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# SORPTION OF GASES AND VAPOURS ON FLOUR, STARCH AND GLUTEN

## A thesis

submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the Degree of Doctor of Philosophy

by

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#### PREFACE

The effect of water on wheat flour appears to be unique in its ability to bring about the important phenomenon of doughing upon which most of the uses of this cereal product depend. The question that immediately arises is whether the interaction of flour particles with water to form the colloidal system referred to as dough involves the formation of chemical bonds, either covalent or electrovalent, or whether the interparticle linkages consist of physical bonds caused by van der Waals attractive forces. Opinions seem to be divided on this question, but it would seem that both physical and chemical bonds, including the hydrogen bond, are formed to some extent during dough formation (1,2). However, most of the theories concerned with the nature of the linkages in flour-water doughs have little direct experimental basis.

Many of the properties of solid surfaces, such as adhesion, are extremely sensitive to the type of material adsorbed on the surface. Accordingly, before the adhesion of solid particles can be understood it is necessary to have some knowledge of the nature of any adsorbed film that might be present. This is particularly true if, as with flour in the doughing process, the adhesion requires the presence of some other material such as water.

It was with this viewpoint that the present studies of the sorption of various vapours on wheat flour and its two main components, starch and gluten were initiated using a high vacuum technique in conjunction with a McBain-Bakr sorption balance. A survey of the literature showed that a similar technique was used in only one investigation of the sorption of water vapour on wheat and wheat flour at one temperature (25°C). The sorption of water vapour was of primary concern, but sorption of some alcohol vapours was also studied, since alcohols may be regarded as structurally related to water, although they do not form flour doughs such as those produced with water. Carbon tetrachloride was included in the sorption studies as an example of a completely symmetrical, non-polar molecule, and sorption studies with ammonia were made because of the similarity in properties between liquid ammonia and water. In addition to the sorption studies, a number of qualitative experiments were made with a variety of liquids to obtain, if possible, some information about three dimensional network formation in flour doughs.

Since the major part of the thesis is concerned with sorption studies, it is necessary for reference purposes, to review briefly the developments in the general field of adsorption by solids, and subsequently to consider specifically some of the more important sorption studies that have been made with flour and related materials.

#### INTRODUCTION

#### ADSORPTION OF GASES ON SOLIDS

Whenever an evacuated solid is exposed to a gas some of the gas is taken up by the solid. If the gas molecules adhere to the surface of the solid they are generally considered to be adsorbed. If the gas molecules enter the solid the term absorption is generally applied, although the less popular term, occlusion has occasionally been used. The term imbibition is still commonly used when solids swell on taking up the gas. In 1909 McBain (3) suggested the use of the term sorption when both adsorption and absorption occur simultaneously and the two processes become indistinguishable. The solid which takes up the gas is called the adsorbent (sorbent) and the gas which is taken up is called the adsorbate (sorbate). The term sorption will be used in this thesis to indicate the overall interaction of vapour or gas with the sorbent. Adsorption will refer to the equilibrium if it is attained by taking up vapour and desorption if equilibrium is attained by loss of vapour.

Two interactions are possible for both absorbed and adsorbed gases. An absorbed gas may dissolve in the solid to form a solid solution or it may react to form a definite chemical compound e.g. a hydrate. On the other hand, an adsorbed gas may be attached to the surface by relatively small

forces comparable in magnitude to those between the molecules in a condensed liquid, or by relatively strong forces similar to those involved in formation of chemical bonds. The former type of surface interaction is generally called physical or van der Waals adsorption and the latter is known as chemical adsorption (chemisorption) or activated adsorption. The term activated adsorption was introduced by Taylor (4) to include processes with definite activation energies that occur on solid surfaces.

Physical adsorption is usually non-specific; all solids adsorb all gases to some extent. Chemisorption, on the other hand, occurs only in specific adsorbent-adsorbate systems. The most reliable way to distinguish between the two is by measurements of the heat of adsorption. Physical adsorption is accompanied by heats of adsorption of the same order of magnitude as the heats of condensation of the adsorbate vapour whereas heats of chemisorption are considerably higher and approximate to heats of chemical reactions. Chemisorption generally occurs at high temperatures whereas physical adsorption occurs most readily at low temperatures. Also, the rate of adsorption may be used as a criterion of the type of mechanism involved. Physical adsorption occurs almost instantaneously, if diffusion is not rate controlling, whereas chemisorption is a comparatively slow process that obeys the

normal laws of chemical kinetics.

The amount of gas or vapour adsorbed when equilibrium is established depends on a number of factors, the most important of which are temperature, pressure, and the physical and chemical properties of the adsorbent and the adsorbate. Hence, for a given system, the amount of gas adsorbed at equilibrium is a function of pressure and temperature only, that is

$$X = f(T, P) \qquad \dots (1)$$

where X is the amount adsorbed per gram of adsorbent, usually expressed in milligrams or millimoles, T is the temperature, and P is the equilibrium pressure.

The most common experimental procedure is to measure the amount of gas adsorbed at various pressures under isothermal conditions, from which an isotherm is obtained as a plot of the amount adsorbed against the equilibrium pressure. If the isotherm is obtained by increasing the pressure of the gas after equilibrium has been established at some lower pressure it is convenient to call it the adsorption isotherm, and if the curve is obtained by decreasing the pressure after equilibrium has been established at some higher pressure it

may be called a desorption isotherm. The adsorption and the desorption branches of the isotherm may or may not coincide. With the readily condensable vapours, it has been found more convenient to plot the amount adsorbed against the relative pressure rather than the absolute pressure. This gives isotherms which are more strictly comparable for a series of adsorbates. A number of the more common, explicit forms of the isotherm functions will be discussed later.

Adsorption data may also be expressed by isobars and isosteres. Isobars show the variation of the amount adsorbed with temperature at constant pressure and isosteres show the variation of equilibrium pressure with temperature for a definite amount of gas adsorbed. Adsorption isosteres are of particular interest since they may be used to determine heats of adsorption.

### Heats of Adsorption

It is generally found that whenever a solid adsorbs a gas, heat is evolved, i.e. the adsorption process is always exothermic. Conversely, the desorption process is always endothermic. The magnitude of the heat of adsorption is usually an indication of the affinity between the particular adsorbent and adsorbate.

Experimentally, heats of adsorption may be determined directly by calorimetry or indirectly from adsorption isosteres.

Both the integral and the differential heats of adsorption may be obtained calorimetrically, whereas the indirect method gives only the differential heats of adsorption.

The integral heat of adsorption is the total heat evolved, usually expressed in calories per gram of adsorbent for adsorption of a definite amount of gas. The differential heat of adsorption is simply the derivative of the integral heat with respect to amount of adsorbate. Hence, it is equal to the slope of the curve obtained when the integral heat is plotted against the amount adsorbed. It is usually expressed in calories per gram (or per mole) of adsorbate.

It can be shown by a mathematical treatment similar to that given by Brunauer (5) that the differential heat of adsorption is related to the thermodynamic isosteric heat of adsorption by the equation

 $Q_{isosteric} = Q_{diff.} + RT$  ....(2)

and, since the value of RT usually does not amount to more than the experimental error in the isosteric heat, it is generally set equal to the differential heat of adsorption. The manner in which isosteric heats can be obtained from adsorption data, by using an equation analogous to the familiar Clausius-Clapeyron equation, will be discussed later.

#### Theories of Adsorption

A number of the more popular adsorption theories which have been proposed deserve brief mention. A more detailed discussion may be found in standard textbooks on the subject (5,6,7).

Essentially, the theories attempt to develop mathematical equations to represent the adsorption isotherm. For an isotherm equation to have any practical as well as theoretical significance, it should fit the isotherm over a reasonable pressure range, and the values of various constants in the equation should agree with values that can be obtained for the same constants by other experimental techniques. Most of the equations that have been proposed are only partially successful in accomplishing these purposes.

#### The Freundlich Isotherm

For historical and practical reasons, mention may first be made of the empirical Freundlich equation (8). If x is the amount adsorbed per gram of adsorbent, the Freundlich Isotherm may be expressed by the equations

$$x = ap \qquad or \log x = n^{-1} \log p + \log a \qquad \dots (3)$$

where a and n are characteristic constants and p is the

equilibrium pressure. In practice, it has been found that over a narrow range of pressures the Freundlich equation satisfies the experimental data in a large number of cases.

#### Langmuir Theory

Langmuir (9) advanced a theory that probably represents the first theoretical approach to adsorption. According to this theory, adsorption is a direct result of a time-lag between condensation and evaporation of a molecule that strikes the surface. For a given temperature and pressure, the amount of adsorption depends on the intensity of the force field surrounding the solid. Langmuir regarded this theory as a "chemical theory" in the sense that the adsorbed layer was considered to be held by forces of the same kind as those responsible for cohesion of the adsorbent.

The isotherm equation proposed by Langmuir may be expressed in the form

$$x = \underline{abp} \dots (4)$$

where x is the amount adsorbed, p is the equilibrium pressure and, a and b are characteristic constants which can be derived from kinetic theory.

Hermans (10) pointed out that the theory underlying

equation (4) implies two conditions; (1) that the adsorption sites are localized, are of equal energy and act independently; and (ii) that the adsorbed layer is only one molecule thick. He derived a similar equation to include the binding energy, E, and the entropy of adsorption,

$$\frac{n}{N} = \frac{cp \exp(E/RT)}{1 + cp \exp(E/RT)} \qquad \dots (5)$$

where n is the number of occupied sites, N is the total number of adsorption sites available and c is a constant at a given temperature. The parameter  $c \exp(E/RT)$  which is equivalent to b in equation (4) can be taken as an indication of the affinity between adsorbent and adsorbate since it includes both the enthalpy and the entropy of adsorption.

The Langmuir isotherm can be represented schematically as an hyperbola, the curvature of which is concave to the pressure axis. This implies a positive heat effect on the basis of equation (5). From equation (5) it is possible to get some idea of what happens to the shape of the isotherm as the affinity decreases. For very low values of the parameter  $c \exp(E/RT)$  the isotherm is almost a straight line. The original Langmuir equation predicts a linear isotherm for very low pressures only. Therefore, the modifications advanced by Hermans extends the possibility of finding a linear isotherm over a much larger range of pressures. It may be of interest to point out that in the Langmuir theory, saturation (n/N = 1) is reached only at infinite pressures. Obviously then, this can never apply to systems which include condensable vapours up to their saturation pressure at temperatures below the critical temperature. Application of the Langmuir equation to such systems is therefore confined to the low pressure region.

#### The Capillary Condensation Theory

It has been known for some time that vapour pressure of a liquid over a meniscus in a capillary is lower than the normal vapour pressure by an amount equal to the pressure exerted by the column of liquid in the capillary. If the diameter r, of the capillary is known, the vapour pressure P, in the capillary is given by the Kelvin equation

$$P = P_0 \exp(-2V) / rRT$$
 ....(6)

where  $\delta$  is the surface tension of the liquid,  $P_0$  is the vapour pressure of a flat liquid surface, and V is the molar volume of the liquid. Equation (6) is based on the assumption that the liquid completely wets the walls of the capillary. Otherwise, the value of r must be corrected by multiplying it by the cosine of the contact angle.

On the basis of the Kelvin equation, Zsigmondy (11)

concluded that, in pores of very small diameter, vapour could condense at much lower pressures than the saturation pressure. If the diameter of the capillary is not uniform but varies continuously, the finest capillaries will be filled first and the coarser ones filled as the vapour pressure is increased.

If it can be assumed that equation (6) holds for very small pores, the normal values for molecular diameters suggest that a pore diameter of about 40Å is the smallest to which the concept of capillary condensation can be expected to apply. For this pore size the equation yields a value of 0.35 for the relative pressure of water at which capillary condensation may be expected at room temperature.

Another, more recent approach to the problem of capillary condensation, particularly in the region of high relative pressures where hysteresis is usually observed, takes account of both pore size and pore distribution. Some of the treatments are based on the original Kelvin equation, others on the Cohan equation (12) which will be given later.

Kistler (13) proposed a basic equation for capillary condensation

$$dA/dV = -\log (P/P_0) RT/M \delta$$
 ....(7)

where A is the pore size,

V is the pore volume,

P is the equilibrium pressure,

 $P_o$  is the saturation vapour pressure at temperature T, R is the gas constant,

M is the molecular weight of adsorbate, and

 $\delta$  is the surface tension of liquid adsorbate.

This equation gives the pore size distribution in the adsorbent. Equation (7) reduces to the Kelvin equation if it is applied to either cylindrical capillaries or spherical pores.

To obtain the pore volume distribution curve directly from the adsorption isotherm, Kubelka (14) proposed the plot of d(Va/Vt)/dlog D versus log D where Va is the volume adsorbed at a given pressure, Vt is the total volume adsorbed at saturation pressure, and D is the pore diameter calculated from the Kelvin equation for the relative pressure corresponding to Va. Schuchowitski (15) objected to this plot because it is based on theory which does not differentiate between physical adsorption and capillary condensation. Foster (16) pointed out that the plot was justifiable if it was applied only to the region where hysteresis occurred.

A number of interesting attempts have been made to integrate multilayer adsorption with capillary condensation. Shull (17) proposed a treatment in which he assumed that multilayer adsorption reduces the pore size by a definite

amount for any given pressure. This is essentially the basic assumption of the Cohan equation (13). A recent paper by Voigt and Tomlinson (18) gives a theoretical treatment covering the distribution of two types of pores, the cylindrical and the "ink bottle" types, on the basis of Maxwellian and Gaussian distribution laws. They found some agreement between the theoretical models and experimental results.

At present, most authors agree that capillary condensation is not important at low pressures, but its importance at higher pressures seems to be controversial. The greatest single triumph of the Capillary Condensation Theory is its ability to account for the hysteresis effect. Some of the explicit theories proposed to explain hysteresis will be discussed later.

#### The Brunauer, Emmett and Teller (BET) Theory

The BET Theory was the first attempt to provide a unified theory of physical adsorption. In the first paper, Brunauer, Emmett and Teller (19) developed an equation to cover the entire course of the adsorption isotherm including unimolecular and multimolecular adsorption. In the second paper, Brunauer and co-workers (20) classified the known isotherms into five general types and extended the isotherm equation developed in the first paper to include capillary condensation.

According to the BET Theory, adsorption is due to

totality of forces designated as van der Waals forces. These include the orientation effect of Keesom (21), the induction effect of Debye (22) and the dispersion effect of London (23). By applying much the same reasoning as Langmuir, Brunauer and co-workers were able to extend the Langmuir equation to include multimolecular adsorption. By assuming that the heats of adsorption in the second and the subsequent layers were equal to the heat of liquefaction, and by realizing that the resultant infinite series were convergent when adsorptions in different layers were added, they were able to derive the following equation to describe multimolecular adsorption

$$X = \frac{Xm \ c \ P}{(P_{o} \ -P) \ \{1 \ + \ (c \ -1)P/P_{o}\}} \qquad \dots (8)$$

where X is the amount of gas adsorbed per gram of adsorbent, Xm is the amount of gas required to cover one gram of the adsorbent with one monomolecular layer, P is the equilibrium pressure, P<sub>o</sub> is the saturation pressure, and c is a constant which is approximately given by

 $c = exp (E_1 - E_L)/RT$  ....(9)

where  $E_1$  is the average heat of adsorption for the first layer,

 $E_{r}$  is the heat of liquefaction of the gas,

R is the gas constant and,

T is the absolute temperature.

For experimental applications, equation (8) is generally put into a linear form

$$\frac{P}{X(P_{O} - P)} = \frac{1}{Xm c} + \frac{c - 1}{Xm c} \frac{P}{P_{O}} \qquad \dots (10)$$

Equation (10) shows that where the BET Equation applies, a plot of  $P/X(P_0 - P)$  against  $P/P_0$  should yield a straight line with 1/Xm c as intercept and (c - 1)/Xm c as the slope. This plot gives a method for obtaining the two constants Xm and c from experimental data. By estimating the surface occupied by a single adsorbate molecule, it is possible to calculate the specific surface of the adsorbent from Xm and  $E_1$  may be calculated from equation (9). Since Xm and  $E_1$  can be obtained by other methods, these two constants provide a means of verifying the BET Theory.

Actually, the BET Equation given above includes the simplification that the number of adsorbed layers at saturation pressure is infinite. This is not always true. With some adsorbents the structure of the solid may limit the number of adsorbed layers to some value considerably less than infinity. To cover this situation equation (8) has to be modified to include an additional constant n, the number of adsorbed layers. If the maximum number of layers that can be adsorbed is n, then the summation of the series is carried to n terms only, and not infinity. The more accurate isotherm equation becomes

$$X = \frac{Xm c x}{1 - x} \frac{1 - (n + 1)x^{n} + nx^{n + 1}}{1 + (c - 1)x - cx^{n + 1}} \qquad \dots (11)$$

where  $x = P/P_0$  and Xm and c have the same significance as before. The value of n is obtained by trial and error after Xm and c have been determined using the range of pressures where equation (10) applies. If the adsorbed layer is monomolecular, the BET equation simplifies to the Langmuir equation.

In practice, it is found that equation (10) applies only in the relative pressure range from 0.05 to 0.35. Brunauer, Emmett and Teller ascribe the discrepancy below  $P/P_0 = 0.05$ to a highly heterogeneous surface, for which the approximation of an average heat of adsorption in the first layer does not hold. At relative pressures above approximately 0.35 two effects may cause deviation from equation (10). In the derivation of this equation it is assumed that adsorption occurs on a perfectly plane surface, but actual adsorbents may contain cracks and crevices which limit the number of layers that may be built up. Hence, at higher relative pressures, less gas is adsorbed than would be predicted by the BET theory. In addition, the approximation that the heat of adsorption in the second layer is equal to the heat of liquefaction is not altogether satisfactory. In this case, at relative pressures above 0.35, more gas is adsorbed than the BET theory would predict.

#### Phase-Change Theories of Adsorption

In the theories described so far, attention was focussed on the process of interchange of gas molecules between the gas phase and the adsorbed phase. Phase-change theories are mainly concerned with the properties of the adsorbed phase, likened to a film such as may exist on water. The behaviour of these films is largely due to the attractive forces acting between the adsorbed molecules and the mobility of the molecules of the surfaces. These phenomena have been assumed non-existent in the development of previous adsorption theories.

