

THE MAGNETIC SUSCEPTIBILITY  
OF STARCH

By

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## INTRODUCTION

At a recent symposium on Starch Chemistry, C. S. Hudson (12) briefly summarized the chemistry of starch as having arisen during three successive periods which he designated as the "early period", the "middle period", and the "recent period".

The more important knowledge gained during the "early period" may be summarized as: 1. the conversion of starch into D-glucose by acid hydrolysis; 2. the conversion of starch into maltose by enzymatic hydrolysis; and 3. the noting of the intense blue color that iodine imparts to starch. Briefly, this information gave a basis for the simplest molecular formula for starch  $(C_6H_{10}O_5)_x$  and a qualitative test. In addition, various empirical treatments of starch such as its use in textile coating, food preparations, and the manufacture of adhesive pastes and dextrans were used industrially during this period. However, this information was of little value in furnishing evidence concerning the chemical structure of starch.

The "middle period" may be considered to have begun about 1893 to coincide with Emil Fischer's early discoveries concerning  $\alpha$ - and  $\beta$ -D-glucopyranosides. The discoveries of principal interest during the period may be summarized as follows: 1. Emil Fischer's establishment of a ring-type structure for maltose and his recognition of the existence of anomers; 2. the discovery of cellobiose by Skraup leading to the general recognition that the structures of starch and cellulose are intimately

related in some way to the structures of maltose and cellobiose respectively; 3. the discovery of crystalline dextrans by Schardinger; 4. the methylation studies on starch, cellulose, maltose, and cellobiose by Haworth, leading to proof of the structures and anomeric configurations of the two disaccharides and to the initial structural formulas of starch and cellulose; 5. indications of the presence of "repeating units" and "end groups" in the structures of starch and cellulose; 6. proof through methylation studies that the ring types of carbohydrates are to be classed as "pyranose" and "furanose"; and 7. the precise chemical synthesis of cellobiose. Thus, at the close of the "middle period" the nature of the linkages between the various glucose residues of starch was shown to be that of an  $\alpha$ -glucopyranoside as contrasted to the  $\beta$ -glucopyranoside of cellulose.

In the present "recent period" of starch research, some of the advances already given recognition are: 1. the enzymatic synthesis of starch-like products from D-glucose-1-phosphate (Cori Ester); 2. the application of periodate oxidation to the study of starches; 3. the recognition of isomaltose as 6-( $\alpha$ -D-glucopyranosyl)-D-glucose; and 4. the crystallization of  $\alpha$ - and  $\beta$ -amylases from various sources.

In addition to these, during the immediate preceding past and at the present time, extensive studies have been and are being made in this laboratory in an effort to correlate the physical and chemical properties of starch. Among the more successful

of these efforts have been the chlorination studies of Barham and Thomson (4,5) as the result of which it was possible to construct a model showing the possible arrangement of the glucose units within the starch granule.

The tendency of electrons to go in pairs is almost universal so that only a relatively few molecules containing unpaired electrons are known. In general, a "free radical" may be defined as any such molecule containing an unpaired electron. However, in organic chemistry, the meaning of the term "free radical" is generally restricted to include only those structures containing an unpaired electron in the valence shell of an atom such as the methyl ( $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot$ ) radical and these radicals are considered to be of special importance in the interpretation of molecular structure. In contrast, the ferric ion ( $\text{Fe}^{+++}$ ), which contains five unpaired electrons in a subshell of the atom, is not considered to be a "free radical" in the restricted definition of the term.

Certain chemical properties of starch which will be reviewed subsequently appear to indicate that free radicals may either be actually present as a functional unit within the starch granule or that the starch granule contains structures which may become free radicals during the course of a chemical reaction. One of the physical methods generally used to detect an actual existence of unpaired electrons in a substance is that of magnetic susceptibility measurement. Walker (24) attempted to establish the actual existence of free radicals in starch through the use of

such magnetic susceptibility studies. The present study was undertaken to test and, if possible, to confirm and expand the conclusions of Walker.

## HISTORICAL

### Chemical Evidences for Free Radicals in Starch

The chemical evidences indicating an existence of free radicals in starch and starch products were very adequately reviewed by Walker (24). Accordingly, an extensive review at this time is probably unnecessary. Briefly, however, these evidences may be classified into the two categories: 1. the alkali consumption of starch during pasting; and 2. the catalytic behavior of starch in certain reactions.

The consumption of alkali by starch during pasting is a well-known phenomenon and this alkali lability is often used as an indication of the source of the starch, its past treatment, and its desirability for various uses. However, the mechanism and focal points of attack by the alkali are not fully understood and are a matter for conjecture. One theory advanced in an effort to explain this consumption of alkali was that the focal points of attack by the alkali were the terminal aldehydic end groups present in the starch molecule. However, such a view is not entirely in accord with other facts concerning starch.

One of the severe inadequacies of this theory is that it does not account for the relatively large amounts of alkali consumed by the starch. That is, the amount of alkali consumed



during pasting is not consistent with a starch molecule having a molecular weight of the order of 200,000 with only one terminal aldehyde group per molecule. Taylor, et al. (20) attempted to explain this difficulty by suggesting that the alkaline decomposition of starch proceeds from an initial attack of the terminal aldehyde group through a progressive destruction of the glucose residues and an eventual increase in aldehydic groups. However, Taylor and Keresztesy (21) found that alkali lability was increased if the starch were ball-milled. This evidence was contrary to the preceding view expressed by Taylor but was explained by contending that ball-milling made existing aldehydic end groups, which were previously shielded from attack by alkali, more available for reaction through the breaking of certain hydrogen bonds. If this explanation were correct, it would be logical to assume that alkali lability would be higher in those starches which have more available water for swelling. However, Barham and Wagoner (6) found that a reduced availability of water for swelling was accompanied by an increase in alkali number in the case of certain sweet potato starches. Subsequently, Campbell (8) using palmitic acid progressively adsorbed on and desorbed from a starch of known history, found that changes in density and specific surface accompanying the adsorption-desorption process formed closed cycles and that the changes in the rate of hydration, alkali number, low temperature maximum viscosity, and gel strength indicated a close approach to reversibility. Barham and Campbell (2) succeeded in resolving

the gelatinization process of starch into slow and fast hydration processes which were manifested quantitatively in a resulting over-all rate of hydration. It was further found that the alkali number was inversely related to the overall rate of hydration and that it was possible to obtain a quantitative resolution of the alkali number in terms of the different rates of hydration as well as a quantitative correlation between the total alkali number and the over-all hydration process. In addition to these quantitative correlations, the rate of hydration was qualitatively correlated with the density, moisture content, low temperature viscosity maximum, and gel strength. From these considerations, in the absence of degradation, it was concluded that the aldehyde group is not alone responsible for alkali consumption by granular starch, but that it was probable that the granule is susceptible to alkaline attack largely through some other structure which represents a condition of strain and is not a reducing group in the usual sense. The concept of activated glucose, a free radical, was used to account for a changing alkali number in the absence of degradation.

The discussion in the previous paragraph does not furnish any direct evidence for the existence of free radicals in starch. However, since the nature of the alkali consuming component in starch is unknown, a free radical structure created by a homolytic scission of a valence bond and suggested by Barham and



Campbell should be considered at least until such time that evidence obtained would indicate such a view to be improbable or impossible.

The catalytic behavior of starch in certain reactions appears to be that of a free radical generator. Inasmuch as this property is commonly attributed to free radicals themselves, such a catalytic behavior would imply the existence of free radicals within the starch itself.

Barham and Thomson (4, 5) noted the formation of a black induction product during the chlorination of starch in liquid chlorine which turned bright yellow on further chlorination. The black color of this product was attributed to the light absorbing properties of free radicals. As a result of this and other characteristics of the chlorination reaction, a free radical mechanism for the reaction was postulated and it was suggested that the initial free radical generator might be located within the starch itself.

Barham, Stickley, and Thompson (3) successfully carried out the addition of chlorine to benzene using starch, and the chlorination products of starch, as catalysts. Further, Rosenberg (17) found that certain starches and starch products had the ability to induce polymerization of acrylonitrile and styrene and also to decompose acrylonitrile. These reactions are generally considered to be catalyzed by free radicals and thus indicate an occurrence of free radicals in the starch. In addition to noting the catalyzing reaction of starch, Rosenberg also found that upon

treatment of starch with such procedures as vacuum drying, solvent extraction, and ball milling, a qualitative correlation was obtained between its catalytic behavior and alkali lability. This correlation adds support to the belief that the alkali consuming component in starch may be of a free radical nature.

In addition to these evidences which are obtained from the reactions of starch, some additional evidence for free radicals may be obtained from substances related to starch. Thus Levene (13) made use of a free radical theory in order to explain the activity of glucose. According to Levene, such a free radical or "active" glucose would be formed by a homolytic scission of the oxygen bridge of the lactal form of glucose. This evidence applied to starch could be interpreted by saying that the strain created within a starch granule might be great enough to weaken or even break these lactal bonds.

#### Magnetic Susceptibility Studies of Starch and Starch Products

The only previous study of the magnetic susceptibility of starch was that of Walker (24) and may be considered to be the basis of the present study.

Briefly, Walker's study consisted of the measurement of the magnetic susceptibility of various starches which were subjected to various treatments. The conclusions as reported in his summary were: 1. The various samples of starch and starch products measured were found to have diamagnetic values ranging from  $-0.33 \times 10^{-6}$  to  $-0.55 \times 10^{-6}$  cgs units (specific suscepti-

bility); 2. Solvent extraction and vacuum drying were found to increase the value of the diamagnetic susceptibility of a starch and that ball-milling under nitrogen was found to lower this value to a much greater degree than ball-milling under air; and 3. Free radicals were found to exist in two and possibly more of the samples. In addition, evidence was presented which indicated that the free radicals present within the granules possessed two degrees of freedom and that two samples of starch were found to have axes of greatest and least paramagnetism which were approximately  $112.5^\circ$  apart.

In anticipation of the results obtained during the present series of experiments, it is believed that certain conclusions of Walker were not justified by the data presented. These criticisms will be presented in the "Discussion" of this thesis.

#### The Nature of Magnetic Properties

In contrast to the review of the chemical evidences presented by Walker indicating the presence of free radicals in starch, it is believed that his survey of magnetic properties was inadequate inasmuch as a knowledge of the theoretical considerations regarding the source of magnetic properties in substances is necessary for a complete understanding of the problem undertaken in this thesis. It is, perhaps, unfortunate that the qualifications of the writer do not permit him to make a critical survey and analysis of these considerations. Consequently, it will be necessary to keep mathematical derivations at a

minimum, with a sacrifice of rigor for the sake of simplicity.

The magnetic properties of all substances can be classified into the three categories (10): 1. paramagnetic, 2. diamagnetic, and 3. ferromagnetic. Substances are generally classified into one of these three categories on the basis of their magnetic permeability ( $\mu'$ ) as compared to that of a vacuum; that is, a substance is diamagnetic if it has a magnetic permeability less than a vacuum, paramagnetic if the permeability is slightly greater than a vacuum, and ferromagnetic if it is very much greater than that of a vacuum. As a standard, the value for the permeability of a vacuum is taken as unity.

