Sorption of hydrogen chloride by wheat flour

Abraham Chu-yang Teng

Iowa State University
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by

Abraham Chu-yang Teng

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Dean of Graduate College

Iowa State University
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The rate of sorption of hydrogen chloride by soft white winter wheat flour from a gaseous mixture of hydrogen chloride and nitrogen was determined under various process conditions. Experimental measurements were carried out in a controlled environment with a dynamic microbalance technique. Due to the inherent complexity of the three component system (hydrogen chloride - flour - moisture), most of the determinations were undertaken at a temperature near the freezing point and at a total pressure of 1 atm., although some were determined at room temperature. The apparent rate of sorption was affected by the principal parameters, such as partial pressure, temperature, flour moisture content, sample depth and gas flow rate inside the balance enclosure. Equilibrium sorption isotherms were recorded for the flour with a set of different moisture levels at $34^\circ$ F. A limited number of measurements on ammonia sorption rates by wheat flour and acid-modified flour, respectively, were also collected in a similar manner.

To simulate the sorption process taking place in a shallow fixed-bed, a mathematical model was formulated under several simplifying assumptions. The overall transport of material was assumed to consist of simultaneous diffusion through the bed and sorption on the flour particles. Instantaneous sorption of hydrogen chloride by wheat flour was postulated as well as isothermal conditions and axial symmetry. The macroscopic mass balance
incorporating a nonlinear sorption isotherm resulted in a non-linear partial differential equation of the parabolic type. Using the predictor-corrector method, the equation with the appropriate boundary conditions was numerically solved to yield an approximate solution. The calculation was performed on a digital computer. The effect of void fraction, effective diffusivity, type of nonlinear isotherm and boundary conditions on computed values were considered. In general, the agreement between the experimental and computed sorption curves was good.

A general tendency was observed that the apparent sorption rate increases as the flour moisture content and hydrogen chloride partial pressure increase. From the analysis, it appears that local equilibrium exists between the free and immobilized sorbate at the gas-solid interface in this particular sorption process.
INTRODUCTION

Recently, a process which involves the sorption of gaseous hydrogen chloride to facilitate the acid modification of moisture laden wheat flour and the subsequent neutralization of the acid-modified product with anhydrous ammonia gas was proposed to produce a tub-sizing agent for paper (60, 61, 62). This process appears to differ from an ordinary catalytic fluid-solid reaction, because flour, a solid, and the contained moisture are the reactants in a hydrolysis reaction, and sorbed hydrogen chloride serves as a catalyst which dissociates to form hydronium ions with water. Needless to say, no hydrolysis could take place without the presence of moisture in the flour particles. Hence, it may be postulated that this process depends upon the amount of hydrogen chloride, transferred to the moisture to form some sort of aqueous acid solution within the flour.

In attempting to develop this promising operation further, a series of investigations (96) was undertaken to determine the important process characteristics so as to provide engineering data for the design of a commercial plant. It was of prime interest in this study to know how fast the reagent is sorbed by flour particles under various physical conditions since the economy of many chemical operations is frequently determined by the rates of transport processes.

One common area of interest in fluid-solid systems is the rate
of interphase transport of material from the source to the sink, that is the kinematics of motion. One step in the transport process is the diffusion from the source in the bulk of the gaseous phase, under the influence of a partial pressure or concentration gradient, to the interface. At the interface discontinuities are usually present. There is a steady drop in concentration across the solid phase because of diffusion within the solids.

At this stage, it seems pertinent to classify the differences among some of the terms which are used to express the transfer of material between two or more phases. The term absorption refers to the mass-transfer operation which involves the transfer of a gas into a liquid absorbent; while the term dissolution, which is often used rather vaguely to represent the transfer of mass from any type of phase into a liquid, refers more accurately to the dispersion of a solid into a liquid. In addition, the transfer of mass from either a gas or a liquid to the surface of a solid is termed as adsorption. The opposite of absorption and adsorption is designated as desorption. It was thought that the general term 'sorption' should be used to include both adsorption at the solid surface and absorption (solution) in solids or in the moisture which is present in the particular system under investigation. Henceforth, the total sorbed weight will be regarded as the amount of sorbate (gas) taken up by the sorbent (moisture laden flour).

The primary objective of the present investigation was to study the hydrogen chloride sorption characteristics of soft white winter
wheat flour with special attention being given to the sorption kinetics. In this investigation the problem of measuring the sorption rate was complicated by the moisture in the flour. Because of this challenging fact, a great deal of thought and planning had to be given to the development of a simple and economical technique for making experimental measurements. Eventually, a combination of the conventional gravimetric and dynamic methods of experimental measurement was adapted to this study though the experimental difficulties were not eliminated entirely.

Data for determining the sorption kinetics was obtained by measuring the overall gain or loss in weight of a sample of flour contained in a shallow pan suspended from a quartz helix microbalance. The work included the determination of the effects of several variables, such as the partial pressure of the sorbate, temperature, flour moisture content, sample depth, and gas flow rate inside the balance enclosure, upon the apparent rates of sorption. Some attention was also given to the sorption of ammonia by wheat flour and acid-modified flour.

In addition to the measurement of the overall sorption rate, the apparent equilibrium data for the hydrogen chloride-flour-water system were collected to provide sorption isotherms at 34° F. Several types of sorption isotherm equations which have been developed experimentally or theoretically were tested to find the best correlation for the data of this particular system.
In order to provide further insight into the sorption process and to assist in analyzing the results, a mathematical model was developed to represent the experimental system. In developing this model it was assumed that the controlling resistance to mass transfer would be the resistance to diffusion through the layers of flour in the balance pan. Consequently at the surface of each particle the gas and solid should be in equilibrium. Furthermore, it was postulated that only hydrogen chloride would be transported and that the system would behave isothermally. A partial differential equation representing the mass balance across a differential layer of flour at any given instant in time was developed and this was combined with an equation representing the equilibrium sorption isotherm. The resulting expression with the appropriate initial and boundary conditions constituted a mathematical representation of the system. This mathematical system was integrated with a digital computer and the results were compared with the experimental data obtained.
LITERATURE REVIEW

In this review, particular attention is devoted to sorption studies involving wheat flour and experimental techniques for measuring the sorption of gases. Some general information concerning the mechanism of sorption of gases and vapors by solids is also included. A review of previous work on the mathematical development and analysis of systems involving simultaneous diffusion and either sorption or reaction is deferred to a later section.

General Theories of Sorption

When a solid is exposed and surrounded by a gas or vapor, there is a boundary layer which exists at the interface between the two phases. For the exploration of the true mechanism of mass transfer through this layer, a number of hypotheses have been proposed. The earlier postulates included the film theory, the penetration theory and the surface renewal theory. Recently a film-penetration model has been developed to generalize the film and penetration theories.

Molecules, after being transported by molecular diffusion through the boundary layer, are sorbed at the solid surface. Two main types of adsorption may occur, due to different forces of attraction existing between the two different phases. These forces depend on the complex physical structure of the solid as well as on the chemical nature of both gas and solid. One type, called physical adsorption or van der Waals adsorption, has a relatively
weak interaction and small energy requirements and is completely reversible. The other type is chemisorption or activated adsorption. It has a strong interaction of a chemical nature and a considerable energy requirement and is, in most cases, not completely reversible.

In other words, the heat released upon physical adsorption is of the same order of magnitude as heats of condensation of the adsorbate; while chemical adsorption requires a certain activation energy and the heat of chemisorption is many times greater than the heat of normal condensation and corresponds to that of a chemical reaction. Consequently, the amount adsorbed increases significantly as the temperature is raised for chemical adsorption but decreases sharply for physical adsorption. There are some other distinguishing characteristics between physical adsorption and chemisorption (35). Adsorption at low partial pressures is unfavorable to physical adsorption but on the contrary it may be favorable to chemisorption. The entire surface, both externally and internally, of the adsorbent (usually solid), is available for physical adsorption; while chemisorption is limited to active sites on the surface only. Because of this, surface coverage is complete and extendible to multilayers for the former, and incomplete and limited to a monomolecular layer for the latter.

Aside from the differences mentioned above, the comparisons on the rate of adsorption are our major concern. Since higher activation energy is required, chemical adsorption has a negligible rate at low temperatures. In some cases, the fast initial physical
adsorption is followed by a slow sorption process that may be due to chemisorption; that is once the higher energy forces have been satisfied by the latter mechanism.

For a given system the equilibrium adsorption data may be expressed as:

\[ f \left( \frac{W_A}{A}, \frac{P_A}{A}, T \right) = 0 \]

A plot of the amount adsorbed versus pressure at constant temperature is called an "adsorption isotherm". When pressure is constant and the temperature varies, the plot is an "adsorption isobar". The plot of the variation of equilibrium pressure with respect to temperature at a constant amount of gas adsorbed is an "adsorption isostere". These are most often obtained as cross-plots of isobars or isotherms since isosteres are not readily measured experimentally. Among these methods of graphical representation of equilibrium adsorption data, the adsorption isotherms represent the most generally useful plot in adsorption studies. Adsorption behavior as illustrated by the isotherm plot was classified by Brunauer (12) into five general types. In some isotherm plots, the adsorption and desorption curves frequently do not coincide—a phenomena termed "hysteresis".

A great amount of theoretical work has been carried out in the field of adsorption (12, 28, 29, 34, 44, 45, 64, 66, 68, 70, 86, 97). Adsorption has been explained on the basis of the monolayer (or monomolecular), multilayer, capillary condensation,
potential, polarization, statistical and thermodynamic theories. Most of the attempts to formulate equations for interpolating and extrapolating available experimental data and understanding clearly the behavior of adsorption have been done on the basis of some predetermined theoretical models for specific systems and conditions of adsorption. Therefore, there is no unified theory or general equation suitable for all types of adsorption isotherms.

From an engineering viewpoint, adsorption of more than one component in industrial processes such as catalysis and gas separation is probably far more important than single component adsorption. A discussion and development of the theoretical aspects of mixed adsorption can be found in a great many references.

The theory of gas absorption has been well established and unified in comparison with that of adsorption. For this mass transfer operation, the partial pressure of the solute in the gas phase which is in equilibrium with a certain liquid-phase concentration is expressed as a function of that concentration. Henry's law and Raoult's law are the two most familiar expressions which are used for predicting vapor-liquid equilibria in gas absorption. The amount of gas sorbed by some moisture laden solids was observed to obey Henry's law for a given moisture level by Nakayama (73).

Barrer (7) presented a detailed discussion and review of the subject of diffusion in and through solids. It is well recognized
that diffusion inside a solid particle can include a variety of transport processes. Many investigators observed that after being physically sorbed at the external surface of solids gaseous molecules may be transported by surface diffusion. The general term, pore diffusion, is usually used to refer to the other types of mass transfer. Flow of gases through porous solids has been dealt with by a great number of researchers in the fields of soil physics, petroleum technology, surface measurement, gas separation, catalysis, and some others, over the years. Two thorough literature surveys on the subject have been written by Carman (16) and Scheidegger (89). The first emphasizes the permeability of porous media to gases and the surface diffusion coefficients, while the second stresses the theoretical aspects of the physical phenomenon by mathematical treatments. Since it is normally found for fine-pored media, that the mean free path of gaseous molecules is an appreciable fraction of the capillary radius, slip flow and Knudsen (or 'free molecule') diffusion occur inside the pore space. Carman (16) reviewed the theoretical development and the experimental verification of this transfer process in detail for consolidated and unconsolidated porous media.

The sequential resistances to the transfer of the sorbate from the bulk of the gas phase to the sorbent particle have been considered separately up to this point. In many instances, it is possible to combine these series resistances into one for the overall transfer process. This concept was developed for fluid-fluid systems.
However, as pointed out by Bosworth (10), this concept may equally well be applied to fluid-solid systems.

Rate of Sorption

The study of sorption, like all physicochemical studies, concerns both rate processes and equilibria. By far, however, most work has been done on equilibria, due to the fact that physical adsorption processes are very rapid, except at high temperatures (28). Unfortunately, there are only a few studies in this area that are comprehensive, especially in the field of physical adsorption. Most of the resulting theoretical rate expressions, which are based on a number of postulates are limited in scope and contain a number of arbitrary constants.

In describing the sorption process, three sequential steps in the mechanism are now generally accepted in accordance with Langmuir's pioneer work (65). These include the motion of the gas molecules to the surface, the sojourn of the molecules on the surface, and the motion of the molecules away from the surface, in other words, sorption, surface migration or reaction, and desorption. With porous sorbents the step of internal diffusion through the pores of the sorbent must be included, of course, as an additional resistance. Comparing physical sorption with chemisorption, most studies have indicated that the former is controlled by resistance to mass transfer at the interface and in and through the solids whereas the latter is controlled by resistance
to surface reaction.

A brief review of early investigations concerned with adsorption kinetics was given by Gregg (44). Texts by McBain (68) and Brunauer (12) presented the kinetics of physical adsorption including the theory of adsorption rates. Ledoux (64) attempted to explain the whole subject of dynamic adsorption by treating it from a practical engineering point of view. In De Boer's contribution (28), he intended to create a picture of sorption from a dynamic approach. Barrer (7) dealt with the transport rate of gaseous sorbates in and through sorbents.

It is not surprising to find that much of the study of sorption rates has been done on chemisorption. It is extensively discussed in various references and text-books (3, 34, 45, 51, 66, 91). For chemisorption is of primary concern to the investigators of chemical kinetics. In developing an overall rate expression for fluid-solid reaction systems, a number of theories concerning chemisorption processes have been suggested. Among the early contributions, Langmuir's treatment (63) based on a kinetic approach has been widely accepted as the most suitable method for gas-solid catalytic reactions. Langmuir's derivation has been modified to obtain expressions for sorption and desorption rates for surface processes in dynamic equilibrium. There are also several other rate equations which were formulated empirically by researchers in this field.

Such diversified fields as chemisorption, soil mechanics, powder metallurgy, gas separation, biochemistry and polymerchemistry,
have contributed a vast amount of literature on sorption kinetics. Most of the existing information, however, concentrates on the rates of processes involving simultaneous diffusion and sorption or reaction in various practical systems.

Experimental Measurement of Sorption

The conventional methods for determining the amount of gas adsorbed are either volumetric or gravimetric. Usually both methods are carried out in a static system. In contrast, the development of gas chromatography has led to methods for measuring sorption in a dynamic system. In addition, various indirect methods have been employed involving accommodation coefficients, the optical properties of the sorbed film, and radiotracer techniques. These methods are discussed in several references (9, 12, 26, 32, 33, 34, 37, 86, 97).

Volumetric

Probably this approach to sorption measurement is the oldest among the common methods. This method which is based on volumetric measurement can be carried out by two different techniques. The one offering the greatest experimental simplicity, but requiring more difficult data reduction, utilizes a constant-volume system. The other, having many of the advantages of the previous method and avoiding the problem of hysteresis encountered due to changing pressure in the other techniques, utilizes a constant-pressure system.
In both techniques a known weight of sorbent is contained in a bulb connected to the necessary manometers and pressure gauges, and the other auxiliary apparatus. After the sorbent is heated and evacuated, a known quantity of the test gas is admitted and brought to equilibrium with the sorbent at a known temperature for the case of the constant volume system. The pressure is then measured. If the volume of the bulb minus that of the sorbent is known, the quantity of the unsorbed gas and the amount sorbed can be calculated. The difficulty in determining the dead space makes the measurement rather inaccurate.

The same procedure in loading sorbent is used in the case of the constant-pressure system. In contrast with the constant-volume technique, after a known quantity of the test gas is admitted, a gas buret filled with mercury, connected with the system at one end and with a leveling bulb at the other must be adjusted occasionally to keep the operating pressure constant. The amount of gas lost to the sorbent at the chosen operating pressure can be measured directly.

The two techniques have been improved and modified constantly by using more accurate control methods such as automatic pressure controllers or regulators. Although rate studies can be carried out by means of the volumetric technique, such studies are more frequently done by using a gravimetric or weighing technique.
Gravimetric

The direct weighing of the amount sorbed by means of a McBain and Baker sorption balance makes it possible to avoid the deadspace difficulty of the volumetric method. This balance consists essentially of a calibrated spring made of fused silica or special metals on the end of which is hung a small pan containing the sorbent. By measuring the increase in the length of the spring the sorbent can be weighed. The buoyancy and damping factors need to be corrected for in this method. The buoyancy factor may be reduced or eliminated by employing cantilever, knife-edge or torsion type micro-balances, and some workers have used these in place of a quartz spring. Recently several new types of vacuum micro-balances have been developed and introduced, which are based on the principle of magnetic balancing or the use of a linear differential transformer to measure extremely small deflections. Automatic recording and controlling vacuum micro-balances have been devised for studying weight change as a function of time, temperature, or other variables. A few early investigators even used ordinary analytical balances. The gravimetric method is well suited for the study of sorption rates providing sorption is not too rapid to follow accurately.