One approach to the development of a Phase-Change theory of adsorption is through the Gibbs'adsorption equation which, in its original form, was applied to adsorption from solution. The Gibbs' equation was first applied to adsorption of gases on solids by Bangham (24) who used it to evaluate the spreading pressure of an adsorbed film on charcoal. One form of the Gibbs' equation is

where  $\langle$  is the surface free energy,

 $\Gamma$  is the surface excess of adsorbate and,

µ is the free energy of the sorbate.

Bangham integrated the above expression and obtained for the spreading pressure of an adsorbed film the expression

$$\mathcal{N} = \Pr_{\overline{VZ}} \int_{0}^{P} \frac{vd}{vd} \log P \qquad \dots (13)$$

where  $\tilde{n}$  is the spreading pressure of the adsorbed film,

- P is the equilibrium adsorption pressure,
- v is the volume of gas adsorbed per gram of adsorbent,
- $\Sigma$  is the specific surface area,
- R is the gas constant,
- T is the absolute temperature, and

V is the molar volume of the adsorbate.

By attributing the expansion of the adsorbent (swelling) to the spreading pressure of the adsorbed molecules, Bangham and his associates (25,26) were able to verify some of the theories embodied in the above considerations.

Gregg (27) used equation (13) to calculate  $\pi \sigma$  versus  $\mathcal{P}_{\mathcal{E}}$  curves ( $\sigma$  is the area per adsorbate molecule) for a number of adsorption isotherms taken from the literature. He showed that there was a close resemblance between these curves and similar curves obtained by spreading oil films on water. Jura and Harkins (28) have followed Gregg in emphasizing the analogy between films adsorbed on solids and insoluble films spread on water. However, instead of plotting  $\pi \mathcal{C}$ - $\pi \mathcal{E}$ :curves, they plotted  $\pi$ - $\mathcal{C}$  curves and distinguished five phases which occur on solids as well as on water.

In another paper, Jura and Harkins (29) presented semi-empirical equations of state to describe all the phases which could occur. Using the values of  $\partial \Pi / \partial \Omega$  obtained from their empirical equations of state, they succeeded in applying their equations to a number of adsorption isotherms.

The practical significance of the work of Jura and Harkins, as far as physical adsorption is concerned, is that their isotherm equation for a liquid condensed film on a solid provides a reasonably good method for calculating the surface area of the adsorbent. Harkins and Jura (30) determined the surface areas of a number of adsorbents and found excellent agreement with surface areas obtained by the BET method. They claim that their method has the advantage that it does not require an estimate of the area occupied by an adsorbate molecule. However, they have introduced the doubtful assumption that the characteristics of a condensed film remain unchanged from substrate to substrate. Ross (31) criticized the theory of Jura and Harkins on the grounds that they have applied empirical equations of state

derived from pressure-area relations for oil films on water to adsorbed films on solids, which are considered to be multimolecular over about 80% of the range of the isotherm.

#### Recent Advances in Adsorption Theories

Recent advances in the field of adsorption have been directed in two general directions. On one hand, efforts are being made to extend and improve the BET model, while on the other hand, certain authors have proposed that the BET theory be abandoned and have suggested completely different models.

Extensions of the BET theory have been based mainly on statistical mechanical approaches similar to Fowler's (32) statistical derivation of the Langmuir equation, Cassie (33) extended the statistical treatment to multilayer adsorption by assuming that the existence of adsorbed liquid at relative pressures less than unity could be justified on the basis of an increase in entropy due to mixing of molecules of the first layer with molecules of the subsequent layers. However, Hill (34) pointed out that there is no entropy of mixing when identical molecules are exchanged between two energy levels. In addition, he proposed modifications in the BET theory to include "vertical" and "horizontal" interactions between the adsorbed molecules. Recent papers by the same author (35-38) extend his original statistical

mechanical treatment to include the above refinements in the BET model.

Dole (39) generalized further the statistical treatment of Cassie (33) and Hill (34) to include variable heats of adsorption in different layers. He showed that under certain conditions multilayer adsorption can give rise to a linear isotherm in addition to the five types considered by Brunauer and his co-workers (21).

McMillan (40) suggested that a better fit of the BET equation at low relative pressures may be obtained if two or more c values are used. This is equivalent to assuming surface heterogeneity. In a more recent paper, McMillan and Teller (41) considered the influence of surface tension forces on multilayer adsorption. Their conclusion was that correction for surface tension effects overcorrects the BET theory.

Instead of modifying the BET model, some authors have proposed completely different models. Thus, Halsey (42), by using a quasi-chemical treatment, showed that the BET theory can lead to substantially no adsorption beyond the first layer if  $E_2 = E_L$ , and stepwise isotherms if  $E_1 > E_2 > \dots > E_L$ . In addition, he showed that a typical multilayer isotherm is composed of three regions; (i) non-cooperative adsorption on a strongly heterogeneous surface; (ii) cooperative adsorption on a heterogeneous surface; and (iii) cooperative multilayer adsorption induced by small van der Waals

perturbations some distance from the surface. He was able to give a mathematical formulation for his theory but, to develop a practical isotherm equation, he had to make a large number of simplifying assumptions. His final simplified isotherm equation was of the same form as the equation proposed earlier by Harkins and Jura (28).

#### Sorption Hysteresis

In a large number of sorbent-sorbate systems the adsorption and the desorption isotherms do not coincide. This phenomenon is known as sorption hysteresis.

Both irreversible and reversible hysteresis have been observed. Irreversible hysteresis generally occurs over the entire pressure range but disappears after proper conditioning of the adsorbent. Accordingly, it has been attributed to non-condensable gases that are initially adsorbed on the surface. Reversible hysteresis may occur only over a very narrow relative pressure range or it may cover almost the entire relative pressure range. The two types of reversible hysteresis have been named limited and linear hysteresis respectively. Furthermore, reversible hysteresis is highly reproducible and persists even after the adsorbent has gone through many adsorption-desorption cycles. Limited hysteresis has been obtained for the system silica gel-water (43) whereas linear hysteresis has been found in sorption of water vapour on

polymers such as cellulose (10) and proteins (44).

One of the first attempts to explain hysteresis was put forward by Zsigmondy (11). He suggested that, since adsorbed gaseous impurities might prevent complete wetting of the surface during adsorption, the adsorption pressure was lower than the desorption pressure. However, this effect disappears after thorough cleansing of the surface and hence this explanation can only account for the irreversible hysteresis.

The theory of Capillary Condensation is the only adsorption theory which offers a reasonable explanation of reversible hysteresis. Two different approaches have been proposed. The first of these is the "delayed meniscus" theory which was first proposed by Foster (11) and later put on a mathematical basis by Cohan (12). The second theory is the so called "ink bottle" theory first suggested by Kraemer (45) and later adopted by McBain (46).

According to Foster (16) adsorption proceeds by a build up of multilayers on the pore walls until the adsorbed layer becomes so thick as to bridge the pore and form a meniscus. Subsequent adsorption in the pore then proceeds by capillary condensation. Thus, adsorption is envisaged as a combination of multilayer adsorption and capillary condensation. At saturation pressure, all pores are completely filled so that during desorption the adsorbate is removed by evaporation from

pores, each of which contains a meniscus. Foster concluded that molecules which are adsorbed on the walls of a pore will have higher vapour pressure than condensed molecules. Hence, the equilibrium pressure will be higher on adsorption than on desorption.

Cohan (12) showed, by simple thermodynamic reasoning, that the vapour pressure of an annulus of adsorbed liquid inside a pore, as postulated by Foster, is given by

$$Pa = P_{o} \exp(-yV/r_{a}RT)$$
 ....(14)

where Pa is the vapour pressure of the molecules adsorbed in form of an annulus, and

ra is the internal radius (radius of the pore less

twice the thickness of the adsorbed layer). The other symbols in equation (14) have their usual significance. Comparison of the Cohan equation with the Kelvin equation, which can be assumed to apply to desorption, shows that desorption pressure will be higher than adsorption pressure, i.e. hysteresis will be observed.

The second approach to the problem of limited hysteresis is to assume that capillary condensation occurs during both adsorption and desorption, and that hysteresis is caused by the shape of internal pores. Kraemer (45) and later, McBain (46) suggested that the adsorbent might contain pores shaped like ink bottles with narrow necks and wide bodies. On adsorption, vapour condenses into the bodies but desorption occurs by evaporation from necks of filled pores. Since the radius of the body is larger than that of the neck, the vapour pressure is higher on adsorption than on desorption.

The linear type of reversible hysteresis is usually encountered with adsorbents which swell considerably during adsorption. This is most common in sorption of certain vapours by high polymers such as cellulose and proteins. Most of the theories proposed to explain this type of hysteresis are based on structural changes in the adsorbent.

A mechanism for hysteresis based on swelling-shrinking phenomena was first suggested by Urquhart (47) and later developed by Filby and Maass (48) for the system cellulosewater vapour. Smith (49) proposed an analogous mechanism for hysteresis in sorption of water vapour by proteins and Hirst (50) used essentially the same explanation for hysteresis in sorption of water by coal.

Hirst pointed out that swelling may bring about distortion of the sorbent in such a manner as to cause a sudden increase in the accessible surface. Many sorbents, particularly those of the "gel" class, consist of elementary micelles of various irregular shapes. These micelles will normally touch at certain points and the mechanical strains induced by swelling will tend to pull them apart. This process is aided by

reduction in the mutual adhesion of the micelles when adsorption occurs. The net effect could easily cause the structure to "spring open" at a certain point and reveal previously inaccessible areas. This could be followed by a new stage of swelling or be limited by elastic restraint of the sorbent.

On desorption, the structure tends to "close up" owing to the shrinking of the adsorbent. However, as surface forces fall off rapidly with distance, they are much less when the structure is "open" than those which originally resisted opening. Therefore when the pressure returns to the value that caused the structure to "open up", there is no sudden closing. The structure remains open until pressure and swelling decrease sufficiently to overcome the reduced surface forces; i.e. hysteresis effect is present.

Another mechanism for hysteresis which is not based on capillary condensation was proposed by Pierce and Smith (51) to explain hysteresis which may occur on plane surfaces.

Their theory is based on the assumption that a drastic change occurs in the adsorbed layer at saturation. One such change could be that isolated clusters of liquid merge into a continuous layer. This could produce a hysteresis effect.

It would appear from above discussion, that no single mechanism is adequate to explain the different types of hysteresis. There is a good possibility that, with heterogeneous

adsorbents such as flour, several factors may be involved simultaneously.

# SORPTION OF GASES AND VAPOURS ON WHEAT FLOUR AND RELATED MATERIALS

One of the first studies of adsorption of water vapour by wheat flour at controlled humidities was reported by Bailey (52) in 1920. He found that the moisture content of flour varied almost linearly from 5.11% at a relative humidity of 29.4% to 15.0% at 80% relative humidity.

Fairbrother (53) pointed out that flour which loses some of its moisture at a lower relative humidity does not regain all the weight when re-exposed to the original relative humidity. He attributed this irreversibility to a change of some of the particles to a permanent gel with a resultant change in hydration capacity. Such an effect is quite possible if the original relative humidity were sufficiently high to produce a permanent change in the flour, such as "case hardening". This would partially inhibit subsequent adsorption.

Adsorption isotherms for flour in equilibrium with water vapour have been reported by Anderson (54), Anker, Geddes and Bailey (55) and Knight and Larmour (56). In addition to flour isotherms, Knight and Larmour reported isotherms for bran, shorts, screenings and middlings from the same mill stream.

In all the cases cited so far, the main object of the

sorption studies was to get some indication of the comparative moisture contents of flour samples stored under different relative humidities. In these experiments, no attempt was made to remove any of the gases and vapours that were originally adsorbed on the flour and in some cases the experimental temperature was not closely controlled. Consequently, there is considerable disagreement between the results from different laboratories.

Babbitt (57,58) has reported the first attempt to obtain isotherms for adsorption of water vapour on wheat and wheat flour, in which the samples were originally dried to a practical limit. Furthermore, he differentiated clearly between the adsorption and desorption branches of the isotherm which did not coincide owing to a hysteresis effect. Babbitt also pointed out that the observed rates of adsorption and desorption could be explained on the basis of diffusion. He did not offer any explanation for the observed hysteresis effect, but did point out that the isotherms for wheat showed considerably more hysteresis than the isotherms for flour.

The isotherm for flour reported by Babbitt is a typical sigmoid shape or Type 11 (according to BET Classification) isotherm showing an almost constant amount of hysteresis over the entire relative pressure range. In the low humidity range, the isotherm is concave to the pressure axis; in the mid range it is almost linear; and, in the high humidity

range it is convex to the pressure axis.

According to the BET theory the first portion of a sigmoid isotherm represents the adsorption of the first layer of vapour, the linear region represents the deposition of a second layer of molecules, and the final portion the build up of multilayers. As will be pointed out later, adsorption on polar substances such as proteins may first take place on highly specific sites, followed by less specific multilayer adsorption.

An alternate hypothesis which explains a sigmoid isotherm is that the vapour is initially adsorbed in clusters on the polar sites, and this is followed by the build up of multilayers (59).

Morey and co-workers (60) studied the effect of temperature on adsorption of water by wheat flour. Over a temperature range from  $50^{\circ}$  to  $90^{\circ}$ C they found a linear relation between the centigrade temperature and the logarithm of the vapour pressure. They estimated the isosteric heat to be 10.7 Kcal./ mole, which is essentially equal to the heat of liquefaction of water vapour. However, this value cannot be taken as indication of the mechanism of adsorption since the measurements did not include the low relative pressure range where the isosteric heat is usually higher than the heat of liquefaction.

Apparently no attempt has yet been made to relate the

sorption of water vapour by flour to the physical structure of the flour particles or to the chemical nature of the components of flour. This approach is difficult since it requires that the various components of flour be separated without altering their chemical and physical properties. Starch which comprises from 50 to 70% of the flour can be isolated without serious damage and several sorption studies on wheat and other starch have been reported (61). However, it was not until quite recently that methods for isolating gluten, the main protein component of wheat flour, have been developed to a degree such that the properties of the isolated material can be assumed to be very similar to the properties of native gluten (62,63). No vapour phase sorption studies on wheat gluten have yet been reported.

Before an attempt can be made to correlate sorption with chemical structure of the components of wheat flour it is necessary to consider the main structural characteristics of the constituent substances and to indicate the functional groups which may be responsible for the behaviour of these substances towards water. Starch and gluten, which comprise the bulk of the flour, have been selected for this discussion. It is assumed that the effect of the lesser components on sorption capacity of flour is negligible.

Starch is a natural high polymer of glucose units. Molecular weight determinations have yielded widely divergent values
that depend upon the source of the starch used and on the method of molecular weight determination. Thus, by the end group analyses Hess and Lung (64) found the chain length of starch to be equivalent to 50 glucose units, i.e. to have a molecular weight of about 9,000. Rodewald (65) obtained molecular weights of 17,000 to 103,000 from heat of wetting measurements whereas viscosity measurements (66) have yielded values ranging between 108,000 and 324,000. A value of 56,000, from the heat of wetting, has been reported recently by Dumanskii (67).

Wheat starch exists in wheat endosperm in the form of granules ranging in size from about 3 to 15 microns in diameter, and consists of two molecular types which are distinguishable by chemical means (68). One of these, comprised mainly of linear molecules, is the water soluble fraction usually called amylose and the second, branched chain type is the less soluble amylopectin.

The general formula for starch may be represented by



Such a molecule is characterized by hydroxyl groups and ring and bridge oxygen atoms, all of which may interact directly with water. Hunter (69) suggested the formation of hydrogen bonds between this polysaccharide and water. With the hydroxyl group, it is possible to have



and with the bridge oxygen atom the hydrogen bond would be



It is apparent then, that there is a variety of possible ways in which water may be attached to molecules of starch.

The proteins, which comprise a very large and extremely important group of natural high polymers, are characterized by a main chain or backbone of amino acids with peptide linkages. This structure can be represented

CO CH NH CH NH CO CH

in which R<sub>1</sub>, R<sub>2</sub>, etc., represent amino acid side chain residues.

Some idea of the variety of functional groups represented by the side chain residues in flour proteins, or more specifically gluten, may be had by considering the amino acids that have been isolated from wheat gluten. Analyses of gluten from wheat flours of widely different baking quality show no significant variations in the amounts and kinds of amino acids (70,71). The most recently published (71) analysis of wheat gluten is reproduced in Table 1.

Examination of the amino acids listed in Table 1 yields the following R groups which may be considered as hydrophilic because of their polar or ionic character,

-OH, in serine, threonine, and tyrosine,

-NH-, in histidine, proline, and tryptophane,

-NH<sub>2</sub>, in lysine and one of the terminal amino acids in the polypeptide chain,

-NH----C
$$^{\rm NH}_{\rm NH}$$
, in arginine,

-COOH, in aspartic and glutamic acids, and one of the terminal amino acids in the polypeptide chain,

### TABLE 1

## Average Composition of Wheat Gluten

		b
Constituent	a Chemical Formula	Gm. amino acid per 100 gm. Proteins
Alanine	сн <sub>3</sub> сн(ин <sub>2</sub> )соон	2.2
Ammonia	NH3	4.5
Arginine	NH <sub>2</sub> c(=NH)NH(CH <sub>2</sub> ) <sub>3</sub> CH(NH <sub>2</sub> )COOH	4.7
Aspartic Acid	HOOCCH <sub>2</sub> CH(NH <sub>2</sub> )COOH	3.7
Cystine	(-sch <sub>2</sub> ch(NH <sub>2</sub> )cooh) <sub>2</sub>	1.9
Glutamic Acid	HOOC(CH <sub>2</sub> ) <sub>2</sub> CH(NH <sub>2</sub> )COOH	35.5
Glycine	сн <sub>2</sub> (NH <sub>2</sub> )соон	3.5
Histidine	N <sup>CH</sup> NH CH———ССH <sub>2</sub> CH(NH <sub>2</sub> )СООН	2•3
Isoleucine	сн <sub>3</sub> сн <sub>2</sub> сн(сн <sub>3</sub> )сн(NH <sub>2</sub> )соон	4.6
Leucine	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH(NH <sub>2</sub> )COOH	7.6
Lysine	NH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> CH(NH <sub>2</sub> )COOH	1.8
Methionine	сн <sub>3</sub> s(сн <sub>2</sub> ) <sub>2</sub> сн(NH <sub>2</sub> )соон	1.9
Phenylalanine	CH2CH(NH2)COOH	5.4
Proline	H <sub>2</sub> C CH <sub>2</sub> H <sub>2</sub> C CHCOOH	12.7
Serine	HOCH <sub>2</sub> CH(NH <sub>2</sub> )COOH	4.7

36

.....continued

		ზ
Constituent	a Chemical Formula	Gm. amino acid per 100 gm. Proteins
Threonine	сн <sub>3</sub> сн(он)сн(ин <sub>2</sub> )соон	2.6
Tryptophane	CCH <sub>2</sub> CH(NH <sub>2</sub> )COOH	1.1
Tyrosine	HO CH <sub>2</sub> CH(NH <sub>2</sub> )COOH	3.1
Valine	(cH <sub>3</sub> ) <sub>2</sub> cHcH(NH <sub>2</sub> ) cooh	4.7

a Formulae from Fieser, L.F., and Fieser, M. Organic Chemistry, D.C. Heath and Co., Boston, 1950.

b Computed from theoretical protein containing 17.5% nitrogen.

