chi_M = \sum \chi_A + \lambda$ , where  $\sum \chi_A$  represents the sum of the atomic susceptibilities of all the atoms in the molecule, and  $\lambda$  is a constitutive correction constant which depends on the nature of the chemical linkages involved. The effect of double bonds, or ring formation, or of strongly polar groups, all of which are recognized as modifying the distribution of electrical charge density, is generally to lower the diamagnetism of the whole molecule (1).

Of the attempts which have been made to extend Pascal's method and put his constitutive factors on a theoretical instead of empirical basis, the most interesting is that of Gray and Cruikshank who express their susceptibilities in terms of atomic and ionic susceptibilities, calculated by a modification of Pauling's method, together with bonding depressions, i.e., decreases produced by various forms of linkage. From the electrical dipole moment of the linkages, they deduce for each atom a "residual charge", given by the ratio of bond



moment to internuclear distance, which represents the fraction of time the atom can be regarded as being in a charged ionic state. By multiplying the time factors, a mean atomic susceptibility of the atom is obtained, and these values, summed for the molecule, give a theoretical value for  $\chi_M$ . The difference between the calculated and observed values is taken as the depression caused by the formation of linkages (15).

Farquharson (10) found that the molecular susceptibility of a polymeride containing  $n$  simple repeating units is  $n$  times the susceptibility of the simple residue plus  $(n-1)$  times the Pascal constitutive correction factor. But, on the other hand, he found that when polymerization involved ring closure, a value very considerably less than the additive value was found.

In spite of the ingenuity used by these men in an attempt to correlate accurately diamagnetism with molecular structure, it is unfortunate that calculations of molecular susceptibility cannot be made with accuracy and for this reason there seems to be no point in using methods developed to calculate molecular susceptibility from atomic values. These methods have seldom yielded results which cannot better be obtained by other means such as the use of molecular refractivities, based on the refractive index, to solve problems of molecular structure (14).

Paramagnetism is attributable to the magnetic moment which each electron within the atom possesses through its orbital motion and spin. These moments cancel out for all completed subgroups of electrons in the atom, that is, when it has in the



same electronic shell two s, six p, 10 d, or 14 f electrons, where the letters s, p, d, and f indicate the second or series quantum numbers of 0, 1, 2, and 3 respectively. Therefore paramagnetism occurs mainly in compounds containing odd number of electrons or containing atoms with incomplete subgroups. Under the influence of a magnetic field, these elementary magnets resulting from odd electrons will tend to orient themselves along the lines of force, in opposition to the effect of thermal agitation which seeks to maintain a random distribution.

The paramagnetic contribution to the susceptibility of a free radical also is due to the spin of the unpaired electron. Paired electrons have no magnetic effect because they have opposite spins. It has been shown that the orbital motion of the electrons has no paramagnetic effect in molecules of the type usually dealt with in organic chemistry. According to quantum mechanics the paramagnetic effect of  $n$  unpaired electrons in a molecule can be stated by saying that the magnetic dipole moment,  $u$ , for one mole, expressed in Bohr magnetons, amounts to

$$u = \sqrt{n(n+2)}.$$

For a radical with a single unpaired electron this is, in Bohr magnetons,

$$u = \sqrt{3} = 1.73.$$

Thus the Bohr magneton may be interpreted as the magnetic moment produced by the orbital motion of a p electron, or the

moment produced by the spin of one unpaired electron. This magnetic moment is precisely analogous to an electrical dipole in an electrostatic field, the resulting effect being a function of temperature, and calculation shows that

$$u = 2.84 \sqrt{x_M T}$$

where  $u$  is the magnetic moment for one mole,  $x_M$  is the molecular susceptibility, and  $T$  is the absolute temperature. An empirical expression of this form,  $x = C/T$ , was advanced by Curie, where  $x$  is the specific susceptibility, and  $C$  is the Curie constant (1). This expression, however, is strictly followed by few substances. A relation of wider validity, the Curie-Weiss law, is  $X = C/T - \Delta$ , in which the term  $\Delta$  probably represents a correction for the intrinsic molecular field--i.e., the mutual interaction of the molecular magnets. Hence, it is evident that paramagnetism due to odd electrons is dependent upon the temperature of the substance whereas diamagnetism is independent of temperature. Van Vleck has shown theoretically that in the case of certain molecules a small contribution,  $x_R$ , due to resonance between the ground state and the higher energy states of the molecule must also be included with the diamagnetism and paramagnetism. Therefore for the general case  $x_M$  will be the sum of three factors, the induced diamagnetic contribution  $x_D$ , which is negative, the paramagnetic contribution  $x_P$ , due to permanent magnetic dipoles, which is positive, and the resonance contribution  $x_R$ , which is again positive, i.e.,  $x_M = x_D + x_P + x_R$ . For the simplest molecules with an even number of extra-nuclear electrons,  $x_P = 0$ ,

and  $x_R$  is less than  $x_D$ ; such substances are therefore diamagnetic. In rare cases only  $x_R$  is greater than  $x_D$  and slight paramagnetism is observed which is invariant with temperature.