Dynamic

In the dynamic or continuous flow method the sorbate is mixed in known concentration with an inert gas and passed continuously
through a packed bed of solid sorbent. The issuing stream is analyzed at definite intervals by employing either a thermal conductivity cell or an ionization gauge. Determining the breakthrough curve for sorption is probably the simplest experimental approach in this dynamic measurement. Observing the sorbate concentration in the effluent gas from a sorbent bed containing a known amount of sorbate is another technique which has been employed. Often the first method follows the second as a check for reversibility of sorption. Several modifications have been employed by a great number of investigators in chromatographic studies. Observing the effluent concentration after introduction of a "pulse" of sorbent into an inert carrier (purge) stream is the third dynamic approach. This is sometimes called "the pulse flow method." It is claimed that this method offers the ability to detect the sorption of small amounts and consequently it is useful for measuring sorption by solids having small surface areas. Some advanced instruments on the market, such as the Perkin-Elmer Sorptometer which applies the new dynamic-measurement concept, are rapid and accurate in operation. This method finds wide-spread application in practical research in the chemical industries.

Optical

A sorbed film on a solid surface may cause an elliptical polarization of an incident beam of light. The ellipticity may then be related to the thickness of the sorbed layer if a dielectric
constant for the sorbed phase is known. This method involves experimental and theoretical difficulties not found in the more direct methods.

Accomodation coefficient

The sorption phenomenon is related to the exchange of energy between the gas and the solid surface. Energy exchange is indicated by the change in temperature of the gas as related to the temperature of the solid. In other words, the accommodation coefficient measures the extent to which a gas of known temperature striking a surface of a different temperature "accommodates" its temperature to that of the surface. Specifically, the temperature of the gas molecules before striking the surface, the temperature of the gas molecules when they leave the surface, and the temperature of the surface define the accommodation coefficient. Precise measurement of small differences in temperature is required.

Radiotracers

A sorption determination may be accomplished by measuring the accumulation of radioactive gas on the solid sorbent or by measuring the loss of radioactivity of the gas phase. This method might be refined to measure the sorption of quantities much below the limit of other methods. This technique would provide an excellent means for determining sorption rates. The radiotracer technique also permits measurement of the sorption of one component of a mixture.
The investigators, however, need knowledge and experience in handling radioactive materials.

Wheat Flour

The amount of gas sorbed per gram of sorbent depends on the partial pressure, temperature, nature of the sorbent, and the preparation and history of the sorbent. In order to understand the role of wheat flour as a sorbent, a brief review was made of cereal chemistry. This review was especially concerned with the physical and chemical properties of flour and methods of analysis for cereal. For this particular project, an attempt was made to determine what techniques have been used in the past for similar investigations and to see what, if any, sorption studies have been made involving wheat flour.

Laboratory methods

It is not intended in this section to give a complete account of the various ways and means of examining flour, since fairly complete information is available in several sources (49, 50, 57). The methods given here only concern the determination of moisture content, particle size and chlorine. Some of these methods were used in the experimental investigation.

A lengthy discussion and evaluation of methods for moisture determination in wheat flour was presented by Hlynka and Robinson (49), and Kent-Jones and Amos (57). It is very important to know
that due to the nature of wheat flour, the moisture contained therein seems to be combined with varying degrees of affinity. Hence the determination of moisture is by no means simple. Initially the loss of moisture is fairly rapid as flour is heated, but it becomes more and more difficult to remove further moisture as the heating proceeds.

A wise selection of a method of determining moisture must be made since different methods of determination tend to give different results. The common methods of moisture determination can be classified under four major headings, oven, distillation, electrical, and chemical or titration methods.

Investigations have shown that the results of moisture determination by the various oven methods were affected not only by the type of oven used, but also by the weight of sample taken and the shape and dimensions of the container. Vacuum ovens on an average tended to give higher results than air ovens.

Much literature is available to show the progress made in measuring particle size and surface area (19, 20, 26, 53, 77). The techniques used to determine fine particle size distribution are important supporting methods for a primary study of sorption. Gravitational sedimentation, centrifugal sedimentation, microscopy, sieving are the major techniques in fine particle measurement. Some other techniques which have been used in rapid and accurate measurement are average size from permeametry, gas adsorption, electrolytic resistivity changes (Coulter Counter), Cascade impactor,
and light scattering. Among the various methods listed above, the estimation of surface areas by gas adsorption has earned considerable attention, for it is closely related to the present sorption study. Although no difficulty would be found in locating information on the gas adsorption methods for evaluating surface areas, the excellent book by Young and Crowell (97) is the most complete and comprehensive in this field.

In this survey, measurement of the particle size distribution of starch or polypolymers in general and flour in particular has been of most interest. Irani and Fong (54) discussed the effect of particle size distribution on the quality of flour. In measuring particle size distribution of soft wheat flour, the gravitational sedimentation, centrifugal sedimentation, sieving, microscopic counting and Electrolytic Resistivity change methods were used and the experimental results were compared. Particle sizes were measured and related to certain flour characteristics by Sullivan et al. (94). By using the Brunauer-Emmett-Teller (gas adsorption) method and a photomicrographic technique, Hellman and Melvin (46) determined the surface area of various starches. The apparent external surface obtained by nitrogen sorption was within the range of 0.1 to 2.6 m$^2$/gm. The specific surfaces of starch granules and its parent flour were measured and found to be 0.7708 and 0.1249 m$^2$/gm. respectively, by Gracza and Greenberg (42), as analyzed from the particle size distribution data using the centrifugal method. The specific surface area of flour obtained from a water-flour
isotherm by employing the Brunauer-Emmet-Teller theory was 235 m²/gm. as reported by Bushuk and Winkler (15) recently. Hess (48) obtained a value of 0.16 to 0.60 sq.m/gm. by the same method from the flour-argon isotherm.

Flour is known to be a heterogeneous mixture of particles of different densities and shapes. Specific gravity values ranging from 1.40 to 1.50 with an average value of 1.44 were collected by Irani and Fong (54) by duplicate determination of five flour samples and air-classified fractions of these samples. However, no information with regard to the moisture content of the flour samples was presented. Gracza and Greenberg (42) suggested a swelling factor to account for the decrease in density of starch granules caused by hydration. In their study of the specific surface of flour and starch granules in a hard winter wheat flour and in its fine subsieve-size fraction, the density of the starch granules at about 10 per cent moisture level was taken as 1.500 gm/ml and of the swollen granules as 1.297 gm/ml.

A gravimetric method for determining chlorine as chloride in flour was suggested by Kent-Jones and Amos (57). The available official method of analyzing for chlorine is for the analysis of chlorine in flour fat (50). No other information relating to this determination was located.
Properties

A great number of publications concerning the chemistry and technology of the cereal industries are available (5, 6, 49, 57, 67, 81), so the brief summary presented here will only provide information of greatest importance to the present study. As summarized by Kent-Jones and Amos (57), the approximate composition of 72 per cent-extraction white flour is:

<table>
<thead>
<tr>
<th>Components</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>13.0-15.5</td>
</tr>
<tr>
<td>Starch</td>
<td>65-70</td>
</tr>
<tr>
<td>Protein</td>
<td>6-13</td>
</tr>
<tr>
<td>Cellulose (fiber)</td>
<td>trace to 0.2</td>
</tr>
<tr>
<td>Fat</td>
<td>0.8-1.5</td>
</tr>
<tr>
<td>Sugar</td>
<td>1.5-2.0</td>
</tr>
<tr>
<td>Mineral matter (ash)</td>
<td>0.3-0.6</td>
</tr>
</tbody>
</table>

Apparently, starch is the constituent that must be given primary consideration in this study of sorption. As may be seen from several electron-microscope photographs of various wheat flour samples (57, 67), wheat starch is composed of two types of granules. The smaller granules are spherical while the large ones are lens-shaped. The diameters of these granules lie between 0.002 mm. and 0.050 mm. but the majority of the granules are close to either the upper or the lower limit in size and granules of intermediate size are much rarer (57). It has long been known that all of the unmodified industrial starch is a natural high polymer built up from the basic glucose unit in two types of molecules, those that are essentially linear chains of 1-4, alpha-glucosidically-linked glucopyranose called
amylose and those that are branched chains through alpha-1, 6 linkage, termed amylopectin. The former, in the case of wheat starch, comprises about 23 per cent of the total starch. The polymer is formed through loss of one molecule of water for each molecule of glucose is represented by the following formula:

\[
\begin{align*}
&\text{CH}_2\text{OH} \\
&\text{H} \\
&\text{OH} \\
&\text{H} \\
&\text{OH} \\
&\text{H} \\
&\text{OH} \\
&\text{H} \\
&\text{H} \\
&\text{O} \\
&\text{n}
\end{align*}
\]

The structure of protein is also that of a high polymer, but the repeating unit is not identical and may be any of the naturally occurring amino acids. A comprehensive review as to the role of protein in wheat flour has been presented elsewhere (57).

**Sorption**

The study of sorption of gases or vapors by wheat flour has been limited in volume and diversified in theoretical interpretation. Most of the work published has centered on sorption problems related to the wheat kernal (4, 35, 49) and to starch (4, 14, 15, 46, 49, 72, 87). Only single component adsorption by evacuated adsorbents appears to have been investigated previously.
One of the earliest studies of gas sorption by starch and cellulose was the work done by Costa (21). He measured the sorption of hydrogen chloride, ammonia, and several other gases by commercial rice starch which had been dried at 100°C to a constant weight. The temperature of the measurements was not stated explicitly while gas pressures were indicated as small, without quantitative statement. The sorption of hydrogen chloride was rapid in the beginning and the amount sorbed in 96 hr. was 0.103 gm./gm. of starch. The rate was slower subsequently and after 792 hr. the total amount sorbed was 0.1855 gm./gm. of starch. The quantity of hydrogen chloride sorbed did not appear to reach any definite limit and a water-soluble black substance was formed indicating chemical reaction. Unlike starch, cellulose showed a definite sorption limit within 100 hours. By the end of this time 0.0532 gm./gm. of cellulose was sorbed. However, in the case of the sorption of ammonia by starch a limit appeared to be reached in 24 hours. A summary of Costa's results is given below:

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>Starch</th>
<th>Cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0.1855</td>
<td>0.0532</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.0894</td>
<td>0.0256</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.0905</td>
<td>0.0140</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0067</td>
<td>0.0004</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0006</td>
<td>-----</td>
</tr>
</tbody>
</table>

From these results, it appears that starch is a better sorbent than cellulose and that it is stable in all of the sorbents except hydrogen chloride.
A recent investigation by Thomson and his associates (43) was the kinetic study of the reaction of hydrogen chloride with rice, corn, wheat, and potato starches at a temperature of 70°C. Using a simple Warburg-type apparatus, they were able to follow the reaction by measuring changes in hydrogen chloride pressure. The behavior of the granules was also studied under a microscope. Definite hexagonally packed structures on the surface of the granule were observed in an electron micrograph of a palladium-carbon shadowed reaction product. Rapid sorption of hydrogen chloride on the surface of the granules took place during the first few minutes. This was followed by a period of constant rate of sorption termed the "induction period". At the end of this period, another straight section with a different slope was recorded on the sorption kinetic curve until the end of the reaction. It was learned that the rate of hydrogen chloride sorption during the induction period increased in the order: potato, wheat, corn, and rice starch. It was also noted that the average particle size and the induction time increased in the same order. Several interesting results were observed. Thus, the starch slowly darkened until it was black, and at the end of the induction period the weight and water solubility of the granules were a maximum. The granules became insoluble and permanently black during the subsequent reaction. It was postulated that the reaction following induction is a cross-linking of starch chains with the elimination of 2.5 to 3 molecules of water per glucose unit. There is, however, little degradation of the starch chains.
During the induction period, hydrogen chloride diffuses into the granules, breaking hydrogen bonds between chains and increasing the disorganization; the start of polymerization is, therefore, delayed until the end of the induction period.

A study on sorption of water vapor by wheat and its milling product was undertaken by Babbit (4). A special arrangement of the McBain quartz spiral balance was used in the measurement of the amount of moisture sorbed by wheat kernels. The time-rate of change of moisture content was related to diffusion and the rate of approach to equilibrium. It was noted that the depth of the sample in the holding pan affected the rate of sorption to a very small degree.

As pointed out earlier, in our investigation the problem of measuring the hydrogen chloride sorption rate is complicated by the moisture in the flour. Since this moisture is not permanently fixed, it may desorb while hydrogen chloride is being sorbed. Consequently an extensive knowledge of the combination of flour with water is needed in order to understand the sorption characteristics of flour.

Until now, very little has been said about the actual relationship between flour and water vapor. Most of the investigations relating to this field are limited in scope to the more practical aspects. The lengthy and comprehensive review by Hlynka and Robinson (49) provides an excellent explanation of the sorption of moisture by cereals in relation to their chemical structure. Water appears to be bound by
polar effects. Accordingly, the points of polarity in the starch molecule, such as hydroxyl groups on the ring, ring oxygen, and bridge oxygen are suitable foci for interaction with water, which is a small molecule with a large permanent dipole moment per unit surface. Similarly the molecules of protein carry a wide variety of polar and ionic groups, therefore, there is ample opportunity for water to interact with them.

It has been observed for sometime that a sigmoid shaped sorption isotherm is common for cereal grains and their products. The sorption isotherms obtained by Babbit (4) and by Bushuk and Winkler (15) have shown sigmoid shaped curves for water vapor sorption by flour at room temperature. In general, an S-shaped or Type II isotherm is characteristic of multilayer adsorption according to Brunauer (12). Hlynka and Robinson (49) made an attempt to interpret the features of such an isotherm for wheat and flour following the Brunauer-Emmett-Teller theory of multilayer adsorption (13). Accordingly, they postulated that the first monomolecular layer of water is adsorbed on active centers only; the second layer is adsorbed on the surface not covered by active centers and on the first layer. The first segment of the isotherm corresponds to a water content of about 6 per cent (approximately 0.07 gm.H₂O/gm. dry flour) and the linear segment of the isotherm represents an additional 10 per cent moisture content (that is a total of 0.18 gm.H₂O/gm. dry flour). The last segment is the continued adsorption of additional layers. Becker and Sallans (8)
and Bushuk and Winkler (15) applied this hypothesis to obtain a number of adsorbed layers at saturation relative pressure.

However, Hellman and Melvin (46) objected to the interpretation of the sorption data for water vapor on starch in terms of an area of adsorption because of the disagreement in the specific surface areas obtained by two different experimental procedures. The surface area of corn starch calculated by the method of Brunauer-Emmett-Teller from experimentally determined sorption isotherms for nitrogen at -195°C is approximately 0.70 m²/gm. of starch, but the value obtained from the isotherms for water vapor is 334 m²/gm. The surface area of the same sorbent determined by employing a photomicrographic technique is 0.483 m²/gm. which is comparable to the value determined by nitrogen sorption. Because of this fact, they concluded that water sorption of starch is not a surface condensation phenomenon and recommended using the alternative interpretations given by Cassie (18) and Rowen and Blaine (87).

In Cassie’s estimation sorption occurs at sites distributed throughout a substance. The explanation given by Rowen and Blaine for the large differences between the sorption capacities of textile fibers for water vapor and nitrogen was more detailed. They attempted to interpret the apparent discrepancy in various ways. It was assumed that the sorbing sites were not restricted to part of a surface; in other words, the entire surface was available for sorption. There might be an additional internal
surface specific to certain sorbates as well as an external surface. The dependency of the internal surface on the presence of a swelling agent such as water and the ability of the small, polar water molecule to penetrate into capillaries not accessible to the nitrogen molecule were other possibilities suggested by Rowen and Blaine. The discrepancy in the specific surface of flour obtained from different sorbates was observed by Bushuk and Winkler (15). Most workers agree that flour containing specific polar groups logically interacts with the sorbate molecules during the sorption process.

The series of investigations conducted by Bushuk and Winkler (15) is one of the most recent works concerning the sorption of water and organic vapors by wheat flour. The conventional McBain-Baker sorption balance was employed to study flour dried under vacuum at 27°C and several other temperatures. The results showed that the rate of sorption was not affected by varying the size of the flour sample; however, the presence of a slight amount of air in the sorption chamber decreased the rate of sorption very markedly. In addition, the sorption was about 75 per cent complete in 15 minutes after the sample was exposed to the vapor and complete equilibrium was established in less than four hours. Based on the results obtained by fitting the rate data of their particular investigation to a first-order rate equation, they concluded that the sorption system is primarily a diffusion controlled process. In addition, according to their experimental results the rate of sorption increased with decreasing molar volume of the sorbate, and
apparently the dipole moment of the sorbate molecule had no effect on the rate of sorption.

**Acid modification**

It has been known in industry that starch can be altered by the use of various physical and chemical procedures. Physically modified starch has moderately improved properties and is more desirable for biological utilization in food. Chemically modified starch has drastically altered properties and finds wide utilization in industry. Matz (67) and Kerr (58) presented a complete discussion of this aspect. Acid-modified starch, which is a primary concern of this study, has shorter chains in both the amylose and amylopectin fractions and an increasing proportion of linear to branched chains. Hence, the modification of starch by acid-treatment is known as breaking off the complexly constituted amylopectine types and results in lower paste viscosity. In starch manufacture, acid-modified products are prepared by different processes so as to have several desirable characteristics for specific applications.

One can easily see, from the following structure of starch, that a cleavage takes place to rupture the carbon-oxygen bond between two adjacent glucose units. As a result, a water molecule splits and adds to the two starch fragments. Kerr (58) stated that, theoretically, the hydrolysis of any starch is a composite of at least two reactions: the hydrolysis of linear chains of comparatively
Kerr (59) reviewed thoroughly some aspects of starch chemistry concerning the utilization of acid-modified starch products for tub-sizing paper. Because of a limited hydrolysis, acid-converted starches show the desired characteristics for sizing purposes. An attempt was made to explain the physical properties and chemical behavior of these starch products in terms of starch composition and chemical structure.