In consequence of this relationship to magnetic permeability, the magnetic properties of a substance may be described as the tendency for magnetic lines of force to pass through the substance. Accordingly, the magnetic lines of force have a greater tendency to pass through paramagnetic and ferromagnetic substances than through a vacuum, and a lesser tendency to pass through a diamagnetic substance than through a vacuum. This difference is made apparent by the behavior of substances when placed in a magnetic field. If the substance is paramagnetic or ferromagnetic, it will align itself with the magnetic field, and will be attracted into the stronger part of the field if the magnetic field is inhomogeneous. In contrast, a diamagnetic substance will align itself across the magnetic field and will be repelled into the weaker part of an inhomogeneous field.

Magnetic permeability is related to the magnetic susceptibility ( $k$ ) by the relationship:  $\mu' = 1 + 4\pi k$ . Thus, for

diamagnetic substances  $k$  is minus and for paramagnetic and ferromagnetic substances  $k$  is positive. Since  $k$  represents a volume susceptibility for the substance, more convenient units for the comparison of different substances are:  $\chi = \frac{k}{\rho}$  where  $\chi$  = specific susceptibility and  $\rho$  = density; and  $\chi_M = \chi M = \frac{Mk}{\rho}$  where:  $\chi_M$  = molecular susceptibility and  $M$  = molecular weight.

In 1905, Langevin (Partington 15) derived a mathematical expression for paramagnetic susceptibility from theoretical considerations. In his derivation, he assumed a system of atoms as illustrated in Fig. 1. If the permanent magnetic moment of an atom were assumed to be  $\mu$ ,\* and made an angle  $\theta$  with an external magnetic field of strength  $H$ ,

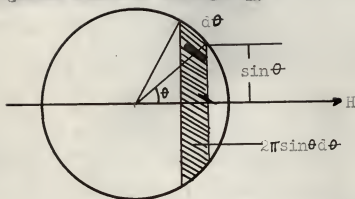


Fig. 1

\*The symbol  $\mu'$  is used in this section to designate magnetic permeability whereas  $\mu$  is used to designate magnetic moment. This distinction is contrary to common practice where  $\mu$  is used as a symbol for both magnetic permeability and magnetic moment.



the energy of each such atomic magnet would be:

$$\epsilon = -\mu H \cos \theta \quad (1)$$

The area cut off a sphere of unit radius by a strip of width  $d\theta$  as in Fig. 1 is  $(2\pi \sin \theta) d\theta$ . The fundamental equation of the Maxwell-Boltzmann statistics is:

$$\eta_r = \frac{1}{c} e^{-\frac{\epsilon_r}{kT}} \quad (2)$$

which relates the number of atoms to a given energy state. Accordingly, for the system described, the number of molecular magnets with axes directed in the solid angle is:

$$\eta = (A'e^{-\frac{\mu H \cos \theta}{kT}}) 2\pi \sin \theta d\theta = Ae^{-\frac{\mu H \cos \theta}{kT}} \sin \theta d\theta \quad (3)$$

where  $A'$  and  $A$  are constants. The mean moment in this direction is:

$$\mu_0 = (\mu \cos \theta) (Ae^{-\frac{\mu H \cos \theta}{kT}} \sin \theta d\theta) \quad (4)$$

The mean moment for the system would be the total moment divided by the total number of molecules or:



$$\bar{\mu} = \frac{\int_0^\pi \frac{\mu H \cos \theta}{kT} A e^{-\frac{\mu H \cos \theta}{kT}} \mu \cos \theta \sin \theta d\theta}{\int_0^\pi \frac{\mu H \cos \theta}{kT} A e^{-\frac{\mu H \cos \theta}{kT}} \sin \theta d\theta} \quad (5)$$

By putting  $a = \frac{\mu H}{kT}$  and  $x = \cos \theta$ , so that  $dx = -\sin \theta d\theta$ ,

$$\bar{\mu} = \frac{\int_{-1}^{+1} \frac{e^{ax}}{e^{-ax}} dx}{\int_{-1}^{+1} e^{ax} dx} = \mu \left( \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} \right) = \left( \cot a - \frac{1}{a} \right) \quad (6)$$

If  $\sigma = N\mu$ , where  $N = \text{Avogadro's number}$ , then

$$\frac{\sigma}{\sigma_\infty} = \cot a - \frac{1}{a} = \cot \frac{\mu H}{kT} - \frac{kT}{\mu H} \quad (7)$$

where  $\sigma_\infty$  represents the value of  $\mu$  at saturation. Equation (7) is commonly known as the Langevin Formula.

In the event that  $a$  is small, the integration of (6) may be simplified by expanding the exponentials so that by retaining only  $1 + ax$  and integrating:

$$\bar{\mu} = \frac{1}{3} a \mu = \frac{\mu^2 H}{3kT} \quad (8)$$

or

$$\chi_M = \frac{N\mu^2}{3kT} \quad (9)$$

magnetic field, all electrons would be in perfect alignment. At ordinary temperatures, such a perfect alignment could be achieved only through the use of high field strengths. The extent of the alignment may be illustrated by evidence presented by Woltjer and Onnes (van Vleck 22), who claim to have achieved an 80 per cent alignment of electrons in the case of gadolinium sulphate using the relatively high field strength of 22,000 gauss at the relatively low temperature of  $1.31^{\circ}$  K.

In addition to equation (7), Langevin was able to derive a theoretical equation for diamagnetic susceptibility by considering the magnetic moment induced in a molecule by an external magnetic field. In this derivation, it is assumed that the molecule has no permanent magnetic moment in the absence of a magnetic field. However, if it is assumed that an electron is travelling about a nucleus with a velocity  $\underline{v}$  (9),

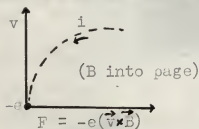


Fig. 2

and the atom is placed into a magnetic field  $\underline{B}$ , the moving electron will be acted on by the so-called Lorentz Force,  $-e(\underline{v} \times \underline{B})$ , and its motion will be modified because of this force. The change in the electronic motion caused by the Lorentz Force is always such that the altered motion tends to weaken the external field  $\underline{B}$  which originally caused this change. (Lenz's Law). In the above Fig. 2, the dotted line represents the line of the path

the moving electron would follow if it were free and the external magnetic field were directed into the page. This motion of the electron would be equivalent to a current flowing in the direction  $\underline{i}$  so that this current would produce an external field which is directed out of the page in accordance with the right hand rule of physics, and which in effect weakens the external field. Actually, in an atom, the electrons are not free but travel in orbits so that an electron possesses both an angular momentum about the nucleus and a magnetic moment, inasmuch as the orbital motion of such an electron would be equivalent to a tiny current loop. The torque of the Lorentz Force on this electron must act at right angles to its angular momentum (since it is a deflecting force) and cannot change the magnitude of the angular momentum. As a result, the angular momentum precesses about the direction of the applied field in a manner similar to the precession of a gyroscope. This precession of the electron orbits induced by a magnetic field is called the "Larmor" precession and gives rise to the diamagnetic behavior of the atom.

The theoretical equation derived by Langevin for the diamagnetic susceptibility of a monatomic molecule as given by Pauli (reported by Van Vleck, 22) is:

$$\chi = - \frac{Ne^2}{6m_1c} \sum \bar{r}_1^2 \quad (10)$$

where  $N$  = Avogadro's number;  $e$  = charge of the electron;  $m_1$  = mass of the electron;  $c$  = velocity of light;  $\bar{r}_1^2$  = time average

orbital radius.

The behaviors of a paramagnetic and a ferromagnetic substance in a magnetic field are similar and differ only in magnitude. Since ferromagnetism is a property of only certain transition elements, it is believed that the source of such ferromagnetism lies in the incomplete orbitals containing unpaired electrons (13). Such a concept, however, does not explain why only certain of these transition elements show ferromagnetism instead of this property being common to all elements in transition groups.

Historically (13), in 1852, Wilhelm suggested that each atom is a permanent magnet, capable of orientation. In 1890, Ewing pointed out the necessity for strong interatomic forces to account for the observed phenomena. Following the concept of the Bohr atom (1913), the shell structure of the atomic electrons, and the fact that inner incomplete shell is responsible for ferromagnetism, were recognized. Subsequent to the formulation of quantum mechanics (1925), it became possible to compute interatomic forces so that in 1928, Werner, Heisenberg, and others computed the magnitudes of the forces between the magnetic moments of adjacent atoms. These computations showed that in the cases of iron, cobalt, and nickel, the atomic properties and the spacing of the atoms in the crystalline lattice are such that there are strong interatomic forces tending to keep the magnetic moments of adjacent atoms lined up parallel to one another, whereas in the case of other transition elements, the interatomic forces

actually tend to prevent the magnetic moments from lining up, and hence prevents these elements from being strongly magnetic.

Several conclusions become apparent from the preceding discussions regarding the nature of magnetic properties.

The most significant of these conclusions is that both the paramagnetic effect and ferromagnetic effect are due to orientations of internal atomic magnetic moments by a magnetic field. In both cases, this orientation is opposed by a thermal disorientating agitation so that the magnetic susceptibility is a function of temperature. Further, in the case of ferromagnetic substances, due to the interaction of internal magnetic moments, the measured susceptibility need not necessarily be a function of the externally applied field strength. In the case of permanent magnets, the interaction of the internal magnetic moments is of sufficient magnitude so as to be able to resist thermal disorientation even after removal of the applied external magnetic field. The magnetic susceptibility of such a substance would depend on its previous history. This dependence is termed hysteresis. In contrast, a paramagnetic substance, which has no (or very little) interaction of internal magnetic moments, would have a measured susceptibility which would be a function of the external applied field strength and the measured susceptibility would be independent of the previous history.

In the case of the diamagnetic effect, it is expressed by Lenz's Law applied to an electron travelling in a magnetic field. Consequently, diamagnetism will be a universal property of all

substances and will be independent of temperature.

### APPARATUS

The apparatus used during the present series of experiments and the techniques used in measurement were essentially the same as described by Walker (24) and were adequately illustrated and described in his thesis.

### EXPERIMENTAL

The present study, as previously stated, was undertaken to test and, if possible, to confirm and expand the conclusions made by Walker (24) with regard to the magnetic properties of starch. Primarily, however, the ultimate aim of both Walker and the present study was to determine the presence or absence of free radicals or unpaired electrons in starch using magnetic susceptibility measurements.

From a consideration of Walker's conclusions, free radicals in starch are capable of orientation and their incidence in starch depends on the history and previous treatment (or condition of strain) of the starch granule.

#### Orientation Effects

Orientation by an Electrical Field. Walker claimed to have orientated starch granules using a strong magnetic field. In lieu of a magnetic field, an attempt was made to utilize the electrical moment of the free radical for orientation through



the use of an external electrical field, since it would be easier to obtain a strong electrical field in the laboratory, if such a course were indicated, than it would be to obtain a magnetic field greater than a certain maximum. However, the data indicated no orientation.

Procedure 1: A chloroform-cornstarch (designated in this laboratory as Cornstarch No. 10) slurry was prepared. A modified Gouy tube with a porous plate in place of the usual glass septum was placed between the plates of an aluminum condenser. A potential across the plates, which were approximately one-half inch apart, was maintained at various voltages using a Type 673A, General Radio power supply. The Gouy tube was filled with starch using small amounts of the starch slurry, the chloroform being removed by the force of gravity through the porous plate of the tube. The time required to fill the Gouy tube was approximately 48 hours. The final traces of chloroform were removed by passing a gentle air stream through the starch until constant weight was obtained.