-S-S-, in cystine, and

-S-CH<sub>3</sub>, in methionine.

In addition to the various groups listed above, water may interact with the -CO- and the -NH- groups in the peptide linkages.

Very little is known about the molecular structure of gluten proteins. The classification of flour proteins into five groups based on solubility (72) has proved unsatisfactory. Gortner, Hoffman and Sinclair (73) and others (74,75,76) have shown that different complexes with the different dispersing agents, and not true solubility, is involved in the separation of gluten proteins.

Investigations with the water soluble proteins of flour have been considerably more successful. Danielsson (77) and others (78) have shown that the globulin fraction consists of three individual components. Recently, it has been shown (79) that the albumin fraction contains at least six electrophoretically distinguishable components. Further details on this subject are contained in a recent review on the physical characteristics of gluten by Sullivan (2).

So far, no attempts have been made to correlate the capacity of flour to bind water with the number of the various polar groups on the flour constituents. The difficulty of so doing is great, since almost nothing is known about the availability of the various groups for interaction with water. Simple summation of all the possible coordinating groups is probably an inadequate approach. For example, Samec (80) has reported that the -OH groups in starch are extensively hydrogen bonded, and it is possible that this intramolecular hydrogen bonding would effect the capacity of starch for binding water.

It appears that with starch and proteins, from sources other than wheat flour, water and other sorbed molecules, may be bonded to various chemical groups in the adsorbent. Thus,

from measurements of heats of wetting on acetylated and untreated starch, Nakagawa (81) was able to show that the heat of wetting can be attributed to the interaction between water molecules and the -OH groups in potato starch. The most likely mechanism for this interaction would be through the hydrogen bond as indicated earlier. A number of authors (82) have suggested the formation of starch hydrates but it has been argued that formation of such hydrates would require a stepwise isotherm and this has not yet been observed experimentally.

Sorption by proteins has been even more difficult to explain in terms of chemical structure, since the protein molecule possesses a large number of polar groups that show various degrees of polarity. Jordan Lloyd (83) attributes the interaction of water with proteins to coordination with free electrons on oxygen and nitrogen atoms in groups such as carbonyl, amide, hydroxyl, amino and imino, or by the formation of hydrogen bonds with the same groupings.

Pauling (84) has suggested that the data of Bull (85) on adsorption of water by proteins can be interpreted quite satisfactorily on the assumption that the initial process is the attachment of one water molecule to each polar amino acid side chain. He did not consider the peptide carbonyl and the imido groups important in water binding. However, Hunter (69) indicated that water may be bound by the peptide

linkage, thus,

Recently, it has been estimated (86) that four to five molecules of water can be bound by the carboxyl group, three by hydroxyl group, and two each by imino and carbonyl group. Mellon, Korn and Hoover (87) have concluded that peptide groups are responsible for about 45% of the vapour phase water adsorption by casein.

Benson and co-workers have recently published an interesting series of papers dealing with adsorption as related to chemical structure. Benson and Seehof (88,89) showed that sorption of polar gases such as ammonia, hydrogen chloride, boron trifluoride and methylamine on egg albumin was independent of the apparent surface areas of the proteins but was related to the specific nature of the protein. They observed also that hydrogen chloride and boron trifluoride formed permanent complexes with the proteins. On the basis of such studies, they have proposed a vapour phase titration technique for distinguishing between "free" basic and "free" amino groups in the protein molecule. This possibility was supported by additional experimental evidence in another publication (90) from the same laboratory. However, a recent paper by Reyerson

and Peterson (91) has indicated that the amount of adsorbed hydrogen chloride retained by insulin decreased with increasing temperature. Hence, a vapour phase titration cannot be used as a measure of the "free" amino groups, at least for this protein.

Seehof, Keilin and Benson (44) have suggested that the constancy of reversible hysteresis in sorption of water by proteins is associated with binding on free basic groups. This is a complete contradiction to a previous report (87) that hysteresis in casein did not depend on free amino groups. Seehof and co-workers based their hypothesis on a significant correlation for a variety of proteins, between the total number of polar groups and maximum hysteresis. Further experimental work is obviously required, preferably with materials other than proteins, which exhibit a similar hysteresis effect.

The concept of "bound" water has been important in considering the interactions of water with biological materials such as starch and proteins. Traditionally this concept implies a stoichiometric relation between water and hydrophilic materials and that the forces of interaction between water molecules and the specific sites on the hydrophilic material are considerably larger than van der Waals adsorption forces. Some authors suggest that bound water could also be called chemisorbed water (92), but Jordan Lloyd (83) preferred to

define it as the water which is incapable of exhibiting the physical and chemical properties of free water.

Moran (93) has showed that, in freezing gelatin gels, there is no further separation of ice at any temperature when the moisture content falls below about 34%. A convincing demonstration of the existence of bound water was reported by Hatschek (94). He observed that when gelatin gels, containing cobaltous chloride, were dried at  $15^{\circ}$  to  $30^{\circ}$ C they turned blue when there remained as much as 30%water in the gel, presumably incapable of forming a hydrate. The ability of winter wheats to resist freezing has been ascribed (95) to the relatively large amounts of bound water held by these wheats. The ability of some plants to resist dessication has been explained on a similar basis (96).

Smith (49) pointed out that water sorbed by hydrophilic high polymers such as cellulose exists partly as bound and partly as condensed water. For sorptions at low pressures most of the sorbed water is bound whereas at higher pressures actual bulk condensation may occur. This type of division appears to imply that water in the first adsorbed layer is equivalent to bound water. Dumanskii and co-workers (97,98,99) have recently shown that bound water decreases the heat of wetting, and from measurements of heats of wetting they estimated values ranging from 28 to 35% bound water for

a variety of flours. These high values seem to suggest that all the water adsorbed at 100% relative humidity is of the bound type (Babbitt (58) showed that the moisture content of flour at 100% relative humidity was 25%). The high value for bound water also seems to be at variance with multimolecular adsorption theories. For instance, to explain the rise in the sigmoid isotherm at high pressures the BET theory (19) postulates the formation of multilayers in which the properties of the sorbate are identical with the properties of bulk liquid.

Reversible swelling of an adsorbent generally occurs when any solid takes up a gas or a vapour. With some adsorbents such as charcoal, the amount of swelling during vapour phase adsorption is so small that it can only be detected by very precise measurements. With lyophilic adsorbents, on the other hand, the extent of swelling during adsorption is so great that it can be readily observed with the naked eye.

Swelling may be considered as the initial phase of solution. Equilibrium may be attained before complete solution occurs (e.g. the limited swelling of cellulose or insoluble proteins in water) if the swelling forces cannot overcome the cohesive forces in the material or if the structure of the adsorbent is sufficiently rigid to prevent diffusion of sorbate molecules to the proper points to effect complete dissolution.

Considerable information, some of which is pertinent to later discussion, is available on liquid phase swelling of starch and proteins. Jordan Lloyd and co-workers (100) made quantitative studies of the swelling of a variety of proteins in aqueous media of different pH. They found that all of the proteins they examined were swelled by water and the degree of swelling varied markedly with pH. More recently, Jordan Lloyd, Dempsey and Garrod (101) reported on the swelling of protein fibers in organic solvents. They found that the proteins they investigated swelled readily in the four lower fatty alcohols and fatty acids, and in thioglycollic and lactic acids. Swelling was slight in higher alcohols and acids and did not occur at all in pyridine, dioxane, paraldehyde, benzene, ether and ammonia. The result with ammonia is of particular interest since, with this liquid an effect might be expected similar to that obtained with water.

A mechanism by which starch grains swell in water has been reviewed recently by Badenhuizen (102). All layers in the starch granule apparently swell at the same rate. The outer layers, however, show a stronger swelling power in the tangential direction than the inner layers and, since all the layers stick together, the inner part is stretched by swelling of the outer part. As a consequence, a cavity

develops in the centre of the granule, and this cavity increases in size with swelling. Heated starch disperses much faster on swelling than unheated starch. Badenhuizen claims that this is due to weakening of cohesive forces caused by a decrease in chain length of starch molecules as a result of the heat treatment.

Density changes that accompany adsorption of water by wheat and endosperm particles have also been used to study their swelling. Sharp (103) found that wheat density decreased markedly as the moisture content increased. Campbell and Jones (104) studied the movement of moisture in wheat by observing the variation in density of endosperm particles. They found a linear decrease in endosperm density with moisture content in the "practical" moisture range (5 to 20%). The change in density was fully reversible if the moisture content did not exceed 20%. Above 20% moisture content, the density decreased at a greater rate than the rate of increase in moisture. This acceleration was ascribed to marked swelling of the endosperm particles at the high moisture levels.

It may be concluded from the foregoing discussion that the various interactions of flour, starch and proteins with water are probably very closely related. However, considerable further work is necessary to correlate the seemingly different effects by a single mechanism.

#### EXPERIMENTAL

#### MATERIALS

The following materials were used as adsorbents:

Flour No. 1: An unbleached, improver-free, straight-run sample, milled from a blend of Canadian hard red spring wheat of the 1954 crop. The protein content of this flour was 14.77%.

Flour No. 2: An unbleached, improver-free, straight-run sample commercially milled from high grade Canadian hard red spring wheat. The protein content of this flour was 14.99%.

Flour No. 3: An unbleached, improver-free, straight-run sample, milled on a laboratory mill from a pure variety (Selkirk) of Canadian hard red spring wheat of the 1954 crop. Its protein content was 15.34%. A portion of this flour was separated on a Rotap Sifter into fractions of different particle-size. The fractions and their protein contents were as follows:

Fraction				Protein	Content	(%)	
Held	on	sieve	No.	120		15.0	
11	11	11	No.	140		15.2	
n	11	<b>#1</b>	No.	170		15.4	
n	11	11	No.	200		16.2	
Pass	sed	throug	zh No	. 200		15.8	

Gluten No. 1: Washed mechanically from flour No. 2 and freezedried in crude form. The protein content of this material was 69.76%.

Gluten No. 2: Washed mechanically from flour No. 2. The wet gluten from 3000 gm. of flour was dispersed in 4 1. of 0.01N acetic acid solution and portions of the dispersion spray-dried using an inlet temperature of  $160^{\circ}$  and an outlet temperature of  $90^{\circ}$ C. The protein content of the dry material was 86.61%.

Starch: Separated from flour No. 2. Approximately 200 gm. of flour was made into a stiff dough and the starch was washed out by working the dough under a slow stream of water. To the resulting suspension, enough sodium chloride was added to make the solution approximately 2N in the salt. This was allowed to stand for several hours to dissolve the salt soluble proteins. The starch was separated by centrifugation, washed several times with ethyl alcohol to remove the alcohol soluble proteins and dried in a vacuum at 65°C. It was stored in a dessicator over silica gel.

The adsorbates were as follows:

Water Vapour: Some of the preliminary work was done by using solutions of sulphuric acid in water to provide a constant water vapour pressure. Six solutions of different sulphuric acid concentration were made to give a range of relative pressures from 0.1 to 0.85. These solutions were prepared from Nicholl's C.P. sulphuric acid and distilled water and were stored in 2 litre bottles.

For the major part of the investigation, pure, distilled water was used as the vapour source. The vapour pressure was varied by admitting a definite amount of vapour into the adsorption chamber.

Methyl Alcohol: Methyl alcohol was Fisher "Reagent" grade.

Ethyl Alcohol: "Super-dry" ethyl alcohol was prepared by the method described by Vogel (105). In accordance with this method, 95% alcohol was refluxed for **six** hours over quicklime and the distillate refluxed for half an hour over granulated zinc and subsequently distilled.

Carbon Tetrachloride: Carbon tetrachloride was Fisher "Spectro" grade.

Ammonia: Ammonia was the anhydrous grade obtained from Canadian Industries Limited in large cylinders. To ensure complete dryness, the ammonia was passed through a 16 inch drying tube filled with soda lime before it was admitted to the storage bulb.

A large number of other liquids and gases were used in the attempts to prepare various doughs. These materials, which will be listed in the appropriate section, were anhydrous and of the highest purity grade. Some were available in the laboratory, the

remainder were obtained either from Brickman Chemical Co., or Fisher Scientific Co.

Quartz Spirals: The quartz spirals used in the adsorption measurements were obtained from Houston Technical Laboratories, Houston, Texas, U.S.A.

Sample dishes: Two types of sample dishes were used. With less sensitive spirals it was possible to use platinum dishes; with more highly sensitive spirals it was necessary to use very light quartz baskets. The platinum dishes were about 12 mm. in diameter and 2 mm. in height and were pressed from 0.001 inch foil on a specially constructed die. The quartz sample dishes were obtained from Houston Technical Laboratories.

#### METHODS

A number of the standard techniques used to measure the extent of vapour adsorption on a solid adsorbent were examined and it was decided that gravimetric techniques would be particularly satisfactory for the present investigation for two reasons: (1) the errors in the determination of the dead space volume inherent in volumetric methods are eliminated; and (i1) they can be readily adapted to kinetic experiments. One minor disadvantage of gravimetric techniques is that very sensitive weighing devices are necessary to measure the extent of adsorption directly. For this purpose the micro torsion balance and the McBain-Bakr quartz spiral balance have been used with considerable success. The relative merits of the two types of balance were examined and it was decided to adopt the quartz spiral balance because of its greater stability, simpler manipulation and commercial availability.

#### Apparatus No. 1

A schematic diagram of the adsorption apparatus which will be referred to as Apparatus No. 1 is shown in Figure 1. It consisted of the following: (i) an adsorption tube, A, constructed from 38 mm. pyrex tubing and to which was connected a mercury manometer of 10 mm. pyrex tubing; (ii) a three litre bulb, D, to increase the total volume of the adsorption chamber (this could also be used as a storage bulb); and, (iii) a bulb, E, for storing

the adsorbate liquid. In the preliminary experiments, in which sulphuric acid solutions were used to provide a constant water vapour pressure, the bulb, E, was connected to the adsorption chamber at G. However, in subsequent experiments in which the pressure in the adsorption chamber was varied by admitting a definite amount of vapour from a flask containing pure water it was found more convenient to have bulb E connected to the manifold as shown in Figure 1. In this way the adsorption chamber was isolated by only one stopcock and one ground-glass joint. This greatly diminished the possibility of leaks developing during prolonged experiments. In all, four such adsorption chambers, in two separate thermostats, were used. Apparatus No. 1 was used in all experiments unless otherwise stated.

Each adsorption chamber was connected to a manifold which included standard equipment used in high vacuum techniques. High vacuum was obtained by a two-stage, all-glass mercury diffusion pump backed by a Cenco Hyvac oil pump. Throughout this investigation care was taken to maintain the desorption vacuum at a maximum exceeding  $10^{-4}$  mm. of mercury. During evacuation, pressure was checked intermittently with a McLeod Gauge which was calibrated to read better than  $10^{-5}$  mm.

An air inlet was provided on the manifold as shown in Figure 1.

Figure 1

Apparatus No. 1

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#### Apparatus No. 2

Since this apparatus was designed to study the effect of temperature on adsorption, precise temperature control of the complete adsorption chamber was important. It was therefore constructed in such a way that it could be immersed completely in a thermostat. A schematic diagram of the apparatus is shown in Figure 2. Its various parts were essentially the same as those described for Apparatus No. 1, except that the three stopcocks, E, were mercury sealed and positioned so that the mercury cup was just above the water in the thermostat. The stopcocks E were arranged in such a way that the adsorption tube A and the bulb B (source of constant vapour pressure) could be evacuated individually or together. The two ground-glass joints, F, lubricated with silicone high vacuum grease, held a vacuum of  $10^{-4}$  mm. when completely immersed in water at 50°C. Apparatus No. 2 was connected to the same manifold as Apparatus No. 1.

High vacuum stopcocks were used throughout in the construction of the gas manifold. This was essential for maintaining high vacuum for periods of one week or longer which were required in some of the experiments. All stopcocks and ground-glass joints were lubricated with Dow Corning High Vacuum Silicone grease.

Temperature control in the various thermostats was obtained in the usual way; the control system consisted of

Figure 2

Apparatus No. 2

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Aminco mercury relays actuated by Aminco mercury thermoregulators. Temperatures were controlled to about + 0.02°C.

### Calibration and Manipulation of Quartz Spirals

Five quartz spirals, with a range of sensitivities, were used. Each spiral was calibrated in air by measuring the extension produced by successive 10 mgm. increments of weight. Five such weights were generally used to provide a calibration curve. The spiral extension was measured with a precision cathetometer, the scale of which was calibrated to 0.5 mm. and provided with a vernier to read 0.01 mm. A micrometer head was also available for direct measurement of extensions up to 10 mm.

For all the spirals, the plots of weight against extension were essentially linear. The sensitivities were as follows:

Spiral No.	Sensitivity (mgm./mm. extension)
l	1.80 <u>+</u> 0.04
2	1.72 <u>+</u> 0.04
3	0.411 + 0.008
4	0.308 <u>+</u> 0.006
5	0.51 <u>+</u> 0.01

The sensitivities were determined from the slopes of the weight-extension relations. The calibration error was estimated on the assumption that cathetometer readings were reproducible

within  $\pm$  0.02 mm. These sensitivities were checked periodically and were found to remain constant, within experimental error, throughout the investigation.

Since spirals of high sensitivity are fabricated from very fine quartz fibres, special procedures must be adopted to handle them if breakage is to be avoided. In this study, the spirals were suspended in the adsorption tube from a small ring made of 0.002 inch tungsten wire sealed into a pyrex rod which, in turn, was sealed to a large glass supporting bulb (F, Figure 1). The bulb rested on a constriction in the adsorption tube. The top of the bulb was provided with a glass hook by which the spiral assembly could be raised from or lowered into the adsorption tube with a nylon thread that passed through a guide directly above the adsorption tube.