Corn starch, one of the most versatile and readily available starches, was the first to be acid modified for commercial use; while wheat starch is not currently modified on an industrial scale, because of processing difficulties and economic factors. Frederickson (38, 39) developed the first commercial process employing a fluidized bed for acid modifying corn starch. The acid was added to the flour by vaporizing a solution of hydrogen chloride into the fluidizing gas stream. Ravindram et al. (83, 84, 85) carried out a series of
investigations, on a process for the depolymerization of starch utilizing a fluidized bed reactor.

Rankin et al. (82) discovered a process for acid-modifying whole flours to produce tub-sizing agents. Lancaster et al. (61) extended this work, to produce a material similar to commercial starch products in paste viscosity and effectiveness as a tub-sizing agent from commercial soft white winter wheat flour. A ribbon blender which held 30 lb. batches of flour was used for this purpose. Small amounts of 4 N hydrochloric acid was sprayed into very dry flour with less than 3 per cent moisture content and the mixture was held at a temperature less than 37° C (100° F) for 30 minutes to 2 hours. The reaction was stopped by spraying in 14 N sodium hydroxide. In other experiments, dry hydrogen chloride was blown into the reactor containing a flour having 10 per cent moisture content, and dry ammonia gas was introduced instead of aqueous sodium hydroxide. The desirable reacting temperature was 80 to 100° F. In another study Lancaster et al. (62) developed a rate equation in terms of product paste viscosity, concentration of acid and reacting temperature. This correlation was for the same process mentioned above. They also noted that a critical variable in processing flour is moisture content, which must range between about 6 per cent, below which the rate decreases, and about 12 per cent, above which localized over-reaction occurs. From the protein solubility test, they found that the protein is not changed appreciably during acid modification.
EXPERIMENTAL INVESTIGATION

Apparatus and Materials

Apparatus

It was foreseen that it would be necessary to have the moisture in the flour under control, therefore no conventional way of measuring sorption could be adopted directly for this particular study. Usually, both the measuring system and the sorbate must be evacuated before undertaking any experimental determinations. Due to the complexity involved in this particular work, the apparatus and method of measurement were modified several times.

In the earliest stage of the investigation, the idea of using a mixture of hydrogen chloride gas and water vapor to contact the flour, was conceived in order to reduce the moisture loss. It seemed, however, that both hydrogen chloride gas and water vapor would be sorbed by the flour in that process. This would require some method for following the sorption of both gases which would be very complicated.

After careful examination, it appeared that a weighing method, in combination with a dynamic approach, would be the most adaptable and simplest technique for this special case. The change in sample weight could be observed and recorded from time to time; and after a given interval the sample could be removed and analyzed. In this dynamic measurement, a stream of gases flowed past the sample so that the concentration of the component of interest could be
maintained constant in the gas phase and the diffusion problem within the tubular enclosure would be eliminated, except within the sample pan. No evacuation system was needed in this arrangement.

The apparatus shown in Figure 1 was used for measuring the rate of gas sorption by flour. It consisted of a quartz spring microbalance\textsuperscript{a} enclosed in a vertical glass tube 3 cm. in diameter and 100 cm. in overall length with a gas inlet at the bottom and an outlet at the top together with gas metering and other auxiliary equipment. The flour samples were suspended from the quartz helix in small plastic flat-bottomed, cylindrical pans having a diameter of 1.75 cm. and different wall heights.

A cathetometer\textsuperscript{b} was used to measure the spring extension to 0.1 mm. which corresponded to a change in sample weight of 1 mg. The gas drying towers contained calcium chloride and magnesium perchlorate respectively. The rotameters were calibrated with a soap bubble method. The helix was calibrated by placing analytical balance weights in the pan. It had a maximum capacity of 2 gm.

The balance enclosure was water jacketed for temperature control and fitted with a sintered-glass gas diffuser plate near the bottom. Water was circulated through the jacket by a pump.\textsuperscript{c}

\textsuperscript{a}Made by Microchemical Specialities Co., Berkeley, California.
\textsuperscript{b}Made by Eberback Corporation, Ann Arbor, Michigan.
\textsuperscript{c}Fisher Scientific Model B-1 centrifugal pump.
Figure 1. Flowsheet of apparatus used for measuring HCl sorption rates at room temperature
For some runs made at room temperature at the beginning of this study, an unjacketed tubular enclosure was used. Either the pure component gases or mixtures could be passed through the balance enclosure. After the gases had passed through the balance enclosure, they were bubbled through a flask of water to remove the noxious components and then vented.

Materials

A straight grade, untreated and unbleached flour milled from Genessee variety, Michigan soft white winter wheat a was used for most measurements. For the study of moisture effect on hydrogen chloride sorption, the moisture content of the original flour was adjusted by several methods to different levels.

One of these was the method used by Hellman and Melvin (47) which involved placing the flour in a desiccator along with a saturated salt solution selected to give the appropriate vapor pressure of water. Two weeks or more were allowed for the flour to reach equilibrium. During this period the desiccator was connected to an operating water aspirator for 30 minutes of each day so the total pressure in the desiccator should have remained close to the water vapor pressure. At the end of the equilibrium period the flour in the desiccator was well mixed. Altogether six

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a Obtained from the King Milling Company, Lowell, Michigan.
different levels of moisture content were obtained by this method using saturated salt solutions of potassium nitrate, potassium chloride, sodium nitrate, sodium bromide, potassium carbonate, and lithium chloride, respectively. A second method, which was used to adjust the moisture content, involved drying the flour in a vacuum oven at 105° C for several hours. In all cases the moisture content of the adjusted flour was determined by measuring the weight loss of a sample heated to 105° C for 24 hours. The various moisture levels obtained by these methods are summarized as follows:

Table 1. Environments used for preparing flour samples of different moisture contents

<table>
<thead>
<tr>
<th>Moisture Content (Gm. H₂O)</th>
<th>Preparation Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gm. Dry Flour</td>
<td></td>
</tr>
<tr>
<td>0.2503</td>
<td>desiccator, room temp., KNO₃</td>
</tr>
<tr>
<td>0.2219</td>
<td>desiccator, room temp., KCl</td>
</tr>
<tr>
<td>0.1994</td>
<td>desiccator, room temp., NaNO₃</td>
</tr>
<tr>
<td>0.1682</td>
<td>desiccator, room temp., NaBr</td>
</tr>
<tr>
<td>0.1364</td>
<td>desiccator, room temp., K₂CO₃</td>
</tr>
<tr>
<td>0.1162</td>
<td>atmosphere, room temp., 24 hr.</td>
</tr>
<tr>
<td>0.0949</td>
<td>atmosphere, room temp., 48 hr.</td>
</tr>
<tr>
<td>0.0841</td>
<td>desiccator, room temp., LiCl</td>
</tr>
<tr>
<td>0.0208</td>
<td>vacuum oven, 105° C, 8 hr.</td>
</tr>
<tr>
<td>0.0068</td>
<td>vacuum oven, 105° C, 20 hr.</td>
</tr>
</tbody>
</table>
A few sorption experiments were carried out with pure wheat starch prepared by the Batter process and supplied by the Northern Utilization Research and Development Division of the United States Department of Agriculture in Peoria, Illinois. The starch ranged from dust sized particles up to lumps 3/8 in. across when received. It was subsequently ground with a mortar and pestle to a more uniformly sized powder. Examination of the powder under a microscope revealed the presence of many individual starch granules, some agglomerators containing up to 50 granules, and some fragments of granules.

The anhydrous hydrogen chloride gas and the anhydrous ammonia gas were obtained from the Matheson Company which claimed that the gases had a minimum purity of 99 per cent. The compressed nitrogen gas was obtained from the Air Reduction Company which claimed the purity of the gas to be 99.9 per cent.

Experimental Procedure

Water vapor desorption rate

The test procedure used for measuring drying rates of flour at room temperature and pressure involved the following steps:

1. A balance pan was loosely filled with flour and the upper surface was left irregular to avoid packing the flour by scraping the surface. Hence, the reported flour depths are only approximate.
2. The balance tube was purged with nitrogen and then taken apart at the center joint to admit the sample pan. After the pan was suspended from the quartz helix microbalance, the tube was reassembled.

3. While the oscillations of the quartz spring were damping out, the initial sample weight was observed and recorded.

4. The nitrogen was taken from a high pressure storage cylinder, dried by passing it through drying towers, metered with a rotameter and then passed through the balance tube containing the flour sample.

5. The sample weight loss was observed at frequent time intervals.

Since conceivably the loss in flour moisture could be reduced by operating at a lower temperature, some moisture desorption runs were made at a temperature near the freezing point of water. For these determinations, the above procedure was used with the following exceptions:

1. The microbalance pans were loaded with wheat flour which had been refrigerated.

2. Ice water was pumped through the jacket of the microbalance enclosure, and the lower end of the enclosure along with several feet of the Tygon plastic tubing which conducted the gas to the enclosure were emersed in an ice bath.

**Hydrogen chloride sorption rate**

The measurements of the sorption rates of hydrogen chloride from a gas mixture at room temperature and pressure were made by using the following procedure:
1. One of the sample pans was loosely filled with flour. The surface was carefully scraped smooth to avoid compacting the bed.

2. The tube, which enclosed the microbalance, was purged with nitrogen and then taken apart at the center joint to admit the sample pan. After attaching the pan to the spring, the tube was reassembled.

3. While the oscillations of the quartz spring were damping out, the nitrogen and hydrogen chloride flow rates were adjusted to provide the desired mixture and total gas flow rate. While the initial adjustments were being made, the gases were vented around the balance enclosure.

4. The initial sample weight was observed and recorded and then the three-way stopcock was turned to pass the gas mixture through the balance enclosure.

5. The weight of the sample was observed and recorded at 1 min. intervals. Time zero was taken as the instant when the first bubble of gas reached the surface of the water in the exhaust absorber.

6. The run was stopped when the weight of the sample became constant or at least was changing very slowly.

It was estimated that less than 3 min. passed between the time the sample was placed in the microbalance and the start of a run.

The experimental sequence involved in the series of determinations at low temperature was similar to that used in the measurement at room temperature. The sample of flour was refrigerated prior to charging the balance pans. As shown in Figure 1, the cooling system was used to maintain the ice water in the enclosure jacket at a temperature of 34° F.
Sorption of ammonia on flour and acid-modified flour

Several runs were made to investigate the sorption of anhydrous ammonia by wheat flour containing 12 per cent moisture under a limited number of conditions. These were made with the same apparatus and using the same experimental procedure as for the hydrogen chloride sorption. In addition, several runs were made in which hydrogen chloride was first sorbed by a sample of flour followed by sorption of ammonia. The procedure was similar to that used where only hydrogen chloride was sorbed except that the flow of hydrogen chloride was interrupted before the sample reached a constant weight and after a 2 min. interval where only nitrogen was flowing through the balance enclosure, addition of ammonia to the nitrogen stream was started. Sorption of ammonia was continued until the sample appeared to reach a constant weight.

Analytical methods

The samples of flour used for each run were analyzed for moisture by weighing, drying under vacuum for 24 hr. at 100°C and reweighing.

In attempting to determine the actual amount of hydrogen chloride in the product, some of the flour samples which had sorbed hydrogen chloride were analyzed for chloride by a gravimetric method. This involved digestion of the sample with nitric acid followed by precipitation with silver nitrate. Blank determinations were run on the untreated flour and the resulting values were applied to
correct the unknown sample values.

The Volhard volumetric method for determining chloride was also used for determining chloride in flour. This involved mixing a sample of flour with distilled water which had been acidified with dilute nitric acid, adding silver nitrate to precipitate the chloride, and then determining the excess silver nitrate by titrating with potassium thiocyanate. Before the titration the silver chloride precipitate must be eliminated either by filtering the sample or by surrounding it with a film of nitrobenzene.

In addition, a potentiometric method for the determination of chloride in flour was used by measuring the potential between a silver chloride coated electrode (Beckman 39048 Silver Electrode) and a calomel reference electrode suspended in a mixture of flour and water. Readings were made with a Beckman, Model 76, expanded-scale pH meter. The following procedure was used:

1. The flour sample was weighed out accurately and mixed with a solution of dilute sodium hydroxide.

2. The resulting slurry was heated in a boiling water bath for 30 min. and continuously stirred. The mixture was then transferred to a volumetric flask and made up to volume.

3. The Beckman pH meter was standardized against a solution of potassium chloride.

4. The pH meter was set to read 25 millivolts when the electrodes were placed in the standard solution.

5. The electrodes were then rinsed and placed in some of the flour mixture which had been prepared. The potential developed across the electrodes was measured and then referred to a calibration curve to obtain the concentration of chloride.
The calibration curve was prepared by making up a series of samples containing known amounts of untreated flour and sodium chloride. These samples were subsequently treated by the above procedure and the corresponding potential readings were plotted against the known chloride concentrations.

Presentation and Discussion of the Experimental Data

**Water vapor desorption rate**

As stated before, an attempt was made to measure the rates of sorption of hydrogen chloride and ammonia by flour containing significant amounts of moisture. This proved to be a very difficult undertaking because there was no way of entirely preventing or accounting for the simultaneous desorption of water vapor as either hydrogen chloride or ammonia was being sorbed. In order to know the weight loss corresponding to the loss of moisture in a quantitative sense, efforts were made to determine the water vapor desorption rate. The initial moisture content of the flour was found to be 11.7 per cent by drying it for one hour at 130°C in an electric oven. The flour depth was investigated to see if it was possible to eliminate the effect of diffusion through the layers of flour on the balance pan. In order to vary the flour bed depth, five different balance pans were used having wall heights of 0.15, 0.20, 0.40, 0.50 and 0.70 cm. respectively. The experiments were carried out at room temperature and pressure with three different
nitrogen flow rates (320, 165 and 31 std. ml./min.) to determine the effect of gas velocity upon the overall drying rate as well.

Some representative results are shown in Figure 2. The fractional weight loss of a sample at room temperature is plotted versus time for a nitrogen flow rate of 320 std. ml./min. Curves for five different sample depths are reproduced. The slope of these curves represents the drying rate and it is apparent that the drying rate decreases as the moisture content decreases. Also it is apparent that the drying rate increases as the flour depth decreases. Hence, the rate of diffusion through the bed of flour particles seems to affect the overall drying rate significantly.

Similar families of curves for nitrogen flow rates of 165 and 31 ml./min. were obtained but are not presented here. At the lower flow rates the drying rates were smaller and the curves representing different flour depths lay closer together. The effect of flow rate upon the overall drying rate appears to be significant.

Although diffusion and mass transfer seemed to have an important bearing on the drying rate, it must be kept in mind that the conditions used in these tests were somewhat unusual in that very dry nitrogen was used so that the driving force was very large. Drying flour with a gas having a higher partial pressure of water vapor could alter the picture considerably.

In attempting to minimize the loss of water vapor from a sample, the water vapor desorption rate was measured at a temperature near the freezing point of water and with a nitrogen flow rate of
Figure 2. Weight lost by flour in nitrogen

flow rate, 320 std. ml./min.
temperature, 80°C
pressure, 1 atm.
gas composition, pure nitrogen
sample depths, 0.15 - 0.70 cm.
sample weights, 0.17 - 0.95 gm.
moisture content, 12%
Flow rate = 320 cc/min.

Bed depth
0.15 cm.
0.20 cm.
0.40 cm.
0.50 cm.
0.70 cm.

GM, H₂O DESORBED/GM, DRY FLOUR

DESORBING TIME, MINUTE
1,050 std. ml./min. However, this did not seem to eliminate the problem completely, as can be seen from the data presented in Figure 3. Although the drying rates were significant, they were much smaller than had been observed previously at room temperature and at lower flow rates. Of course, in the presence of either hydrogen chloride or ammonia the rate of moisture loss would be expected to be different from that shown here because of the interaction of these compounds with water in the flour phase. The water jacket temperature during the runs was 34° F and it is assumed that the flour sample must have been close to this temperature at the start of a run. The flour contained 12.0 per cent moisture initially. Balance pans having three different wall heights (0.15, 0.40 and 0.70 cm) were used. All of the measurements were made at a atmospheric pressure.

**Hydrogen chloride sorption rate**

When pure hydrogen chloride gas was passed over samples of flour, with a normal moisture content, suspended from the micro-balance at room temperature, the rate of sorption was extremely rapid and the sorption process appeared to be virtually complete within a period of about 5 min. The depth of the flour in the balance pans had very little effect on the rate. During the process the samples underwent a marked change in appearance so that the material remaining after a run was in the form of a hard, black cake which was shrunken away from the sides of the balance pan. The amount of
Figure 3. Weight lost by flour in nitrogen

- Flow rate, 1050 std. ml./min.
- Temperature, 34° F
- Pressure, 1 atm.
- Gas composition, pure nitrogen
- Sample depths, 0.15 - 0.70 cm.
- Sample weights, 0.19 - 0.98 gm.
- Moisture content, 12%
hydrogen chloride sorbed was about five times that which would be used in the proposed process for manufacturing a tub sizing agent. In these experiments the sorption rates were so rapid that the measurements were of doubtful accuracy. However, they did provide at least an indication of the order of magnitude.