Table 1. Magnetic susceptibility of starch orientated by an electrical field. (Cornstarch No. 10).

Condenser potential	:	Specific susceptibility
	:	
	:	
0 Volts		$-49.01 \times 10^{-8}$ cgsu.
1000 Volts		$-47.38 \times 10^{-8}$ cgsu.
1500 Volts		$-47.72 \times 10^{-8}$ cgsu.

The slight differences in susceptibility are probably not significant and are within the limits of the accuracy of the Gouy apparatus. In any event, it is believed that the above data does not indicate an orientating effect by the electrical fields used.

Effect of Rotation of the Gouy Tube. The above readings were taken using only one position of the Gouy tube. If orientation of the granules had occurred, the susceptibility of the starch measured would depend on the position of the Gouy tube in accordance with the findings of Walker. However, no such dependence was found in the case of the above samples.

Table 2. Effect of rotation of orientated granules on magnetic susceptibility. (Cornstarch No. 10).

Condensor potential :	Observed lines deflection on Gouy balance				
	0°	90°	180°	270°	Average
0 Volts	-20.52	-20.98	-20.88	-21.14	-20.88
1000 Volts	-19.88	-19.58	-19.98	-19.46	-19.73
1500 Volts	-19.60	-19.84	-19.96	-19.72	-19.80

In each case, the deviations at various positions appeared to be within the limits of accuracy of the readings and are believed to be without significance.

Orientation by a Magnetic Field Superimposed on an Electrical Field. In order to increase the orientating impetus given to the free radicals, an attempt was made to orientate the starch granules using a magnetic field superimposed on an electrical field. However, data indicated no orientation.

Procedure 2: The procedure was essentially that used in Procedure 1 except that a magnetic field was passed through the condenser at right angles to that of the electrical field. The electrical field was maintained at 1500 volts. The strength of the magnetic field was not determined but it is believed to have been of an order similar to or greater than that used during the Gouy measurements.

Table 3. Magnetic susceptibility of starch orientated by an electrical field superimposed on a magnetic field. (Cornstarch No. 10).

Treatment	:	Specific susceptibility
None	:	$-49.01 \times 10^{-8}$ cgsu.
Magnetic field superimposed on an electrical field.	:	$-52.41 \times 10^{-8}$ cgsu.

The difference of  $-3.40 \times 10^{-8}$  cgsu. appears to be greater than the experimental error of a typical Gouy measurement. However, the procedure employed in this measurement requires two additional sources of error not usually found in a typical Gouy measurement. These errors are the possibility of an incomplete removal of the chloroform used and a difference in packing procedure. In order that chloroform contamination account for this difference, approximately 0.1 gm. chloroform per gram of starch would have to be localized at the effective portion of the Gouy tube. Inasmuch as the Gouy tube was brought to constant weight before the susceptibility was measured, this amount of chloroform

would appear to be excessive. Perhaps a better criterion for comparing the two susceptibilities would be in terms of lines of deflection of the Gouy apparatus. The observed lines of deflection for the two starches were -20.52 and -20.08 lines for the native and orientated starch respectively. These readings are, for all practical purposes, identical. However, the average weight of the starches in the Gouy tubes was 4.8815 gms. and 4.4407 gms. for the native and orientated starch respectively. As a result, it is believed that the difference in susceptibilities was due to the lack of a uniform packing of the Gouy tube. During usual susceptibility measurements, uniform packing of a Gouy tube is insured by technique. In a modified procedure such as the one used to obtain the data of Table 3, inherent difficulties do not permit the usual uniform packing. As a consequence, the usual limits of error are not applicable. It is believed that the difference of  $-3.40 \times 10^{-8}$  cgsu would be within appropriate limits of experimental error and without significance. This conclusion is substantiated by the data of Table 4 which indicated no change in susceptibility on rotation of the Gouy tube in the magnetic field of the Gouy apparatus, thus indicating no orientation.

Table 4. Effect of rotation of granules orientated by a magnetic field superimposed on a magnetic field on magnetic susceptibility. (Cornstarch No. 10).

Treatment	: Observed lines deflection on balance				
	: 0°	90°	180°	270°	Average
Magnetic field superimposed on an electrical field	-19.5	-20.2	-20.5	-20.1	-20.1

Orientation of Starch Granules by a Magnetic Field. Inasmuch as Walker originally claimed orientation using a magnetic field, it was attempted to orientate the granules using only such a field. No significant orientation was indicated by magnetic susceptibility data.

Procedure 3: The procedure was essentially that used in Procedure 1 except that a magnetic field was passed through the condensor instead of the electrical field. The strength of the magnetic field was not determined but it is believed to have been of an order similar to or greater than that used during the Gouy measurements. The data obtained is presented in Table 5.

Table 5. Magnetic susceptibility of starch orientated by a magnetic field. (Cornstarch No. 10).

Treatment	Specific susceptibility
None	$-49.01 \times 10^{-8}$ cgsu.
Magnetic field	$-47.78 \times 10^{-8}$ cgsu.

Further, no significant change was noted in the observed deflections upon rotation of the Gouy tube during susceptibility measurements, thereby indicating no orientation.

Time Effect on Orientation. Inasmuch as no orientation was achieved using either a magnetic or an electrical field, it was thought that the factor of time might have an influence on the orientation effects.

Procedure 4: A cornstarch-distilled water starch slurry was prepared and placed in a sintered glass Gouy tube. The tube and



starch were then exposed to magnetic and electrical fields for various lengths of time. However, no significant data were obtained inasmuch as caking of the starch and similar difficulties made it impossible to completely dry the starch without disturbing any possible orientation.

#### Effect of Treatment

Inasmuch as it was not possible to obtain any orientation effects for the starch granule, an attempt was made to determine the effects of various treatments on the magnetic susceptibility of starch.

Apparent Effect of Hot Methanol Extraction. The presence of fatty acids in the starch granule probably influence the condition of strain within the granule. If a relationship exists between strain and the incidence of free radicals, this relationship should be manifested in a correlation between magnetic susceptibility measurements and extraction.

Procedure 5: Cornstarch No. 10 was treated for two-hour periods with successive portions of hot 85 per cent laboratory stock methanol using three parts methanol to one part of starch by weight. The data obtained indicated a significant change in susceptibility.



Table 6. Effect of hot laboratory stock methanol on magnetic susceptibility of starch. (Cornstarch No. 10).

Number of extractions	Specific susceptibility
0	$-49.01 \times 10^{-8}$ cgsu.
5	$-47.15 \times 10^{-8}$ cgsu.
15	$-23.60 \times 10^{-8}$ cgsu.

Apparent Effect of Cold Methanol Extraction. It would be expected that cold methanol would not be as efficient an extracting agent as hot methanol. Consequently, cold methanol extraction would not be expected to influence internal strain nor magnetic susceptibility of starch greatly. However, cold laboratory stock methanol extraction resulted in a probable decrease in susceptibility.

Table 7. Effect of cold laboratory stock methanol on magnetic susceptibility of starch. (Cornstarch No. 10).

Number of extractions	Specific susceptibility
0	$-49.01 \times 10^{-8}$ cgsu.
5	$-50.68 \times 10^{-8}$ cgsu.
10	$-44.04 \times 10^{-8}$ cgsu.

The difference in susceptibility between native and ten times extracted Cornstarch No. 10 is probably real. This belief is substantiated by a comparison of the lines deflection observed on the Gouy balance. For the native and extracted cornstarch, these readings were  $-20.32$  and  $-13.10$  lines

respectively. This difference in deflection is real and is probably a better means of comparison than is the calculated susceptibility. In any event, the data in this particular experiment were unlike those recorded in Table 3 where the readings were similar but the calculated susceptibilities were different.

Apparent Effect of Ammonium Hydroxide on Starch. Treatment of starch with ammonium hydroxide results in a fatty acid extraction similar to that resulting from extraction with methanol.

Procedure 6: A 20:1 ratio of concentrated ammonium hydroxide-Cornstarch No. 10 slurry was stirred for a period of twenty-four hours. The slurry was then filtered and dried in air until free of ammonia odor. The data seemed to indicate a very pronounced change in susceptibility.

Table 8. Effect of laboratory ammonium hydroxide on magnetic susceptibility of starch. (Cornstarch No. 10).

Treatment	:	Specific susceptibility
None	:	$-49.01 \times 10^{-8}$ cgsu.
Concentrated ammonium hydroxide	:	$- 7.70 \times 10^{-8}$ cgsu.

Effect of Magnetic Field Strength on Measured Susceptibility of treated starches: In the case of the ammonium hydroxide treated starch, the deflection from which the specific susceptibility was calculated was -2.5 lines at an electromagnet

current of three amperes. Accordingly, it was decided to use a greater field strength and then calculate the deflections to a common field strength.

Table 9. Effect of magnetic field strength on observed Gouy deflections. ( $\text{NH}_4\text{OH}$  treated -Cornstarch No. 10).

Electromagnet current	Observed deflection	Deflection calc. to 10 amperes.
1 Ampere	0.9 Lines	90.0 Lines
3	- 2.8	-31.0
4	- 8.8	-55.0
5	-17.3	-69.2

From the data obtained, it is evident that the susceptibility of this starch was not independent of the field strength. Consequently, it was decided to verify the susceptibility of the laboratory stock methanol treated starches. These also seemed to show a dependence of susceptibility on field strength.

Table 10. Effect of magnetic field strength on observed Gouy deflections. (Hot 85% Laboratory Stock Methanol - Cornstarch No. 10).

Electromagnet current	Observed deflection	Deflection calc. to 10 amperes.
1 Ampere	0 Lines	0 Lines
2	- 1.62	- 40.
3	- 6.60	- 73.3
4	-14.12	- 88.1
5	-25.48	-102.0

Chemical Evidence for Iron Contamination of Starch Samples.

The above variations of magnetic susceptibility, according to present concepts, are due to the presence of ferromagnetic substances. The following chemical test was used in order to establish the presence of iron as a contaminant in the starch samples.

Procedure 6: A 1:1 concentrated HCl:distilled H<sub>2</sub>O solution was prepared in one depression of a spot plate. A few crystals of NaSCN were placed in the solution and stirred with a glass stirring rod. The solution turned a slight red due to the presence of traces of iron in the HCl, distilled water, etc.

The test solution was then divided into two equal portions (i.e., one-half was transferred to a neighboring spot). A small amount of the starch to be tested was placed in one spot and a sample of untreated starch was placed in the second spot. Each spot was then filled to volume using distilled water.

The test was made by comparing the intensity of color in the two neighboring spots. The deeper color supposedly indicated the presence of a larger amount of iron. In the event of a doubtful test, it was generally possible to distinguish the two by the addition of one or two crystals of NaSCN to each spot without stirring and then comparing the color.

The test performed on the starches treated with ammonium hydroxide and methanol in the present series of experiments showed that a decrease in diamagnetic susceptibility was accompanied by an increased incidence of iron. Further, Cornstarch No. 10, itself, showed a greater incidence of iron when compared with

sucrose.

Extraction of Cornstarch No. 10 with purified ammonium hydroxide resulted in only a slight change in magnetic susceptibility.