Removal of the sample dish from the spiral at the conclusion of an experiment was readily accomplished by resting the dish on a small, rigid card, which was then raised slowly until the spiral was disengaged. This procedure was reversed when a charged sample dish was suspended from the spiral.

#### Storage of Flour and Gluten

It is highly essential in adsorption studies, to have reproducible adsorbent samples. Reproducible flour samples are best obtained from a single milling. However, if stored under normal atmospheric conditions, the samples undergo

progressive changes with storage time and the effect of these changes on the sorptive capacity of flour has not yet been investigated. Consequently, the flour must be stored under conditions that minimize the changes during storage. In the present study, 5 gm. samples of flour (or gluten) were stored at low temperatures (about  $4^{\circ}$ C) in 25 ml. round-bottom flasks which were sealed after four hours evacuation. A new sample was used for each set of experiments.

#### Procedure for a Typical Experiment

The experimental procedure for obtaining isotherms was essentially identical for all the adsorbates used. Accordingly, a general outline of the procedure will be given here without reference to particular experiments; specific deviations from this routine procedure will be included in appropriate sections.

Experimental work was usually arranged so that each experiment was begun in the latter part of the afternoon. An appropriately weighed sample of adsorbent (usually 100 mgm. for spirals No. 1 and 2, 50 mgm. for spirals No. 3 and 4 and 75 mgm. for spiral No. 5), was placed in the adsorption tube and allowed to attain temperature equilibrium after the adsorption tube was properly sealed. It was found more practical to weigh the samples on a laboratory balance than to determine the sample weight from the spiral extension, although either method might have been used.

After the adsorbent had attained equilibrium (about 1 hour) the position of a reference point on the lower end of the spiral was determined with the cathetometer and recorded. It was found that the bottom of the hook on the spiral was a very good reference point. Also, it was found convenient to have a series of thin scratches on the adsorption tube to serve as reference points for positioning the cathetometer.

The pumps were turned on usually at about 8.00 p.m., and the system enclosing the adsorbent was evacuated overnight at a temperature of  $27^{\circ}$ C. After about four to six hours, the pressure remained essentially constant at  $10^{-4}$  mm. or lower. After about 12 to 14 hours of evacuation, the extension of the spiral was measured a number of times at hourly intervals to ascertain that desorption equilibrium has been attained. Desorption was assumed to be complete if two additional hours of evacuation produced no further decrease in the weight of the adsorbent. This initial treatment of the adsorbent will be referred to as the "conditioning" period.

It was necessary to determine accurately the decrease in weight during the conditioning period to obtain the dry weight of the adsorbent since the adsorption was estimated on a "dry weight" basis. Since it is very difficult to obtain absolute dryness of highly hygroscopic materials such as flour, it was necessary to establish a relative criterion of dryness.

Accordingly, the term "dry" adsorbent, as used in this thesis, refers to the state of the adsorbent after the conditioning period described above.

The pure liquids from which the adsorbate vapours were drawn were degassed by repeated freezing, evacuation and melting. Three such degassing treatments were found sufficient to remove all the dissolved non-condensable gases. Sulphuric acid-water solutions were degassed in a similar manner.

After the conditioning treatment, the vapour was admitted to the adsorption chamber by opening slowly the stopcock which connected the flask containing the sulphuric acid-water solution or by admitting a definite amount of vapour from the pure liquid. The increase in weight of the adsorbent was reflected in an increased extension of the spiral, until equilibrium was established, at which time the pressure inside the adsorption chamber was also recorded. Pressures were measured on mercury manometers. The mercury levels could be measured either with a cathetometer or with an ordinary meter stick graduated in 1 mm. divisions.

The weight of vapour adsorbed per gram of dry adsorbent was determined from the extension of the spiral. This gives one point on the adsorption isotherm. To get a succeeding point, the pressure inside the adsorption chamber was increased by admitting more vapour or by replacing the sulphuric acid solution with one of lower concentration, and again

measuring the equilibrium extension and pressure. To obtain kinetic data at higher pressures, the original sample was again conditioned overnight and used in the same way to obtain the equilibration curve at the higher pressure. Actual experimental data illustrating the various phases of this procedure will be presented later.

It was found unnecessary to make corrections for the effect of buoyancy on the sample and the container. With the size of the sample used the correction, in all cases, was less than experimental error. It was also found unnecessary to correct for adsorption on the spiral or the sample dish. Blank experiments showed that there was no adsorption on the spiral or on the empty container until the relative pressure of 0.9 (for water vapour) was exceeded.

#### RESULTS

#### Conditioning of Samples

In all adsorption measurements the first step is to free the surface of the adsorbent from gases and vapours which are initially adsorbed on it. If the surface impurities are held by van der Waals forces, complete removal may be effected by evacuation of the system until a good vacuum is obtained. The rate of removal may be increased by applying slight heat to the adsorbent. If the impurities are chemisorbed, complete removal is considerably more difficult.

In the present investigation, water was the main impurity which had to be removed as completely as possible. To retain the original characteristics of the flour, starch or gluten it was not possible to use elevated temperatures to facilitate purification of the surface, and it was therefore decided that the same temperature should be used for the initial conditioning as for the corresponding adsorption experiment. The temperature used was 27°C., unless otherwise specified. To remove most of the water at this temperature required long periods of evacuation with the mechanical and diffusion pumps.

It was of interest to study the initial removal of moisture by the technique adopted, and to compare the moisture content obtained by this method with the value obtained by the standard air oven method.

Table 11 gives the complete experimental data for one conditioning treatment using duplicate samples of flour No. 2. The pressure in the system after about the first three to four hours of evacuation remained constant at less than  $10^{-4}$  mm. of mercury. The values of moisture removed, in percent, are plotted against evacuation time in Figure 3.

Figure 3 shows that the rate of decrease of sample weight became essentially constant after about six hours of evacuation. This was generally observed in subsequent experiments. The equilibrium moisture content according to this technique was 9.85% compared with 10.5\% by the standard air oven method. No attempt was made to reach the same moisture content by the two methods since this would probably have required temperatures in the order of  $100^{\circ}$ C and this would have altered the physical characteristics of the adsorbent.

The rate at which the moisture was removed was not affected noticeably by using larger samples or by packing them more compactly in the sample dish. That is, the observed rate is probably due to diffusion out of individual flour particles and not to diffusion from the mass of flour used. Gluten and starch gave very similar initial conditioning curves (Figure 3), although the moisture content of these materials was considerably less than that of the flour used.

On the basis of the results shown in Figure 3 it was

## TABLE 11

# Initial Conditioning of Flour

	Spiral-1	(1.80 mgm./mm.)		Spiral-2	gm./mm.)	
Evacu- ation Time	Cathe- tometer Reading	Δh	∆W= AhxS <sub>1</sub>	Cathe- tometer Reading	Δh	∆W= ∆hxS <sub>2</sub>
(Hr)	(cm.)	(mm.)	(mgm.)	(cm.)	(mm.)	(mgm.)
0 0.25 0.5 1.0 1.5 2.0 3.0 4.0 10.0 12.0	39.157 39.500 39.561 39.610 39.631 39.649 39.659 39.695 39.697 39.697 39.702	0 3 4 3 4 3 4 4 5 5 5 5 5 5 5 5 5 5 5 5 5	0 6.21 7.31 7.78 8.20 8.56 8.90 9.42 9.55 9.42 9.55 9.77 9.86	40.017 40.383 40.440 40.462 40.481 40.516 40.531 40.536 40.553 40.569 40.577 40.582	0635494962051 3444555555555555555555555555555555555	0 6.30 7.28 7.98 8.892 9.503 9.632 9.632 9.632

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Figure 3

Initial Conditioning of Flour (Duplicate Samples)



decided that a twelve hour initial evacuation period at 27°C was sufficient to give a reproducibly "dry" adsorbent. This conditioning procedure was therefore adopted for the remainder of the investigation.

### Rates of Adsorption

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A study of the rates of adsorption was necessary to determine the length of time required for equilibrium adsorption at each pressure and for each adsorbate since equilibrium values were necessary for plotting the adsorption isotherms.

Table 111 gives the complete experimental data for the adsorption of water vapour by flour No. 2 at 27<sup>o</sup>C at a relative pressure of 0.1. The method for calculating the data shown in columns 3 and 4 can be most easily demonstrated by an example.

- $\Delta$ h, the extension (cm.) of the spiral was obtained from the appropriate cathetometer readings.
  - k, a characteristic multiplying constant for each spiral to convert spiral extension to amount adsorbed, X, in mgm./gm., was dependent on the sensitivity of the particular spiral and the weight of the dry adsorbent. Its evaluation may be illustrated by the calculation of k shown in Table 111. Sensitivity of spiral No. 1 = 1.80 mgm./gm. Decrease in spiral extension during conditioning of the adsorbent (of 100 mgm. initial weight) = 5.56 mm.
#### TABLE 111

Adsorption of Water Vapour by Flour No. 2

(Initial weight of adsorbent = 100 mgm; T = 27°C) "Dry" weight of adsorbent = 90 mgm.

489 <u>000000000000000000000000000000000000</u>	Spiral-1	(k = 200.0) P = P/P <sub>0</sub>	= 2.8 mm. = 0.1
Time (Hr)	Cathetometer Reading (cm.)	△h (cm.)	X (mgm./gm.)
0 5 1.5 2.5 3 4 5 6 8	39.173 38.921 38.900 38.888 38.884 38.883 38.883 38.882 38.881 38.882 38.882 38.882	0 0.252 0.273 0.285 0.289 0.290 0.291 0.290 0.291 0.291 0.291	0 50.4 54.6 57.0 57.0 57.8 58.0 58.2 58.4 58.2 58.2 58.2

Decrease in weight =  $5.56 \times 1.80 = 10.0 \text{ mgm}$ . Weight of dry adsorbent = 100 - 10 = 90 mgm.  $\Delta h$  = extension due to adsorption of vapour by 90 mgm. of flour.

Extension for one gm. of dry adsorbent would be

$$\Delta h \ge \frac{1000}{90}$$
 cm. =  $\Delta h \ge \frac{10^4}{90}$  mm.

Increase in weight for one gm. of adsorbent would be

$$\Delta h \ge \frac{10^4}{90}$$
 x Sensitivity of Spiral, S, in mgm./mm.

Hence, 
$$k = \frac{10^4}{90} \times S$$
 or simply = Sensitivity(mgm./mm.) x 10  
Weight of dry adsorbent  
(mgm.)

Table 1V gives the data for the rates of adsorption of water vapour on flour at seven different relative pressures. In this experiment the vapour pressure was varied by admitting additional vapour from the pure liquid. These data are plotted in Figure 4.

Figure 4 shows that, in the system used, the adsorption of water was quite rapid and complete equilibrium was established in about three hours. The rate of adsorption was not affected by the pressure of water vapour.

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# TABLE 1V

Adsorption of Water Vapour by Flour No. 2

(T = 27<sup>o</sup>C; Vapour Source - Pure Water)

Time			X(mgm./	(gm.)			
(Hr.)	$P/P_0 = 0.1$	$P/P_0 = 0.20$	$P/P_0 = 0.34$	$P/P_0 = 0.47$	$P/P_0 = 0.61$	$P/P_0 = 0.73$	$P/P_0 = 0.84$
_	_	_					_
0	0	0	0	0	0	0	0
0.5	50.4	63.2	79.6	99.6	115.9	136.3	174.5
1.0	54.6	71.2	89.2	109.5	128.3	145.5	189.3
1.5	57.0	73.8	92.2	114.1	131.9	153.5	194.7
2.0	57.8	74.2	03.4	115.5	134.0	154.0	195.5
2 5		75.0		116 5	125 3	155 7	105 7
2.0	50.0	75.0	94.0	110.5	125 7	156 1	105 7
5.0	20.2	12.0	94.2	110.2	132.1	100.1	192.1
4.0	58.0	75.2	93.8	116.7	135.5	150.5	195.1
5.0	58.4	75.4	93.8	116.7	135.5	156.1	196.1
6.0	58.2	75.2	94.0	117.1	135.7	156.5	195.9
8.0	58.2	75.6	94.0	116.9	135.7	156.5	195.9

Adsorption of Water Vapour on Flour at Various Relative Pressures (Relative pressures shown in circles)



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Table V compares kinetic data for the adsorption on flour of water, methyl alcohol and ethyl alcohol vapours at approximately the same relative pressures. These data are plotted in Figure 5.

Figure 5 shows that while two to three hours were adequate to establish equilibrium with water vapour, the same process with methyl alcohol vapour required about six hours and more than eight hours were required to attain equilibrium with ethyl alcohol vapour. These results, in addition to the fact that the kinetic data fit a first order rate equation, suggest that diffusion is the rate controlling factor.

Rate experiments with starch and gluten gave results that were closely parallel to those obtained with flour. Kinetic data were not recorded during the whole time required for attainment of equilibrium with carbon tetrachloride and ammonia on flour. When adsorption had proceeded until the spiral extension remained constant during a two hour period, the final value was used to plot the isotherms for these two adsorbates. It was observed that ammonia required only about two hours to reach equilibrium. With carbon tetrachloride adsorption was usually complete after about eight hours.

Although the results of the kinetic experiments served as a reasonably reliable guide, much longer equilibration periods than those indicated above were generally used to obtain data for the isotherms. The fact that complete ad-

### TABLE V

Adsorption of Water, Methyl Alcohol and Ethyl Alcohol by Flour

(T = 27°C; Adsorbent - Flour No. 2)

 ጥነ mo	Water $(P/P_{-}=0.72)$	Methyl Alcohol (P/P_= 0.72	Ethyl Alcohol (P/P_= 0.70
(Hr)	X(m.moles/gm.)	X(m.moles/gm.)	X(m.moles/gm.)
++++++-=++++++++++++++++++++++++++++++			
0	0	0	0
0.25	7.15	1.32	0.30
0.5	8.12	2.17	0.48
0.75	8,28	2.74	-
1.0	8.35	3.13	-
1.25	8,45	3.34	1.03
1.5	8.57	3.53	-
1.75	_	3.65	-
2.0	8.64	3.74	1.44
3.0	8.45	3.85	-
4.0	8.45	3.87	2.00
5.0	8.64	3.95	-
6.0	8.64	-	2,15
7.0	8.64	3.95	_
8.0	8.64	3.95	2.24

#### Rates of Adsorption on Flour

- -0-0- Water vapour at 0.72 relative pressure - $\Delta$ - $\Delta$ - Methyl alcohol vapour at 0.72 relative pressure
- -D-D- Ethyl alcohol vapour at 0.70 relative pressure



sorption should correspond to attainment of constant weight was still the main criterion of equilibrium.

It was generally observed that the time required to reach equilibrium on desorption was considerably shorter than that required for adsorption equilibrium with the same adsorbate. However, it is doubtful that true thermodynamic equilibrium was attained during desorption; the position of the desorption branch of the isotherm probably corresponds to a metastable condition of the adsorbent.

#### Effect of Air on the Adsorption Process

Peculiar effects were usually observed if slight amounts of air leaked into the adsorption chamber during the equilibration period. If the leak occurred after equilibrium had been established the weight of the sample either decreased or increased slowly, depending on the vapour pressure in the system. If the leak were stopped, a constant sample weight was again recorded after a few minutes.

Two controlled experiments were made to investigate further this effect. In the first experiment, a small amount of air was admitted after equilibrium was established at 17 mm. pressure of water vapour. When equilibrium was again established at the new, higher total pressure, an additional small amount of air was admitted. In the second experiment, the solution of constant vapour pressure was not degassed, so that the total pressure in the adsorption chamber was 101.5 mm.

instead of 17 mm.

The results of the two experiments are given in Table VI. Figure 6 shows the variations in increase of the weight of the adsorbent as a function of time.

Figure 6 reveals a number of effects, all of which could be explained on the basis of diffusion. The upper curve shows that, as soon as air was admitted, the adsorbent suddenly increased in weight; however, it returned to its original weight after about fifteen minutes of equilibration. A similar effect was observed when more air was admitted to the adsorption chamber. These results suggest that the incoming air acted as a piston and increased the partial pressure of water vapour in the immediate vicinity of the adsorbent. This effect disappeared as soon as the air and the vapour had sufficient time to mix. Hence, such an effect may be regarded as characteristic of the present system when air is admitted at the top of the adsorption tube.

The effects shown by the second curve can also be attributed to diffusion. Immediately after the adsorption chamber was opened to the vapour source, a relatively high partial pressure of water vapour was present in the homogeneous airvapour mixture around the adsorbent. However, as water vapour was rapidly adsorbed its partial pressure decreased to a considerably lower value and an apparent equilibrium was then established at this lower partial pressure of water vapour.

#### TABLE V1

Effect of Air on Adsorption of Water Vapour by Flour

Time (Hr)	Total Pressure (mm.)	X (mgm./mm.)	Time (Hr)	Total Pressure (mm.)	X (mgm./mm.)
0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 17 17 17 17 17 17 17 17 17 17 17 17 17	0 137.1 146.7 149.1 150.0 149.9 149.9 149.9 150.0 150.0 150.0 150.0 171.2 160.3 156.5 154.5 150.6 150.4 163.4 155.9 147.0 145.8 145.8	0 1.0 1.5 2.0 3.0 5.0	101.5 101.5 101.5 101.5 101.5 101.5 101.5	0 38.1 40.3 43.8 42.0 44.0 48.7 48.7

(T = 27<sup>o</sup>C; Adsorbent - Flour No. 2)

<sup>x</sup>Air admitted to increase total pressure immediately after the indicated readings.

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Effect of Air on Adsorption of Water Vapour on Flour

- -o-o- Air admitted into the system after equilibrium was established with water vapour.
- $-\Delta \Delta$  Vapour source not degassed.



Further adsorption then depended upon the rate at which water vapour was able to diffuse through the air to the adsorption sites.

On the basis of these observations, it is obvious that traces of air in the adsorption chamber may markedly effect the rate of adsorption and in certain cases may make attainment of true equilibrium practically impossible in any reasonable time. During the remainder of the investigation, results were discarded if an increase in pressure in the adsorption chamber was observed at any time during the equilibration period.