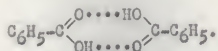
Certain particles respond to a magnetic field by an orientation with respect to its axes. This orientation takes place whenever the magnetic properties of the particle are different along different axes, either when the particle is intrinsically magnetically anisotropic, as in many crystals, or when the particle, although intrinsically isotropic, is not a sphere. This latter effect, due to asymmetry in external shape alone, is usually negligibly small. The axis of greatest paramagnetism, or of smallest diamagnetism, orients itself along the direction of field lines (19). Thus a knowledge of the resultant dipole moment of a molecular species or particle can be utilized with respect to the elucidation of the structure of the particle as well as the electronic configuration of the atoms. Paramagnetism occurs only in the following two classes of molecular species: those containing atoms of the transitional group of the periodic system; and those containing an uneven number of electrons, the "odd molecules" or free radicals (19). In organic chemistry, the main concern with magnetism lies in the study of the free radicals. Provided no heavy metal atom of the transitional group is present, paramagnetism is an unambiguous criterion for free radicals, the biradicals being included in this group, and can be utilized for their identification and even for their quantitative determination in mixtures with other molecules which are not free radicals (19).

Another achievement of the magnetic method has to do with the color of the free radicals. Free radical solutions are generally colored and it has been long believed that the intensity of the color is a measure of the degree of dissociation. But magnetic measurements have shown that the free radical may be completely destroyed by heating, yet the color of the solution remains approximately the same. Evidently the color of the solution is not only an uncertain measure of the degree of dissociation, but it may not be related in any way to the presence or absence of free radicals (14).

Extensive investigation has been conducted within the last few years in order to determine the effect of various chemical and physical changes upon the susceptibility of the molecule or particle. For example, Angus and Hill (3) found that the diamagnetic susceptibility of an isomeride with a branched hydrocarbon chain is greater than that of the corresponding straight chain compound; the sequence appears to be that tertiary is slightly greater than secondary, secondary greater than iso-, and iso- greater than normal. Also the magnetic susceptibilities of compounds containing 3, 4, 5, and 6 membered carbon rings and the related open chain compounds have been measured (10). Constitutive correcting constants calculated for the rings differ from those of Pascal. The effect of ring closure is to cause a fall in diamagnetism in each case except in the five membered ring where there is a rise. The necessity for correcting constants is interpreted as being due to changes in the value of the susceptibility of the carbon atom when it

is a member of different sized rings.

The fact that ring closure causes a fall in diamagnetism is also verified by Angus and Hill (2) who polymerized benzoic acid in benzene:



They found that the diamagnetic susceptibility of benzoic acid decreases (becomes more positive) upon polymerization. However if ethyl acetate is used as the solvent instead of benzene, the diamagnetic susceptibility increases since ring closure is reduced and addition compounds increase.

It has been known for some time that hydrogen bonding has a definite effect upon the magnetic susceptibility of a substance. Angus and Hill (2) found that the diamagnetic susceptibility of a substance decreases when the concentration of the substance is increased. This evidently is due to ring closure (inter or intra molecular hydrogen bonding) which results in a decrease of diamagnetism. On the other hand "open" addition compounds (intermolecular) results in increased diamagnetism as concentration increases. They also found that the diamagnetic susceptibility of ice is less than the diamagnetic susceptibility of water and the diamagnetic susceptibility of water increases as the temperature increases, due to breakdown of hydrogen bonding.

Perhaps one of the most interesting contributions to the elucidation of molecular structure by magnetic susceptibility is that by Mayr (12). Certain paramagnetic salt-hydrates were



crystallized inside a magnetic field and the magnetic susceptibility of the polycrystalline mass was compared with that of the same substance crystallized outside the magnetic field. It was found that for the less paramagnetic salt the difference of the magnetic susceptibility inside and outside the magnetic field is within the experimental error; for the other salts, the difference is between two and four percent. Mayr believes that the magnetic field causes some orientation in the polycrystalline mass, whose crystalline elements put themselves with the axis of greatest magnetic susceptibility in the same direction of the field, although the idea of a formation of some crystalline element with a different magnetic susceptibility cannot be rejected.

## METHODS

### Apparatus

Out of the great number of methods that have been used for the measurement of magnetic susceptibility, the method of Gouy was selected. This method seemed to be the most convenient for the purpose since it was relatively simple and temperature control, if required, could be more easily applied than other methods. The equipment consisted of an electromagnet, a balance, a suspension and cylindrical vessel, a generator of direct current, an adjustable resistance, and an ammeter. Plate I is a schematic presentation of the equipment.