Effect of Purified Methanol on Starch. The stock methanol used was received in a fifty-gallon steel drum and withdrawn from this drum as needed. In the previous mentioned starch-methanol treatments, the methanol was used as it was received without additional treatment. In order to verify the source of contamination of the starch samples, Cornstarch No. 10 was treated with specially purified reagents.

Procedure 7: The distilled water used was twice distilled from a potassium permanganate solution; twice from a potassium flouride solution, followed by a final redistillation. The methanol was distilled three times using a long fractionating column. Pyrex was used in both procedures.

Table 11. Effect of hot purified methanol on the magnetic susceptibility of starch. (Cornstarch No. 10).

No. ex- tractions	: Deflections calc. to 10 amps. :			: Specific susceptibility
	: 3 Amp	: 4 Amp	: 5 Amp	
0	-186.0	-186.7	: Off Scale	-55.74 x 10 <sup>-8</sup> cgsu
5	-164.4	-163.7	-171.6	-53.95 x 10 <sup>-8</sup> cgsu
10	-167.6	-166.5	-165.6	-52.19 x 10 <sup>-8</sup> cgsu
15	-163.7	-163.3	-163.8	-49.70 x 10 <sup>-8</sup> cgsu

The difference in the susceptibility between native cornstarch No. 10 and solvent extracted cornstarch appears to be significant and real in this case. This difference will be



considered extensively in the "Discussion" of this thesis.

Effect of Methanol Extraction on Susceptibility of Various Starches. An attempt to extend the solvent extraction effect noted in the case of Cornstarch No. 10 was made. However, the data obtained was not conclusive.

Table 12. Effect of hot purified methanol on magnetic susceptibility of various starches.

Starch	: $X_M$ (Native)	: $X_M$ - Five extractions
Cornstarch	-93. x 10 <sup>-6</sup> cgsu	-87. x 10 <sup>-6</sup> cgsu.
Cody milo	-74. x 10 <sup>-6</sup>	-75. x 10 <sup>-6</sup>
Pink kafir	-69. x 10 <sup>-6</sup>	-74. x 10 <sup>-6</sup>

In this comparison, it is apparent that hot methanol may cause either an increase, decrease, or have no effect on the magnetic susceptibility of starch. In each case, the change due to extraction is small. It will be shown subsequently that the presence of uncontrolled variables in different starches may cause small increases or decreases in the observed magnetic susceptibility. As a result of these uncontrolled variables, it is not possible to interpret satisfactorily the data in Table 12.

The data presented in Table 12 is also of interest in that it provides an opportunity to correlate alkali lability with magnetic susceptibility. Inasmuch as the alkali lability is of the sequence cornstarch pink kafir cody milo whereas the magnetic susceptibility is of the sequence cornstarch cody milo



pink kafir, there would appear to be no such correlation. However, the presence of uncontrollable factors previously mentioned do not permit such a definite conclusion.

The susceptibilities of these starches appeared to be independent of field strength indicating no ferromagnetic impurity.

Reduction of Ferrous Ion with Starch. Assuming that the ferromagnetism present in the starches previously mentioned was due to iron (or a magnetic modification of an iron compound), starch was treated with ferrous ion in order to determine whether or not the ferromagnetism was due to a reduction of iron salts by the starch. The data obtained did not indicate such a reduction.

Procedure 8: Cornstarch No. 10 was treated with a methanol- $\text{FeCl}_2$  solution with stirring for a period of two hours under a carbon dioxide atmosphere. The alcohol- $\text{FeCl}_2$  solution was removed by filtering. The starch was then washed with additional methanol.

Table 12. Gouy deflections of ferrous chloride treated Cornstarch No. 10.

Treatment	: : Lines deflection : (Calc. to 10 Amps.)
$\text{FeCl}_2$	297.2
$\text{FeCl}_2$ - 1 Washing	-154.9
$\text{FeCl}_2$ - 4 Washings	-157.2

The color of each of the above starches remained white after

treatment except, perhaps, the unwashed starch. This starch became very slightly discolored to a very delicate light yellow. However, it is not believed that iron contamination would have been suspected on the basis of color during ordinary laboratory procedures.

Further, the magnetic susceptibility did not appear to have any dependence on field strength, thus indicating an absence of ferromagnetism. Actually, this independence of susceptibility with field strength does not establish that reduction of ferrous ion by free radicals did not occur inasmuch as a localized iron atom would not exhibit ferromagnetism. However, it does establish that the laboratory methanol treated starches did not become ferromagnetic as a result of reduction of ferrous ion.

Corrosion effects of Methanol on Steel Wool. Inasmuch as the starch did not become ferromagnetic in the presence of ferrous ion, the source of the ferromagnetic impurities may be assumed to be present in the methanol used.

Procedure 9: The purified methanol prepared was placed in a carboy containing steel wool which was washed free of fine particles. The methanol was then permitted to stand in contact with the steel wool for a period of one month.

Small particles were noted to accumulate on the bottom of the carboy during the period of standing. In general, these particles were attracted by a small Alinco magnet passed on the outside of the carboy. On pouring the alcohol from the carboy into

a beaker, these same fine particles could be accumulated using the same magnet. However, the number and size of these particles were such that it is believed that they would not have been noticed in the methanol during the course of normal laboratory experiments.

Effect of Iron-Exposed Methanol on Starch. Cornstarch No. 10 was treated with the above mentioned methanol which had been exposed to steel wool. In general, all samples of starch treated with this alcohol became ferromagnetic. As a typical example, the following data are presented.

Table 14. Gouy deflections of iron-exposed methanol treated starch.

Electromagnet current	Observed deflection	Deflection calculated to 10 amperes.
1 Ampere	1.12 Lines	112. Lines
2	1.66	41.5
3	- 1.84	- 20.44
4	- 7.12	- 44.5
5	-14.8	- 59.4

Effect of Filtration on Iron-Exposed Methanol. On filtering the iron-exposed alcohol through a sintered glass funnel, particles of metallic iron gradually accumulated. However, after filtering two liters of this alcohol, the amount of iron which accumulated in the funnel was small and was estimated to be less than one milligram. Ferromagnetism was noted in the starch samples treated with this alcohol only after a prolonged treatment.

Table 15. Gouy deflections of iron-exposed methanol treated starch. Filtered after exposure).

Number of Extractions :	Deflections calculated to 10 amperes					- Lines
	1 amp	2 amp	3 amp	4 amp	5 amp	
1	-160.	-175.	-177.	-172.		
5	-132.	-144.	-150.	-152.		-154.
10	-150.	-147.	-150.	-153.		-154.
15	- 50.	- 73.	- 88.	-106.		-113.

Determination of Magnitude of Susceptibility due to Iron Contamination. One of the characteristics of the magnetic susceptibility of a ferromagnetic substance is that the substance becomes magnetically saturated at relatively low field strengths. Accordingly, once a critical value is reached, the slope of the deflection vs. a (current)<sup>2</sup> plot should represent the true slope due to diamagnetic and paramagnetic contributions. However, the position of the line on the graph would be altered by the contamination of the ferromagnetic impurity. By extrapolation of the true slope to zero current, the deflection due to the ferromagnetic impurity may be estimated. This is shown for native Cornstarch No. 10 and an impure methanol treated starch in Fig. 3. The native Cornstarch No. 10 appears to intercept the  $I^2 = 0$  axis slightly below zero, although this deviation may or may not be significant. In the case of the extracted cornstarch, the intercept is approximately at 4 lines deflection. The significance of this value can be seen by subtracting this value from the observed deflection and then calculating the deflection at ten amperes.

Table 16. Correction of gony deflections of substances containing ferromagnetic impurities. (Laboratory methanol treated starch).

Electromagnet current	: Observed deflection	:	: Corrected deflection	:	: Calculated to 10 amperes.
1 Ampere	- 0.	Line	- 4.0	Lines	-400. Lines
2	- 1.62		- 5.62		-140.5
3	- 6.60		-10.60		-117.8
4	-14.12		-18.12		-113.3
5	-25.48		-29.48		-117.6

At three, four, and five amperes, the calculated deflection at ten amperes appears to be constant. Below three amperes, the ferromagnetic substance is not magnetically saturated so that anomalous results are obtained.

The difference in slope between the two lines on Fig. 2 represents a true change in magnetic susceptibility due to diamagnetic and paramagnetic causes as contrasted with a change in susceptibility due to ferromagnetism. However, whether this change in slope is due to a difference in packing or contamination by a paramagnetic ion such as Fe cannot be determined from the graph.

The usual method of determining the susceptibility of a substance contaminated with ferromagnetic impurities is to use an electromagnet current great enough so that the deflection due to the impurity is small as compared to the total observed deflection. However, the procedure described above has the advantage in that it corrects for the impurity present rather than

DETERMINATION OF FERROMAGNETIC  
IMPURITIES IN STARCH

- Native Cornstarch No. 10
- Cornstarch No. 10 extracted  
15 times with laboratory  
methanol.

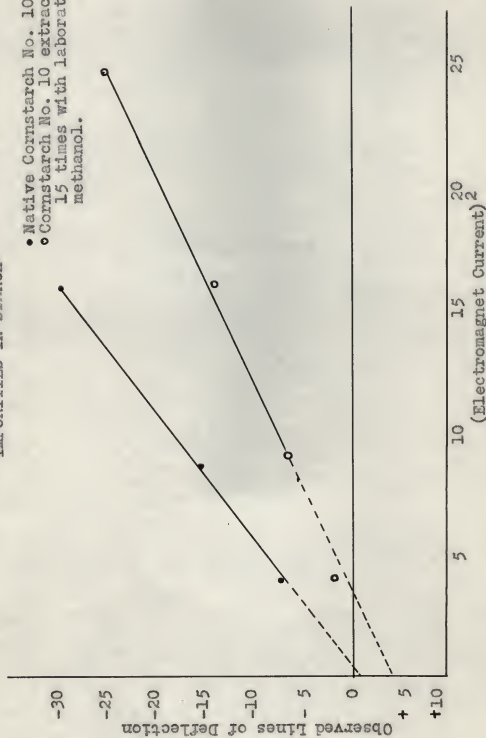


FIG. 3



neglecting it.

#### DISCUSSION

From a consideration of the data contained in Tables 1, 2, 3, 4, and 5, it is apparent that no orientation effects of starch granules were obtained during the present series of experiments. Further, from a consideration of the data contained in Tables 9, 10, and 11, certain anomalous magnetic susceptibility data obtained were shown to be due to the presence of ferromagnetic impurities. These impurities were shown to be iron by the application of a chemical test described in Procedure 6.

Walker on obtaining certain anomalous magnetic susceptibility data (i.e., paramagnetic values for starch and a variation of susceptibility with orientation) attributed these results to the presence of free radicals present in the starch granule. If it is postulated that the anomalous results obtained in both series of experiments were due to similar causes, it is apparent that the conclusions of Walker and the author are contradictory. It is believed that such a postulate is valid and that certain conclusions made by Walker are in error.

Walker, in his thesis, makes only one mention of ferromagnetism and this only insofar as it may be present as a contaminant in solid organic materials. More significant, however, is the lack of any mention of ferromagnetism in the discussion of his Samples 11 and 12 in which he stated: "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". These free radicals could have been attributed to starch only if it were assumed "a priori" that the samples did not contain impurities capable of giving such paramagnetic values, or if it were shown that the starch samples did not contain such impurities. There is no evidence presented in Walker's thesis to show that impurities were absent in the particular starch samples used. Accordingly, it must have been assumed that the starch samples being used were pure samples.