A number of preliminary runs were made at room temperature in order to investigate the effects of the hydrogen chloride concentration in the gas mixture, the gas flow rate and the depth of the flour sample on the rate of sorption of hydrogen chloride. These parameters were varied over the following ranges:

- HCl concentration: 2.5 - 75%
- Gas flow rate: 100 - 1455 ml./min.
- Sample depth: 0.15 - 0.70 cm.

All measurements were made at room temperature (76°F) and pressure (1 atm.) starting with flour containing approximately 12 per cent moisture. For each run the gain in sample weight due to sorption was found as a function of time. Some of the resulting curves representing the gain in weight are plotted in Figures 4 to 7.

Inspection of the various weight gain curves leads to the following general observations:

1. The flour sorbs hydrogen chloride most rapidly at the start. The sorption rate decreases with the amount sorbed and approaches zero within a few minutes.

2. An equilibrium concentration of sorbed hydrogen chloride appears to be reached which is related to the concentration of hydrogen chloride in the vapor. Figure 6 shows that the relative amount sorbed increases with the concentration in the gas.
Figure 4. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen

- flow rates, 400 std. ml./min.
- temperature, 80° F
- pressure, 1 atm.
- gas composition, 50 - 75% HCl
- sample depths, 0.15 - 0.70 cm.
- sample weights, 0.17 - 0.95 gm.
- moisture content, 12%
COMPOSITION OF GAS MIXTURE

- X - 50 % HCl BY VOLUME 0.70 cm BED
- △ - 75 % HCl BY VOLUME 0.40 cm BED
- ○ - 50 % HCl BY VOLUME 0.15 cm BED
- △ - 75 % HCl BY VOLUME 0.15 cm BED

GRAMS ADSORBED PER GRAM OF SAMPLE

SORPTION TIME - MINUTES
Figure 5. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen

flow rates, 100 - 300 std. ml./min.
temperature, 80° F
pressure, 1 atm.
gas composition, 10 - 30% HCl
sample depths, 0.40 cm.
moisture content, 12%
COMPOSITION OF GAS MIXTURE

- 10% HCl by volume 300 cc feed/minute
- 30% HCl by volume 100 cc feed/minute
- 20% HCl by volume 200 cc feed/minute
- 20% HCl by volume 300 cc feed/minute
- 30% HCl by volume 200 cc feed/minute

GRAMS ADSORBED PER GRAM OF SAMPLE

Sorption time - minutes

Graph showing the adsorption of different gas mixtures over time.
Figure 6. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen

flow rates, 1210 - 1455 std. ml./min.
temperature, 80° F
pressure, 1 atm.
gas compositions, 2.5 - 20% HCl
sample depths, 0.40 cm.
moisture content, 12%
COMPOSITION OF GAS MIXTURE

- 2.5% HCl BY VOLUME 1210 cc FEED/MINUTE
- 5.6% HCl BY VOLUME 1250 cc FEED/MINUTE
- 9.2% HCl BY VOLUME 1300 cc FEED/MINUTE
- 14.2% HCl BY VOLUME 1375 cc FEED/MINUTE
- 20.0% HCl BY VOLUME 1455 cc FEED/MINUTE
Figure 7. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen

flow rate, 1,050 std. ml./min.
temperature, 80° F
pressure, 1 atm.
gas composition, 3% HCl
sample depths, 0.15 - 0.70 cm.
moisture content, 12%
GM. ADSORBED PER GM. OF SAMPLE

SORPTION TIME - MINUTES

BED DEPTH

\( \nabla \) 0.15 cm.

\( \circ \) 0.40 cm.

\( \triangle \) 0.70 cm.
It appears that the sorbed equilibrium concentration may be roughly equal to the equilibrium concentration of an aqueous solution.

3. The initial sorption rate increases with the concentration of hydrogen chloride in the gas phase and with gas velocity.

When the overall initial sorption rates were plotted against the hydrogen chloride concentration, it appeared that the overall initial rate might be a linear function of the concentration or a first order rate process, though there was considerable scatter in the data. The initial rate increased as the bed depth decreased and as the gas flow rate increased, indicating that the overall initial sorption rate is controlled partly by mass transport in the vapor phase and partly by diffusion in the bed.

In order to confirm a suspicion that adequate control over flour moisture content was not exercised in the measurements of hydrogen chloride sorption at room temperature, several experimental runs were made with flour which had been adjusted to the relatively high moisture content of 18.16 per cent. The experimental procedure and conditions used for the determinations were the same as before. The resulting changes in sample weights for the experiments are plotted as a function of time in Figure 8. In each case the samples actually lost weight during the first two or three minutes but then they gained weight for a period which varied with the bed depth or sample size.

Figure 9 shows the resulting curves of sample weight plotted against time for a study of hydrogen chloride sorption reversibility.
Figure 8. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen

flow rate, 1,050 std. ml./min.
temperature, 80° F
pressure, 1 atm.
gas composition, 3% HCl
sample depths, 0.15 - 0.70 cm.
moisture content, 18.16%
GM, HCl SORBED / GM. SAMPLE

SORPTION TIME, MIN

BED DEPTH
△ 0.15 CM.
○ 0.40 CM.
△ 0.70 CM.
Figure 9. Weight gained and lost by flour from a mixture of hydrogen chloride and nitrogen and pure nitrogen, respectively

- flow rate, 1,050 std. ml./min.
- temperature, 80° F
- pressure, 1 atm.
- gas composition, 3% HCl at first part of each run
- sample depths, 0.15 - 0.70 cm.
- moisture content, 12%
Sorption data showing the amount of gas adsorbed per gram of sample over time. The graph shows curves for different bed depths and sample weights:

- **0.15 cm.** 0.1721 gm.
- **0.40 cm.** 0.4420 gm.
- **0.70 cm.** 0.7330 gm.

A downward arrow indicates the introduction of pure nitrogen.
When the hydrogen chloride content of the gas stream was reduced to zero after a normal sorption period, the sample weight loss was very pronounced. The rate of weight loss was greatest at first and then gradually slowed down. The rate of weight loss also appeared to vary inversely with sample bed depth. The general characteristics of these curves indicated that hydrogen chloride was desorbed.

Several runs were made at low temperature to measure the sorption rate of hydrogen chloride by flour under conditions where the desorption of water vapor would be negligible. It was assumed that at the start of a run the flour sample must have been close to a temperature of 34° F which was the temperature of the enclosure. A dry, cooled gas mixture containing 3.0 per cent hydrogen chloride was passed over the sample at a flow of 1,050 std. ml./min. and the pressure in the balance enclosure was essentially atmospheric. Runs were made using bed depths of 0.15, 0.40 and 0.70 cm. The sample flour had a normal moisture content of 12 per cent. It should be noted that the bulk density of the cold flour was greater than the flour at room temperature so the microbalance pans contained from 25 to 35 per cent more flour by weight than where the pans were loaded at room temperature. The resulting curves of sample weight plotted against time are shown in Figure 10 for sorption rate of hydrogen chloride at low temperature. These curves are similar in appearance to those obtained at room temperature. However, the rates of weight gain were much greater and the total weight gains were larger than
Figure 10. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen.

- Flow rate: 1,050 std. ml./min.
- Temperature: 34° F
- Pressure: 1 atm.
- Gas composition: 3% HCl
- Sample depths: 0.15 - 0.70 cm.
- Moisture content: 12%
SORPTION TIME MINUTES

GM. ADSORBED PER GM. OF SAMPLE

BED DEPTH          SAMPLE WEIGHT
△ 0.15 cm.      0.2229 gm.
○ 0.40 cm.      0.6012 gm.
△ 0.70 cm.      0.9122 gm.
for comparable runs made at room temperature (see Figure 9 for comparison). These effects are in keeping with the anticipated effect of temperature on the partial pressure of hydrogen chloride in equilibrium with moisture laden flour.

Effect of moisture on HCl sorption A number of runs were made at a temperature of about $34^\circ F$ to determine the effect of flour moisture on the sorption of hydrogen chloride. The measurements were continued until the samples appeared to reach a constant weight. Ten levels of flour moisture ranging from 20.0 to 0.7 per cent were investigated as well as three different sample bed depths. The experimental technique and conditions were the same as before.

The weight gain curves for three of the moisture contents are presented in Figure 11, 12 and 13. These curves were similar to those obtained before and they provided both rate and apparent equilibrium data. These results showed that the samples gained weight rapidly at first but as the flour became saturated the rate of gain diminished and finally approached zero. If the gain in sample weight was truly representative of the amount sorbed, the slope of the curves representing the gain in weight as a function of time should correspond to the sorption rate. Assuming this to be the situation, the results for the three different sample depths indicated that increases in depth greatly reduce the rate of sorption. This in turn would seem to indicate that the rate of sorption was at least partially controlled by the rate of diffusion through the sample bed.
Figure 11. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen

- flow rate, 1,050 std. ml./min.
- temperature, 34° F
- pressure, 1 atm.
- gas composition, 3% HCl
- sample depths, 0.15 - 0.70 cm.
- moisture content, 20.02%
BED DEPTH

- ▼ 0.15 cm.
- ○ 0.40 cm.
- △ 0.70 cm.
Figure 12. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen

flow rate, 1,050 std. ml./min.
temperature, 34° F
pressure, 1 atm.
gas composition, 3% HCl
sample depths, 0.15 - 0.70 cm.
moisture content, 12.00%
Figure 13. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen

- flow rate, 1,050 std. ml./min.
- temperature, 34°F
- pressure, 1 atm.
- gas composition, 3% HCl
- sample depths, 0.15 - 0.70 cm.
- moisture content, 0.677%
BED DEPTH

Δ 0.15 cm.

○ 0.40 cm.

▽ 0.70 cm.

GM. SORBED / GM. SAMPLE

SORPTION TIME, MIN.
The results of this series of runs revealed that the flour moisture content affects both the rate of hydrogen chloride sorption and the amount of hydrogen chloride sorbed under equilibrium conditions. Estimates of sorption rates and equilibrium values were made by assuming that the weight gain curves did represent hydrogen chloride sorption curves. Figure 14 illustrates clearly the effects of flour moisture content and sample depth on the initial rate of sorption. The average rate of sorption which prevailed during the first 10 min. of sorption is plotted against the flour moisture content for three different sample depths. Another function of sorption rate, the time required for a sample to reach an apparent steady-state weight, was also plotted against moisture content. The results, not presented here, showed that at the lowest sample depth the total time required to reach a steady-weight is not affected very much by the moisture content.

The amount of hydrogen chloride sorbed per unit mass of dry flour under apparent equilibrium conditions at 34° F and a hydrogen chloride concentration of 3 per cent in the gas phase is plotted as a function of flour moisture content in Figure 15. This shows that the amount of hydrogen chloride sorbed increases with moisture content. It also shows a change in the sorption characteristics at a moisture content of about 0.08 gm. H₂O/gm. dry flour. Thus, below this moisture content the effect of moisture on hydrogen chloride sorption is relatively small, while above, it is relatively large. These effects are even more pronounced on a semilogarithmic plot.
Figure 14. Average hydrogen chloride sorption rate during the first 10 min. of sorption

flow rate, 1,050 std. ml./min.
temperature, 34°F
pressure, 1 atm.
gas composition, 3% HCl
sample depths, 0.15 - 0.70 cm.
Figure 15. Equilibrium sorption of hydrogen chloride

flow rate, 1,050 std. ml./min.
temperature, 34° F
pressure, 1 atm.
gas composition, 3% HCl
sample depths, 0.15 - 0.70 cm.
MOISTURE CONTENT, GM. H₂O / GM. DRY FLOUR

GM. HCl SORBED / GM. DRY FLOUR

BED DEPTH

▽ 0.15 cm.
○ 0.40 cm.
△ 0.70 cm.
The apparent equilibrium data is presented in another manner in Figure 17 where the mass ratio of hydrogen chloride sorbed to flour moisture is plotted against the flour moisture content. It is apparent that this ratio becomes nearly constant for moisture contents exceeding about 0.1 gm. $H_2O/gm.$ dry flour. Hence, it appears that the sorption mechanism is greatly affected by the moisture content. Below the critical moisture content the sorption appears to be largely controlled by the solid, while above the critical value it appears to depend almost entirely on the moisture present.

**Effect of partial pressure and moisture on HCl sorption**

Additional equilibrium and sorption rate data for the water-flour-hydrogen chloride system were sought under different combinations of moisture content and partial pressure at a temperature of about 34° F and a total pressure of 1 atm. Nine levels of flour moisture ranging from 19.2 to 0.9 per cent and six levels of hydrogen chloride partial pressure ranging from 15.8 to 3 mm. of mercury were investigated. The same procedure was used as before.

Some typical results obtained with a single sample depth of 0.40 cm. for different partial pressures of hydrogen chloride and recorded in Figures 18, 19, and 20 for three different moisture contents respectively. These indicate that both the rate of sorption
Figure 16. Semilogarithmic plot of the equilibrium sorption of hydrogen chloride

flow rate, 1,050 std. ml./min.
temperature, 34° F
pressure, 1 atm.
gas composition, 3% HCl
sample depths, 0.15 - 0.70 cm.
Figure 17. Mass ratio of HCl adsorbed to flour moisture content

flow rate, 1,050 std. ml./min.
temperature, 34° F
pressure, 1 atm.
gas composition, 3% HCl
sample depths, 0.15 - 0.70 cm.
BED DEPTH

- 0.15 cm.
- 0.40 cm.
- 0.70 cm.

MOISTURE CONTENT, GM. $H_2O$ / GM. DRY FLOUR
Figure 18. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen

- Flow rate, 1,050 std. ml./min.
- Temperature, 34° F
- Pressure, 1 atm.
- Gas compositions, 0.41 - 2.14% HCl
- Sample depth, 0.40 cm.
- Moisture content, 19.22%
Figure 19. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen gas compositions, 0.41 - 2.14% HCl.

- flow rate, 1,050 std. ml./min.
- temperature, 34° F
- pressure, 1 atm.
- sample depth, 0.40 cm.
- moisture content, 11.49%
SORPTION TIME, MIN.

GM. HCl ADSORBED / GM. SAMPLE

% HCl

○ 2.14
□ 1.64
△ 1.33
Θ 0.96
□ 0.61
△ 0.41
Figure 20. Weight gained by flour from a gaseous mixture of hydrogen chloride and nitrogen

flow rate, 1,050 std. ml./min.
temperature, 34° F
pressure, 1 atm.
gas compositions, 0.41 - 2.14% HCl
sample depth, 0.40 cm.
moisture content, 6.36%
and apparent equilibrium quantity sorbed increase markedly with increasing hydrogen chloride partial pressure. Curves similar to those shown were obtained at several other moisture levels, and are not presented here. In general, the rate of sorption and total quantity sorbed increased as the moisture content increased. Flour having 9 per cent moisture or less behaved somewhat differently in that there was a lag of several minutes before it started to sorb.

The summary shown in Table 2 provides a comparison of the effects of the various system parameters on the initial sorption rate. This show the interval of time required for samples to sorb 0.02 gm. HCl/gm. flour and the average rate of sorption during this interval for the indicated values of the parameters. The data given in the table confirm the effects previously attributed to partial pressure, sample depth, and moisture content and, in addition, show that the sorption rate was slower at room temperature than that at 34° F.