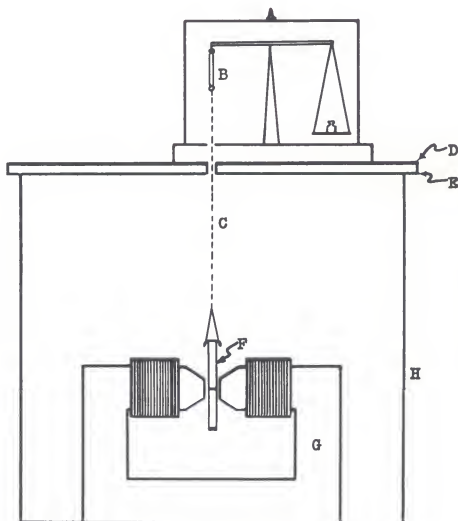
Electromagnet and Vessel. The electromagnet used in this



#### EXPLANATION OF PLATE I

- A - Magnetically damped chainomatic balance
- B - Counter weight
- C - Silver suspension chain
- D - Iron plate;  $1/8$  inch
- E - Galvanized sheet iron; 23 gauge
- F - Double cylindrical vessel
- G - Electromagnet
- H - Box to protect system from air currents

PLATE I



investigation was specially constructed for the purpose. If used intermittently, it was able to use 10 amperes of current without overheating although only 3.5 amperes were used for most of the measurements. At 10 amperes the magnet was capable of developing a field strength of approximately 10,000 gauss. The pole pieces tapered to a diameter of 3.18 cm at the faces, which were about 1.2 cm apart. This distance allowed freedom of unobstructive movement for the vessel which was approximately two mm distant from each pole piece.

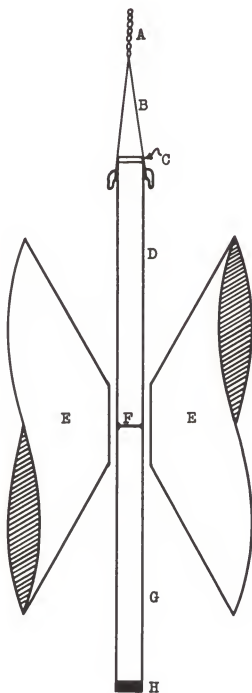
Instead of a single cylindrical vessel, a double vessel was used; it consisted of a cylinder of uniform cross section, double the length of the single one, with a glass septum dividing it into two compartments as shown in Plate II. The reason for using a double vessel instead of a single one is obvious. When the substances in the two compartments are of nearly the same susceptibility, the pull of the magnetic field is in opposite directions and component forces are nearly cancelled. The difference in susceptibility was obtained as a difference of two magnitudes one of which was almost zero, whereby the limits of error were diminished considerably.

The vessel was made from 8 mm (inside diameter) pyrex glass tubing. The upper compartment was 10.5 cm in length and had a volume of 5.0139 ml. The lower compartment was 12 cm in length. The top of the vessel was ground flat and fitted with a glass disk of the same diameter of the tube. The lower end of the tube was sealed shut with a thin rubber stopper.

#### EXPLANATION OF PLATE II

- A - Lower end of silver suspension chain
- B - Nylon stirrup
- C - Glass disk
- D - Upper compartment of double vessel in which sample  
is packed
- E - Poles of electromagnet
- F - Glass septum
- G - Lower compartment of double vessel which contains air
- H - Thin rubber stopper

## PLATE II



Balance and Suspension. The balance was of the chainomatic type, and magnetically damped. The scale was removed and another having 150 divisions was put in its place. This scale was made by drawing a large scale of sufficient size on white cardboard, photographing, and then printing to the correct size. A scale magnifier was used to facilitate reading and to minimize error due to parallax. The left pan of the balance was removed and a counter weight hung in its place. A light silver chain was attached to the lower end of this counter weight and hung down through a hole in the floor of the balance. At the lower end of the suspension was a nylon stirrup to which the cylindrical vessel could be conveniently attached and detached. The entire length of the suspension was approximately 20 inches.

Generator and Resistance. The direct current generator was capable of producing a constant voltage of 150 volts. The voltage was found to fluctuate slightly, but this fluctuation was minimized by putting a heating element ( $R_2$  of Plate III) in the circuit. In order to attain a pull on the cylindrical vessel within the range of the scale on the balance, the amperage was first adjusted roughly with the generator rheostat and then finely with the slide rheostats. The ammeter used was a Weston D.C. ammeter calibrated from zero to 15 amperes, accurate to one-half of one percent.