In the case of starch, such an assumption can hardly be valid inasmuch as iron is a common industrial contaminant. This is especially true of starch which may undergo a steeping process using water purified only with regard to human consumption; is ground, pulverized, etc., in most cases using steel rollers, hammers, etc.; and in certain but not all instances magnetic devices are even employed to remove metallic impurities. During routine laboratory studies, this contamination is of little significance. However, due to the nature of the magnetic properties of iron, this contamination manifests itself during magnetic susceptibility studies from 100-1,000,000 times greater than its presence would indicate on a quantitative basis.

In any event, the data presented by Walker may or may not be valid depending upon whether or not the samples used in his

experiments were free from iron. In certain instances it may be possible to establish the presence of iron by an analysis of the characteristics of the experimental data obtained. Unfortunately, the data recorded by Walker in both his thesis and laboratory notebook are in terms of calculated specific susceptibilities. As a result, it is difficult to analyze these data in terms of possible contamination. However, some analysis is possible to show that Walker used contaminated samples.

One such indication appears to be contained in Fig. 6 of his thesis which shows the change of paramagnetism of sample No. 14 (Blackhull starch - solvent extracted, adsorbed in 0.3 per cent palmitic acid, rolled and packed in a magnetic field) with rotation of the Gouy vessel in a magnetic field. The difference between the maxima and minima of the sine curve is approximately  $4.05 \times 10^{-6}$  cgsu. Such a value, which was said to represent the difference due to orientation of the radicals, is unreasonable when it is compared with the specific susceptibility of  $K_3Fe(CN)_6$  which is of the order  $+6.82 \times 10^{-6}$  cgsu. It would seem that if the difference in susceptibility of this magnitude were due to orientation of free radicals, such orientation effects would be a more common phenomenon than they appear to be. In actual practice, paramagnetic anisotropy is generally not considered in the usual magnetic susceptibility studies.

A second indication of contamination in the starch samples used by Walker is the magnitude of the paramagnetic susceptibility

which was obtained. That is, Walker's values would indicate an incidence of 0.88 odd electrons per glucose unit for his Sample No. 14. Such a high incidence would indicate a highly reactive structure and a low degree of polymerization for starch. Neither of these properties are in accord with the facts.

A third indication that the data obtained by Walker are unreliable is the decrease in diamagnetism which was reported during successive measurements of the same portion of starch sample. If such a decrease were a true property of either diamagnetism or paramagnetism, the recorded values for magnetic susceptibility which are available in the literature would be of little significance except in those cases where the previous magnetic history of a substance were reported with the data presented. However, literature data do not consider the previous magnetic history of a substance as a variable except in a limited number of cases such as ferromagnetism. The phenomenon of decrease in diamagnetism observed by Walker was not observed during the present series of experiments.

In addition to these criticisms pertaining to Walker's data, it is believed that his conclusions are inconsistent with the present theories regarding magnetic properties. Although such an inconsistency would not necessarily invalidate the conclusions of Walker from a standpoint of logic, the evidence supporting these theories and their consistence with facts lend support to their validity. Accordingly, they should at least be considered in cases of apparent discrepancy. The conclusions of Walker which

are believed to be inconsistent with present magnetic theories are those pertaining to anisotropy and orientation effects of free radicals.

According to present concepts, paramagnetism is due to the magnetic moment of the spin of an unpaired electron. The spin of this electron is limited with respect to the atom by the spin quantum number to values of  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . Without respect to the atom, the spin quantum number has no meaning in the absence of a magnetic field, but in the presence of an external magnetic field it is again restricted to the values of  $+\frac{1}{2}$  and  $-\frac{1}{2}$  (11). Accordingly, it would appear that a magnetic field has an aligning effect upon electrons. This alignment was discussed in terms of the Langevin formula on page 14. In effect, Walker assigned spin quantum numbers of all values from  $+\frac{1}{2}$  to  $-\frac{1}{2}$  to the odd electrons in the absence of the magnetic field, fixed the axis of spin with reference to the molecule as a whole, and then utilized the magnetic moment of the electron to orientate the molecule until the electron itself had a spin of either  $+\frac{1}{2}$  or  $-\frac{1}{2}$  with respect to the field. Such an assumption would require a large moment of inertia resisting the orientation of the electron as compared to the moment of inertia resisting the orientation of the molecule as a whole. Such a view is inconsistent with the small energy considerations involved in the hyperfine structure of spectral lines attributed to spin. In any event, it would appear that paramagnetism due to odd electrons is caused by an alignment of the electrons by the magnetic field giving rise



to a magnetic effect which is absent in a random arrangement of electrons.

It is believed that the conclusion of the previous paragraph attributing the paramagnetic effect to an alignment is substantiated by certain concepts regarding magnetism. Among these is the phenomenon of "quenching" which occurs in certain elements of the transitional group. Michaelis (Weissberger 26) explaining quenching states: "the quenching is due to the facts that the motion of electrons takes place in an electrostatic field produced by the electrons and nuclei in the environment and that this field can never be spherically symmetric. This field, because of its assymetry, restrains the orientation of the orbitals and prevents them from being influenced by the applied magnetic field. However, this restraining effect is not complete. For the rare earth metals, the orbital contributions are of the same importance as spin contributions because here, the shell is surrounded by a complete electron shell which shields the electrostatic effect of the surrounding molecular electrostatic field and allows the orbitals to orientate themselves freely in a magnetic field". Clearly, the paramagnetism due to the orbital magnetic moment of an electron is the result of an orientated orbit similar to that of an orientated spin in the case of true paramagnetism.

The behavior of an electron in a magnetic field may also be considered with respect to entropy. Blesny (7) in his summary on the use of paramagnetic salts in cooling states: "When the

salt is magnetized in a very strong magnetic field at  $1^{\circ}$  K., the electronic entropy is completely removed. On demagnetizing to zero field, the entropy remains constant, but is divided between electron and nuclear spins". Thus, it is again clearly seen that a magnetic field has an aligning effect on electrons since a system can have zero electronic entropy only when there perfect alignment of electron spin.

In contrast to the preceding conclusions, Waters (25) claims that a molecule will orientate in a magnetic field due to the paramagnetic moment. It would appear that such a view would support Walker's conclusions. However, it is believed that Waters did not intend that his statement be evaluated critically. It should, however, be given consideration.

The basis of Waters' statement appears to be the Stern-Gerlach experiment in which a beam of silver atoms is passed through a heterogeneous magnetic field and made to split into two beams each of equal intensity. This splitting is generally attributed to the existence of electrons of opposite spin in silver atoms. In actual effect, the splitting is due to the presence of a permanent magnetic moment within the atom. The magnetic moment of an atom or molecule is limited by the relationship  $J = L \pm S$  where  $J$ ,  $L$ , and  $S$  are the molecular magnetic, azimuthal, and spin quantum numbers, respectively. It so happens that in the case of the silver atom,  $L = 0$ , and since there is only one odd electron,  $J$  is limited to the values of only  $\pm \frac{1}{2}$  and the splitting may be attributed to the spin.

However, the conditions of the Stern-Gerlach experiment are not those under which paramagnetic susceptibility is measured. In the first place, the silver atoms used are thermally excited atoms in a gaseous state. According to the Langevin equation, thermal excitation would inhibit the aligning of an electron by an external magnetic field. Inasmuch as the Stern-Gerlach experiment indicates an equal splitting of the beam, evidently the thermal excitation is sufficient to resist alignment of the electron spin by the magnetic fields used. Secondly, a more basic requirement of an electron in a magnetic field is that it assume a state of least energy. This state of state of least energy need not necessarily be one of alignment. Under the conditions of the Stern-Gerlach experiment, the gaseous atoms in a vacuum can apparently satisfy this energy requirement by a displacement effect. However, it should be pointed out that this displacement is not an orientation effect in the sense claimed by Walker and Waters since the conditions of the Stern-Gerlach experiment do not require that the magnetic moment of an atom be orientated with respect to the atom itself. Instead, the displacement effect noted in the Stern-Gerlach experiment appears to be the one always measured in the Gouy apparatus.

Thus far, reasons have been presented in criticism of Walker's conclusions both from the standpoint of the data presented and from theoretical considerations. In all fairness, the data presented in his thesis should be reviewed in the light of

conclusions obtained from the present series of experiments. It is believed that his data represent a consistent picture when reviewed under these conditions.

To begin, it is believed that in those cases where paramagnetic values for starch or starch products were obtained by Walker, these paramagnetic values were obtained using contaminated samples and that the contamination was the primary cause for the extreme paramagnetic values obtained. The source of the contamination is undetermined but in the case of Sample No. 14 the contamination may have occurred during the alcohol treatment. Further, in view of the magnitude of the values obtained, in certain cases at least, the contaminant was a ferromagnetic impurity as contrasted with ferrous or ferric ion.

Assuming that Walker had such contaminated samples, the data obtained are reasonable. The positive values obtained are due to the presence of iron. At this point, it may be postulated that these values were obtained at low electromagnetic currents if the contaminant was ferromagnetic. However, this postulate cannot be verified.

The sine curve obtained by Walker is also readily explained. The magnetic field utilized in the Gouy apparatus is a global field. Accordingly, along a horizontal plane, the field strength would vary. This can be shown by the variation of  $r_1$ ,  $r_2$ , and  $r_3$  from a central point as illustrated in Fig. 4.

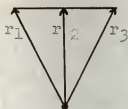


Fig. 4

In effect, the sine curve obtained by Walker may be attributed to the variation of susceptibility with field strength of a localized ferromagnetic substance. Such a variation would exhibit the characteristics of a sine curve. This view is also consistent with the fact that packing of the Gouy tube in a magnetic field resulted in an accentuated sine curve inasmuch as such packing would tend to localize any ferromagnetic particles present toward the outer portions of the tube. Further, it would account for a continual decrease in diamagnetic susceptibility inasmuch as there would be a residual magnetism left on removal of the magnetic field except in the case of very pure iron.

There are two requirements necessary in order to obtain a sine curve of the magnitude obtained by Walker. The first of these requirements is a ferromagnetic impurity not in the center of the Gouy tube as explained above. The second requirement is that the current used in the electromagnet be less than the saturation current for the iron particle. However, the second requirement can be assumed to be met if the iron contamination is



assumed to be present throughout the length of the Gouy tube. A sine curve similar to that of Walker may be readily obtained by fastening a minute iron filing to the outside of a Gouy tube with scotch tape and then measuring the susceptibility at different positions.

Inasmuch as Walker concluded that the starch granule was magnetically anisotropic, the causes and nature of anisotropy should also be considered in this thesis. The phenomenon of magnetic anisotropy is not an uncommon experience inasmuch as the common magnet represents a magnetically anisotropic substance. This anisotropy is attributed to an alignment of magnetic moments due to an interaction between electrons. In order to have anisotropy of this type, it is necessary to have the interactions of such a magnitude that they will exist even in the absence of an external magnetic field in accordance with the considerations previously discussed with regard to ferromagnetism. Consequently, a piece of hard iron will show magnetic anisotropy upon magnetization inasmuch as such interaction is possible. In contrast, a piece of soft iron will not be anisotropic (at least less than hard iron) inasmuch as electronic interaction occurs only under the influence of a magnetic field. In order that a free radical be magnetically anisotropic, it would, of necessity, be caused by an interaction of this type. However, as it was previously shown, a favorable spatial orientation would be necessary in order that such an interaction occur. It is hardly probable that the free radicals postulated in the

starch granule have such a spatial orientation. Accordingly, it must be concluded that the free radicals present in starch are not magnetically anisotropic.