All of the apparent equilibrium data obtained for sorption of hydrogen chloride on flour at 34° F using a sample depth of 0.40 cm. are summarized in Figure 21. These data show that the amount sorbed depends on both the flour moisture content and hydrogen chloride partial pressure, the amount increasing as either parameter is increased. At low moisture contents the amount sorbed is very small and the sorption isotherms are nearly linear, while at higher moisture contents the overall isotherms are nonlinear. However, the portion of the isotherms corresponding to partial pressures
Table 2. Average rate of sorption while sorbing 0.02 gm. HCl/gm. of sample

<table>
<thead>
<tr>
<th>Sample Depth cm.</th>
<th>Temp. °F</th>
<th>HCl %</th>
<th>Moisture %</th>
<th>Time Min.</th>
<th>Rate ( \frac{gm. HCl}{(gm.) (Min.)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>Room</td>
<td>3</td>
<td>14</td>
<td>2</td>
<td>0.010</td>
</tr>
<tr>
<td>0.40</td>
<td>Room</td>
<td>3</td>
<td>14</td>
<td>7</td>
<td>0.003</td>
</tr>
<tr>
<td>0.70</td>
<td>Room</td>
<td>3</td>
<td>14</td>
<td>13</td>
<td>0.002</td>
</tr>
<tr>
<td>0.15</td>
<td>34</td>
<td>3</td>
<td>14</td>
<td>1</td>
<td>0.020</td>
</tr>
<tr>
<td>0.40</td>
<td>34</td>
<td>3</td>
<td>14</td>
<td>4</td>
<td>0.005</td>
</tr>
<tr>
<td>0.70</td>
<td>34</td>
<td>3</td>
<td>14</td>
<td>7</td>
<td>0.003</td>
</tr>
<tr>
<td>0.15</td>
<td>34</td>
<td>3</td>
<td>9</td>
<td>3</td>
<td>0.007</td>
</tr>
<tr>
<td>0.40</td>
<td>34</td>
<td>3</td>
<td>9</td>
<td>7</td>
<td>0.003</td>
</tr>
<tr>
<td>0.70</td>
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<td>10</td>
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<tr>
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<td>34</td>
<td>0.4</td>
<td>14</td>
<td>73</td>
<td>----</td>
</tr>
</tbody>
</table>

greater than 5 mm. of mercury are linear and of very moderate slope. The apparent equilibrium values are plotted against other pairs of coordinates in Figures 22 and 23. In the first of these diagrams the apparent equilibrium concentration of hydrogen chloride in the flour is plotted as a function of moisture content for different partial pressures. In the second diagram the ratio of hydrogen chloride to water in the flour is plotted against moisture content for various hydrogen chloride partial pressures. The sorption characteristics of flour containing less than 0.07 gm. \( H_2O/gm. \) dry flour appear to be different than those containing more (Figure 22). Thus, below this critical moisture content very little hydrogen
Figure 21. Apparent equilibrium sorption isotherm of hydrogen chloride by flour

flow rate, 1,050 std. ml./min.
temperature, 34° F
pressure, 1 atm.
sample depth, 0.40 cm.
moisture contents, 0.0071 - 0.2379 gm. H₂O/gm. dry flour
MOISTURE CONTENT, GM. H₂O / GM. DRY FLOUR

PARTIAL PRESSURE OF HCl, MM. OF MERCURY
Figure 22. Effect of moisture content on apparent equilibrium sorption of hydrogen chloride by flour

flow rate, 1,050 std. ml./min.
temperature, 34° F
pressure, 1 atm.
gas compositions, 0.41 - 3.02% HCl
sample depth, 0.40 cm.
MOISTURE CONTENT, GM. H₂O/GM. DRY FLOUR

% HCl

- 3.02
- 1.64
- 0.96
- 0.41
Figure 23. Mass ratio of hydrogen chloride sorbed to flour moisture content under apparent equilibrium conditions

- flow rate, 1,050 std. ml./min.
- temperature, 34°F
- pressure, 1 atm.
- gas compositions, 0.41 – 3.02% HCl
- sample depth, 0.40 cm.
chloride is sorbed and changes in the moisture content have little
effect on the amount sorbed while above this critical value the
amount sorbed increases greatly as the moisture content increases.
Changes in the ratio of sorbed hydrogen chloride to water are
illustrated by Figure 23. If the system is considered to consist
of the three components, flour, water, and hydrogen chloride, it
would seem that at low moisture contents the flour should exert a
greater influence than at higher moisture contents and vice versa.

At the end of the measurements, an attempt was made to
determine the amount of chloride in an aqueous slurry of the sample
by chemical analysis. None of the methods of analysis for chloride
appeared to give meaningful results.

**Temperature effects accompanying sorption of HCl**

For the purpose of determining the temperature rise accompanying
the sorption of hydrogen chloride by flour samples held by the
microbalance pans, several experiments were carried out at room
temperature as well as low temperature. It was hoped that these
would provide an indication of the suitability (or lack of it) of
an isothermal model.

**Room temperature** Two tests were carried out to determine
the apparent temperature rise of the flour samples under conditions
similar to those used for measuring sorptions rates at room
temperature. The flour samples with a normal moisture content
were contained in the usual cylindrical pans which were suspended in the tubular enclosure for the microbalance but the pans were supported by plastic covered copper wire instead of the quartz spring. An iron-constantan thermocouple made of 30 gauge wire was inserted in the center of each sample. The procedure used was similar to that used for determining sorption rates except that changes in sample temperature were measured instead of weight changes. A dry gas mixture containing 3.0 per cent hydrogen chloride was passed over a sample at a rate of 1,050 std. ml./min. Initially the flour samples and the gas mixture were at room temperature.

The results for both runs shown in Figure 24 were similar. The sample reached a maximum temperature rise of 2.7°C within the first 8 min. and then the temperature of the samples remained constant for the next 8 min., whereupon the observations were discontinued. The similarity in results was remarkable inasmuch as the grams of hydrogen chloride sorbed per gram of flour for the shallower sample should have been twice that for the deeper sample during the first 8 min.

Low temperature The test conditions and procedure were similar to those described above except for the temperature. For the present tests the flour containing 12.0 per cent moisture was stored in a refrigerator until it was placed in the balance pans. The cooling system was used for this low temperature
Figure 24. Temperature changes occurring in flour undergoing the room temperature sorption

flow rate, 1,050 std. ml./min.
temperature, 26° C
pressure, 1 atm.
gas composition, 3% HCl
sample depths, 0.40 - 0.70 cm.
moisture content, 12.0%
BED DEPTH

- 0.40 cm.
- 0.70 cm.

TEMPERATURE, °C

SORPTION TIME, MIN.
determination. When the flow of dry, cool gas was started, thermocouples imbedded in the flour samples indicated a temperature of $34^\circ F$.

The subsequent changes in bed temperature during sorption were recorded in Figure 25. For both 0.4 and 0.7 cm. sample depths the temperature dropped $2^\circ F$ during the first 1 to 2 min. and then rose very quickly to between 37 and $38^\circ F$, whereupon it dropped more gradually. Although both samples reached their peak temperature in about 10 min., the shallower sample cooled off more rapidly. It is noteworthy that the peak temperature was reached at a time when perhaps only 20 to 40 per cent of the hydrogen chloride should have been sorbed. This can be seen from the sorption curves in Figure 12. It is also worth noting that the bed temperatures leveled out at 32 and $33^\circ F$ respectively within 40 to 60 min. Consequently, any sorption runs continued for this length of time should be in temperature equilibrium by the end of the run.

**Sorption of HCl by wheat starch**

The sorption of hydrogen chlorides by pure wheat starch was investigated to see if the starch component of flour is the controlling component as far as sorption of hydrogen chloride is concerned. Since the bulk density of the wheat starch with about 12 per cent moisture was considerably greater than that of flour, the microbalance pans were loaded more heavily and it was not
Figure 25. Temperature changes occurring in flour undergoing the low temperature sorption
flow rate, 1,050 std. ml./min.
temperature, 34° F
pressure, 1 atm.
gas composition, 3% HCl
moisture content, 12.0%
possible to sorb the maximum amount of hydrogen chloride without exceeding the capacity of the microbalance. Whereas cold flour had a greater bulk density than warm flour, the opposite was apparently true in the case of starch, for the pans loaded with starch at room temperature weighed from 1 to 9 per cent more than ones loaded with cold starch. The resulting curves of sample weight plotted against time for runs made at room temperature are shown in Figure 26. These agree fairly well with the curves presented in Figure 7 for flour under similar conditions. The curves representing runs made with starch at 34° F are given in Figure 27. The agreement between these curves and those for flour under similar conditions (see Figure 10) is poor. Perhaps this lack of agreement was due to differences in moisture content of the starch and flour. There may not have been sufficient control over this important parameter.

Sorption of ammonia on flour

One set of experiments for the study of ammonia sorption by wheat flour was conducted at room temperature while passing a gas stream containing 6.3 per cent ammonia at a rate of 1,089 std. ml./min. over the sample. A second set was made at 34° F while passing a gas stream containing 3 per cent ammonia at a rate of 1,050 std. ml./min. over the sample. The results are presented in the form of weight gain curves in Figure 28 and 29, respectively. The weight gain curves are similar in appearance to those obtained with hydrogen chloride. They indicate that the rate of sorption
Figure 26. Weight gained by wheat starch from a gaseous mixture of hydrogen chloride and nitrogen

flow rate, 1,050 std. ml./min.
temperature, 80° F
pressure, 1 atm.
gas composition, 3% HCl
sample depths, 0.15 - 0.70 cm.
moisture content, 12%
Figure 27. Weight gained by wheat starch from a gaseous mixture of hydrogen chloride and nitrogen

- flow rate, 1,050 std. ml./min.
- temperature, 34° F
- pressure, 1 atm.
- gas composition, 3% HCl
- sample depths, 0.15 - 0.70 cm.
- moisture content, 12%
BED DEPTH

- 0.15 cm.
- 0.40 cm.
- 0.70 cm.

SAMPLE WEIGHT

- 0.3149 gm.
- 0.7457 gm.
- 1.2092 gm.

GM. ADSORBED PER GM. OF SAMPLE

SORPTION TIME - MINUTES
Figure 28. Weight gained by flour from a gaseous mixture of ammonia and nitrogen

flow rate, 1,050 std. ml./min.
temperatures, 34 and 80° F
pressure, 1 atm.
gas composition, 6.3% NH₃
sample depths, 0.15 - 0.40 cm.
moisture content, 12.0%
SORPTION TIME, MIN

GM. NH₃ SORBED / GM. SAMPLE

SORPTION TEMPERATURE

AT ROOM TEMP.

AT 34°F

BED DEPTH

△ 0.15 CM.
△ 0.40 CM.
△ 0.70 CM.

△ 0.15 CM.
△ 0.40 CM.
△ 0.70 CM.
Figure 29. Weight gained by flour from a gaseous mixture of ammonia and nitrogen

flow rate, 1,050 std. ml./min.
temperature, 80° F
pressure, 1 atm.
gas composition, 3% NH₃
sample depths, 0.15 - 0.70 cm.
moisture content, 12.0%
GM. NH$_3$ SORBED / GM. SAMPLE

SORPTION TIME, MIN.

BED DEPTH

• 0.15 CM.

○ 0.40 CM.

△ 0.70 CM.
increased greatly as the sample depth decreased. They also displayed considerable variation in the steady-state or apparent equilibrium quantity of ammonia sorbed for different sample depths. Under the same partial pressure and temperature the flour sorbed much less ammonia and the rate of sorption was smaller than for the case of hydrogen chloride. On the other hand, the rate of sorption and total quantity of ammonia sorbed increased markedly when either the partial pressure was increased or the temperature decreased, which again was similar to the behavior of hydrogen chloride.

Sequential sorption of HCl and NH₃

Several runs were made in which hydrogen chloride and ammonia were sorbed in sequence by flour. These runs were made with the following conditions in common:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial moisture content</td>
<td>0.1298 g H₂O/g dry flour</td>
</tr>
<tr>
<td>Temperature</td>
<td>34°F</td>
</tr>
<tr>
<td>Pressure</td>
<td>735 mm Hg</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>1,050 std. ml./min.</td>
</tr>
<tr>
<td>Sample depth</td>
<td>0.40 cm.</td>
</tr>
<tr>
<td>HCl concentration</td>
<td>0.96 vol. %</td>
</tr>
<tr>
<td>NH₃ concentration</td>
<td>3.66 vol. %</td>
</tr>
</tbody>
</table>

Dried nitrogen was used throughout this series of experiments. The results of a typical run are shown in Figure 30 where the weight gained by the sample is plotted against time. The overall curve has the general appearance of one which could result from superimposing separate sorption curves for hydrogen chloride and ammonia, respectively. Similar curves were obtained for other experiments where the period of time allowed for hydrogen chloride
Figure 30. Results of a typical run (10-5) for sorption of hydrogen chloride followed by sorption of ammonia by flour

flow rate, 1,050 std. ml./min.
temperature, 34° F
gas compositions, 0.96 vol. % HCl and 3.66 vol. % NH₃
sample depth, 0.40 cm.
moisture content, 12%
sorption differed. All of these curves are plotted in Figure 31 for comparison. One interesting aspect of the results is the mole ratio of the total ammonia sorbed to the total hydrogen chloride sorbed. The ratio is listed below for the various runs.

<table>
<thead>
<tr>
<th>Mole HCl Adsorbed</th>
<th>Mole NH₃ Adsorbed</th>
<th>Mole NH₃ Mole HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gm. Dry Flour</td>
<td>Gm. Dry Flour</td>
<td></td>
</tr>
<tr>
<td>0.0003516</td>
<td>0.000870</td>
<td>2.47</td>
</tr>
<tr>
<td>0.0006379</td>
<td>0.001621</td>
<td>2.54</td>
</tr>
<tr>
<td>0.0007601</td>
<td>0.001392</td>
<td>1.78</td>
</tr>
<tr>
<td>0.0009904</td>
<td>0.001650</td>
<td>1.67</td>
</tr>
<tr>
<td>0.0011460</td>
<td>0.001897</td>
<td>1.66</td>
</tr>
<tr>
<td>0.0018356</td>
<td>0.003033</td>
<td>1.65</td>
</tr>
</tbody>
</table>

The ratio reaches a constant value when the amount of hydrogen chloride sorbed exceeds a certain value. This is similar to the behavior observed where the ratio of hydrogen chloride to water sorbed also approaches a constant value.
Figure 31. Summary of results for sorption of hydrogen chloride followed by sorption of ammonia by flour

flow rate, 1,050 std. ml./min.
temperature, 34° F
pressure, 1 atm.
gas compositions, 0.96 vol. % HCl and 3.66 vol. % NH₃
sample depth, 0.40 cm.
moisture content, 12%
Several special and/or simple, empirical equations which have been used to represent sorption kinetic relationships in other systems were investigated first to determine whether they might be applicable to the sorption of hydrogen chloride by flour. Usually, such empirical expressions were developed by incorporating a series of physical and chemical processes into one overall rate representation. The reason for taking such an approach is that frequently the concentration of materials at intermediate positions is not known, but instead only the overall concentration difference across several steps in a process is known. Therefore, it is convenient to express the rate in terms of the overall concentration difference. In most cases, however, it is not possible to interpret the physical process from an empirical representation which is usually limited in applicability to a certain system.

An empirical equation represented by the following expression, as cited in Brunauer's text (12), was tested:

\[
\ln \left( \frac{W_A^*}{W_A} \right) = kt^m
\]

This model relates the amount of sorbate sorbed by unit weight of sorbent, \( W_A \), at time \( t \) with that sorbed in the equilibrium state, \( W_A^* \). In the case of the sorption of hydrogen chloride by flour the values of the two empirical constants, \( k \) and \( m \), seemed to vary from one run to another as the important system parameters were changed.
This indicated some inadequacy in the model to represent the overall process. Another model (12) which was tested is:

\[ \ln W_A = kt^m \]  

(2)

For some runs this appeared to fit the data well but for others it appeared inadequate.

According to De Boer (28) the process of physical adsorption is likely to be much faster than the process of diffusion through the capillary pores of a solid adsorbent. Consequently, whenever the overall process is controlled by the rate of capillary diffusion the rate equation will be of the form:

\[ \frac{dW_A}{dt} = k (W_A^* - W_A) \]  

(3)

If initially the sorbent is free of sorbate, this expression can be integrated to yield:

\[ \ln \frac{W_A^*}{W_A^* - W_A} = kt \]  

(4)

As time becomes very large, \( W_A \) should approach \( W_A^* \). Most of the sorption experiments were usually carried sufficiently long so that equilibrium should have been nearly attained. Theoretically, the equilibrium value of \( W_A \) is only reached after an infinitely long time. There have been observations that in some cases sorption equilibria are reached only after many hours or even days. However, in order to obtain a reasonably good fit of this equation to the data obtained in this experimental investigation, it was usually necessary to revise the apparent equilibrium value. Then it was
found that the specific sorption rate $k$ varied with the bed depth, flour moisture content, and hydrogen chloride concentration in the gas phase. In some other cases, the specific sorption rate is proportional to the diffusivity in the solid particle according to De Boer (28). Because of the temperature dependence of the diffusivity the parameter $k$ in Equation 4 may also depend on temperature. After proper adjustment of the apparent equilibrium value, it appeared that this model is inadequate to represent the phenomena taking place in the present system. In general, an increase in either the hydrogen chloride concentration or the moisture content or a decrease in the bed depth produced an increase in the specific rate.

Since the above empirical models did not fit the experimental data, a fresh approach based on a more rigorous analysis of the system was undertaken. As in most physical systems, if the model corresponds closely to what really takes place, the rate expression derived from the model will closely predict and describe the actual kinetics.

From the discussion of the experimental investigation, it was clear that diffusion through the bed of flour did have an effect on the sorption rate. During the measurements of sorption rate with high partial pressures of hydrogen chloride, a gradual change in the color of the flour from the top of the sample downward was observed. It indicated that more gas had been sorbed at the top than at the bottom. This picture of molecular transport closely resembles the dispersion of gas through a porous media without the effect of bulk flow.
Fundamental Rate Equations

A mathematical development was undertaken for the purpose of obtaining a fundamentally based mathematical representation of the sorption process taking place in a bed of flour. The procedure used involved obtaining an equation to represent the concentration of hydrogen chloride in the gas phase as a function of the bed depth and time. This equation was then used to calculate the total amount of hydrogen chloride sorbed by the flour as a function of time. This provided results which could be compared with the experimental data.

Following a conventional plan of attack, the mass, energy, and momentum balances were examined first. In this particular system, due to the absence of bulk flow through the interstices of the particles the pressure drop could be neglected and the momentum balance could be excluded from the analysis. Although the heat effects were not negligible in this system, the observed temperature variations (Figure 25) in samples of flour undergoing sorption in a stream containing 3 per cent hydrogen chloride appeared small. Consequently for a first approximation isothermal conditions were assumed and this eliminated the energy balance from consideration.