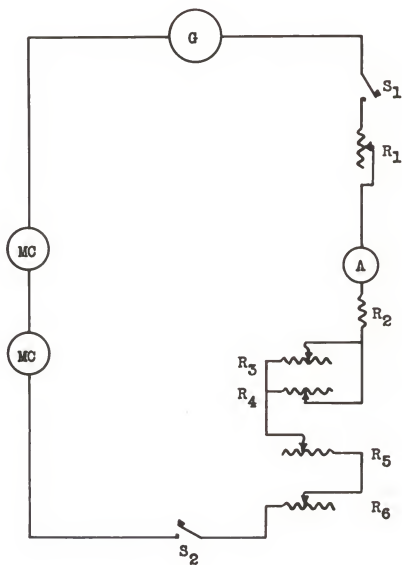
Assembly and Operation. The vessel was hung from the suspension so that the glass septum was approximately in the center of the homogeneous part of the magnetic field. In



### EXPLANATION OF PLATE III

- G - Direct current generator
- MC - Coil of electromagnet; 1.5 ohms
- A - Ammeter
- S<sub>1</sub> - Main generator switch
- S<sub>2</sub> - Switch on apparatus
- R<sub>1</sub> - Main generator rheostat
- R<sub>2</sub> - Heating element; 660 watts, 110 volts
- R<sub>3</sub> - Slide rheostat; 7.1 ohms, 5 amperes
- R<sub>4</sub> - Slide rheostat; 46 ohms, 3.1 amperes
- R<sub>5</sub> - Slide rheostat; 2.5 ohms, 13 amperes
- R<sub>6</sub> - Slide rheostat; 2.5 ohms, 13 amperes

PLATE III



order to carefully protect the whole system from air currents, the suspension and magnet were surrounded by a box which had the front wall removable for opening and closing. The space from around the top of the box to the lower surface of the balance case was surrounded by a mantle of thin wood. A heavy iron plate and a sheet of galvanized iron were placed under the balance in order to shield the balance from the magnetic field of the magnet.

The pull upon the vessel was measured in terms of change in weight. This pull was independent of the length of the cylinder because the cylinder reached from the region of the homogeneous field to the region of vanishingly small field strength. Instead of compensating the magnetic pull by weights, however, the pull was measured by determining the maximum deflection on the microscopic scale. In order to attain a pull within the desired range, the amperage was adjusted adequately for each measurement.

The unknown substance to be measured was packed into the upper compartment of the vessel by adding the substance slowly and tapping the lower end of the tube lightly on a solid surface. When as much as possible of the substance had been added, the tube was leveled off and the glass disk put in place on top of the tube. The tube was then wiped clean with a cloth and suspended between the poles of the magnet.

Calibration. The deflection of the balance by the pull of the magnet upon the vessel was always recalculated for one standard amperage, in this case 10 amperes. This required a

knowledge of the relationship of amperage to magnetic pull for the actual conditions of the apparatus. This relationship was obtained by measuring the pull upon the vessel at different amperages and then plotting. Figure 4 shows that the magnetic pull was directly proportional to the square of the amperage or field strength.

The method used for measuring magnetic susceptibility was relative, comparing the effect of the magnetic field upon an unknown substance with the effect of the same magnetic field upon a reference substance of known susceptibility. Since the susceptibility of the substance was measured in the cylindrical glass vessel, the magnetic properties of the vessel also had to be considered. This was circumvented by measuring successively in the same glass container two different substances of known susceptibilities, in this case air and water. Air is slightly paramagnetic, due to oxygen; pure water is diamagnetic. The difference is  $0.749 \times 10^{-6}$  c.g.s.u. Thus, when the difference between the magnetic pulls on water and on air was found to be  $n$  scale divisions, each scale division corresponded to an increment of susceptibility amounting to  $0.749 \times 10^{-6}$  per  $n$  divisions c.g.s.u. of volume susceptibility for the conditions of the apparatus. The actual calibration of the apparatus and a sample calculation of magnetic susceptibility appears in the appendix. The accuracy of the apparatus was determined by measuring the susceptibilities of potassium ferricyanide and benzene. In each case, the measured susceptibility was within a margin of error of one-half of one percent.