# Sorption of Water, Methyl Alcohol, Ethyl Alcohol and Carbon Tetrachloride Vapours on Flour

While sulphuric acid-water solutions were useful as sources of constant vapour pressure when water vapour was the adsorbate, control of the vapour pressure with other adsorbates was not possible by similar means since it was not possible to dissolve sufficient non-volatile substances in the alcohols or carbon tetrachloride to obtain relative pressures of the order of 0.1. Hence, with these adsorbates, the pressure of the vapour in the adsorption chamber was varied by admitting vapour from a flask containing a pure liquid. Since Pidgeon (106) has pointed out that the two procedures for controlling the pressures of the vapour may give different results when water vapour is the adsorbate, it was obviously of interest to examine this point with the present type of system.

Data for the flour-water isotherms, when the two techniques were used to vary the vapour pressure, are given in Table VII and plotted in Figure 7.

Figure 7 shows that the two methods give essentially equivalent isotherms with practically identical hysteresis loops. Accordingly, it is obvious that the objections raised by Pidgeon do not apply to the present system. Presumably, the size of the adsorption chamber was so large in comparison with the amount of adsorbent that the pressure remained essentially constant throughout the equilibration period. Periodic checks of the pressure during an experiment indicated that this was indeed true.

Table VII also gives data for a second sorption cycle on each of the two samples. Comparison of these data with those in the first part of Table VII will show that the reproducibility is well within the experimental error. It may also be pointed out that both the adsorption and the desorption branches of the isotherm were completely reversible in the range of pressures used.

Visual examination of the adsorbent after these adsorptiondesorption experiments showed that the flour was transformed

# TABLE VII

# Sorption of Water Vapour by Flour No. 2 at 27°C.

Sulphuric	Acid Solutions	Pure	e Water
P/P <sub>o</sub>	Amount Adsorbed X(mgm./gm.)	P/P <sub>o</sub>	Amount Adsorbed X(mgm./mm.)
			· ·
Adsorption:			
0.09	58.5 81.8	0.10 0.20	58.2 75.6
0.39 0.52	106.7 124.7	0.34 0.47	94.0 116.9
0.83	198.0	0.73 0.84	150.7 156.5 195.9
Desorption:			
0.64 0.52 0.39 0.22 0.09	156. 139.4 121.2 95.8 72.0	0.70 0.55 0.42 0.25 0.10	162.1 140.2 121.9 99.5 70.1
	Second C	ycle	
Adsorption:			
0.39 0.83	107.4 198.9	0.45 0.83	112.3 192.4
Desorption:			
0.52	140.6	0.60	147.3

#### Sorption Isotherm for Water Vapour on Flour

- -o-o- Adsorption) Vapour source - H<sub>2</sub>SO<sub>4</sub> solutions
- $-\Delta \Delta -$  Adsorption Vapour source - pure water - $\Delta - \Delta -$  Desorption



**..**.

from a powder to a compact cake which was firm enough to be lifted from the container. This effect, which will be referred to as "vapour phase cross-linking", will be discussed further in a later section. It is important to note at this point, however, that formation of the flour cake, which apparently had no effect on the adsorption process, occurred only at higher relative pressures, but below the pressure at which bulk condensation occurred. Visible condensation occurred at relative pressures above about 0.9 and since this completely altered the physical characteristics of the adsorbent, relative pressures above 0.9 were not used in the sorption studies.

Table VIII gives the isotherm data for flour No. 2 and four adsorbates: water vapour; methyl alcohol vapour; ethyl alcohol vapour; and, carbon tetrachloride vapour. The data for water vapour, recorded in this table are taken from Table VII (note the difference in units). The isotherms for the four adsorbates are shown in Figure 8.

The following features of the isotherms may be emphasized for later discussion:

1. Water, methyl alcohol and ethyl alcohol, all yielded sigmoid isotherms with hysteresis over the entire range of pressures investigated.

2. For the same three adsorbates, the amount of sorption

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# TABLE VIII

# Sorption by Flour No. 2 at 27°C.

Water		Methyl Alcohol		Ethyl Alcohol		Carbon Tetrachloride	
P/P <sub>o</sub>	X(m.moles/gm.)	P/P <sub>o</sub>	X(m.moles/gm.)	P/P <sub>o</sub>	X(m.moles/gm.)	P/P <sub>o</sub>	X(m.moles/gm.)
Adsor	ption:						
0.10 0.20 0.34 0.47 0.61 0.73 0.84 Desor	3.23 4.20 5.22 6.49 7.53 8.68 10.87	0.05 0.20 0.30 0.44 0.59 0.73 0.88	0.63 1.81 2.17 2.96 3.41 3.87 4.87	0.19 0.41 0.51 0.70 0.72 0.906 0.905 0.91	0.64 1.14 1.52 2.32 2.55 3.00 2.94 3.08	0.12 0.19 0.33 0.47 0.56 0.70 0.76 0.84	0.06 0.08 0.12 0.18 0.21 0.29 0.29 0.34
0.70 0.55 0.42 0.25 0.10	9.00 7.78 6.76 5.52 3.89	0.68 0.45 0.27 0.15 0.06	4.08 3.73 3.03 2.50 1.80	0.78 0.65 0.49 0.33 0.20	2.91 2.78 2.62 2.54 2.21	0.72 0.59 0.50 0.39 0.28	0.29 0.24 0.20 0.15 0.12

### Sorption Isotherms for Various

#### Adsorbates on Flour

- Empty adsorption
- Filled desorption



varied directly with polarity and inversely with molar volume.

3. The degree of hysteresis increased with molar volume of the polar adsorbate.

4. Carbon tetrachloride was only slightly adsorbed; its isotherm was essentially linear and showed no hysteresis.

# Apparent Irreversibility in Sorption of Methyl Alcohol Vapour on Flour

It was noted in the course of the experiments reported in the previous section that adsorbed alcohols could not be removed by evacuation for any practical length of time, whereas adsorbed water could be completely removed by evacuation for about six to eight hours. An experiment was therefore made to examine further the apparent irreversibility of alcohol adsorption.

Methyl alcohol vapour was adsorbed on a sample of flour, which had been conditioned in the usual way, until equilibrium adsorption was attained. The system was then evacuated for twenty-two hours. After this desorption, the adsorbent retained about 3% adsorbed alcohol. Water vapour was then adsorbed on the sample and after equilibrium had been established, the system was again evacuated for eight hours to desorb the water vapour. About 1% of adsorbed materials remained on the sample. Water vapour was then adsorbed a second time until equilibrium was attained, after which the desorption process was repeated. The original weight of dry adsorbent was then reproduced within experimental error. In Table 1X and Figure 9 are recorded the data obtained by these various manipulations.

#### Sorption of Ammonia on Flour

Isotherm data for the sorption of ammonia on flour No. 2 are given in Table X. A plot of the amount sorbed against the absolute pressure of ammonia is shown in Figure 10. This isotherm was not included with isotherms for the other adsorbates since at  $27^{\circ}$ C. the highest pressure of ammonia (69.3 cm.) corresponds to only 0.1 relative pressure. However, to compare the sorption of ammonia with that of water it is necessary to use the relative pressure scale and such a comparison shows that that flour adsorbs slightly more ammonia than water.

# Sorption of Water and Methyl Alcohol Vapours on Starch and Gluten

Isotherm data for sorption of water and methyl alcohol vapours by starch, and freeze-dried and spray-dried gluten, are given in Table X1 and Table X11 respectively. Figure 11 shows the two isotherms for starch and Figure 12 shows the analogous isotherms for the glutens.

The isotherms for starch and gluten are very similar to the flour isotherms for the same two adsorbates. Figure 13 compares the water isotherms for the four adsorbents. The

# TABLE 1X

# Descrption Irreversibility with Methyl Alcohol

 $(T = 27^{\circ}C; Adsorbent - Flour No. 2)$ 

Time	Methyl Alcohol (P=118)	Water (P=21 mm.)	Water (P=21 mm.)
(Hr)	X(mgm./gm.)	X(mgm./gm.)	X(mgm./gm.)
Adsor	ption:		
0	Q	27.0	8.0
0.25	94.6	143.0	
0.50	120.	199•1	190.0
0.75	157.2	1610	168 5
1.0	144.5	172 0	186 0
2.0	162 1	172.0	187.6
3.0	164.2	-	187.6
4.0	164.2	172.2	188.0
5.0	164.2		187.6
6.0	-	_	-
7.0	164.2	-	-
Desor	ption:		
0	164.2	172.2	187.6
0.25	72.0	-	-
0.50	65.6	37.0	
0.75	62.3		
1.0	61.0	26.1	13.6
1.5	58.2	21.2	6.0
2.0		16 1	0.2
5.0	59.6	TO•T	_
8.0	-	8	2.2
22.0	27.0		

#### Desorption Irreversibility with Methyl Alcohol

on Flour

- -o-o- Initial adsorption of MeOH (1)
- ---- Desorption after (1)
- - $\triangle$ - $\triangle$  Adsorption of  $H_20$  (2)
- $\blacktriangle \blacktriangle -$  Desorption after (2)
- - $\Box$ - $\Box$  Adsorption of H<sub>2</sub>O (3)
- - Desorption after (3)



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# TABLE X

Sorption of Ammonia by Flour No. 2 at 27°C.

Pressure (mm.)	X(mgm./gm.)
Adsorption:	
50 105 155 190 246 305 310 392 436 452 577 693	31.5 44.4 50.0 54.8 61.5 67.8 68.5 76.4 78.3 78. 86.2 95.0
Desorption:	
495 220 90 42 0 <b>x</b>	83.5 62.1 46.8 38.6 4.0

After 12 ho	urs of	f evacuatio	n
-------------	--------	-------------	---

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### Sorption Isotherm for Ammonia on Flour

# Legend

- -o-o- Adsorption
- -e-e- Desorption

.



# TABLE X1

# Sorption of Water and Methyl Alcohol by Starch at 27°C.

	Water	Methyl Alcohol			
P/Po	X(m.moles/gm.)	P/P <sub>o</sub>	X(m.moles/gm.)		
Adsorpti	.on:				
0.10 0.20 0.34 0.47 0.61 0.73 0.84	3.19 4.17 5.32 6.84 8.00 9.81 11.64	0.05 0.20 0.30 0.44 0.59 0.73 0.88	0.88 1.99 2.54 2.99 3.43 3.94 4.84		
Desorpti	on:				
0.70 0.55 0.42 0.25 0.10	9.83 8.61 7.14 5.52 3.87	0.68 0.45 0.27 0.15 0.06	4.16 3.84 3.28 2.65 1.94		

Sorption Isotherms for Water and Methyl Alcohol Vapours on Starch

- Empty adsorption
- Filled desorption



### TABLE X11

Sorption of Water and Methyl Alcohol by Gluten at 27°C.

	Gluten (1)			Gluten (2)			
Water	? 	Methyl	Alcohol	Water	?	Methyl	Alcohol
P/P <sub>o</sub>	X	P/P <sub>o</sub>	х	P/P <sub>o</sub>	х	P/P <sub>o</sub>	Х
Adsorpt	tion:						
0.15 0.27 0.43 0.60 0.72 0.82	2.35 3.58 4.98 6.61 8.00 9.40	0.07 0.15 0.23 0.37 0.45 0.52 0.65 0.73 0.76 0.82	0.82 1.50 1.92 2.64 2.94 3.10 3.72 4.12 4.70 5.51	0.15 0.27 0.43 0.60 0.72 0.82	1.91 2.74 3.98 5.35 6.54 7.75	0.07 0.15 0.24 0.38 0.45 0.51 0.63 0.76 0.82	0.95 1.46 1.80 2.47 2.78 2.90 3.48 4.35 6.30
Desorpt	tion:						
0.76 0.67 0.60 0.51 0.42 0.35 0.31 0.24 0.18 0.13 0.09	8.68 7.96 7.38 6.07 5.08 5.08 3.80 4.30 2.36	0.63 0.58 0.35 0.26 0.06	4.79 4.31 3.82 3.33 1.30	0.76 0.67 0.51 0.42 0.35 0.31 0.24 0.18 0.13 0.09	6.90 5.76 5.76 4.25 3.79 2.62 2.10 1.51	0.80 0.59 0.35 0.26 0.12 0.06	5.31 4.40 3.79 3.26 2.31 1.64

X is given in millimoles/gm.

Sorption Isotherms for Water and Methyl Alcohol Vapours on Gluten.

- Empty adsorption
- Filled desorption


Sorption Isotherms for Water Vapour on Flour, Starch, Gluten (1) and Gluten (2).

### Legend

- Empty adsorption
- Filled desorption



small differences probably reflect real differences in the sorptive capacity of the various materials. The glutens showed vapour phase cross-linking with water vapour similar to that observed with flour but no comparable behavior was observed with starch.

#### Sorption of Water Vapour on Modified Freeze-Dried Gluten

The sample of gluten used as adsorbent in this experiment was treated as follows. A 2 gm. sample of freeze-dried gluten was placed in a 50 ml. beaker and completely covered with water. This was allowed to remain at room temperature until the water had completely wetted the gluten. After this treatment, the gluten was in the form of a coherent mass similar to that which is readily obtained by kneading gluten with a small amount of water. The wet, cross-linked gluten was dried in an Abderhalden Drying Apparatus for twelve hours, using methyl alcohol as the heating vapour. A portion of the dry, brittle material was then used as the adsorbent. Further reference to the glassy, brittle material which results from this treatment will be made later.

The effect of such treatment on the adsorption isotherm is of practical interest since the change in gluten resembles, to a certain extent, the changes which gluten undergoes during the doughing process. It is realized, however, that the difference in the isotherm of the original and the treated glutens

has no theoretical significance since the physical properties of the two materials are entirely different.

Table X111 and Figure 14 give the equilibrium weights of water vapour that were sorbed at various relative pressures.

The significant difference between the isotherm shown in Figure 14 and isotherm for the sorption of water vapour by the untreated gluten (Figure 13) was the decrease in concavity to the pressure axis in the low relative pressure region. Actually, the isotherm for the modified gluten was essentially linear to relative pressures of about 0.7. A very similar type of isotherm was reported (58) for the sorption of water vapour on whole wheat. On the basis of these results, it may be speculated that cross-linking eliminates the sorption sites which are responsible for the rapidly increasing initial portion of the isotherm for the original gluten. Much more evidence would be necessary, however, for a critical examination of this possibility.

# Effect of Particle Size and Heat Treatment on Sorptive Capacity of Flour for Water Vapour

It was of interest to examine the effect of particle size on adsorption since it might be expected that the extent of adsorption would depend upon the external surface area of the adsorbent. Moreover, particle size is a relatively important factor in flour technology. Its effects on a number of flour

#### TABLE X111

Sorption of Water Vapour by Modified Gluten at 27°C.

P/P <sub>o</sub>	X(mgm./gm.)
Adsorption:	
0.067 0.20 0.36 0.54 0.68 0.79 0.89	15.32 42.31 67.93 94.31 118.76 146.86 225.44
Desorption:	
0.80 0.66 0.38 0.21 0.09	158.4 125.7 90.4 65.7 42.3

# Sorption Isotherm for Water Vapour on Modified Gluten.

# Legend

Empty - adsorption

Filled - desorption



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properties have been investigated (107, 108).

Table XIV gives the sorption data for five fractions of different particle size and for the unfractionated flour. The maximum extent of variation is illustrated by the data plotted in Figure 15.

A rough estimate of the relative variation in external surface area of the five fractions may be obtained by calculating the surface area on the assumption that the diameter of the particles in each fraction corresponded to the size of the holes in the sieve through which the fraction passed. The pertinent data for such a comparison are collected in Table XV.

The data in the last column of Table XV show that the total variation in surface was about twofold. However, the adsorption isotherms indicate that the specific adsorption surface was essentially the same for all the fractions and the original flour.

The colloidal nature of proteins, which undoubtedly plays an important role in adsorption, can be readily altered by heat treatment. Accordingly, it was also of interest to study the effect of moderate heat treatment on the sorptive capacity of flour.

The flour samples which were used as adsorbents in this experiment (flour No. 1) were prepared as follows. Approximately 5 gm. of flour was placed into a series of small glass vials,

#### TABLE XIV

#### Effect of Particle Size on Adsorption of Water Vapour

at  $27^{\circ}$ C.

Origir Flour	nal	н.о.	120	H.O.	140	н.о.	170	н.о.	200	Р.Т.	200
P/P <sub>o</sub>	x X	P/P <sub>o</sub>	Х	P/P <sub>o</sub>	X	P/P <sub>o</sub>	X	P/P <sub>o</sub>	х	P/P <sub>o</sub>	x
0.20 0.42 0.69 0.78	80.0 112.7 152.5 166.7	0.20 0.42 0.69 0.78	75.9 108.2 149.3 170.7	0.17 0.45 0.62 0.71	65.6 111.1 140.9 158.3	0.17 0.45 0.62 0.71	63.5 107.1 138.6 155.3	0.18 0.47 0.62 0.71	67.9 112.0 141.0 152.4	0.18 0.47 0.62 0.71	75.8 125.8 151.6 164.1

x(mgm./gm.)

#### TABLE XV

Variation of Surface Area With Particle Size

Fraction	Diameter of Particles (microns)	Relative Specifi Surface Area		
P.T. 200 H.O. 200 H.O. 170 H.O. 140	<74 74 - 88 88 -105 105 -120	> 8.0 8.0 - 6.7 6.7 - 5.7 5.7 - 5.9		
H.O. 120	>120	<5.0		

Adsorption Isotherms for Water Vapour on Various Particle Size Fractions of Flour

#### Legend

- Fraction
- -o-o- Passed through sieve 200
- ---- Held on sieve 200
- $-\Delta \Delta -$  Unfractionated flour
- - $\triangle$ - $\triangle$  Held on sieve 120



which were evacuated and sealed. These were then held in an oven at  $100^{\circ}$ C for various periods of time.

Table XVI gives the sorption data for the untreated flour and for samples which were heated for 4, 8, and 24 hours. The adsorption isotherms in Figure 16 show that heat treatment caused a definite decrease in the sorptive capacity of the flour. A 24-hour treatment at  $100^{\circ}$ C decreased the sorptive capacity by about 20%.

# Effect of Temperature on Adsorption of Water Vapour on Flour, Gluten (1) and Starch

Adsorption isotherms for water vapour on flour, gluten (1) and starch were determined at four temperatures to obtain data for calculating the isosteric heats of adsorption. Apparatus No. 2 was used in these experiments.