The mass balance for the hydrogen chloride in the gas phase of a differential element of the packed bed was represented by the expression:

$$-e \nabla \cdot J - (1 - e) \frac{\partial W_A}{\partial t} = e \frac{\partial C_A}{\partial t} \quad (5)$$
This expression reduced to the following because of axial symmetry and the assumption that only axial diffusion occurred:

$$\varepsilon \frac{\partial}{\partial z} \left( D_e \frac{\partial C_A}{\partial z} \right) - (1-\varepsilon) \frac{\partial W}{\partial t} = \varepsilon \frac{\partial C_A}{\partial t}$$

(6)

This equation was subject to the following conditions:

$$C_A = W_A = 0 \quad \text{at } t = 0 \text{ and } z \geq 0$$

$$C_A = C_0 \quad \text{at } t > 0 \text{ and } z = 0$$

(7)

$$\frac{\partial C_A}{\partial z} = 0 \quad \text{at } t > 0 \text{ and } z = L$$

The effective diffusivity was contained within the parentheses since it might depend on the concentration of hydrogen chloride.

For high polymer substances characterized by swelling while undergoing sorption, there is abundant evidence of a concentration dependency (24). Such a concentration dependence exists in most systems, but often, (for example in dilute solutions), the dependence is slight and the diffusion coefficient can be assumed constant for practical purposes. Of course, the diffusion coefficient may also depend on other factors which are often neglected.

It is worth noting that there are numerous practical examples of processes, such as gas separation, ion exchange, gas chromatography, heterogeneous reaction in fixed beds, gas diffusion through porous media and membranes, and dyeing, which lead to similar mathematical expression. Although no difficulty was encountered in locating earlier studies in these fields, Crank's work (23) was the one most closely related to the present investigation. Many
mathematical attempts have been made to describe quantitatively single-component diffusion through media in which some of the diffusing substance becomes immobilized, physically or chemically, as diffusion proceeds. Each mathematical development has been based upon a particular set of assumptions, which in turn determined the ability of the resulting equations to describe dynamic sorption realistically.

In order to obtain an equation relating only the composition of the gas phase, time and position it was necessary to find another expression relating the sorption rate to the composition of the gas phase. This could be done for either the case where sorption was instantaneous or for the case where it proceeded at a finite rate.

If the transfer of the sorbate from the gas phase to the solid took place at a finite rate, there were several possible functional representations of the rate. One of the simplest was for the case of first order irreversible sorption which is represented by the expression:

$$\frac{\partial W_A}{\partial t} = kC_A$$  \hspace{1cm} (8)

Solutions of the equation obtained by substituting the expression in Equation 6 have been published in standard monographs on diffusion and adsorption (7, 12, 23) in terms of a series of exponential terms or error functions. Danckwerts (27) has also presented a method of solving the equation, by a simple transformation of the solution obtained for the case where the sorption is neglected.
This model was tested for the sorption of hydrogen chloride by flour, but it appeared inadequate.

Another functional representation of the sorption rate is given by the following expression for the case of higher order, irreversible sorption:

\[
\frac{dW_A}{dt} = kC_A^n
\]  

(8a)

This might be observed where sorption is accompanied by chemical reaction. Kalaba (55) has developed a quasilinearization method for obtaining approximate solutions or (more easily) numerical solutions of the equation obtained by combining Equation 6 and 8a.

Reversible adsorption has been represented commonly by a linear driving force expression. This expression has taken one of the following forms, the form depending on whether the gas phase, solid phase or both provide rate controlling resistances (95):

\[
\frac{dW_A}{dt} = k_g (C_A - C_A^*)
\]  

(9)

\[
\frac{dW_A}{dt} = k_p (W_A^* - W_A)
\]  

(10)

and

\[
\frac{dW_A}{dt} = k_{pg} (C_A - W_A)
\]  

(11)

Equation 9 has been applied historically to mass transfer operations where the gas film was presumed to be the controlling resistance. On the other hand, Equation 10 has been used where the solid phase resistance was controlling and Equation 11 where both phases were controlling. In these rate equations, the problem of correlating
and predicting the mass transfer rate constants, that is $k_g$, $k_p$, and $k_{pg}$, is not an easy task, since the constants depend on conditions such as gas velocity in a flow system, sorbent particle size, type of sorbate, temperature, pressure, and some others. Numerous papers in the field of dynamic adsorption have analyzed cases where the mass balance contained a bulk flow term instead of a longitudinal diffusion term. Crank (23) has presented a mathematical analysis of Equation 6 combined with a rate equation of the type:

$$\frac{\partial W_A}{\partial t} = k_s C_A - k_d W_A \quad (12)$$

This described a transfer situation where the immobilized solute was formed at a rate proportional to the concentration of solute free to diffuse, and disappeared at a rate proportional to its own concentration. When the sorption process has a linear isotherm, the general rate expression (Equation 9) reduces to Equation 12 since $C^* = RW_A$. Since the isotherms for sorption of hydrogen chloride by flour were not linear and since the mass transfer coefficients could not be estimated readily, no attempt was made to utilize one of the linear driving force expressions for reversible sorption.

In some sorption processes where the resistance to diffusion is large compared to the resistance to sorption it is possible to assume that local equilibrium exists between the free and immobilized sorbate. In other words, diffusion is the rate-controlling step in such a process.
Houghton (52) rearranged Equation 12 into the form:

\[
\frac{1}{k_d} \frac{dW_A}{dt} = K_C A - W_A \quad (13)
\]

and called attention to the fact that where \( k_d \) is very large compared to the rate of adsorption the equation reduces to a linear sorption isotherm expressed as:

\[
W_A = K_C A \quad (14)
\]

Crank (23, 24) used a numerical approximation method to solve a problem involving adsorption controlled by the diffusion rate for the case of the Freundlich type adsorption isotherm shown below.

\[
W_A = K_C A^\alpha \quad (15)
\]

For the special case where \( \frac{\partial C_A}{\partial t} \) may be neglected compared with \( \frac{\partial W_A}{\partial t} \), Equation 6 reduces to:

\[
\frac{1 - e}{e} \frac{\partial W_A}{\partial t} = \frac{\partial}{\partial z} \left( D_e \frac{\partial C_A}{\partial z} \right) \quad (16)
\]

If the sorption is instantaneous, it is possible to substitute an expression for the sorption isotherm for \( C_A \). Equation 16 then becomes an expression for a simple diffusion process with variable diffusivity. The possibilities for solving such non-linear diffusion equations have been discussed in several papers (1, 2, 24, 78). An exact solution is obtainable only for the diffusion equation with semi-or doubly infinite boundary conditions by use of the classical Boltzman similarity transformation. Ames has presented a detailed
discussion of this subject (1, 2). The methods exploited by many others (24, 79) are approximate or numerical in nature.

Crank and Henry (24) developed a method for calculating the rates of adsorption and desorption for the preceding case with finite boundary conditions. In their work, an assumption was made that in the early stages of diffusion when the concentration of penetrant has not become appreciable inside the medium, the problem reduces to one of diffusion into a semi-infinite medium. In the later stages, an approximate numerical solution can be used for evaluation. In another study Crank and Park (25) developed a sophisticated method to obtain the diffusivity-concentration relation for the preceding problem from the overall sorption-time curves which were experimentally obtained.

An application of the weighted residual methods, which belong to one of the approximate methods for obtaining solutions of non-linear partial differential equations in the form of functions, has been published by Fujita (40) for the general case of a concentration-dependent diffusion coefficient problem. This method of moments was developed for a diffusion problem with finite boundary conditions.

For the analysis of the present system, the assumption was made that the instantaneous sorption model discussed above could be used to represent the simultaneous diffusion and sorption process under investigation. Thus Equation 6 with its associated boundary conditions were used to mathematically represent the present sorption
process. On substituting for $\frac{\partial W_A}{\partial t}$ from the non-linear equilibrium isotherm, which is developed in the next section, Equation 6 became a non-linear partial differential equation of the parabolic type. No analytical methods were located for solving this non-linear system with its finite boundary conditions, however, there exist several methods for numerically approximating the equations or for simulating the process by a Monte Carlo technique.

Sorption Isotherm Equations

As discussed earlier there are several expressions which can be used to fit experimental equilibrium isotherm data for either physical or chemical sorption. Some of the well-known ones are the Freundlich, Brunauer-Emmett-Teller and Langmuir equations. Of the three, the first one is rather empirical while the last two are theoretically based. An attempt was made to fit these equations to the data presented in Figure 20 for the sorption of hydrogen chloride by flour at 34° F.

The Freundlich equation (Equation 15 in the preceding section) which is relatively simple in form was the first one tested. This model appeared to fit the experimental data reasonably well except at the lowest hydrogen chloride partial pressure. Both the empirical constants varied with flour moisture content but in a different way, $K$ increasing and $n$ decreasing as the moisture content increased. For the minimum and maximum moisture contents tested, the constants had
the following values:

<table>
<thead>
<tr>
<th>Gm. H₂O</th>
<th>Gm. Dry Flour</th>
<th>K</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0071</td>
<td>0.0016</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>0.2379</td>
<td>0.0520</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

The Brunauer-Emmett-Teller equation shown below also fits the experimental data reasonably well.

\[
\frac{D_A^*}{W_A^* (P_o - P_A^*)} = \frac{1}{W_{Am} S} + \frac{S-1}{W_{Am} S P_o} \quad (17)
\]

The greatest deviation from this equation was exhibited by the data which correspond to the lowest moisture content and smallest hydrogen chloride partial pressure. For moisture contents equal to or greater than 0.095 gm. H₂O/gm. dry flour, the intercept of the preceding equation correlated well with moisture content as follows:

\[
\frac{1}{W_{Am} S} = -0.167 M + 0.049 \quad (18)
\]

For moisture contents equal to or greater than 0.068 the slope of the Brunauer-Emmett-Teller equation was correlated with moisture content by the following expression:

\[
\frac{S-1}{W_{Am} S} = 3.5 M^{-0.14} \quad (19)
\]

By combining the last two equations the following equation was obtained which correlates the constant S with the moisture content M.
\[ S = 1 - 0.585 M^{0.86} + 0.17 M^{-0.14} \quad (20) \]

A somewhat more complicated expression can also be obtained which relates \( W_{Am} \) to the moisture content.

The following equation which is basically a form of the Langmuir relation was also tested:

\[ W_A^* = \frac{A C_A^*}{1 + E C_A^*} \quad (21) \]

Here again the best fit was obtained with data taken with flour having the higher moisture contents.

The following relation which is a general extension of the preceding equation was also investigated:

\[ \frac{C_A^*}{W_A^*} = k_1 + k_2 C_A^* + k_3 (C_A^*)^2 + \quad (22) \]

The method of least squares was used to fit this equation to the apparent equilibrium data. A digital computer program (Appendix B) was prepared and used for this purpose.

The coefficients in Equation 31 were determined for a series of different order fits up to the fourth order respectively. The typical curves are given in Figures 32 and 33 for the first order, linear equations. The coefficients \( k_1 \) and \( k_2 \) for the first order case are plotted against flour moisture content in Figures 34 and 35. It is apparent that both of these coefficients were greatly affected by the flour moisture content, the greatest changes taking place at lower moisture levels. Above a moisture content of about 0.1 \( \text{gm.} \ H_2O/\text{gm. dry flour} \) the coefficients were nearly independent.
Figure 32. Langmuir isotherm for flour with larger moisture content at 34°F.
Figure 33. Langmuir isotherm for flour with smaller moisture content at $34^\circ$ F
MOISTURE CONTENT

GM. $\text{H}_2\text{O} / \text{GM. DRY FLOUR}$

- $\bigcirc$ 0.0679
- $\bigcirc$ 0.0334
- $\triangle$ 0.0071

$\frac{C_A^*}{W_A' \times 10^4}$, (gm. HCl/cm$^3$) (gm. HCl/cbm$^3$ flour)

$C_A^* \times 10^5$, gm. HCl/cm$^3$
Figure 34. Effect of moisture content on the isotherm coefficient $k_1$. 
VALUE OF COEFFICIENT, $K_1 \times 10^4$

MOISTURE CONTENT, GM. H₂O/GM. DRY SAMPLE

0.1

0.2

0

∞

12

2

4

∞
Figure 35. Effect of moisture content on isotherm coefficient $k_2$, $\text{cm}^3/\text{gm}$. 
Moisture content, g/m. H₂O/gm. dry flour

Value of coefficient, k₂

0.2

0.1
of the moisture content. A visual comparison of the fit obtained with higher orders did not seem to justify the use of an expression of order higher than one.

Numerical Analysis and Computer Programming

This section is devoted to presenting the procedure used to convert the differential equation into a finite difference form and the subsequent programming for computer solution. Equation 22 truncated to the first order as shown below was differentiated and combined with Equation 6.

\[
W_A = \frac{C_A}{k_1 + k_2 C_A}
\]

The resulting differential equation appeared as follows when the effective diffusivity was assumed to be constant:

\[
\varepsilon D_e \frac{\partial^2 C_A}{\partial z^2} = \varepsilon \frac{\partial C_A}{\partial t} + (1 - \varepsilon) \frac{k_1}{(k_1 + k_2 C_A)^2} \frac{\partial C_A}{\partial t}
\]

or

\[
\frac{\partial C_A}{\partial z} = \frac{1}{D_e} \left\{ 1 + \frac{(1 - \varepsilon) k_1}{(k_1 + k_2 C_A)^2} \right\} \frac{\partial C_A}{\partial t}
\]

The following dimensionless variables and parameters were introduced:

\[
\frac{C_A}{C_0}, \quad \frac{z}{L} = \gamma, \quad \frac{D_e t}{L^2} = \tau, \quad k_2 = k_2 C_0
\]

In terms of the dimensionless quantities the differential equation
became:
\[
\frac{\partial^2 C}{\partial \eta^2} = \left\{ 1 + \frac{(1-e)}{e} \frac{k_1}{(k_1 + k_2 \epsilon)^2} \right\} \frac{\partial C}{\partial \tau} \tag{27}
\]

with the initial and boundary conditions
\[
\begin{align*}
C &= 0 \quad \text{at } \tau = 0 \text{ and } \eta \geq 0 \\
C &= 1 \quad \text{at } \tau > 0 \text{ and } \eta = 0 \\
\frac{\partial C}{\partial \eta} &= 0 \quad \text{at } \tau > 0 \text{ and } \eta = 1
\end{align*} \tag{28}
\]

There are a number of numerical methods for solving partial differential equations of the parabolic type. Of the various methods only that of finite differences stands out as being universally applicable to both linear and non-linear systems. An excellent survey of numerical methods for parabolic differential equations has been prepared by Douglas (30). By using a predictor-corrector modification of the Crank-Nicolson difference equation, Douglas and Jones (31) obtained a solution of the following boundary value problem:
\[
\frac{\partial^2 U}{\partial \eta^2} = F(\eta, \tau, U, \frac{\partial U}{\partial \eta}, \frac{\partial U}{\partial \tau}) \tag{29}
\]
\[
u(\eta, 0), \ u(0, \tau), \ u(1, \tau) \text{ specified at}
\]
\[
0 < \eta < 1 \\
0 < \tau \leq T_s
\]

Many applications of predictor-corrector methods for the numerical solution of ordinary differential equations have been published (36, 71).
For a function of the form
\[ F = g_1(\gamma, \tau, U, \frac{\partial U}{\partial \gamma}) \frac{\partial U}{\partial \tau} + g_2(\gamma, \tau, U, \frac{\partial U}{\partial \gamma}) \]  
(30)
the predictor
\[ \frac{\Delta^2 U_{i,j+1/2}}{\Delta \tau^2} = F \left( \eta_i, \tau_{j+1/2}, U_{i,j}, \frac{\Delta U_{i,j}}{\Delta \eta}, \frac{2(U_{i,j+1/2} - U_{i,j})}{\Delta \tau} \right) \]  
(31)
for \( i = 1, 2, \ldots, N + 2 \)
followed by the corrector
\[ \frac{\Delta^2(U_{i,j+1} + U_{i,j})}{2\Delta \eta^2} = F \left( \eta_i, \tau_{j+1/2}, U_{i,j+1/2}, \frac{\Delta U_{i,j+1/2}}{\Delta \eta}, \frac{(U_{i,j+1} - U_{i,j})}{\Delta \tau} \right) \]  
(32)
leads to a set of linear algebraic equations which can be used for the prediction of the independent variable. Instead of Equation 31, a modified Crank-Nicolson predictor
\[ \frac{\Delta^2(U_{i,j+1/2} + U_{i,j})}{\Delta \eta^2} = F \left( \eta_i, \tau_{j+1/2}, U_{i,j}, \frac{\Delta U_{i,j}}{\Delta \eta}, \frac{2(U_{i,j+1/2} - U_{i,j})}{\Delta \tau} \right) \]  
(33)
may be used to obtain equivalent results. The following notation applies to the preceding relations:
\[
\frac{\Delta^2 U_{i,j}}{\Delta \tau^2} = (\Delta \tau)^{-2} (U_{i+1,j} - 2U_{i,j} + U_{i-1,j})
\]

\[
\frac{\Delta U_{i,j}}{\Delta \tau} = \left(2 \Delta \tau \right)^{-1} (U_{i+1,j} - U_{i-1,j})
\]

where \(N\) and \(M\) are positive integers.

Douglas and Jones have proved that the predictor-corrector method defined previously converges uniformly to the solution of Equation 29 with an error of the order \(O \left( \left( \Delta \tau \right)^2 + \left( \Delta \tau \right)^{3/2} \right)\).

The modified Crank-Nicolson predictor (Equation 33) and the corrector (Equation 32) were used in the numerical integration of Equation 27 for the given boundary conditions. Details are presented in Appendix A.