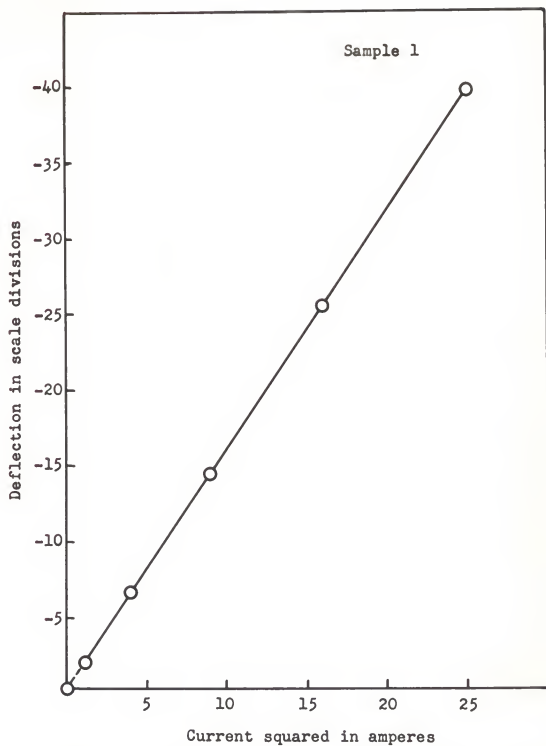


Fig. 4. Relationship of strength of magnetic field to current through magnet.

### Preparation of Samples

Fourteen different samples of starch, starch products, and glucose were treated as described below. Each sample was packed into the upper compartment of the double vessel by adding the sample slowly while tapping the lower end of the vessel on a solid surface. Individual samples always were packed under the same conditions which prevailed during their preparation; for example, if the sample was prepared in dry nitrogen, it was also packed in dry nitrogen.

The susceptibility of each sample was measured five times. Samples 1 to 10, inclusive, were measured by packing a different portion of the sample each time. Samples 11 to 14, inclusive, were measured by packing the same portion of the sample each time.

Sample 1. This was a commercial corn starch (laboratory code no. 7). It was measured in its original form.

Sample 2. Sample 1 was solvent extracted by refluxing it in 85 percent methanol (by volume) for five two-hour periods. The methanol was removed by washing with distilled water and the starch was thoroughly dried in air and pulverized.

Sample 3. Sample 2 was further dried by placing the sample in a desiccator over  $P_2O_5$ , while alternately evacuating and filling the desiccator with dry air three times a day for one week.

Sample 4. Sample 3 was treated by ball-milling it for two weeks without interruption except for daily evacuation of the ball-mill jar and filling with dry air.

Sample 5. Sample 2 was put over  $P_2O_5$  in a desiccator filled



with dry nitrogen. The desiccator was then alternately evacuated and filled with dry nitrogen three times a day for one week. After drying, the sample was transferred in an atmosphere of dry nitrogen to a ball-mill jar. The sample was then ball-milled for two weeks without interruption.

Sample 6. This was a sample of Cody starch made in the laboratory from Cody milo. It was solvent extracted the same as Sample 2 and dried the same as Sample 3.

Sample 7. This sample was a Blackhull kafir starch (laboratory code no. C-8) which was milled and purified in this laboratory. It was also solvent extracted the same as Sample 2 and dried the same as Sample 3.

Sample 8. This was a commercial Belgain rice starch. It was also solvent extracted and dried over  $P_2O_5$  as described above.

Sample 9. This sample was a Pink kafir starch which was milled and purified in this laboratory, solvent extracted, and dried over  $P_2O_5$ .

Sample 10. This was pure crystalline glucose. It was measured in its original form.

Sample 11. This sample was a starch chloride, prepared according to the method of Barham and Thomson (5) and pyrolyzed for 48 hours at  $70^{\circ}C$  and 15 mm pressure. Analysis showed its structure approached the dichloride of starch (laboratory code no. CA-8).

Sample 12. Sample 11 was rolled for one hour inside a tube between specially constructed poles of a powerful electromagnet. After rolling, the starch chloride was carefully packed into

the upper compartment of the vessel in presence of the same magnetic field.

Sample 13. This sample was prepared by Campbell (8). It was a solvent extracted Blackhull kafir starch (laboratory code no. CC-10) which subsequently had been permitted to adsorb palmitic acid from a 0.3 percent solution of palmitic acid in 85 percent methanol. The sample contained 0.42 percent fat by hydrolysis, of which 0.11 percent was palmitic acid.

Sample 14. This sample was prepared by the same method used on Sample 11 to obtain Sample 12.

#### RESULTS AND DISCUSSION

The measured magnetic susceptibilities of the samples are given in Table 1, arranged in order of decreasing diamagnetic values. The value obtained after each packing for Samples 1 to 10, inclusive, do not deviate from the average values by more than two percent, which is the highest accuracy that can be expected in the measurement of the susceptibility of solids. The significance of the diamagnetic susceptibilities of Samples 1 to 10, inclusive, will be discussed later.

As the magnetic susceptibilities of Samples 11 and 13 were measured, a general decrease in diamagnetism was noted, as indicated in Fig. 5. This lowering of diamagnetism caused no noticeable change in the physical appearance of the samples, and was apparently due to the effect of the magnetic field upon the samples. The most logical explanation for such a lowering of diamagnetism seemed to be the orientation of the

Table 1. Magnetic susceptibility of samples.