This conclusion, however, does not imply that the starch granule itself is not magnetically anisotropic. L. Michaelis (Weissburger 26) discusses magnetic anisotropy in organic compounds at great length. However, the anisotropy discussed is not of the type described above but is due to the diamagnetic properties of the substance. Accordingly, such anisotropy can be only of the magnitude associated with diamagnetic susceptibility and not the relatively large value obtained by Walker. This anisotropy is caused by the fixation of electron paths through valence bonds. In the case of starch, the helical structure postulated for the starch granule would probably exhibit this type of anisotropy. Cellulose was shown to exhibit this type of anisotropy (16). Likewise, if these helices were favorably orientated within the starch granule, the starch granule would also exhibit magnetic anisotropy. However, it would be possible to demonstrate this anisotropy only by using an apparatus capable of detecting the small differences in magnetic properties which would be present. The behavior of the hilum of a starch granule under the influence of a magnetic field might possibly serve as a basis for the study of granule orientation. However, any anisotropy so demonstrated would be diamagnetic anisotropy and not the type postulated by Walker.

Certain data presented in this thesis appear to indicate

that the magnetic susceptibility of starch is dependent on the history of the starch. Accordingly, it might, perhaps, be possible to interpret this data with regard to the possible existence of free radicals or unpaired electrons as a functional unit in the starch granule.

Table 1 of this thesis shows that the untreated Cornstarch No. 10 had a specific susceptibility of  $-49.01 \times 10^{-8}$  cgsu. However, Table 11 shows that Cornstarch No. 10 had a specific susceptibility of  $-55.78 \times 10^{-8}$  cgsu. In each case, the susceptibility determinations were repeated so that the values recorded may be considered to be experimentally accurate. The only difference in the history of the two samples that is known is that the sample recorded in Table 11 was stored in a bottle recorded in this laboratory as "Cornstarch No. 10, Bottle No. 6". The source of the starch recorded in Table 1 was not recorded but it was definitely not taken from Bottle No. 6. In addition, Table 11 records a change in the specific susceptibility for Cornstarch No. 10 from  $-55.74 \times 10^{-8}$  cgsu. to  $-49.70 \times 10^{-8}$  cgsu. upon extraction with purified hot methanol and Table 12 records an attempt to extend the findings of Table 11 to other starches.

In attempting to interpret the data listed in these tables, it should be noted that the magnetic susceptibilities recorded are those obtained using the laboratory starches described. The absence of ferromagnetic impurities was established and special precautions were taken to prevent further contamination in each

case so that the data may be considered to be experimentally accurate. However, contamination during the original preparation of the starches, etc., might have occurred so that the magnetic susceptibility values recorded need not necessarily be the true values for the starch itself. However, differences in the susceptibility of a given starch subjected to various treatments would, perhaps, retain their significance. Consequently, an attempt will be made to interpret such differences rather than the actual values themselves. It will be apparent, however, that the discussion will be analogously applicable to the total susceptibility measured. Similarly, the discussion will concern itself primarily with the difference in susceptibility noted upon the extraction of Cornstarch No. 10 with methanol, but it will also be analogously applicable to the other cases previously mentioned.

Table 11 records a decrease in magnetic susceptibility of Cornstarch No. 10 from  $-55.74 \times 10^{-8}$  cgsu. to  $-49.70 \times 10^{-8}$  cgsu. It is believed that the difference in susceptibility of  $6.04 \times 10^{-8}$  cgsu. is real and significant. Four possible explanations for this difference are possible.

First of all, it may be reasoned that the decrease in susceptibility upon extraction of Cornstarch No. 10 with purified methanol was due to the formation of unpaired electrons or free radicals during the extraction process which were stabilized. This reasoning would establish the existence of free radicals in the extracted starch and indirectly in the native starch. If

this reasoning is accepted, it can be shown that in order to achieve a decrease in diamagnetism of  $6.04 \times 10^{-8}$  cgsu., the creation of one free radical for approximately each 130 glucose units would be necessary. However, if it is assumed that these free radicals were created by the homolytic scission of a typical C-C or C-O bond, the data would indicate that 65 such bonds were ruptured. In effect, an explanation similar to the above was utilized by Mueller and Dammerau (14) as a possible explanation for the deviation of the magnetic susceptibility of olefins from the theoretical values calculated through the use of Pascal's values. This explanation proposed that certain of the olefin molecules existed in a biradical form so that the experimental diamagnetic susceptibility of the olefin would always be less than the theoretical value.

In addition to the previous reasoning, the change in the magnetic susceptibility of Cornstarch No. 10 upon alcohol extraction may also be attributed to a change in the diamagnetic properties of the starch. Such a phenomenon is not uncommon and represents the major difficulty in applying Pascal's atomic magnetic increments. In accordance with the theoretical considerations previously presented concerning the nature of diamagnetism, any factor capable of altering the orbital motion of an electron would in effect alter the diamagnetic susceptibility of the substance. However, reasonable consistent values can usually be obtained except in certain cases. Among other causes, the incidence of hydrogen bonding and ring formation appear to be



especially significant factors in causing deviations from theoretical values. As an example of possible deviations which were attributed to these causes, Angus and Hill (1) record different molar susceptibility values for benzoic acid from a minimum of  $-43.2 \times 10^{-8}$  cgsu. to a maximum of  $-72.0 \times 10^{-8}$  cgsu. depending on whether ethyl acetate or benzene was used as a solvent. For different concentrations of benzoic acid in benzene, values from  $-65.0 \times 10^{-8}$  cgsu. to  $-72.0 \times 10^{-8}$  cgsu. are reported. These values compare with  $-57.9 \times 10^{-8}$  cgsu. for solid benzoic acid. Similar data was presented for various other compounds. Inasmuch as starch is known to contain extensive hydrogen bonding and since such constitutional factors may cause either an increase or decrease in magnetic susceptibility, it is reasonably permissible to attribute the decrease in diamagnetism noted in Table 11 to such constitutional factors. Similarly, it would have been permissible to explain an increase in magnetic susceptibility to such causes had an increase occurred.

During a typical starch-alcohol extraction procedure, it is known that fatty acids, etc., are removed from the starch. In addition, it may be difficult to remove the final traces of solvent. Accordingly, it may be reasoned that the differences in the magnetic susceptibility noted in Cornstarch No. 10 upon solvent extraction were due to such extraneous causes. However, it is believed that the differences due to these causes would be negligible except in those cases where a paramagnetic or a ferromagnetic substance were being removed from or added to the starch.

Inasmuch as the data does not indicate the removal of such a substance and since special precautions were taken to prevent contamination by such a substance, the decrease in diamagnetism resulting from such causes will be considered only as a possibility but not a probability in the data under discussion.

The fourth possible explanation for the decrease in the diamagnetism of Cornstarch No. 10 upon extraction with purified hot methanol would attribute the observed decrease as the summation of changes due to the three causes immediately previously considered. This may be expressed by the notation:

$$\Delta X_{\text{Observed}} = \Delta X_{\text{par.}} \pm \Delta X_{\text{diamag.}} \pm \Delta X_{\text{extraneous}} \quad (11)$$

where  $\Delta X_{\text{Observed}}$  is the observed difference in susceptibility and  $\Delta X_{\text{par.}}$ ,  $\Delta X_{\text{diamag.}}$ , and  $\Delta X_{\text{extraneous}}$ , are the changes due to paramagnetic, diamagnetic, and extraneous contributions. The sign associated with each contribution indicates the direction of change possible by each factor concerned. It is apparent that the explanation for an observed change in susceptibility noted in Equation 11 is more general than either of the three previously considered and that in the limiting cases it may become identical with any one of the three. It is further apparent, that in order to establish an incidence of free radicals as a functional unit of a modified starch, it will be necessary to establish the existence of a  $\Delta X_{\text{par.}}$  contribution in an experimental sample. It is believed that the data of Table

11 neither justifies nor denies the existence of such a contribution.

As an example of the difficulty involved in attempting to interpret the data of Table 11, it was previously shown that a decrease in diamagnetism of  $6.04 \times 10^{-8}$  cgsu. would require approximately one additional free radical for each 130 glucose units in the extracted starch as compared with the native starch. If it is arbitrarily assumed that there was a 10 per cent increase in free radicals as the result of alcohol extraction, one free radical would be required in the native starch for each thirteen glucose units. This appears to be a relatively high incidence of free radicals. At least such a high incidence would seem to require a greater deviation from Pascal's theoretical diamagnetic values for atomic increments for the starch. Actually, there is a remarkable agreement between the  $-88.35 \times 10^{-6}$  cgsu. per glucose unit obtained using Pascal's values and the  $-93. \times 10^{-6}$  cgsu. per glucose unit obtained experimentally for native Cornstarch No. 10. The agreement is not as satisfactory for the other starches listed in Table 12, but even the extreme case of pink kafir shows  $-69. \times 10^{-6}$  cgsu. which is in fair agreement with theoretical values.

At this point, it must be admitted that there is no logical reason to assume a ten per cent increase in free radicals except that such an increase appears to be more reasonable than does a thousand per cent increase. In actual fact, the exact per cent increase appears to have little significance in the present

discussion since an incidence of one free radical for each 130 glucose units required by the observed change in susceptibility also appears to indicate a higher than expected incidence. The important conclusion which appears to be necessary at this time is that the observed difference in the magnetic susceptibility of Cornstarch No. 10 recorded in Table 11 could not have been due entirely to an increased incidence of free radicals in the extracted starch. Accordingly, the change in magnetic susceptibility represented by  $\Delta X_{\text{diamag.}}$  and  $\Delta X_{\text{ext.}}$  of Equation 11 is not equal to zero and  $\Delta X_{\text{Observed}}$  does not represent the limiting case which consists only of a paramagnetic contribution. Since only the value of  $\Delta X_{\text{Observed}}$  is known, it is impossible to either deny or establish the existence of a  $\Delta X_{\text{par.}}$  contribution using Equation 11 unless it is possible to evaluate the change in susceptibility due to diamagnetic and extraneous changes. A method for evaluating a paramagnetic contribution independent of diamagnetic and extraneous contributions will be presented in a subsequent section of this thesis. However, this method would require data unobtainable at the present time so that for the purposes of the present discussion it will be considered that  $\Delta X_{\text{par.}}$  cannot be evaluated.

The dilemma of interpreting an observed change in susceptibility may be readily illustrated. Even though the effect of methanol on the hydrogen bonding of starch was not determined, it may be assumed for purposes of the present discussion that methanol extraction of starch increases the extent of such bonding.