A problem arose because of the singularity or discontinuity in the hydrogen chloride concentration function at the surface of the bed. At the beginning of a run it was assumed that the concentration jumped instantaneously from \(C_0 = 0\) to \(C_0 = 1\). In this analysis two different methods were applied to obtain a solution near the point of discontinuity. One approach was to assign a value of \(C_0 = 0.5\) at the beginning and after the first increment \(C_0 = 1\) for all subsequent increments. Another approach was to use an exact solution of the simple diffusion equation obtained by neglecting the sorption rate term in Equation 27. As a result, the equation to be solved was simply:
When this was solved with the appropriate boundary conditions the solution obtained was:

\[
\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \eta^2} \tag{35}
\]

The procedure of approximating the full equation (Equation 27) by the predictor-corrector method started after the hydrogen chloride concentration profile was predicted by Equation 36 at \( \tau = 0.00001 \).

The details of solving Equation 35 are not presented here, since several publications (17, 23) present methods of solution. In evaluating Equation 36 the complimentary error functions were evaluated by the following series which applies for small values of \( x \):

\[
\text{erfc } x = 1 - \text{erf} x = 1 - \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{(2n+1)!} \tag{37}
\]

An approach, which was not tried, involves the adoption of new independent variables. The classical similarity transformations are often useful or suggestive of other transformations. In the present analysis, there were no significant differences in the results obtained by the first two methods. Therefore, the simplest approach of selecting a fixed value for the initial point was adopted for all computations.

After the hydrogen chloride concentration profile in the gas phase was found at any time, the total amount of material sorbed by
the wheat flour was obtained by using the following relation:

\[ H = \frac{C_0 A (1 - e) L}{M_f} \int_0^t \frac{C \gamma}{k_1 + K_2 C} \, d \gamma \]  

The procedure used for numerically integrating this equation is given in Appendix A.

The numerical procedure developed in Appendix A for the predictor-corrector method followed by the integration process to obtain the total amount sorbed was written in Fortran language. The grid points for a given sorption time were calculated first and then an iteration scheme was used to march the calculation toward the end of the sorption time. These calculations were performed on the IBM 360/50 digital computer. The complete computer program is shown in Appendix C.

Since the implicit finite difference method used in this work is stable for any positive value of the ratio \( \frac{\Delta z}{(\Delta \gamma)^2} \), there were no stability problems. However, the respective increment sizes do affect the computation time and accuracy of the results. Consequently, some compromise must be made between the computation time and the accuracy. In this work, the following increment sizes were used:

<table>
<thead>
<tr>
<th>( \Delta z )</th>
<th>( \Delta t )</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.025</td>
<td>used up to ( t = 2 ) min.</td>
</tr>
<tr>
<td>0.02</td>
<td>0.025</td>
<td>used after ( t = 2 ) min.</td>
</tr>
</tbody>
</table>
Comparison of Results

In simulating the sorption process taking place in a shallow fixed-bed, several simplifying assumptions were made, partly because complete information about the complicated system was lacking. A comparison of experimental data with predicted values was the main concern of this analysis. In addition, the effect of various system parameters and conditions were studied and are presented in that section.

Quantitative information on the equilibrium isotherms and other physical constants such as the effective diffusivity and void fraction were needed as computer input data. These were provided by the experimental results and by estimation. The least squares fit of the isotherm data was discussed earlier for the simplest form, that is, the Langmuir equation.

An approximate method was used to evaluate the void fraction or ratio of flour volume to bed volume. Obviously, the flour volume can be calculated, if the value of the true density is available. However, no attempts were made in the present study to experimentally determine the true densities of the flour samples with different moisture levels. As mentioned in the literature review, the use of a swelling factor for estimating the true density of swollen flour granules was suggested by Gracza and Greenberg (41). Irani and Fong (54) reported an average value of 1.44 for the specific gravity of flour in their determination. In
his work, the well-known partial volume rule was used for estimating the total volume of moisture laden flour. Thus it was assumed that the volume of the flour is the sum of the volume of dry flour and volume of associated condensed water. This assumption would be valid if the addition of water to flour behaved as an ideal solution.

The density of the flour particles was calculated for different moisture contents by using the following formula:

\[ \rho_f = \frac{\rho_{H_2O} \rho_f (1+M) \rho \, df}{\rho_{H_2O} + M \rho \, df} = \frac{1.44(1+M)}{1 + 1.44M} \quad (38) \]

The values obtained for particles of different moisture content are shown below:

<table>
<thead>
<tr>
<th>M</th>
<th>( \rho_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2379</td>
<td>1.32</td>
</tr>
<tr>
<td>0.2118</td>
<td>1.33</td>
</tr>
<tr>
<td>0.1980</td>
<td>1.34</td>
</tr>
<tr>
<td>0.1653</td>
<td>1.35</td>
</tr>
<tr>
<td>0.1298</td>
<td>1.37</td>
</tr>
<tr>
<td>0.0953</td>
<td>1.39</td>
</tr>
<tr>
<td>0.0679</td>
<td>1.40</td>
</tr>
<tr>
<td>0.0334</td>
<td>1.42</td>
</tr>
<tr>
<td>0.0071</td>
<td>1.43</td>
</tr>
</tbody>
</table>

In order to estimate the porosity of the individual sample the following expression was used:

\[ \varepsilon = 1 - \frac{M_f}{\rho_f V_f} \quad (39) \]
where $M_f$ was the sample weight and $V_f$ was the pan volume. The void fraction determined in this manner for the various runs are listed in Appendix D.

Since diffusion through the tortuous passages of a packed bed is not the same as diffusion through a stagnant volume of gas, an effective diffusivity $D_e$ was used in place of the normal diffusivity. No experimental measurements of diffusivity were carried out in this study, although conventionally it must be measured experimentally. In general, the effective diffusivity depends on pressure, temperature, concentration, and pore structure of the bed. Since the actual mechanism for diffusion through interstices between particles and in porous media is complex, it is very difficult to predict values of effective diffusivity. For transient flow of gas through unconsolidated beds, the permeability coefficient $K_p$ is related to the diffusivity by

$$K_p = \varepsilon D$$

The above relationship is obtained by comparing Fick's second law of diffusion with a general differential equation for transient flow which results from substituting Darcy's law into the equation of continuity (16). For non-uniform pore structures, a tortuosity factor $q$ should be included in Equation 48 which results in the relation:

$$K_p = \frac{\varepsilon D}{q}$$  \hspace{1cm} (41)
The reduced rate of diffusion through a porous body is due in part to the reduced cross-sectional area available for gas movement and in part to the increased path length imposed by the tortuous nature of the channels. Thus, the relation between diffusion and porosity may be expressed in the form (76):

\[ D_e = D \cdot f(\varepsilon) \]  \hspace{1cm} (42)

Where, for certain systems, \( f(\varepsilon) = \varepsilon^2 \) or \( \varepsilon/\sqrt{2} \). It has also been suggested that the effective diffusivity for some system may be given by (17):

\[ D_e = D \cdot \varepsilon \]  \hspace{1cm} (43)

which is a form similar to Equation 40 while \( D_e \) is taken as \( K_p \).

This relationship was used in the present study as basis for a first approximation.

The Chapman-Enskog formula was used for estimating the normal diffusivity of the gaseous hydrogen chloride-nitrogen pair. A value of 7.968 cm.\(^2\)/min. was obtained for the experimental conditions.

The calculated results of the preliminary computer runs deviated somewhat from the experimental runs. It was anticipated that the inaccuracy of the physical constants might turn out to be the major source of error. Consequently several different values of void fraction and diffusivity were used to determine the effects produced by changes in these parameters. Of course, the sorption isotherms were subject to error and this is discussed later. In addition some errors were introduced by the numerical approximation.

As argued in the last section, the computational errors may
cause the approximate numerical solution to be incorrect. Usually the truncation error is relatively less serious than other types of computational errors resulting from the use of implicit finite difference formula. Another type of error in the course of a numerical computation is the one produced by rounding-off of numbers. This round-off error is inevitable although some procedures can be used to minimize it. In order to yield accurate results, rather fine increments were required. Within the allowance of computer time, several sizes of increments were tested, then a reasonable value was selected for the computations which followed.

The single Runge-Kutta integral process produces some errors if the increments are not fine enough. There are some ways available for compensating for these errors, such as an automatic monitoring scheme to maintain the magnitude of the errors within preassigned bounds as the computation marches from point to point. However, the error compensating methods did not appear very applicable for the present case because they require a lot of computer time.

Effect of diffusivity

The effect of the diffusivity on the predicted values was investigated by varying the effective diffusivity while holding the other conditions constant. Some representative results are shown in Figures 36 to 41 for different hydrogen chloride concentrations and flour moisture levels. Experimental values are also shown for
Figure 36. Comparison of calculated and experimental sorption curves under various effective diffusivities. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
GM. HCl SORBED / GM. SAMPLE

SORPTION TIME, MIN.

MOIST. CONTENT
0.2379 gm.H_2O/gm. dry flour

HCl CONC.
- O 0.0000348 gm/cm^3
- △ 0.0000217 gm/cm^3

POROSITY, ε
- O 0.558
- △ 0.527

De
- - De
- - De +0.5
- - De +1.0
- - De +2.0
- - De +3.0
Figure 37. Comparison of calculated and experimental sorption curves under various effective diffusivities. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
Figure 38. Comparison of calculated and experimental sorption curves under various effective diffusivities. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
De
- De = 2.0
- De = 2.5
- De = 3.0

Porosity, ε
0.554

Moisture content
0.0953 g m H₂O/g m dry flour

HCl concentration
0.0000384 gm/cm³
Figure 39. Comparison of calculated and experimental sorption curves under various effective diffusivities. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
POROSITY, \( \varepsilon \) = 0.576

MOISTURE CONTENT:

\[
0.0953 \text{ gm. } H_2O / \text{gm. dry flour}
\]

HCl CONC.:

\[
0.0000217 \text{ gm. } / \text{cm}^3
\]
Figure 40. Comparison of calculated and experimental sorption curves under various effective diffusivities. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
POROSITY, $\varepsilon$

0.526

MOISTURE CONTENT

0.0679 gm. H$_2$O/gm. dry flour

HCl CONC.

0.0000348 gm./cm$^3$

SORPTION TIME, MIN.
Figure 41. Comparison of calculated and experimental sorption curves under various effective diffusivities. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
GM HCl SORBED / GM. SAMPLE

MOISTURE CONTENT
0.0334 gm. H₂O / gm. dry flour

HCl CONC.
0.0000348 gm./cm³

POROSITY, ε
0.536

Sorption Time, Min.
comparison. The results for the higher moisture levels are shown in Figures 36 and 37. As was to be expected, increasing the diffusivity increased the sorption rate. A closer correspondence between the predicted and experimental values was obtained in the beginning when the diffusivity was small while near the end of the sorption period a better fit was obtained when the diffusivity was large. The results for the intermediate moisture levels are shown in Figures 38 and 39. A close correspondence was obtained between the observed and predicted values when a relatively small diffusivity was used. The results for the lower moisture levels are presented in Figures 40 and 41. The agreement between the measured and predicted values was poorest for this case. However, it appeared that the value of the diffusivity should be about the same for the lower and intermediate moisture levels. On the other hand, the diffusivity appeared to increase with moisture content at higher levels. It is suspected that the greater discrepancy between the observed and calculated values in the case of samples with smaller moisture contents and/or lower hydrogen chloride concentrations may have resulted from an inaccurate representation of the sorption isotherms, especially at the lower sorbate concentrations. Further discussion of this will be presented later.

From these studies it is apparent that the resistance to diffusion is greater for flour with the lower moisture contents. This seems to imply that flour with the higher moisture contents may have a larger pore size, because of swelling effects, which makes
diffusion through and into the sorbent easier.

Although it was assumed in the above analysis that the effective diffusivity is constant throughout the sorption process, it is possible that it actually varies. In order to investigate this possibility the effective diffusivity was taken to be a function of the hydrogen chloride concentration in the gas phase. Two different functional relationships were assumed. In the first case it was assumed to be a linearly increasing function of the concentration while in the second an exponential function. The linear function did not give reasonable results. However, the exponential function did appear to give reasonable results as illustrated by Figure 42. The question of variable diffusivity was not pursued farther because it would have required a lot of computer time.

**Effect of void fraction**

In the work discussed up to this point, values of the porosity $\epsilon$ were based on a specific gravity of 1.44 for dry flour particles. In order to investigate the effect of varying the porosity, two additional values for the specific gravity of dry flour were assumed. Values of 1.6 and 1.3 respectively were chosen to represent possible extremes. Again the porosity of moisture laden flour was calculated on the basis of the partial volume rule. Some typical results obtained by varying the porosity are presented in Figures 43 to 46.
Figure 42. Comparison of calculated and experimental sorption curves under an assumption of variable diffusion coefficients. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
POROSITY, $\varepsilon$

$\varepsilon = 0.578$

MOISTURE CONTENT

$0.2118 \text{ gm. } H_2O / \text{ gm. dry flour}$

HCl CONC.

$0.0000267 \text{ gm. } / \text{ cm}^3$

Sorption Time, Min.
Figure 43. Comparison of calculated and experimental sorption curves under various void fractions. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
Figure 44. Comparison of calculated and experimental sorption curves under various void fractions. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
POROSITY, $\varepsilon$

- 0.537
- 0.573
- 0.498

$D_e = D\varepsilon$

MOIST. CONTENT
0.1980 gm H$_2$O/gm dry flour

HCl CONC.
0.00000267 gm/cm$^3$

GM, HCl SORBED / GM. SAMPLE

SORPTION TIME, MIN.
Figure 45. Comparison of calculated and experimental sorption curves under various void fractions. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
POROSITY, $\epsilon$

- $0.566$ $0.584$
- $0.487$ $0.508$

$D_e = D \epsilon$

MOIST. CONTENT

- $0.1653$ gm H$_2$O/gm dry flour

HCl CONC.

- $0.0000267$ gm/cm$^3$
- $0.0000067$ gm/cm$^3$

GM. HCl SORBED / GM. SAMPLE

SORPTION TIME, MIN.
Figure 46. Comparison of calculated and experimental sorption curves under various void fractions. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
POROSITY, $\varepsilon$

- 0.585
- 0.506 0.504
- 0.547 0.542

$D_e = D\varepsilon$

MOIST. CONTENT

- 0.1298 gm.H$_2$O/gm. dry flour

HCl CONC.

- 0.0000267 gm/cc
- 0.0000067 gm/cc

SORPTION TIME, MIN.
In general, increasing the porosity increased the sorption rate. Of course, this was to be expected because increasing the void fraction should increase the space available for diffusion and consequently reduce the resistance to diffusion. Moreover, the effective diffusivity was taken to be the product of the normal diffusivity and the porosity. From the given results it was difficult to distinguish between the effects produced by increasing either the effective diffusivity or porosity. For example, the calculated curves were closer to the experimental curves for large moisture contents when larger values of porosity were used while just the opposite was true for small moisture contents. In addition, changes in porosity produced changes in the curves similar to the changes produced by varying the effective diffusivity.

**Effects of non-linear isotherms**

Some attention was given to the possibility that the Langmuir equation does not adequately represent the sorption isotherms for the sorption of hydrogen chloride by flour and the consequent error introduced in the predicted curves. A fourth order polynomial expression (Equation 22) was applied for a couple of computer runs. The results obtained by using this alternative isotherm did not change the calculated values significantly.

Since experimental equilibrium data were not obtained for small hydrogen chloride partial pressures, the exact shape of the sorption isotherms was not known for the low pressure range. Instead of the
straight lines assumed in the construction of Figure 21 a better representation of the isotherms might have been an elongated "S" form as suggested by De Boer (28). Thus, the use of the Langmuir equation to extrapolate into the low pressure range may have introduced some error.

Effects of boundary conditions

It was suspected that the assumption of a constant concentration at the surface of the bed may not have been an accurate picture of the actual process. Crank (24) described a physical process of diffusion and sorption with variable surface concentration.

The change in surface concentration was represented by the relation:

$$C_A = C_0 (1 - e^{-\beta t})$$

at $t > 0$ and $z = 0$

(44)

For finite values of $\beta$ the resulting sorption-time curves, which showed the total amount sorbed as a function of time, were sigmoid shaped. On the other hand, when $\beta$ was chosen to be infinitely large the sorption-time curve was linear in the beginning.

Due to the similarity between the experimental results of the present study and the sorption-time curves obtained by Crank it was thought that the present process might be represented more accurately by using the same relation (Equation 44) to represent the concentration of hydrogen chloride in the gas phase at the bed surface. Three values of the arbitrary constant $\beta$ were tested in order to see if the
computed sorption-time curves could be brought closer to the measured curves. The results are presented in Figures 47 to 50. It can be seen that a good fit was obtained in most cases when was chosen equal to 0.10. In order to determine the effects of apparent diffusivity on the computed values while and are held constant, a couple of computer runs were made for the flour sample with rather low moisture contents. Figures 51 and 52 shows that a better agreement was obtainable as a lower value of and a higher diffusivity were used in the analysis.