Sample:	Description	Portion of : : sample : measured : each time	Magnetic susceptibility in c.g.s. units $\times 10^6$					
			I	II	III	IV	V : average	
10	Glucose--- original form	different	-0.558	-0.554	-0.547	-0.555	-0.561	-0.555
3	Corn starch--- solvent extracted, dried over $P_2O_5$	different	-0.541	-0.527	-0.534	-0.532	-0.541	-0.535
4	Corn starch--- solvent extracted, dried over $P_2O_5$ , ball-milled in air	different	-0.523	-0.536	-0.531	-0.539	-0.530	-0.532
2	Corn starch--- solvent extracted	different	-0.530	-0.529	-0.537	-0.524	-0.534	-0.531
8	Belgain rice starch--- solvent extracted, dried over $P_2O_5$	different	-0.526	-0.535	-0.530	-0.536	-0.528	-0.531
1	Corn starch--- original form	different	-0.513	-0.521	-0.519	-0.524	-0.521	-0.520
5	Corn starch--- solvent extracted, dried over $P_2O_5$ in nitrogen, ball <sup>2</sup> milled in nitrogen	different	-0.517	-0.519	-0.510	-0.504	-0.520	-0.512

Table 1 (cont.)

Sample:	Description	Portion of : : sample : measured : : each time :	Magnetic susceptibility in c.g.s. units $\times 10^5$					
			I	II	III	IV	V : average	
9	Pink kafir starch-- solvent extracted, dried over $P_2O_5$	different	-0.492	-0.500	-0.506	-0.507	-0.510	-0.503
7	Blackhull starch-- solvent extracted, dried over $P_2O_5$	different	-0.440	-0.452	-0.441	-0.448	-0.449	-0.446
6	Cody starch-- solvent extracted, dried over $P_2O_5$	different	-0.435	-0.431	-0.432	-0.435	-0.429	-0.432
11	Starch chloride-- original form	same	-0.379	-0.274	-0.235	-0.169	-0.112	-
12	Starch chloride-- rolled and packed in magnetic field	same	-0.213	+0.111	+1.138	+6.873	+9.005	-
13	Blackhull starch-- solvent extracted, adsorbed in 3% palmitic acid	same	-0.334	-0.290	-0.276	-0.264	-0.198	-
14	Blackhull starch-- solvent extracted, adsorbed in 3% palmitic acid, rolled and packed in magnetic field	same	+0.078	+0.570	+0.258	+0.920	+6.526	-

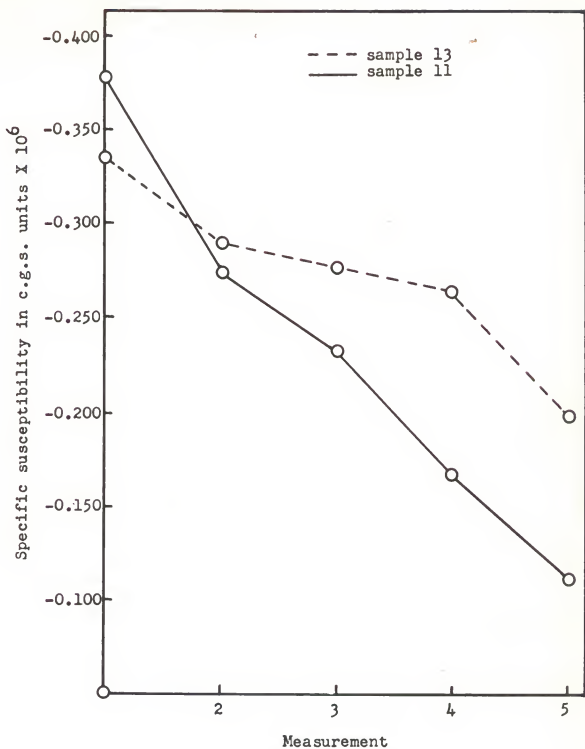


Fig. 5. The decrease in diamagnetism during successive measurements of the same portion of sample.

individual granules during packing in the tube. However, this would be possible only if, at the time the tube was packed, there were enough residual magnetism remaining in the granules after previous exposure to the magnetic field of the Gouy apparatus.