The usual experimental procedure had to be slightly modified for this series of experiments. It was found more convenient to condition the samples at the highest temperature to be used subsequently for adsorption, namely  $50.2^{\circ}$ C. Also, instead of determining the complete isotherm at one temperature, it was found more practical to determine the equilibrium adsorption at the four temperatures with constant relative pressure. The temperatures could be reproduced quite easily by using four thermoregulators set at  $20.2^{\circ}$ ,  $30.1^{\circ}$ ,  $40.8^{\circ}$  and  $50.2^{\circ}$ C. For the experiments with gluten and starch the third thermoregulator

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#### TABLE XV1

Effect of Heat Treatment on Sorptive Capacity of Flour for Water Vapour

(T = 27<sup>°</sup>C; Adsorbent - Flour No. 1; Vapour Source - Pure Water)

	0 <sup>x</sup>		4 <sup>x</sup>		8 <b>x</b>	24 <sup>x</sup>		
P/P <sub>o</sub>	X(mgm./gm.)	P/P <sub>o</sub>	X(mgm./gm.)	P/P <sub>o</sub>	X(mgm./gm.)	P/P <sub>o</sub>	X(mgm./gm.)	
0.07 0.22 0.29 0.58 0.55	46.1 81.8 101.3 143.6 169.7	0.16 0.29 0.51 0.69 0.80	65.0 87.4 122.1 173.4 207.0	0.29 0.51 0.62 0.73	78.8 128.0 148.6 174.4	0.15 0.51 0.62 0.73 0.91	50.0 111.2 132.6 154.8 242.2	

x Hours of heat treatment.

# Effect of Heat Treatment at 100°C on Sorptive Capacity of Flour for Water Vapour.

### Legend

- -D-D- Untreated flour.
- $-\Delta \Delta 4$  hours
- -0-0- 8 hours
- -O-O- 24 hours



was set at 40.6°C.

For adsorption, rather than desorption, to occur at each temperature the experiment with each solution was begun at the highest temperature and the temperature successively decreased. If the procedure was reversed, the process at the lowest temperature would be adsorption and the processes at the higher temperatures would be desorption. The results by the two methods would not be the same owing to the hysteresis effect. Although the absolute pressure decreased markedly (relative pressure only slightly) with decrease of temperature, the amount adsorbed increased as the temperature was decreased owing to the exothermicity of the process.

After equilibrium adsorption data were obtained for the four temperatures with one solution as the vapour source, the solution was replaced by another which gave a higher vapour pressure and the extent of adsorption again determined at each temperature. Altogether six sulphuric acid solutions were used to provide six points on each isotherm at each temperature.

Table XVII gives the isotherm data for flour at the four temperatures. These data are plotted in the usual way in Figure 17. Figure 18 shows the same data plotted with the abscissa as absolute rather than relative pressure of water vapour.

Table XVIII gives pertinent data for plotting the Clausius-Clapeyron equation (log P vs. 1/T). The equilibrium pressures,

### TABLE XV11

Adsorption of Water on Flour at Four Temperatures

20.2 <sup>°</sup> C (P <sub>0</sub> = 17.75)		30.1°C (P <sub>o</sub> = 32.00)			40.8°C (P <sub>o</sub> = 57.72)			50.2°C (P <sub>o</sub> = 93.5)			
P (mm)	P/P <sub>o</sub>	x <sup>x</sup>	P(mm)	P/P <sub>o</sub>	X	P(mm)	P/P <sub>o</sub>	X	P(mm)	P/P <sub>o</sub>	X
2.21 4.11 7.57 11.00 13.58 15.85	0.12 0.23 0.43 0.62 0.76 0.89	68.8 85.5 104.9 138.6 173.9 250.0	4.35 8.39 13.77 18.90 25.02 28.90	0.14 0.26 0.43 0.63 0.78 0.90	64.3 79.9 102.8 134.9 172.3 245.9	7.58 16.69 25.93 36.08 44.84 51.50	0.13 0.29 0.45 0.63 0.78 0.90	59.3 76.8 99.6 131.0 168.4 241.8	14.89 28.90 44.03 59.77 74.27 84.16	0.16 0.31 0.47 0.64 0.79 0.90	54.3 73.5 96.0 125.5 162.6 239.5

X<sup>X</sup> in mgm./gm.

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Flour - Water Vapour Adsorption Isotherms at Four Temperatures.

Legend	
-0-0-	20 <b>.</b> 2°c
- Δ-Δ-	30.1°c
	40.8 <sup>°</sup> c
-0-0-	50.2 <sup>°</sup> C



Amount of Water Vapour Adsorbed on Flour at Different Temperatures Plotted Against the Absolute Vapour Pressure.



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# TABLE XV111

Data IOP FIOULING CLAUSIUS=CLADEVPOIL EQUAL	Data	for	Plotting	Clausius-Clapeyron	Equation
---	------	-----	----------	--------------------	----------

	20.2 <sup>0</sup> C (1/T=3.4	1x10 <sup>-3</sup> )	30.1°C (1/T=3	.30x10 <sup>-3</sup> )	40.8 <sup>0</sup> C (1	/T=3.19x10 <sup>-3</sup> )	50.2 <sup>0</sup> C	(1/T=3.09x10 <sup>-3</sup> )
<u>x</u>	P(mm)	log P	P(mm)	log P	P(mm)	log P	P(mm)	log P
60 80 100 120 140 160 180 200 220 240	1.349 3.319 6.443 9.408 11.16 12.60 13.76 14.50 15.09 15.62	0.130 0.521 0.809 0.974 1.048 1.100 1.139 1.161 1.179 1.194	3.07 7.04 12.99 17.60 20.74 23.26 25.12 26.40 27.52 28.32	0.487 0.848 1.114 1.246 1.317 1.367 1.400 1.422 1.440 1.452	6.35 14.43 25.40 32.78 38.15 42.66 45.66 47.97 49.99 51.37	0.803 1.159 1.405 1.516 1.581 1.630 1.660 1.681 1.699 1.711	13.18 26.27 43.94 54.98 63.39 70.31 75.17 78.63 81.81 83.40	1.120 1.419 1.643 1.740 1.802 1.847 1.876 1.896 1.913 1.921

Adsorption Isosteres for Water Vapour on Flour (Figures indicate the amount adsorbed in mgm./gm.)



at constant adsorption, for the four temperatures shown in Table XVIII were obtained from Figure 18. The Clausius-Clapeyron lines are shown in Figure 19. The slopes of these lines, given in Table XIX, were calculated by the least squares method although they could also be obtained from the graph. The third column in Table XIX gives the isosteric heats of adsorption on flour for different amounts adsorbed.

Analogous data for gluten(1) and starch are given in Tables XX, XX1 and XX11 and Tables XX111, XX1V and XXV respectively. The plots of these data are essentially the same as the corresponding plots for flour and are therefore not presented. The isosteric heats of adsorption for each of the three adsorbents are plotted as functions of the extents of adsorption in Figure 20.

# Application of the BET Equation to the Flour-Water Vapour Isotherm

To use the BET equation to obtain an explicit mathematical equation for a sigmoid isotherm, it is first necessary to obtain the values of the constants  $X_m$ (the amount of water vapour adsorbed in the first monomolecular layer) and, c(which is approximately equal to  $\exp(E_1 - E_L)/RT$ . The data for plotting the linear form of the BET equation (10) are given in Table XXVI. The amounts adsorbed at different pressures shown in column 4 were taken from the adsorption isotherm in

### TABLE X1X

Isosteric Heats at Different Adsorptions on Flour

X(mgm./gm.)	Slope x 10 <sup>-3</sup>	-∆H (k.cal)
60 80 100 120 140 160 180 200 220 240	3.07 2.81 2.61 2.40 2.36 2.34 2.35 2.30 2.30 2.28	14.06 12.85 11.94 10.98 10.80 10.71 10.75 10.50 10.50 10.43

.

# TABLE XX

Adsorption of Water on Gluten (1) at Four Temperatures

20	.2°c		30	.1°c		40.6°c	( <sup>P</sup> o = 57	.11)	50	.2 <sup>°</sup> C	
P(mm)	P/P <sub>o</sub>	Х	P(mm)	P/P <sub>o</sub>	x	P(mm)	P/P <sub>o</sub>	x	P(mm)	P/P <sub>o</sub>	X
1.30 2.04 4.82 7.43 13.00 16.36	0.07 0.12 0.27 0.42 0.73 0.92	34.2 51.9 71.9 88.4 151.2 257.4	2.77 4.19 8.62 14.09 23.63 29.44	0.09 0.13 0.27 0.44 0.74 0.92	31.7 48.4 69.1 85.5 146.5 254.4	5.57 8.15 16.48 26.52 42.46 52.54	0.10 0.14 0.29 0.46 0.74 0.92	28.8 45.0 66.2 81.6 143.2 252.1	11.55 15.12 28.81 44.99 70.75 86.17	0.12 0.16 0.30 0.48 0.76 0.92	26.2 39.7 63.9 76.7 139.0 249.7

### TABLE XX1

# Data for Plotting the Clausius-Clapeyron Equation

20.2 <sup>0</sup> C		°c	30.1	°c	40.6	°c	50.2°C	
x	P(mm)	log P	P(mm)	log P	P(mm)	log P	P(mm)	log P
40 60 100 120 140 160 180 200 220	1.53 2.80 5.25 9.16 10.97 12.30 13.37 14.20 14.84 15.44	0.1835 0.4478 0.7205 0.9618 1.0403 1.0899 1.1261 1.1523 1.1714 1.1887	3.07 5.63 10.69 17.22 20.35 22.72 24.51 25.92 27.10 28.10	0.4874 0.7507 1.0289 1.2360 1.3086 1.3564 1.3893 1.4136 1.4330 1.4437	5.99 10.97 21.70 31.98 37.12 41.23 44.20 46.66 48.66 50.26	0.7779 1.0403 1.3365 1.5049 1.5708 1.6152 1.6454 1.6689 1.6872 1.7012	10.94 20.10 41.14 54.14 59.84 68.44 73.40 77.23 80.41 82.75	1.0390 1.3032 1.6143 1.7335 1.7770 1.8353 1.8657 1.8878 1.9053 1.9178

# TABLE XX11

# Isosteric Heats at Different Adsorptions on Gluten

X(mgm./gm.)	-3 Slope x 10	- △H (k. cal)
.*		
40	2.67	12.21
60	2.67	12.21
80	2.79	12.76
100	2.42	11.07
120	2.31	10.57
140	2.33	10.76
160	2.31	10.57
180	2.30	10,50
200	2,29	10.48
220	2.28	10.43
240	2.20	10.39
270	L • L [	

# TABLE XX111

Adsorption of Water on Starch at Four Temperatures

20.2 <sup>0</sup> C			30.1 <sup>0</sup> C			40.6°c			50.2 <sup>0</sup> C		
P(mm)	P/P <sub>o</sub>	X	P(mm)	P/P <sub>o</sub>	X	P(mm)	P/P <sub>o</sub>	X	P(mm)	P/P <sub>o</sub>	X
1.75 5.75 8.55 11.75 13.32 16.33	0.10 0.32 0.48 0.66 0.75 0.92	54.3 90.3 119.0 160.6 201.3 260.6	3.30 9.83 15.10 21.13 24.04 29.30	0.10 0.31 0.47 0.66 0.75 0.92	50.5 86.43 114.8 151.9 189.7 253.8	6.23 17.81 27.49 37.80 45.48 52.93	0.11 0.31 0.48 0.66 0.79 0.92	46.7 83.0 110.3 140.9 182.0 247.3	10.89 30.37 45.07 62.72 70.81 85.11	0.12 0.32 0.48 0.67 0.76 0.91	43.6 80.6 106.2 132.9 164.0 243.5

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### TABLE XX1V

# Data for Plotting the Clausius-Clapeyron Equation

<u>x</u>	20.2 <sup>0</sup> C		30.1°c		40.6 <sup>°</sup> c		50.2 <sup>0</sup> C	
	P(mm)	log P	P(mm)	log P	P(mm)	log P	P(mm)	log P
l. a	- 0-	_ _	- 05				0	
40 60	0.85 2.24	1.9304 0.3404	1.86 4 70	0.2686	4.00 9.48	0.6021	8.23	0.9153 1.2404
80	4.17	0.6202	8.64	0.9365	13.93	1.1440	29.73	1.4732
100	6.46	0.8103	12.80	1.0719	24.56	1.3902	42.07	1.6240
120	8.59	0.9340	16.38	1.2143	31.35	1.4962	54.76	1.7385
140	10.40	1.0170	19.74	1.2953	37.69	1.5762	66.38	1.8220
180	12.40	1.0759	22.70	1,028	42.95	1.6820	( <b>5</b> •92 80 78	1 0073
200	14.68	1,1667	27.14	1,4336	40.09	1.6942	83,59	1,9222
220	15.44	1.1887	28.32	1.4521	51.28	1.7100	85.55	1,9322
240	16.01	1.2044	29.25	1.4661	52.71	1.7219	86.96	1.9393

### TABLE XXV

# Isosteric Heats at Different Adsorptions on Starch

X(mgm./gm.)	Slope x $10^{-3}$	- △H (k.cal)
40	3.07	14.05
60	2.81	12.85
80	2.58	11.81
100	2.58	11.81
120	2.52	11.52
140	2.52	11.52
160	2.51	11.50
180	2.45	11.20
200	2.36	10.81
220	2.32	10.64
240	2.30	10.53

Isosteric Heat of Adsorption as a Function of Amount Adsorbed.

Legend

- -o-o- Flour
- -A-A- Starch
- -0-0- Gluten(1)



# TABLE XXV1

# Data for the BET Equation

P/P <sub>o</sub>	P(mm)	P <sub>o</sub> -P	X(mgm./gm.)	-3 X(P <sub>0</sub> -P)x10	$\frac{P}{X(P_0-P)x10}^{3}$
0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4 0.45	P(mm) 1.37 2.75 4.12 5.50 6.88 8.25 9.62 11.00 12.38	P <sub>0</sub> -P 26.13 24.75 23.38 22.00 20.60 19.25 17.90 16.50 15.12	46.0 58.0 67.2 75.6 82.6 89.2 96.0 103.3 110.6	1.20 1.44 1.57 1.66 1.70 1.72 1.72 1.70 1.67	$ \begin{array}{r}     1.14 \\     1.91 \\     2.62 \\     3.31 \\     4.05 \\     4.80 \\     5.59 \\     6.47 \\     7.41 \\     7.41     $
0.5 0.55 0.6 0.65 0.7 0.75 0.8	13.75 15.12 16.50 17.88 19.25 20.62 22.00	13.75 12.38 11.00 9.60 8.25 6.9 5.5	118.0 125.2 133.0 142.0 151.6 162.8 176.0	1.62 1.55 1.46 1.36 1.25 1.12 0.97	8.49 9.75 11.30 13.15 15.40 18.41 22.68
Figure 7.

Figure 21 shows that linear form of the BET equation applies to the flour-water isotherm in the relative pressure range below 0.4. The values for the constants  $X_m$  and c can be evaluated from the intercept and the slope of the straight line shown in Figure 21 as follows:

Intercept = 
$$\frac{1}{X_{mc}}$$
 = 0.4 x 10<sup>-3</sup>

Slope =  $\frac{c-1}{X_{m}c}$  = 1.51 x 10<sup>-2</sup>

Hence,

$$x_{m} = 66.2 \text{ mgm}./\text{gm}.$$
  
c = 37.7

From these values for c and  $X_m$ , it is possible to determine the heat of adsorption of the first layer and also the specific surface area.

Heat of adsorption:

$$c = \exp(E_1 - E_L)/RT$$
  
or ln c =  $(E_1 - E_L)/RT$   
and substituting c = 37.7  
 $R = 1.987$  cal.deg.<sup>-1</sup>mole<sup>-1</sup>  
 $T = 300$ 

# Figure 21

Adsorption Isotherm for Water Vapour on Flour Plotted According to the Straight Line Equation (10) of the BET theory.



$$E_{\rm L} = -10.5 \text{ Kcal.mole}^{-1}$$
  
 $\therefore E_{\rm l} = -12.6 \text{ Kcal.mole}^{-1}$ 

Specific Surface Area:  

$$X_{m} = 66.2 \text{ mgm}./\text{gm}.$$
  
 $= \frac{66.2 \times 10^{-3} \times 6.02 \times 10^{23}}{18} = 2.22 \times 10^{21} \text{ molecules}$ 

If liquid packing in the adsorbed layer is assumed, the area occupied by a single molecule may be calculated from the equation of Brunauer (5) and is  $1.06 \times 10^{-15} \text{ cm.}^2$ . Hence, the specific surface area according to the BET theory becomes,

$$A = 2.22 \times 10^{21} \times 1.06 \times 10^{-15}$$
$$= 2.35 \times 10^{6} \text{ cm.}^{2}/\text{gm.}$$

To improve the agreement with the BET theory it is necessary to insert different values of n (the number of adsorbed layers at saturation pressure), into the more accurate BET equation i.e. equation (11) until a reasonably good representation of the experimental data is obtained. Using the values of  ${\rm X}_{\rm m}$  and c given above it is possible to construct a family of sigmoid isotherms such as those in Figure 22 for different values of n. For comparison, the experimental data are plotted in the same figure.

## Figure 22

Adsorption Isotherm of Water on Flour Plotted According to the Three Constant BET Equation (11)

## Legend

Solid lines - BET plots for various n Empty circles - Experimental points



Figure 22 shows that the adsorption isotherm for water vapour on flour can be represented reasonably well to 0.8 relative pressure by the BET equation if n is set equal to 5. This agreement is somewhat fortuitous since the assumptions embodied in the BET theory cannot be applied rigorously to the present system. Consequently, the BET equation was not applied to any of the other isotherms.

#### Cross-linking and Swelling Experiments

As indicated earlier, considerable cross-linking, which transformed the powdered adsorbent to a firm "cake" occurred with flour and gluten, but not with starch, when water vapour was adsorbed at high relative pressures and subsequently desorbed by evacuation. This vapour phase cross-linking was not observed with any other adsorbate than water.

If it can be assumed that the degree of cross-linking is directly related to the firmness of the resulting "cake", the qualitative observations during these experiments suggested that gluten undergoes considerably more cross-linking than flour. Furthermore, since starch showed no apparent change, it can be inferred that only the protein component was involved in the cross-linking.

An experiment was made to measure the amount of water bound in the cross-links. The approach was to determine the amount of water that remained after an adsorption-desorption cycle, and to ascertain whether this amount increased with subsequent adsorption-desorption cycles on the same sample. Results from previous experiments indicated that the residual amount of water was too small to be detected with the less sensitive spirals; accordingly, these experiments were made in Apparatus No. 2 with a highly sensitive spiral (No. 5).