At the present time, both an increase and a decrease in diamagnetism has been attributed to the existence of hydrogen bonding. In addition, it was previously shown that the magnitude of a paramagnetic contribution in an observed change in the susceptibility of starch would be small. However, a change in the diamagnetic susceptibility of a substance amounting to as much as fifty per cent of the originally measured value would not be considered unreasonable. The decrease in diamagnetism noted in Table 11 for Cornstarch No. 10, consequently, may be attributed entirely or partially to the decrease in susceptibility resulting from additional hydrogen bonding in the starch and the conclusion regarding the presence or absence of a paramagnetic contribution would depend on the view taken. However, neither view can be entirely justified on the basis of experimental evidence of accepted concepts. As a result, it would be impossible to justify an existence or absence of a paramagnetic contribution in the observed difference for Cornstarch No. 10.

Actually, the dilemma mentioned in the preceding paragraph represents a simplification of the actual interpretation required. Actually, an increase in diamagnetism could also have been attributed to a change in magnetic susceptibility due to hydrogen bonding, inasmuch as the conditions under which hydrogen bonding may increase or decrease magnetic susceptibility are not known. It is readily apparent that a consideration of additional factors such as ring formation, structural changes, etc., which may influence magnetic susceptibility values, would further



complicate the evaluation of magnetic susceptibility changes which may be due to these causes.

It was previously stated that an incidence of one free radical per each thirteen glucose units appeared to be a high incidence for these free radicals in native starch. From this premise, it was concluded that paramagnetic contributions in an observed change in magnetic susceptibility would be small if present and that these contributions could not be detected in the presence of possible larger diamagnetic changes. It was also stated previously that the alkali consuming group in starch might possibly be a free radical and that it would not be unreasonable to assume a relationship between the consumption of alkali and the incidence of free radicals. As a result, it may be argued that the previous conclusions concerning the interpretation of observed changes in susceptibility are not valid since an alkali number of 10 for a starch would represent one free radical for approximately each 6.2 glucose units and represent a specific susceptibility of approximately  $1.26 \times 10^{-6}$  cgsu. Similarly, if it were possible to change the alkali number of a given starch from 10 to 11, the difference in alkali number would represent an increase of one free radical for each .62 glucose units present in the starch and would represent a change in specific susceptibility of  $12.57 \times 10^{-8}$  cgsu. A change in the alkali number of a given starch from 10 to 11 is reasonably possible. Since the magnitude of the susceptibility which is represented by such a reasonable change in alkali number is

comparatively large and almost twice the value of the observed difference in susceptibility noted for Cornstarch No. 10 in Table 11, it may be concluded the observed change in susceptibility noted for Cornstarch No.10 could have been due entirely to a change in the paramagnetic contribution.

However, it is believed that the conclusions of the preceding paragraph are not valid. It is the characteristic of magnetic susceptibility measurements to give a measure of properties during the instantaneous period during which the measurement is taken. In contrast, alkali number is a cumulative measurement of the alkali consumed during a finite interval of time. As a result, there would be a relationship between alkali number and magnetic susceptibility only with respect to the initial attack of the alkali (which is impossible to measure using procedures similar to those used in determining alkali number) and the rate of consumption of alkali. Further, in order to correlate the rate of consumption of alkali with magnetic susceptibility, it would be necessary to use a time interval comparable with the length of life of the free radical postulated for the pasting process. Although the length of life of such a free radical is not known, it is assumed that it would be short. This view is somewhat substantiated by preliminary experiments which did not appear to show a change in susceptibility during a pasting process. However, inherent difficulties in the procedure do not permit a definite conclusion to that effect. In any event, the total alkali number does not appear to give a true measure of

free radicals actually existing at a given moment. Further, it can be shown that if it is assumed that alkali consumption is a linear function of time, and that if the life of the free radical chain assumed during pasting is even as long as one second, it would be virtually impossible to detect these free radicals with the apparatus used. The amount of alkali consumed during the initial attack is not known but it must be assumed to be small. Consequently, it is believed that the original conclusions, indicating at best that only a small paramagnetic contribution can be present in an observed change in the magnetic susceptibility of starch are valid.

In the immediately previous sections, it was shown that it would not be possible to demonstrate a paramagnetic contribution in an observed change in the magnetic susceptibility of starch using the apparatus and techniques utilized during the current series of experiments. However, perhaps it should be pointed out at this time that it is not absolutely necessary to establish the existence of such a contribution in an observed change in susceptibility in order to establish the existence of free radicals in starch, since a paramagnetic contribution in the total measured susceptibility may be considered to be sufficient for such a purpose. However, the difficulties inherent in establishing a paramagnetic contribution in the total measured susceptibility would be similar to those inherent in establishing a paramagnetic contribution in an observed change. Accordingly, it is believed that the reasoning followed in the preceding paragraphs in the

interpretation of changes in magnetic susceptibilities, would also be applicable to the general case of the magnetic susceptibilities themselves.

In summary, it is believed that the magnetic susceptibility data submitted by Walker and that obtained in the current series of experiments are inadequate to serve as a basis for any interpretation regarding the presence or absence of odd electrons or free radicals existing as a functional unit in starch. Further, it is believed that this inadequacy is due to certain difficulties inherent in the method of obtaining the susceptibility data and that each of these difficulties must be eliminated or at least considered when obtaining susceptibility data in the future.

The first of these difficulties is the presence of external interferences which give unreliable susceptibility data. The contamination of the starch samples caused by reagents possibly can be avoided through the use of proper techniques. This type of contamination was previously considered. However, certain impurities were not considered. These impurities are the trace elements generally present in all starches to a greater or lesser extent. The presence of these impurities affects the actual magnetic susceptibility measured. Most of the impurities present will affect the measured susceptibility only slightly or suitable corrections can be made. However, the presence of traces of iron may or may not be a significant factor in the measured susceptibility depending on the form in which the iron is present.

In addition, it is difficult to allow a correction for iron inasmuch as it is not possible to determine the state of the iron present in natural starches.

The second factor causing the existing magnetic susceptibility data for starch to be of little value in establishing an incidence of free radicals within the starch granule are the presence of internal complicating factors. It is possible to obtain a rough approximation for the diamagnetic susceptibility of a hypothetical glucose unit by using Pascal's diamagnetic values for atomic increments. The diamagnetic susceptibility of such a glucose unit is calculated to be  $-88.35 \times 10^{-6}$  cgsu. However, it is difficult to apply this value. For instance, the molar susceptibility actually measured for glucose is  $-61.38 \times 10^{-6}$  cgsu. which can be corrected to  $-52.16 \times 10^{-6}$  cgsu. as the repeating glucose unit in starch. Further, the molar susceptibility of an extracted cornstarch as reported in Table 12 is  $-87. \times 10^{-6}$  cgsu. An analysis of these data would indicate that the glucose units of starch resemble the hypothetical glucose unit more than does glucose itself. This conclusion is unreasonable but illustrates the difficulties involved in establishing a standard for comparison of magnetic susceptibility data. At the present time, sufficient knowledge is not available to correct for deviations from Pascal's values.

The third factor causing the magnetic susceptibility data for starch, which thus far have been obtained, to be of little value is the limits of accuracy of the Gouy apparatus used.

Michaelis claims an accuracy of  $\pm 2$  per cent for the Gouy



apparatus used in his laboratory. However, his instrument used a scale with 200 lines with each line representing 0.01 mg. The scale and balance used in the Gouy apparatus of this laboratory contained 80 lines with each line representing approximately 0.04 mg. Accordingly, the degree of error of the apparatus used in this laboratory under ordinary conditions is not less than 5 per cent. The limitations of the instrument used may be illustrated if it is assumed that one free radical exists for each one thousand glucose units. These free radicals would manifest themselves only as approximately  $0.8 \times 10^{-8}$  cgsu. in terms of specific susceptibility of starch, or approximately 1.5 per cent of the magnitude of the measured diamagnetic susceptibility. In terms of scale deflections of the Gouy apparatus used in the current series of experiments,  $0.8 \times 10^{-8}$  cgsu. would manifest itself as a deflection of only approximately 0.4 line at an electromagnet current of 3.5 amperes. In general, a series of readings are considered reliable if they are within one line of each other.

In addition to the sensitivity of the balance, the accuracy of the Gouy apparatus is determined somewhat by the density of the substance being measured. It so happens that the density of starch is such that the accuracy of the instrument is diminished as compared to the accuracy of the instrument when it is used to measure the susceptibility of a high density substance. In any event, it is believed that the overall accuracy of the instrument is not sufficient to detect a low incidence of free

radicals in the presence of additional complicating factors.

In order to apply magnetic susceptibility data to establish the existence of free radicals within the starch granule, each of the three factors previously discussed must be corrected for or considered. A method has been shown in Fig. 3 which makes it possible to correct for contamination by ferromagnetic iron. Further, it may be possible to assume that all trace iron in starch is present in a particular oxidation state and thus make it possible to apply an appropriate correction. However, the application of these would require further study. At the present time, there appears to be no way to correct for constitutional changes. With regard to the instrument used to determine susceptibility measurements, it is admitted generally that the advantage of the method of Gouy lies in its convenience rather than its accuracy. Accordingly, the use of an instrument where convenience is sacrificed for the advantage of accuracy might perhaps provide data of sufficient accuracy to detect a certain postulated minimum of odd electrons. This aspect would likewise require additional study.

#### SUGGESTIONS FOR FURTHER STUDY

It has been previously implied that direct magnetic susceptibility measurements cannot be used as a criterion to positively establish the existence of free radicals as a functional unit of the starch granule. One of the principal factors limiting the interpretation of such data was the presence of an

interfering diamagnetic contribution in the measured susceptibility. However, from theoretical considerations, it is possible to postulate the following indirect method for establishing the existence of free radicals in starch quantitatively utilizing the temperature effect of paramagnetism.

Figure 5 represents published data (26) showing the variation of the molar susceptibility with temperature of a paramagnetic substance containing one odd electron per molecule. From the characteristics of the data, it is believed that a correction has been made for the diamagnetic contribution of the molecule so that the susceptibility values shown are a measure of the effective magnetic moment due to an odd electron at a given temperature. At  $23^{\circ}$  C. ( $296^{\circ}$  K) the molar susceptibility for a substance containing one odd electron per molecule would be  $1257 \times 10^{-6}$  cgsu. and at  $-129^{\circ}$  C. ( $144^{\circ}$  K) the susceptibility for such a substance would be  $2514 \times 10^{-6}$  cgsu. It is readily apparent that the difference in susceptibility between these two temperatures is  $1257 \times 10^{-6}$  cgsu and would represent a quantitative measure of the susceptibility at the higher temperature. In this instance, the two temperatures were purposely selected to illustrate this quantitative relationship. However, an appropriate quantitative relationship would exist in the difference in susceptibility between any two temperatures.

The application of this method to starch is readily apparent. From theoretical considerations, it would be expected that true free radicals in starch would represent a temperature

dependence identical to that illustrated in Fig. 5 and that the difference in the molar susceptibility of starch between two temperatures could be compared with the difference in susceptibility between the same two temperatures using Fig. 5. For the temperature interval  $-129^{\circ}$  C. and  $23^{\circ}$  C., the observed difference in susceptibility per glucose unit divided by  $1.257 \times 10^{-6}$  would represent the incidence of odd elections per glucose unit. Even though the measured susceptibilities for starch would contain a diamagnetic contribution in contrast to the data presented in Fig. 5, the difference in measured susceptibilities at two different temperatures would still represent only paramagnetic contributions, inasmuch as diamagnetism is not affected by temperature.