Working on the assumption that the individual starch granules would orient in a magnetic field, Samples 11 and 12 were rolled and packed between the poles of a separate electromagnet. In both cases the samples became highly paramagnetic. The fact alone that both samples did exhibit paramagnetism is positive evidence of free radical existence within the granule, since only an electron with unpaired spin could account for this magnitude of paramagnetism. By using the formulas given on pages 13 and 14, the highest paramagnetic value for Sample 12, namely,  $+9.005 \times 10^{-6}$  c.g.s.u., was calculated to be representative of approximately 1.43 odd electrons per glucose unit. Likewise, the highest paramagnetic value for Sample 14,  $+6.536 \times 10^{-6}$  c.g.s.u., represents approximately 0.88 of an odd electron per glucose unit. Although these values represent the highest paramagnetic values obtained in five packings, they are not necessarily the limiting paramagnetic values. The maximum or limiting paramagnetic value will be obtained only when some method is devised to orient every starch granule with the magnetic field.

In an attempt to determine the nature of the free radicals present in Samples 12 and 14, the fifth, or most paramagnetic, packing of Sample 14 was rotated in the magnetic field of the



apparatus and its susceptibility measured every 22.5 degrees, zero degrees being taken as the position of the tube maintained during packing in the magnetic field. The specific paramagnetic susceptibilities were then plotted against rotation of the tube as shown in Fig. 6. Since the paramagnetic values at zero and 180 degrees are of approximately the same magnitude, it suggests that the free radicals within the granule have only two degrees of freedom.

Figure 6 also suggests that there are more than 0.88 of an odd electron per glucose unit in Sample 12 and 1.43 odd electrons per glucose unit in Sample 14. These values probably represent the over-all vector sum of all the odd electrons within the granule. It is highly probable that this is an axis of greatest paramagnetism through the granule. At approximately 112.5 degrees to this axis is the axis of least paramagnetism.

The actual significance of the magnitude of the diamagnetic values given for Samples 1 to 10, inclusive, is somewhat obscure. The granules of each sample were always arranged at random since each portion of the sample measured had not been previously exposed to a magnetic field. Thus, the magnitude of the diamagnetic values may depend upon the tendency of the free radicals, if present, to orient with the magnetic field. However, if the free radicals within the granules were so hindered that they could not orient, each free radical would cancel out the next and the magnitude of the diamagnetic value of the starch would be independent of any free radical character and would depend only upon the atomic, bond, and resonance contributions within



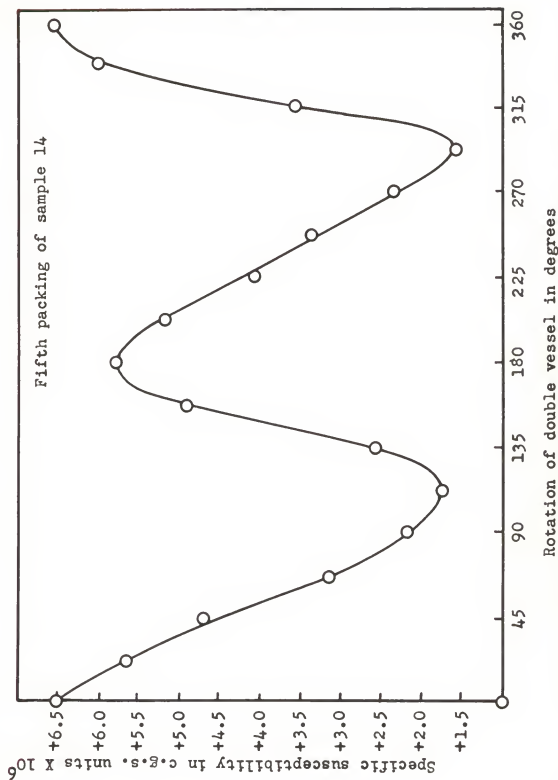


Fig. 6. Change of paramagnetism with rotation of double vessel in magnetic field.

the granule. Nevertheless, the results presented in Table 1, in addition to those found in the literature, suggests that various treatments of starch modify its structure in such a manner as to affect certain of its activities. One of these activities, its alkali consumption, has been at least partially attributed to a free radical structure existing in starch. In this investigation, no general relationship was found between magnetic susceptibility and alkali number. This fact is not surprising, however, since the nature and behavior of the base consuming points and their possible dependence upon strains set up in the gross structure of the granule are not well understood. It is possible that these base consuming points may be produced during adsorption of the alkali and, as free radicals, would be detected by magnetic measurement only during gelatinization.

The only correlation between alkali number and diamagnetic susceptibility was that of glucose, which has the highest alkali number and diamagnetic susceptibility of the samples measured. This could indicate that the diamagnetic value of glucose may be the limiting value which the rest of the samples would tend to approach; or, it seems that the arrangement of the glucose residues in the glucose crystal would be the condition a starch would approach if there were no strain present within the granule.

It can be seen from Table 1 that solvent extraction caused an increase in diamagnetism of the starch. It is suggested that solvent extraction of a starch releases the strain within the granule which was produced by the lipids present. This

would effectively decrease the possibility of free radical existence within the granule and the starch would become more diamagnetic.