The experimental procedure was the same as that used previously. When the sample attained to equilibrium adsorption, the water vapour was desorbed by evacuation overnight or until constant weight was reached. The adsorption-desorption cycle was repeated a number of times; one sample of flour was cycled six times and a sample of freeze-dried gluten five times. The same source of vapour (sulphuric acid solution) was used for each set of experiments. The relative pressure was checked during each adsorption and was found to remain constant for all the cycles to within  $\pm$  0.02, i.e., it did not show a tendency to decrease as the number of cycles increased. Visual examination of the gluten and flour adsorbents after these experiments indicated that the samples were extensively cross-linked (caked).

Experimental results obtained with flour are shown in Table XXVII and analogous data for gluten are given in Table XXVIII. The amounts adsorbed during the second and subsequent cycles include the small amount of water which was retained

# TABLE XXV11

# Six Adsorption Cycles with One Sample of Flour

 $(T = 30.1^{\circ}C; P/P_{\circ} = 0.88)$ 

Time		X (mgm./gm.)						
(Hr.)	1	2	3	4	5	6		
0 0.25 0.50 0.75 1.0 1.5 2.0 3.0 5.0 7.0 8.0	0 162.9 186.3 200.3 220.7 231.2 232.4 232.4 232.8	3.6 157.0 190.1 203.7 213.1 221.0 229.1 229.8 229.9 229.9	2.9 161.0 193.3 215.2 229.4 233.3 234.6 234.6 234.6 234.6	2.8 161.4 193.8 209.3 223.8 230.6 234.3 235.0 235.4 235.4 235.4	1.9x 164.9x 193.6 208.2 226.4 - 234.3 234.7 - 234.7	4.4 164.7 <sup>x</sup> 195.8 209.7 218.2 - - 235.7 235.7 235.7 235.7		

x 4 minutes later than 0.25 hr.

Desorption Cycle	Residual Weight (mgm./gm.)
1 2 3	3.6 2.9 2.8 1.9
<b>F</b> 56	4.4 0.1

# TABLE XXV111

Five Adsorption Cycles with One Sample of Gluten(1) (T =  $30.1^{\circ}C$ ; P/P<sub>o</sub> = 0.88)

Time		2	X (mgm./gm.	)	
(Hr.)	1	2	3	4	5
0 25 0.50 0.75 1.5 2.0 3.0 5.0 7.0 5.0 7.0 8.0	0 138.1 173.5 191.2 202.2 217.1 228.1 230.4 230.9 230.9 230.9	-4.0 142.0 168.3 191.7 202.9 - - 229.2 230.4 230.5 - 230.5	-4.9 150.5x 174.4 189.4 - 220.1 - 228.9 230.2 230.6 231.0 230.5	-2.1 137.1 178.2 - 225.9 228.3 229.2 230.6 230.6 230.6	0 - - 224.6 - - 229.8 230.4 230.4

x 3 minutes later than 0.25 hr. reading.

Desorption Cycle	Residual Weight (mgm./gm.)
1 2	-4.0 -4.9
2 4 5	0.2

after the preceding desorption (with gluten these were negative). The residual weight shown for each desorption cycle was the excess weight of the adsorbent over the initial dry weight, i.e., the total weight of water retained by flour after six cycles was 0.1 mgm./gm. and not the sum of the residual weight for each cycle. A representative part of the data given in Tables XXVII and XXVIII are shown in Figure 23. It was not possible to plot all the data since some of the values for different cycles were exactly the same.

The results give clear indication that, if water is involved as such in a cross-link, the amount of water so bound is too small to be accurately measured by the technique used. The highly reproducible results obtained substantiate further the previous observations that adsorption and desorption of water vapour on flour and gluten appear to be completely reversible.

In the next series of experiments, attempts were made to break down the cross-linked structure by immersing the flour cakes, produced by vapour phase cross-linking, in various liquids. It was assumed that if water were actually bound in the cross-link, the cake should disperse if the water could be replaced by some other molecule that was incapable of promoting the cross-link.

Accordingly, a series of flour and gluten "cakes" of approximately 1 inch in diameter and 1/8 inch in height were prepared by adsorbing water at 0.85 relative pressure on a

# Figure 23

Adsorption of Water Vapour on Flour and Gluten for a Series of Cycles.

Legend

Flour			Gluten		
-0-0-	cycle	l	-0-0-	cycle	1
-0-0-	\$1	2	-[]-[]-	н	2
	11	3	&	Π	3
- <b>Δ</b> - <b>Δ</b> -	11	4	-0-0-	ù	4
- 🗶 🗮	11	5	<u>Δ</u> Δ	"	5
-0-0-	<b>f1</b>	6			



conditioned adsorbent sample followed by removal of the adsorbed water by evacuation. During desorption the cakes suffered shrinkage to a much smaller size than the sample dish, so that they could be lifted from the dish quite easily. The resulting cakes were then placed into a variety of liquids contained in 100 ml. beakers. Table XXIX lists the liquids used and the observed immediate changes in the cakes.

Table XXIX shows that only methyl and ethyl alcohol could disperse the flour cakes. Gluten cakes, which seemed to be more extensively cross-linked, did not disperse as rapidly as the flour cakes in these two liquids. In one experiment, a gluten cake still retained its shape even after immersion in ethyl alcohol overnight.

These observations suggested that it might be possible to break up the cross-linked cake by a vapour phase adsorption of methyl alcohol on the flour cake. However, as many as four adsorption-desorption cycles with methyl alcohol as sorbate did not produce any dispersing effect.

During the preparation of the "cakes" used in the preceding experiment it was possible to observe the swelling of flour or gluten as it adsorbed water vapour at a high relative pressure (about 0.8). These qualitative experiments were extended to include starch and the various adsorbates that were used in the sorption experiments. It was found that flour, starch and gluten all swelled visibly in the presence

TABLE XX1X

Effect of Various Liquids on Flour "Cakes"

LIQUID AND EFFECT

Complete Dispersion

methyl alcohol ethyl alcohol

No Immediate Effect

n-propyl alcohol isopropyl alcohol acetone methylethylketone formaldehyde carbon tetrachloride chloroform benzene toluene o-nitrotoluene nitromethane dimethylformamide o-toluidine di-N-amylamine diethylamine glycerol

of water, methyl alcohol and ethyl alcohol vapours, provided the experiments were made with relative pressures of about 0.80. Carbon tetrachloride at 0.88 relative pressure, and ammonia at an absolute pressure of one atmosphere did not cause observable swelling of any of the three materials.

Gluten was then treated with a number of liquids to determine whether any other liquid could affect gluten in a manner similar to that observed with water. The criterion for a water-like effect on gluten was the formation of a glassy, brittle material similar to that obtained after moistened gluten was dried in a vacuum (modified gluten). On the other hand if the liquid produced only slight caking it was classified as having an alcohol-like (methyl alcohol) effect on gluten.

In choosing the liquids for these experiments the guiding assumption was that hydrogen bond might play a major role in the interaction of water with gluten. Accordingly, the liquids were chosen to possess hydrogen atoms with partially positive character or related behavior. If the particular substance was a gas at ordinary temperatures and pressures it was condensed into a tube that contained about 0.5 gm. of dry gluten, by surrounding the tube with liquid nitrogen. Since traces of water could very easily invalidate the results of such an experiment, special precautions were taken to dry the gluten as well as was possible without serious denaturation and to

use anhydrous chemicals. After the gluten was completely wetted with the appropriate liquid by several condensations and evaporations, it was dried in a vacuum for several hours before it was removed from the vacuum system for examination.

Table XXX gives the various liquids that were used and the observed effects. The results with ammonia and hydrazine were strikingly similar to the results with water. Methylamine was the only other liquid that showed a water-like effect on gluten. Since hydrazine is a liquid at ordinary temperatures and pressures, it was possible to use it to mix a dough with flour. The handling properties of such a flour-hydrazine dough were quite similar to the properties of a flour-water dough.

The fact that ammonia cross-links flour in a manner similar to water suggested that it might provide a means to determine whether the cross-linking liquid was actually involved in the linkage, since it is feasible to analyse for a possible increase in nitrogen content of the dried cake. It is impossible to do an analogous analysis for water. It was therefore of interest to compare the free ammonia and the total nitrogen contents of ammonia-treated and the untreated flour.

The dry, brittle mass that resulted after treatment of a sample of flour with liquid ammonia was ground in a mortar to approximately the same particle size as flour and kept in

TABLE XXX

Effect of Various Liquids on Gluten

### LIQUID and EFFECT

### Water-like

hydrazine ammonia methylamine

Alcohol-like

dimethylamine ethylamine isopropylamine hydrogen cyanide acetonitrile

None

trimethylamine

<sup>x</sup>Dimethylamine caused considerable peptization if the liquid was allowed to remain in contact with the gluten for a short period of time. a dessicator with a sample of the original flour for about three weeks (to establish moisture equilibrium) before the analyses were made. The results obtained are shown in Table XXX1. Total nitrogen was determined by the Micro Kjeldahl method and the amount of base distilled from an alkali suspension of the material is recorded as free ammonia.

Table XXX1 shows that flour which had been cross-linked with ammonia showed a 0.15% increase in "free" ammonia content over that of untreated flour. A similar increase was also reflected in total nitrogen contents of the same samples. This increase is of the same order of magnitude as the amount of residual ammonia on flour, observed in the sorption experiments, which was ascribed to chemical reaction of ammonia with the small amount of water in the adsorbent. Accordingly, the increase in "free" ammonia observed in this experiment can be explained on similar basis.

#### TABLE XXX1

Free Ammonia and Total Nitrogen of Ammonia-Treated and Untreated Flour

		Treated	Untreated
Free ammonia	(%)	0.86, 0.92	0.75, 0.74
Total nitrogen	(%)	2.90, 2.83	2.72, 2.41

### DISCUSSION

## SORPTION ISOTHERMS

It seems apparent from the results that have been presented (c.f. Figure 13) that the isotherms for adsorption of water vapour on flour, freeze-dried gluten, spray-dried gluten and starch are of the same general type. It can be assumed therefore, that the same adsorption mechanism holds for the four materials. Hence, the discussion of the flourwater isotherm which follows should apply equally well for the other materials.

Sorption of water vapour on wheat flour yields a sigmoid isotherm. This type of isotherm is classified as Type 11 according to the BET theory. Such an isotherm is typified by a region in which it is concave to the pressure axis at low relative pressures, an almost linear intermediate region and a region in which the isotherm is convex to the pressure axis at the higher relative pressures.

The BET theory predicts a sigmoid isotherm for multilayer adsorption if the value of the characteristic constant  $\underline{c}$  in the BET equation is greater than unity. The actual magnitude of this constant is reflected in the degree of concavity of the isotherm in the low pressure region. If the basic assumptions embodied in the BET theory can be assumed to apply

to the present system, a value of c>>l implies that the average heat of adsorption of the first layer,  $E_1$ , is greater than the heat of liquefaction of the adsorbate,  $E_L$ . Such a system is sometime referred to as one which has a positive net heat of adsorption. As presented in greater detail later, the isosteric data indicate that this is actually true for the adsorbents used in this study. The linear intermediate portion of the isotherm represents the build-up of the second adsorbed layer and the final convex region the build up of multilayers.

The extent to which the adsorption data for the flourwater system conform to the simplified, linear form of the BET equation (10) is shown in Figure 21. Brunauer (5) pointed out that a deviation such as that shown in Figure 21 can usually be taken to mean that the number of adsorbed layers at saturation pressure is finite rather than infinite as assumed in the development of the linear equation. The linear portion of the curve in Figure 21 can be used to evaluate the constants  $\underline{Xm}$  and  $\underline{c}$  which, in turn, can be used to improve the BET fit in the higher pressure region by assuming different values for n (the number of adsorbed layers at saturation pressure).

The solid lines in Figure 22 represent plots of the BET equation in more general form (three constants) using the values of  $\underline{Xm}$  and  $\underline{c}$  obtained and varying the values of  $\underline{n}$  as indicated. A reasonably good mathematical representation of the flour-water

isotherm may be had up to a relative pressure of about 0.8 by assuming that the number of adsorbed layers is five. At still higher relative pressures, the experimental results are higher than predicted by the BET theory.

By considering only the adsorption isotherm, with a treatment such as outlined above, it is quite possible to reach the conclusion that adsorption of water vapour on flour can be represented by the BET model. If the assumptions embodied in the BET theory are considered, it becomes apparent that the agreement is fortuitous. It was pointed out by Hailwood and Horrobin (109) that any mathematical equation with three arbitrary constants can be fitted to a sigmoid isotherm. It is of interest, however, that the values of  $\underline{Xm}$  and  $\underline{c}$  obtained from the BET plot seem reasonable.

Apart from the usual criticisms of the BET theory mentioned earlier, the hysteresis in the present system is an important aspect that cannot be represented by the theory in its present form. In the development of this theory it is assumed that the surface available for adsorption remains constant throughout the isotherm. This is not true for adsorbents that swell during adsorption. It is necessary therefore, to have a model that will explain the hysteresis effect in addition to the sigmoid shape of the isotherm.

It seems likely that the shape of the isotherms for adsorption of vapours on flour, starch and gluten is a direct

consequence of swelling of the adsorbent during the sorption process. It is possible to obtain an estimate of the specific surface area from the values of the constants  $\underline{Xm}$  and  $\underline{c}$  obtained from the slope and the intercept of the linear BET plot (Figure 21). The BET area obtained for flour was 235 sq.m./gm.; this may be compared with 0.16-0.60 sq.m./gm. determined by the BET method from a flour-argon isotherm. These values suggest that water, and probably the other sorbates used in this study, caused a relatively large increase in surface area due to swelling.

Adsorption accompanied by swelling is amenable to mathematical formulation, but this requires quantitative measurements of the changes in apparent volume of the adsorbent with adsorption, and these have not yet been made for the materials in question. A general qualitative description of the process can nevertheless be attempted.

For the purpose of this discussion, the isotherm can be conveniently considered in three parts: (i) The initial rapidly rising portion; (ii) the intermediate linear portion; and, (iii) the final rapidly rising portion.

The initial part of the isotherm is ascribed to adsorption on sites that are accessible to adsorbate molecules before swelling occurs. The fact that the adsorption process is not instantaneous but has a definite rate that decreases as the molar volume of the adsorbate increases (Figure 5) indicates that the initially available sorption sites become accessible to the molecules of adsorbate only after they have diffused through fairly small openings. Since the rates of adsorption given by the curves in Figure 5 are not affected by using larger samples or by packing the sample more compactly, the controlling factor cannot be diffusion between the particles. On the other hand, additional adsorption sites were apparently made available by the swelling since the adsorption cannot be represented by a Langmuir type of hyperbolic isotherm The openings through which diffusion occurred, and equation. by which additional sites were exposed can be envisaged as tiny cracks developed in the flour particles during the milling process. A similar intra-particle diffusion can be assumed to be the rate controlling factor of the adsorption on starch and gluten.

As the additional sites become occupied, the swelling proceeds further to create progressively more surface for adsorption. This effect would yield an almost linear isotherm since, in this range the swelling is apparently directly proportional to the relative pressure. This is indicated by the density measurements of Campbell and Jones (104) who showed that over the equivalent range of moisture contents the change in density, which may be attributed to swelling, decreases linearly with moisture content. A linear relation between the

degree of swelling and the relative pressure might therefore be expected in the range where the isotherm is linear. There is also a possibility that the linear part of the isotherm might represent adsorption on less active sites or on sites that are not involved in the formation cross-links when flour is wetted with water. This possibility is suggested by the isotherm for modified gluten (Figure 14).

The deviation of the isotherm from linearity in the high relative pressure region could be due to one or both of two possible factors: (i) A significant change in the physical structure of the adsorbent might occur. Such a change could be induced very easily by excessive swelling. In flour for instance, such a change could be a conversion of a semi-crystalline structure to a more amorphous structure. It is not known how such a change would effect the sorptive capacity of flour, but it is known that with cellulose, which also yields a sigmoid isotherm for the adsorption of water vapour, the amorphous form adsorbs considerably more water vapour than the crystalline form (10). This hypothesis is also in general agreement with the observation made by Campbell and Jones (104) during their density experiments, that if the moisture content of wheat endosperm exceeded 20% there is a sudden development of "mealiness". (ii) The increase in the slope of the isotherm at higher relative pressures might, in part,

be due to capillary condensation. Control experiments showed that no condensation on the spiral or the empty sample dish could be detected at any relative pressure below 0.9. This does not eliminate the possibility of condensation taking place in the narrow cracks in the flour particles or in the inter-particle spaces. As a result of swelling, the distance between flour particles would tend to decrease with adsorption. The cross-linking observed at relative pressures of about 0.8 suggests that the appearance of liquid water between flour particles at pressures less than saturation is quite probable.

The observed hysteresis effect might be explained, in part, by an argument analogous to that given by Hirst (50) for the hysteresis in sorption of water vapour on coal. In a swelling-shrinking system, the closing of a structure on desorption occurs at a lower pressure than the pressure at which the structure opens during adsorption. This could produce a hysteresis effect. In addition to the irreversible structural changes in the adsorbent (plastic deformation), there is also the possibility that sorbate molecules might be trapped inside the cracks and crevices as the outer parts of the flour particles shrink, during desorption, at a higher rate than the inner parts. This effect would be particularly important with larger adsorbate molecules. This explanation for the hysteresis effect is supported by experimental results.

Figure 8 shows that the flour-methyl alcohol isotherm exhibits considerably greater hysteresis effect than the flourwater isotherm and also the flour-ethyl alcohol isotherm shows a greater hysteresis than the flour-methyl alcohol isotherm. The lack of hysteresis in the flour-carbon tetrachloride isotherm also suggests that hysteresis is a direct consequence of swelling, since it was observed that carbon tetrachloride did not cause swelling similar to that observed with water, methyl alcohol and ethyl alcohol vapours (c.f. swelling experiments).

Figure 9 presents additional evidence that at least part of the hysteresis effect, particularly for the larger adsorbate molecules, is due to trapping of adsorbed molecules in the adsorbent. Flour retains about 3.5% adsorbed methyl alcohol even after 22 hours of evacuation. It is possible that adsorbed alcohol could be removed completely by a very long period of evacuation. Adsorbed water, on the other hand, was reversibly removed after about six to eight hours of evacuation. Apparently, some diffusion process limits the removal of the adsorbed alcohol.

Complete removal of the adsorbed methyl alcohol was possible by "opening up" the structure of the adsorbent by adsorbing water on the same sample. Figure 9 shows that after two subsequent adsorption-desorption cycles, using water vapour as the sorbate, the original dry weight of the adsorbent

was reproduced within experimental error.