It is believed that this method represents a more advantageous method in establishing a positive existence of free radicals in starch than do direct susceptibility measurements or the use of the anisotropic properties postulated by Walker. However, the application of this procedure would require further study from a practical standpoint in view of certain technical and theoretical limitations. It is, perhaps, beyond the scope of this thesis to discuss the technical difficulties of low temperature magnetic susceptibility measurements except to mention that the techniques are fairly well established. Consequently, even though the Gouy apparatus used during the current series of experiments is not suitable for modification to low temperature techniques, it is believed that a suitable apparatus and procedure

VARIATION OF PARAMAGNETIC SUSCEPTIBILITY WITH TEMPERATURE  
(One odd electron per molecule)

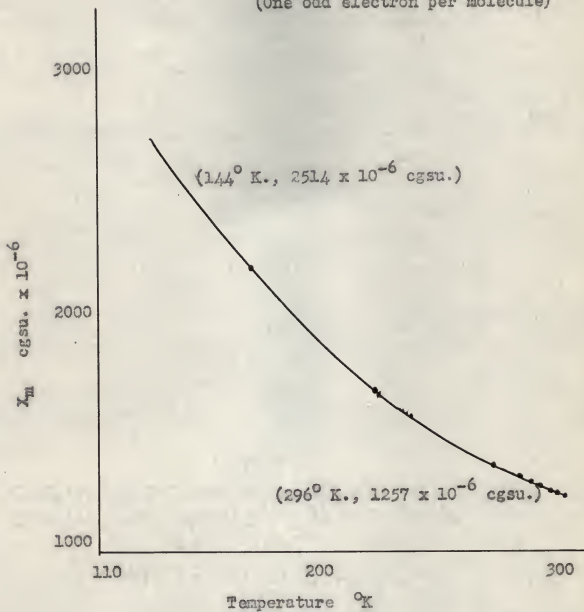


Fig. 5



can be made available. However, certain theoretical limitations should probably be discussed.

The first theoretical limitation which should be considered in utilizing temperature difference susceptibility measurements for the detection of free radicals is the diamagnetic contribution of molecules. The conclusions of the temperature difference method discussed above are based on the assumption that the diamagnetic contribution of a substance is constant at all temperatures. This assumption is valid from theoretical considerations for an ideal substance which does not undergo a structural change during the temperature interval. If such a structural change does occur, then the measured difference in susceptibility could not necessarily be contributed to a change in paramagnetism. There is very little reason to suspect that starch would undergo such a change during the short time interval required for a susceptibility measurement at a low temperature. However, this suspicion should probably be verified through the use of suitable tests.

A second theoretical limitation is found in the magnitude of the difference in susceptibility which may be expected over a temperature interval. It can be shown that if an instrument similar in sensitivity to the one used during the current series of experiments is used, a difference in susceptibility between  $-129^{\circ}$  C. and  $23^{\circ}$  C. for starch containing one odd electron per glucose unit would be manifested as 200 lines on the balance. It is apparent that for a starch containing one odd electron for

each one thousand glucose units, the deflection would be 0.2 lines. This difference would probably not be detected. The magnitude of the deflection difference may be increased by utilizing a more sensitive apparatus or greater temperature differences. However, the magnitude of the difference which may be achieved would require further study.

In addition, various other limitations such as the existence of paramagnetic impurities, trace elements, etc., should also be given consideration. In general, these limitations can be considered with respect to obtaining a chemically pure starch suitable for magnetic susceptibility measurements. The method of obtaining such a starch would likewise require further study.

#### CONCLUSIONS

On the basis of the experimental data furnished and the discussion presented, the following conclusions are made:

1. The magnetic susceptibility of starch data presented by Walker in his Master's Thesis are unreliable as an indication of the existence of free radicals as a functional unit within the starch granule in view of the possible contamination of the starch samples used with paramagnetic and ferromagnetic impurities.
2. The anisotropic properties which were attributed to free radicals by Walker, are not true properties of free radicals. However, the phenomenon described by Walker may be explained by assuming the presence of a ferromagnetic impurity in the starch

samples used for certain magnetic susceptibility measurements. Accordingly, it is postulated that certain starch samples used by Walker may have contained ferromagnetic impurities.

3. The decrease in the diamagnetism of a starch sample upon exposure to a magnetic field is not a true property of the type of free radicals postulated as a functional unit in the starch granule and it is not a true property of diamagnetism. However, the decrease in magnetism described by Walker can be explained by assuming the presence of a ferromagnetic impurity in certain starch samples used for magnetic susceptibility measurements. Accordingly, it is postulated that certain starch samples used by Walker may have contained ferromagnetic impurities.

4. The magnetic susceptibility data obtained during the present series of experiments are inadequate to establish the existence of free radicals within the starch granule.

5. The magnetic susceptibility data obtained during the present series of experiments and that presented by Walker are inadequate to deny the existence of free radicals within the starch granule.

In addition to the evidence leading to the above conclusions, this thesis presents a method for the estimation of the susceptibility due to the presence of a ferromagnetic impurity in a substance and a method for correcting for such an impurity, as well as a possible method for the detection of free radicals using the temperature dependence property of paramagnetism.

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## APPENDIX

One of the factors affecting the validity of some of the conclusions of this thesis is the validity of certain calculations which were presented. It is, perhaps, unnecessary to justify each of the calculations presented. In lieu of such justification, an illustration of the method used during these calculations will be presented.

Figure 5 shows that the susceptibility for one odd electron per molecule per mole of substance is  $1257 \times 10^{-6}$  cgsu. at  $23^{\circ}$  C. This value was accepted as the standard molar susceptibility at room temperature for one unpaired electron. However, the actual measurement of susceptibility in the Gouy apparatus is that of volume susceptibility. Therefore, it is necessary to convert molar susceptibility into volume susceptibility. In order to calculate such a volume susceptibility, a starch containing one unpaired electron for each glucose unit was postulated. Accordingly, for such a substance, the specific paramagnetic susceptibility would be  $(1257 \times 10^{-6} \text{ cgsu.}) / (\text{molecular weight}) = (1257 \times 10^{-6}) / (162) = 7.8 \times 10^{-6}$  cgsu. This susceptibility may be defined as the specific paramagnetic susceptibility to differentiate from a similar value pertaining to diamagnetic susceptibility which will be calculated later. In order to convert this value into volume susceptibility, it is necessary to multiply the specific susceptibility by the apparent density of the starch. Even though the apparent density of starch is variable, for purposes of approximation a value of  $0.9 \text{ gm/cm}^2$  would give sufficiently

accurate values. Accordingly, the volume paramagnetic susceptibility of a starch containing one odd electron per glucose unit would be the specific paramagnetic susceptibility multiplied by the density or  $(7.8 \times 10^{-6} \text{ cgsu})(0.9) = 7. \times 10^{-6} \text{ cgsu/cm}^3$ .

In order to determine the extent to which the above calculated volume paramagnetic susceptibility would be manifested on the Gouy apparatus, it is necessary to take the characteristics of the instrument into consideration. These characteristics are essentially included in the calibration of the vessel constant. Even though several Gouy vessels were used during the current series of experiments, a vessel constant of  $3. \times 10^{-8} \text{ cgsu/line}$  at an electromagnet current of 3 amperes would serve as a suitable approximation. Accordingly, a volume susceptibility of  $7. \times 10^{-6} \text{ cgsu.}$  would be manifested on the apparatus as  $(7. \times 10^{-6}) / (3. \times 10^{-8}) = 233 \text{ lines.}$

The above calculation was recorded on page 68 of this thesis as "a difference in susceptibility between  $-129^{\circ} \text{ C.}$  and  $23^{\circ} \text{ C.}$  for a starch containing one odd electron per glucose unit would be manifested as 200 lines on the balance". In this instance, the temperature interval was purposely selected to represent the magnetic susceptibility at room temperature.

In certain calculations it was necessary to include a diamagnetic contribution for the starch. This contribution was estimated through the use of Pascal's atomic increments to magnetic susceptibility. For a glucose unit, the molar diamagnetic



contribution would be:

$$\begin{array}{rcl}
 10 \text{ H} & = & (10)(-2.93) = -29.30 \times 10^{-6} \text{ cgsu.} \\
 5 \text{ O} & = & (5)(-4.61) = -23.05 \\
 6 \text{ C} & = & (6)(6.00) = -36.00 \\
 & & \text{Total} = \underline{-88.35 \times 10^{-6}}
 \end{array}$$

This molar diamagnetic susceptibility may be converted into specific and volume susceptibility using the procedure previously outlined for the paramagnetic contribution. These values will be  $-5.5 \times 10^{-7}$  and  $5. \times 10^{-8}$  cgsu. for the specific and volume diamagnetic contributions, respectively.

Using these theoretical values, it is believed that their application in obtaining calculated values throughout this thesis is readily apparent.

THE MAGNETIC SUSCEPTIBILITY  
OF STARCH

By

JOHN APOLLINARIS WRONKA

B. S., Saint Louis University, 1948

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AN ABSTRACT OF A THESIS

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The tendency of electrons to go in pairs is almost universal so that only a relatively few molecules containing unpaired electrons are known. A "free radical" is generally defined as any molecule containing such an unpaired electron. However, in organic chemistry the meaning of the term "free radical" is generally restricted to those structures containing an unpaired electron in the valence shell of the atom and these radicals are considered to be of special significance in the interpretation of molecular structure.

From a consideration of certain properties of starch such as alkali number; catalysis in the addition of chlorine to benzene, decomposition of acrylonitrile, and the polymerization of styrene; and the characteristics of certain induction products formed during the chlorination of starch in liquid chlorine; an actual incidence of free radicals or a structure which may become a free radical during the course of a chemical reaction may be postulated for starch. One of the physical methods which may be used to verify the existence of free radicals is that of magnetic susceptibility measurements. Walker, in a Master's Thesis, attempted to verify the existence of free radicals in starch using such magnetic susceptibility measurements. The present series of experiments was undertaken to test, and, if possible, to confirm and expand the conclusions of Walker.

Although Walker presented paramagnetic values for certain starches which would have indicated an existence of free radicals, similar data obtained during the current series of experiments

were shown to be due to the presence of ferromagnetic impurities.

In addition, it was shown that the magnitude of the paramagnetic values presented by Walker as well as certain properties such as free radical anisotropy which were described could not be considered reasonable from the standpoint of theoretical considerations. As a result, it was concluded that the data presented by Walker could not be used as a valid justification for the establishment of an actual incidence of free radicals in starch.

In an attempt to obtain additional data for use in an attempt to establish the existence of free radicals in starch, it was shown that changes in magnetic susceptibility could be achieved in starch. However, the presence of complicating factors made an interpretation of these changes as well as the interpretation of the total measured susceptibility not possible. Further, it was concluded that the limitations inherent in the procedure used and the data obtained would have limited the interpretation of any data which would be obtained.

In lieu of direct magnetic susceptibility measurements, a method utilizing the temperature effect of paramagnetism was suggested as a possible means by which suitable data might be obtained to verify an existence of free radicals in starch. However, this procedure would require equipment which is unavailable in this laboratory at the present time.

In summary, it was concluded that the available data neither confirm nor deny the existence of free radicals in starch. In addition, methods were presented for the estimation of ferro-

magnetic contributions in magnetic susceptibility measurements and the detection of free radicals using the temperature effect of paramagnetism.