Drying of a starch was found to also increase the diamagnetic susceptibility of the starch. An explanation may be found in the opinion that starch molecules are in a semi-crumpled condition in the granule, and dehydration causes them to contract while hydration impels them to extend. It is suggested that in their contracted condition, strain would be decreased and therefore the diamagnetism would increase. In the extended condition, strain would be increased within the granule and the diamagnetism would be decreased.

The ball-milling of starch generally produces a condition of increased alkali lability. In this investigation, ball-milling was found to decrease the diamagnetism of the starch. It would seem that the "crushing-strain" of the ball-mill produced a higher incidence of free radicals. It was found that ball-milling under air lowered the diamagnetism only slightly, while, on the other hand, ball-milling under nitrogen lowered the diamagnetism to a much greater extent. It would seem that the oxygen in air in some way neutralized part of the free radicals produced during ball-milling.

## SUMMARY

1. The magnetic susceptibility of ten different samples of starch, starch products, and glucose were measured by the Gouy method. All samples were found to have diamagnetic values ranging from  $-0.334 \times 10^{-6}$  to  $-0.555 \times 10^{-6}$  c.g.s. units. Glucose was found to have the highest diamagnetic value.

2. Solvent extraction and vacuum-drying were found to increase the diamagnetism of a starch. Ball-milling under nitrogen was found to lower the diamagnetism to a much greater degree than ball-milling under air.

3. Free radicals were found to exist in two and possibly more of the samples. The granules of these two samples, namely, starch chloride and Blackhull kafir starch adsorbed in 0.3 percent palmitic acid solution, were found to have axes of greatest and least paramagnetism which were approximately  $112.5^\circ$  apart. In addition, evidence indicated that the free radicals present within the granules possessed two degrees of freedom.

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## APPENDIX

## Calibration

Both compartments of the double vessel were filled with air. The deflection at 5.0 amp. was -1.15 lines, as an average of ten readings, which deviated from the average value in general by not more than  $\pm 0.3$  line. Since the pull, under the conditions of the instrument, was proportional to the square of the amperage, the pull at 10 amp., which was chosen as standard, was:

$$- \frac{1.15(10.0)^2}{(5.0)^2} = -4.6 \text{ lines}$$

## Vessel Constant

The lower compartment was again filled with air and the upper with pure water. The deflection, measured at 3.5 amp., recalculated for 10 amp., was -263.7 lines.

The difference between volume susceptibilities,  $k$ , for water and air is  $0.749 \times 10^{-6}$  c.g.s.u. This corresponded to  $-263.7 - (-4.6)$ , or -259.1 lines. Hence one line of deflection at 10 amp. signified an increment of volume susceptibility equal to:

$$\frac{0.749 \times 10^{-6}}{259.1} = 2.891 \times 10^{-9} \text{ c.g.s.u.}$$

This was the "vessel constant."

### Susceptibility of Sample 3

The starch was placed in the upper compartment and air in the lower. The weight of the empty vessel was 13.9435 g.; the weight after filling with the starch to the top was 23.4054 g. Hence, the weight of the starch was 4.4619 g. Since the capacity of the vessel was 5.0139 cc., the amount of starch in 1 cc. of the vessel was 0.8899 g. The deflection measured at 3.5 amp. and recalculated to 10 amp., was -177.1 lines. So:

the starch gave -177.1 lines  
and air gave        -4.6 lines

Hence, the difference between the susceptibility of 1 cc. of the starch and that of 1 cc. of air was represented by -172.5 lines, which corresponded to an increment of volume susceptibility equal to  $172.5 \times 2.891 \times 10^{-9} = -0.498 \times 10^{-6}$  c.g.s.u. For air,  $k = +0.029 \times 10^{-6}$  c.g.s.u.; hence,  $k$  for 1 cc. of the starch equaled  $-0.469 \times 10^{-6}$  c.g.s.u.

The starch contained in 1 cc. of the cylinder consisted of 0.8899 g. or (density taken = 1.475\*) 0.603 cc. of solid substance, and 0.397 cc. of air. The 0.397 cc. of air contributed  $0.397 \times 0.029 \times 10^{-6} = +0.012 \times 10^{-6}$  c.g.s.u. Hence, the 0.8899 g. of the starch had a susceptibility  $(-0.469 - 0.012) \times 10^{-6} = -0.481 \times 10^{-6}$  c.g.s.u. Thus, the susceptibility per gram (specific susceptibility),  $x = -0.541 \times 10^{-6}$  c.g.s.u.

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\*This is the density of the starch taken in benzene according to the method given by Barham and Wagoner (7).