An estimate of the "affinity" of flour for water, methyl alcohol, ethyl alcohol and carbon tetrachloride may be had by comparing the initial slopes of the adsorption isotherms. According to Hermans (10), the slope of the initial part of the adsorption isotherm, which is generally assumed to represent monomolecular adsorption, is directly related to the parameter cexp(E/RT) which, in turn, is a direct measure of the affinity of the adsorbent for the adsorbate. The approximate initial slopes of the isotherms shown in Figure 8 are 10, 1.6, 0.8 and 0.01 respectively for the four adsorbates mentioned above.

To make these affinity numbers strictly comparable they should be corrected for the accessibility of adsorption sites to the different adsorbates. This accessibility correction would be directly dependent on the molar volume of the adsorbate. The importance of the accessibility factor is clearly demonstrated by the sorptive capacity of flour for methyl and ethyl alcohol vapours. In this case, the two molecules have essentially the same dipole moments (1.69D and 1.70D, respectively), and therefore, the observed difference in their sorption isotherms must be due to the difference in their molar volumes.

The accessibility factor will account for only a small

portion of the observed difference in the isotherms for water and carbon tetrachloride. Accordingly, the major part of the difference must be due to the difference in polarity of the two molecules. It may be concluded, therefore, that most of the adsorption on flour is due to dipole-dipole interaction, probably by the formation of hydrogen bonds.

Further experimental evidence to indicate that adsorption on the adsorbents used in this investigation depends on the specific nature of the adsorbent rather than on the external surface is provided by Figure 15 which shows the adsorption isotherms for water vapour on flour fractions of different particle size. The total variation in external surface area provided by the five fractions was approximately two-fold, but the adsorption data indicate that the sorptive capacity of all the fractions was about the same as that of the original unfractionated flour. That is, the specific number of adsorption sites was independent of particle size.

If, from the foregoing discussion, it is concluded that the extent of adsorption on flour, starch and gluten depends mainly on the polarity and the molar volume of the adsorbate, it would be predicted that flour should adsorb less ammonia than water. However, comparison of the ammonia (Figure 10) and water isotherms shows that ammonia is adsorbed to a slightly greater extent than water.

The ammonia isotherm also shows a definite hysteresis effect although the swelling experiments showed that ammonia (at one atmosphere pressure) did not cause any observable swelling. This appears to be in contradiction to the hypothesis that the hysteresis effect was a direct consequence of the swelling of the adsorbent.

A possible explanation for these discrepancies is that some of the ammonia enters into an interaction in which water molecules cannot participate. Figure 3 shows that the equilibrium moisture content of the flour by the initial conditioning technique was 9.85% while the standard air oven method gave a moisture content of 10.5%. It is quite possible that the "dry" adsorbents used in this study actually contained about 0.7% moisture, and that the retention of about 4% of the adsorbed ammonia after 12 hours of evacuation was due to reaction of ammonia with the residual water in the flour.

The observed differences in the sorptive capacity of the starch, flour, and gluten can be explained, at least in part, by the relative number of specific adsorption sites. In starch, each glucose unit has three free hydroxyl groups which could interact with water, whereas a similar structural unit in gluten would have one or at most two such highly polar groups as the hydroxyl group. On this basis, starch would be expected to adsorb more water than gluten since

the number of polar groups per unit mass in starch is larger than in gluten. This simple explanation does not include the fact that some of the groups might interact with each other in such a way as to decrease their ability to bind water. There is, as yet, very little information on the extent to which the various polar groups in starch and gluten interact with each other and there is no satisfactory basis therefore, to attempt a correlation of the adsorption data with the number of polar groups. Such a correlation might become possible, however, when more complete knowledge of the structure of flour is available.

The lower sorptive capacity of the spray-dried, compared with that of the freeze-dried gluten, seems to indicate that the spray-dried sample might be slightly denatured. Some heat denaturation is quite possible since the final step in the preparation of this type of gluten consisted of spraydrying a gluten slurry at temperatures between  $90^{\circ}$  and  $160^{\circ}$ C. It was observed that heat treatment of flour for 24 hours at  $100^{\circ}$ C in a vacuum caused about 20% decrease in its sorptive capacity (Figure 16). These observations are in general agreement with the observations made by Astbury (110) that during heat denaturation of proteins some of the polar groups interact in such a way as to change a globular type of protein into a more fibrous type. Decrease in the number of

polar groups would therefore cause a reduction in sorptive capacity.

The variation of isosteric heat of adsorption with the amount adsorbed (Figure 20) has been observed with a large variety of adsorbents (7). To explain the decrease of isosteric heat with extent of adsorption it is generally assumed that adsorption, at very low pressures, occurs on the most active sites, and these would give rise to the highest heat of adsorption. This is followed by adsorption on the less active sites which would tend to give a lower heat of adsorption. With some adsorbents, such as charcoal, there is some difficulty, perhaps, in visualizing the existence of adsorption sites with different energies. However, it is usually assumed that the adsorbent possesses surface imperfections which give rise to corners and edges of greater interaction energies than plane surfaces. With materials such as starch and proteins, the existence of adsorption sites with variable energies is considerably more probable. If the variety of polar groups in starch and gluten (enumerated in the Introduction) are considered, the existence of a series of sorption sites with different interaction energies is obvious. In addition, some of the polar groups on the adsorbent might interact with each other to various degrees. This would decrease further their interaction energies with adsorbate molecules.

Variation in the isosteric heat of adsorption may also be due partly to the swelling process. Swelling is an endothermic process and therefore would tend to decrease the true heat of adsorption. Cassie (111) showed that swelling may use as much as 50% of the heat produced by the adsorption process. Correction of the observed isosteric heats of adsorption to include the swelling effect requires a number of physical constants for the adsorbent which are not yet available for any of the materials used in this investigation.

The extrapolated value of the isosteric heat at zero adsorption is about 14.8 Kcal./mole and the value obtained from the BET equation is 12.6 Kcal./mole. Too much significance cannot be attached to the actual magnitude of either of these values. The shortcomings of the BET theory have already been discussed. Likewise, an extrapolation such as that indicated by the dotted line in Figure 20 can give an entirely erroneous result. Calorimetric studies of other systems (7) have shown that a plot of the differential heat of adsorption against the amount adsorbed frequently shows a very steep rise at very low adsorptions.

There is little doubt, however, that the initial heats of adsorption of water vapour on the materials used are higher than the heat of liquefaction of water. It may be inferred that, at low adsorptions, the interaction energy

between water molecules and the adsorption sites is greater than the energy which holds the water molecules together in the liquid state. At higher adsorption, however, the isosteric heat of adsorption is essentially equal to the heat of liquefaction which suggests that adsorbed water vapour in excess of 12% is very similar to liquid water, i.e., adsorption beyond 12% releases the same amount of energy as the condensation of vapour to liquid. A value of about 15 Kcal./mole for the incipient heat of adsorption would indicate that water is attached initially to the adsorption sites by hydrogen bonds. Formation of the hydrogen bond would release about 5 Kcal./mole in excess of the heat of liquefaction.

### CROSS-LINKING IN FLOUR

To formulate a mechanism for the formation of a threedimensional network in flour (or gluten), the following summary of the experimental observations is useful:

1. Flour adsorbed water, methyl alcohol, ethyl alcohol and ammonia (polar molecules) quite strongly whereas nonpolar carbon tetrachloride was adsorbed only slightly.

2. At high relative pressures, but below the pressure at which bulk condensation could occur, water vapour caused flour and gluten, but not starch, to cross-link. No other sorbate produced similar vapour-phase cross-linking.

3. No increase in weight, as a result of the vapourphase cross-linking, could be detected in flour or gluten.

4. Flour and gluten swell to a high degree, starch to a lesser degree, during adsorption of water, methyl alcohol and ethyl alcohol vapours at relative pressures about 0.8. No swelling was observed with carbon tetrachloride at 0.88 relative pressure. Ammonia, at an absolute pressure of one atmosphere (about 0.1 relative pressure) also did not produce any swelling.

5. In the liquid-phase cross-linking experiments with gluten, a similar effect to that obtained with water was observed with ammonia, hydrazine, and methylamine. On the other hand, hydrogen cyanide, acetonitrile and dimethylamine

produced only slight caking similar to that obtained with methyl alcohol. Apparently, the ability of primary amines to promote cross-links in gluten disappears completely if the substituted group is larger than methyl.

6. Flour that had been cross-linked with liquid ammonia showed an increase of 0.15% in the "free" ammonia content over that of untreated flour. This increase is of the same order of magnitude as the amount of residual ammonia (0.4%) on flour after an adsorption-desorption experiment, and may be ascribed to chemical reaction of ammonia with residual water in the adsorbent.

It is possible to draw a number of further inferences from the foregoing summary. Apparently, not all liquids that swell flour can induce it to cross-link. Since water can produce cross-links through vapour phase adsorption only at high relative pressures, it appears that "free" water (in contrast to "bound" water) or water which possesses its bulk properties must be present to produce the cross-links. Cross-linking was not observed after adsorption-desorption of ammonia, probably because all of the adsorbed ammonia was of the "bound" type owing to the low range of relative pressures investigated. Gas-phase cross-linking with ammonia might well be observed at higher relative pressures.

From visual observations (admittedly not a rigorous criterion) the cross-linking observed with water, ammonia,
hydrazine and methylamine may be assumed to be of the same type.

The liquids that caused gluten to cross-link were all ionizing solvents, i.e., good solvents for polar chain ends. This suggests that the cross-links might be salt linkages, the formation of which would require an ionizing solvent to permit adequate mobility of the ionized groups to form the linkage. The fact that gluten doughs can be readily dispersed by dilute alkalis or acids is generally cited as evidence for the existence of salt linkages in that colloidal system (113). However, if this were the type of cross-link involved and an ionizing solvent were the only requirement, it would be expected that liquid hydrogen cyanide, acetonitrile or dimethylamine (particularly liquid hydrogen cyanide) should cause gluten to cross-link. No cross-linking of the type obtained with water was observed when gluten was treated with any of these three liquids.

Formation of hydrogen bonds between polar end groups in the gluten proteins, with the liquid acting as a solvent, is ruled out on a similar basis, since this type of crosslink should form in any ionizing solvent.

The one feature common to the liquids that promoted cross-links in gluten, but which is absent in the other ionizing solvents or the alcohols, is the presence in the molecule of at least two hydrogen atoms that show partially positive character and are therefore capable of forming hydrogen bonds. Accordingly, it may be postulated that, rather than salt linkages, cross-links in the dough network are mainly of the type

where  $R_1$  and  $R_2$  are polar amino acid side chains. A second type of cross-link involving two hydrogen bonds, which could also be formed with hydrogen cyanide,



is improbable because of steric effects.

Cross-links of type 1 between two hydroxyl groups on the starch molecule or between the carbonyl or the imido groups in the peptide linkages would be considerably less probable owing to steric hindrance effects even though these groups probably play an important role in the binding of water molecules during adsorption. Cross-linking of these various groups to the polar side chains would be slightly more probable.

To form a cross-link of type 1 the liquid presumably must be a good solvent for polar groups to facilitate the mobility of these groups. This is a necessary, but not sufficient, condition for cross-link formation.

If the cross-links were of type 1, i.e., the liquid molecule formed an integral part of the linkage, it would be expected that flour or gluten cross-linked by a vapour phase adsorption of water vapour should show a residual increase in weight and this was not observed experimentally. It is true that the "free" ammonia content of a sample of flour cross-linked with liquid ammonia was increased over that of untreated flour but, as pointed out earlier, this increase was probably due to reaction of ammonia with water in the flour. If, however, the number of cross-links necessary to account for the observed caking effect is very small, the increase in weight due to water or ammonia bound in the cross-links would not be detected. It is not yet possible to estimate the number of cross-links formed in networks of gluten, but it might well be quite small. It is interesting, perhaps, to note that the rheological properties of mechanically mixed doughs can be very drastically altered by the addition of minute amounts of materials

such as potassium bromate (viz., 5 parts per million), and it might be that this reflects a small concentration of cross-links in the dough.

In conclusion, it might be emphasized that if the crosslinks in flour obtained with ammonia, hydrazine and methylamine are analogous to those formed with water in a normal dough a new and interesting approach to the fundamental aspects of dough chemistry becomes possible. It is proposed to attempt an extension of the observations made in the present investigation in a number of ways. For example; (i) a further study might be made of the effect of doughing and baking on the adsorption properties of flour (or gluten) as suggested by the modified gluten-water vapour isotherm; (ii) an extension of the sorption studies might be made to include other polar gases such as hydrazine, various amines, hydrogen chloride and boron trifluoride; (iii) the flour-ammonia isotherm might be extended to higher relative pressures (by using lower temperatures) to investigate the possibility of gas-phase cross-linking with ammonia; and, (iv) quantitative measurements might be made of the extent of swelling due to adsorption of various sorbates (this would involve measurements of surface areas with sorbates such as nitrogen or argon). In particular, it is proposed to attempt mixing and baking studies with doughs formed in non-aqueous media.

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## SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. The McBain-Bakr sorption balance, in conjunction with a high vacuum technique, has been used to obtain the following sorption isotherms: (i) Water, methyl alcohol, ethyl alcohol, carbon tetrachloride and ammonia on flour; (ii) water and methyl alcohol on starch; (iii) water and methyl alcohol on freeze-dried and spray-dried gluten; and, (iv) water on modified freeze-dried gluten.

2. The sorptive capacity of flour for the five sorbates showed the following trend:  $NH_3H_2O>CH_3OH>C_2H_5OH>CCl_4$ . Starch, freeze-dried and spray-dried gluten showed the same trend in sorptive capacity for water and methyl alcohol.

3. On all sorbents, water, methyl alcohol and ethyl alcohol (on flour only) yielded sigmoid isotherms with hysteresis loops over the entire pressure range investigated. With these sorbates, the amount of hysteresis was directly related to the molar volume of the sorbate.

4. Vapour phase swelling was observed in all adsorbents in the presence of water, methyl alcohol and ethyl alcohol vapours at about 0.85 relative pressure. 5. Sorption of water vapour at high relative pressures (about 0.8) caused the flour and gluten, but not starch, to cross-link.

6. Sorption of carbon tetrachloride on flour gave a linear isotherm with no hysteresis loop.

7. Sorption of ammonia on flour gave an isotherm concave to the pressure axis with slight hysteresis.

8. Carbon tetrachloride at 0.88 relative pressure and ammonia at one atmosphere pressure did not swell any of the adsorbents.

9. The modified gluten-water vapour adsorption isotherm was practically linear in the pressure range to about 0.70. At higher pressures, the isotherm showed a sharp rise. This isotherm was more like type lll (BET classification) rather than the type ll isotherm that was obtained for the adsorption of water vapour on the original, freeze-dried gluten. The desorption branch of the modified gluten-water isotherm showed a peculiar hysteresis effect.

10. It was found that the extent of adsorption on flour, starch and gluten depended directly on the polarity and inversely on the molar volume of the sorbate. It is therefore postulated that adsorption on these materials is mainly due to attractive forces between permanent dipoles. The sorbate molecules are probably bound by hydrogen bonds.

11. The sigmoid shape of the isotherm is explained as follows: (1) The initial, rapidly rising portion is ascribed to adsorption on the available sites before swelling; (11) the intermediate, linear portion is attributed to adsorption on additional sites that are exposed by swelling; and, (111) the final rapidly rising portion is ascribed to either (or both) a marked change in the structure of the adsorbent or capillary condensation.

12. The hysteresis effect is attributed to irreversible structural changes in the sorbent induced by swelling.

13. On the basis of the postulated sorption mechanism, flour should sorb more water vapour than ammonia. This is in disagreement with experimental results obtained. This discrepancy is ascribed to chemical reaction of ammonia with the small amount of residual water on the adsorbent. The hysteresis in the flour-ammonia isotherm can be explained on the same basis.

14. The sorptive capacity of the sorbents used for water showed the following trend: Starch > flour > freeze-dried gluten > spray-dried gluten. The higher capacity of starch compared with that of gluten is at**t**ributed to the higher

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concentration of polar groups in starch, and the lower capacity of spray-dried as compared with freeze-dried gluten suggests that the spray-dried sample was probably slightly denatured.

15. Adsorption of water vapour on flour was found to be independent of the external surface area of the flour particles, i.e., it appears that adsorption depends only on the specific nature of the sorbent.

16. The sorptive capacity of flour for water vapour was reduced by about 20% after 24-hour treatment at 100°C in a vacuum.

17. The isosteric heats of adsorption of water vapour on flour, starch and gluten(1) were found to be higher than the heat of liquefaction at low adsorptions but approached the heat of liquefaction at higher adsorptions.

18. The flour-water vapour isotherm conformed to the BET equation if n, the number of adsorbed layers at saturation pressure, was set equal to five. The BET surface area of flour was found to be about 235 sq.m./gm., and the BET heat of adsorption for the first adsorbed layer 12.6 Kcal./mole.

19. Liquid ammonia, hydrazine and liquid methylamine caused gluten to cross-link in a manner similar to water.

20. On the basis of the results obtained, it is postulated that the cross-links in flour (gluten) are



where  $R_1$  and  $R_2$  are the amino acid side chains with polar groups that have atoms with free electrons, e.g., the O atom in the -OH groups, or the N atom in the -NH<sub>2</sub> groups.

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## APPENDIX I

Since the thesis was written a paper has appeared in the literature which, although not directly related to the results reported herein since the adsorbent was coarsely ground wheat (presumably equivalent to whole wheat), is worthy of mention. Becker and Sallans (114) reported sigmoid desorption isotherms for water vapour at 25° and 50°C. Presumably there is a typographical error since they report their isotherm as type III rather than type II according to BET classification. Instead of applying the BET equation to the overall isotherm (by varying the value of n), as was attempted in this thesis, they preferred to divide the isotherm into three parts and applied a different equation to each part. They found that to 0.3 relative pressure the simplified (two constant) BET equation applied; between 0.12 and 0.65 relative pressure the straight line equation applied; and, between 0.5 and 0.95 relative pressure the semi-logarithmic Smith equation (115) applied. It might be pointed out also that the differential heats of adsorption reported in this thesis are of the same order of magnitude as the heats of desorption reported by Becker and Sallans. (Note: Figure 20 in thesis shows total differential heat as a function of moisture content; Figure 5 of B. & S. shows net differential heat of desorption; net differential heat = total differential heat - heat of liquefaction).

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