From these studies it appears that the sorption-time curves can be closely approximated by using the exponential relation to represent the surface concentration and an effective diffusivity which increases with the flour moisture content.
Figure 47. Comparison of calculated and experimental sorption curves under an assumption of variable surface concentrations. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
\[ D_e = D_0 - 3.0 \]

Porosity, \( \varepsilon \) = 0.554

Moisture content: 0.0953 g m. H\( _2 \)O / g m. dry flour

HCl conc.: 0.0000348 g m./cm\(^3\)

Sorption time, min.
Figure 48. Comparison of calculated and experimental sorption curves under an assumption of variable surface concentrations. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
GM. HCl SORBED / GM. SAMPLE

SORPTION TIME, MIN.

$\beta$

- 1.50
- 0.30
- 0.10

$D_e = DG - 3.0$

POROSITY, $e$

0.526

MOISTURE CONTENT

0.0679 gm. H$_2$O / gm. dry flour

HCl CONC.

0.0000348 gm./cm$^3$

185
Figure 49. Comparison of calculated and experimental sorption curves under an assumption of variable surface concentrations. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
GM. HCl SORBED / GM. SAMPLE

0.010
0.008
0.006
0.004
0.002
0.000
0

SORPTION TIME, MIN.

0 10 20 30 40 50

β

1.50

0.30

0.10

De = De - 3.0

POROSITY, e

0.554

MOISTURE CONTENT

0.0334 gm. H₂O / gm. dry flour

HCl CONC.

0.00000217 gm./cm³
Figure 50. Comparison of calculated and experimental sorption curves under an assumption of variable surface concentrations. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
GM. HCl SORBED / GM. SAMPLE

- B = 1.50
- B = 0.30
- B = 0.10

DM = DE - 3.0

POROSITY, ε

0.526

MOISTURE CONTENT

0.0071 gm. H₂O / gm. dry flour

HCl CONC.

0.0000348 gm./cm³

SORPTION TIME, MIN.
Figure 51. Comparison of calculated and experimental sorption curves under an assumption of variable surface concentration and various effective diffusivity. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
POROSITY, $\varepsilon$ = 0.554

MOISTURE CONTENT
0.0953 gm. $H_2O$ / gm. dry flour

HCl CONC.
0.0000348 gm. / cm$^3$

GM. HCl SORBED / GM. SAMPLE

SORPTION TIME, MIN.
Figure 52. Comparison of calculated and experimental sorption curves under an assumption of variable surface concentration and various effective diffusivities. The measured values are shown as geometrical symbols, the calculated curves are shown as lines.
POROSITY, $\varepsilon$  
0.526

MOISTURE CONTENT  
0.0071 gm. $H_2O$ / gm. dry flour

HCl CONC.  
0.0000348 gm./cm$^3$

GM. HCl SORBED / GM. SAMPLE

SORPTION TIME, MIN.
SUMMARY AND CONCLUSIONS

An experimental investigation was carried out to measure the overall sorption rate of hydrogen chloride by soft white winter wheat flour using a quartz spring microbalance. The determination was made by continuously weighing a sample of flour contained in a small, flat-bottomed, cylindrical pan suspended from a quartz helix in a controlled environment. The principal parameters varied were sample depth, temperature, hydrogen chloride partial pressure, and flour moisture content. The apparent sorption rate of ammonia by soft white wheat flour and acid-modified flour, respectively, was also measured in a similar manner for a limited set of conditions. Due to the experimental difficulty of controlling the moisture present in flour, most of the sorption measurements were undertaken at 34° F, although some of the measurements were conducted at room temperature. Apparent equilibrium data for the hydrogen chloride-flour-water system was also obtained for 34° F. Conclusions derived from the experimental results were:

1. All of the parameters had an important affect on the sorption rate.

2. The apparent sorption rate increases as the flour moisture content and hydrogen chloride partial pressure increase and as the temperature and sample depth decrease.

3. With a sample depth of 0.15 cm., temperature of 34° F, and a flour moisture content of 14 per cent, the rate of sorption from a gas stream containing 5 per cent hydrogen chloride was quite rapid and it required only 1 min. to attain the concentration of 0.02 gm. HCl/gm. of sample.
4. The sample temperature was observed to rise several degrees during the first 10 min. of hydrogen chloride sorption and then gradually subside.

5. There was no way of entirely preventing the simultaneous sorption or desorption of water vapor as either hydrogen chloride or ammonia were being sorbed. The amount lost appeared to be small at 34° F.

6. The rate of ammonia sorption appeared to be slower than that of hydrogen chloride sorption and this was probably due to a smaller driving force because the total quantity of ammonia sorbed under equilibrium conditions was much smaller than the quantity of hydrogen chloride.

7. When hydrogen chloride and ammonia were sorbed sequentially by the same sample, the sorption rates for both gases appeared to be of the same order of magnitude. As a result, when ammonia is used to neutralize flour which has been treated previously with hydrogen chloride, very high rates of ammonia sorption can be anticipated.

The sorption of hydrogen chloride by soft white wheat flour in a shallow fixed-bed at low temperature was simulated with a mathematical model. The conditions and assumptions used in the formulation of the problem are stated below.

1. The non-linear equilibrium isotherms obtained experimentally were used in the form of the Langmuir equation.

2. The system was assumed to be isothermal.

3. The sorbed component was assumed to be in equilibrium.

4. Diffusion of hydrogen chloride through the bed was assumed to be the rate controlling step in the process.

5. Both the case of a constant surface concentration and the case of a variable surface concentration were considered.

A computer program was developed for solving the mathematical equations to predict sorption-time curves. These curves were compared with the experimental sorption data. Good agreement between the calculated and measured values was obtained when a
variable surface concentration and proper values of the effective diffusivity were selected for the prediction. From this analysis it appears that the effective diffusivity increases with the flour moisture content.

Since the experimental data were consistent with the proposed mechanism, it appears that the rate of sorption of hydrogen chloride by flour in shallow beds may be controlled by the rate of diffusion through the bed.


96. Wheelock, T. D. Investigation on the application of fluidized systems to chemical reactions of wheat flour and design of a system for modifying flour with hydrogen chloride: final report. Engineering Experiment Station, Iowa State University of Science and Technology, Ames, Iowa. 1966.

ACKNOWLEDGMENTS

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The author is indebted to his wife, Chibi, for her assistance in the preparation of this manuscript. Her patience and encouragement during the years of graduate study are gratefully appreciated.
NOMENCLATURE

A = a constant defined by Equation 21
B = a constant defined by Equation 21
C = dimensionless concentration

C_A = concentration of sorbate in gas phase, gm./ml of gas
C*_A = equilibrium concentration of sorbate in gas phase, gm./ml of gas
C_0 = concentration of sorbate at the surface of bed, gm./ml of gas

D = diffusion coefficient, diffusivity, cm^2/min
D_e = effective diffusivity, cm^2/min
f = an algebraic function
F = an algebraic function

\( g_1 \) = an algebraic function
\( g_2 \) = an algebraic function

H = sorbed HCl concentration, gm.HCl/gm. flour

i = subscript in z direction
j = subscripts in time direction

k = rate constant

\( k_1, k_2 \) = constants defined by Equation 22

k_d = rate constant for desorption

k_g = rate constant for the gas phase control mechanism

k_{pg} = rate constant for the combination mechanism

k_s = rate constant for sorption

K = equilibrium constant for the linear isotherm

k_p = rate constant for the particle control mechanism
K_p = permeability coefficient
L = total bed depth, cm.
m = a constant defined by Equations 1 and 2
M = moisture content, gm. H_2O/gm. dry sorbent
M_f = mass of flour, gm.
n = a constant defined by Equation 15
P_A = partial pressure of component A, mm Hg
P*_A = partial pressure of component A at equilibrium, mm Hg
P_Q = saturation pressure of sorbate, mm Hg
q = tortuosity factor
R = equilibrium constant for linear isotherm
S = a constant defined by Equation 17
t = sorption time, min.
T = sorption temperature, °C
T_s = total sorption time, min
U = dependent variable defined by Equation 29
V_f = volume of sample pan, ml.
W_A = amount of sorbate sorbed by sorbent, gm of sorbate/gm. of dry sorbent or cm^3 of sorbent
W*_A = equilibrium amount of sorbate sorbed by sorbent, gm. of sorbate/gm. of dry sorbent or cm^3 of sorbent
W_Am = amount of sorbate sorbed in the monolayer sorption, gm of sorbate/gm of dry sorbent
W_Q = amount of sorbate sorbed at the surface of bed, gm of sorbate/gm of dry sorbent or cm^3 of sorbent
z = length of fixed bed or distance in z direction, cm
β = a constant defined by Equation 44
\( \varepsilon \) = void fraction in the fixed bed, dimensionless
\( \eta \) = dimensionless length
\( \rho_{df} \) = density of dry flour particles, gm./ml.
\( \rho_f \) = density of moist flour particles, gm./ml.
\( \rho_{H_2O} \) = density of liquid water, gm./ml.
\( \tau \) = dimensionless time
APPENDIX A. DETAILED PRESENTATION OF NUMERICAL ANALYSIS

The following equation for predicting values of concentration at the intermediate time point \((j+1/2)\) was obtained by combining Equations 27 and 33 and using the notation of Equation 34:

\[
\frac{1}{2} \left\{ \left( \frac{C_{i+1,j+1/2} + C_{i+1,j}}{2} \right) - 2 \left( \frac{C_{i,j+1/2} + C_{i,j}}{2} \right) + \left( \frac{C_{i-1,j+1/2} + C_{i-1,j}}{2} \right) \right\} \left( \Delta t \right)^2
\]

\[
= \left\{ 1 + \frac{(1 - \epsilon) k_1}{\left( k_1 + k_2 C_{i,j} \right)^2} \right\} \frac{\left( C_{i,j+1/2} - C_{i,j} \right)}{\Delta t/2}
\]

(A-1)

Similarly the equation shown below for correcting the concentration at the point \(j+1\) was obtained by combining Equation 27 and 32:

\[
\frac{1}{2} \left\{ \left( \frac{C_{i+1,j+1} + C_{i+1,j}}{2} \right) - 2 \left( \frac{C_{i,j+1} + C_{i,j}}{2} \right) + \left( \frac{C_{i-1,j+1} + C_{i-1,j}}{2} \right) \right\} \left( \Delta t \right)^2
\]

\[
= 1 + \frac{(1 - \epsilon) k_1}{\left( k_1 + k_2 C_{i,j+1/2} \right)^2} \frac{\left( C_{i,j+1} - C_{i,j} \right)}{\Delta t/2}
\]

(A-2)

It is clear that, by virtue of this approach, the first approximation given by the 'predictor' can be improved by the use of more accurate values given by the 'corrector' formula. Equations (A-1) and (A-2) produce linear algebraic equations for the calculation of the finite difference approximation. Rearrangement of those equations leads to the following for the predictor and corrector respectively:

\[
C_{i+1, j+1/2} - \mathcal{L}_{p,i} C_{i, j+1/2} + C_{i-1, j+1/2} = \delta_{p,i}
\]

(A-3)

\[
C_{i+1, j+1} - \mathcal{L}_{c,i} C_{i, j+1} + C_{i-1, j+1} = \delta_{c,i}
\]

(A-4)
where the symbols are defined as follows:

\[ L_{p,i} = 2(1 + \gamma_{p,i}) \]
\[ L_{c,i} = 2(1 + \gamma_{c,i}) \]
\[ \beta_{p,i} = 2(1 - \gamma_{p,i}) \]
\[ \beta_{c,i} = 2(1 - \gamma_{c,i}) \]

\[ \gamma_{p,i} = \left\{ 1 + \frac{(1 - \epsilon) \frac{k_l}{(k_1 + k_2 C_{i,j})^2}}{\frac{\epsilon}{k_1 + k_2 C_{i,j} + 1/2}} \right\} \left(\frac{\Delta \eta}{\Delta \xi}\right)^2 \]  \hspace{1cm} (A-5)

\[ \gamma_{c,i} = \left\{ 1 + \frac{(1 - \epsilon) \frac{k_l}{(k_1 + k_2 C_{i,j+1/2})^2}}{\frac{\epsilon}{k_1 + k_2 C_{i,j+1/2}} \right\} \left(\frac{\Delta \eta}{\Delta \xi}\right)^2 \]

\[ \delta_{p,i} = \beta_{p,i} C_{i,j} - (C_{i+1, j} + C_{i-1, j}) \]
\[ \delta_{c,i} = \beta_{c,i} C_{i,j} - (C_{i+1, j} + C_{i-1, j}) \]

The initial and boundary conditions associated with Equation 27 can also be converted to the finite difference form.

\[ C_{i,j} = 0 \hspace{1cm} \text{at } j = 1 \text{ and } l \leq i \leq N + 1 \]
\[ C_{i,j} = 1 \hspace{1cm} \text{at } j > 1 \text{ and } i = 1 \]  \hspace{1cm} (A-6)

\[ \frac{\partial C}{\partial \eta}|_{i,j} = \frac{C_{i+1, j} - C_{i-1, j}}{2(\Delta \eta)} \hspace{1cm} 0 \hspace{1cm} \text{at } j > 1 \text{ and } i = N + 1 \]

where \( i = 1, 2, \ldots, N+2 \) and \( j = 1, 2, \ldots, M+2 \).

Upon rearranging, the last boundary condition in Equation A-6 leads to:

\[ \begin{cases} C_{i+1, j} = C_{i-1, j} \end{cases} \text{ at } i = N+1 \]

which is applicable to any mesh points in the \( \xi \) -direction.

Applying these known conditions to Equation A-3 results in the
following set of simultaneous linear equations which correspond to
the N+1 mesh rows in the η direction:

\[-\mathbf{L}_{p,2} c_{2, j+1/2} + c_{3, j+1/2} = \delta_{p,2}
\]

\[c_{2, j+1/2} - \mathbf{L}_{p,3} c_{3, j+1/2} + c_{4, j+1/2} = \delta_{p,3}\]

\[c_{3, j+1/2} - \mathbf{L}_{p,4} c_{4, j+1/2} + c_{5, j+1/2} = \delta_{p,4}\]

\[\vdots\]

\[c_{N-1, j+1/2} - \mathbf{L}_{p,N} c_{N, j+1/2} + c_{N+1, j+1/2} = \delta_{p,N}\]

\[2c_{N, j+1/2} - \mathbf{L}_{p,N+1} c_{N+1, j+1/2} = \delta_{p,N+1}\]

where

\[\delta_{p,2} = \beta_{p,2} c_{2, j} - (c_{3, j} + c_{4, j}) - c_{1, j+1/2}\]

\[\delta_{p,i} = \beta_{p,i} c_{i, j} - (c_{i+1, j} + c_{i-1, j}) \text{ for } i = 3, 4, \ldots, N\]

\[\delta_{p,N+1} = \beta_{p,N+1} c_{N+1, j} - 2c_{N, j}\]

(A-7)

(A-8)

The matrix of the coefficients also has a tridiagonal appearance.

Obviously, the Thomas algorithm can be employed to solve this system
of simultaneous equations (11). Without presenting in detail, the
following relations are utilized,

\[c_{N+1} = \varepsilon_{p, N+1}\]

\[c_{i} = \varepsilon_{p,i} - q_{p,i} c_{i+1} \quad 0 \leq i \leq N\]

(A-9)

where

\[q_{p,2} = \frac{1}{-\mathbf{L}_{p,2}}\]

\[\varepsilon_{p,2} = \frac{\delta_{p,2}}{-\mathbf{L}_{p,2}}\]
The coefficients, \( q \)'s and \( g \)'s are successively calculated in the order of increasing \( i \) and the values of the concentration are then calculated in the order of decreasing \( i \).

After introducing the computed results from the predictor into the corrector, one is able to move from the \((j+1/2)\) to \((j+1)\) time row.

The same procedure applies to another set of simultaneous equations produced from the corrector.

Once the concentration profile for hydrogen chloride in the gas phase is known from the preceding for any \( j+1 \) time row, it is possible to calculate the total amount of hydrogen chloride sorbed by the entire bed of flour at that particular time. This evaluation can be done by integrating the concentration of sorbate in the solid phase over the entire bed as shown below.

\[
\int dH = \frac{A(1 - \varepsilon)}{M_F} \int W_A \, dz \quad (A-10)
\]

Because of the equilibrium assumption it is possible to substitute the expression for the sorption isotherm in place of \( W_A \).

\[
\int dH = \frac{A(1 - \varepsilon)}{M_F} \int \frac{C_A}{k_1 + k_2 C_A} \, dz \quad (A-11)
\]
After converting into dimensionless variables, the equation becomes

$$
\int_0^H dH = \frac{A(L(1-\varepsilon)) C_0}{M_f} \int_0^1 \frac{C_\tau}{k_1 + k_2 C_\tau} d\gamma \quad (A-12)
$$

which is approximated by

$$
H_{N+1, \tau} = \frac{A(L(1-\varepsilon)) C_0}{M_f} \sum_{i=1}^{N+1} \frac{C_i, \tau}{k_1 + k_2 C_i, \tau} \Delta \gamma_i \quad (A-13)
$$

In order to correct this analysis with the predictor-corrector analogue, Equation A-12 can be numerically approximated by the "Runge-Kutta single-step integration process". Starting with \( H_{i, j+1} = 0 \), \( \gamma_{i, j+1} = 0 \) and a specific \( \Delta \gamma \), the third-order process calculates

$$
\lambda_1 = \gamma \left\{ \frac{C_{i, j+1}}{k_1 + k_2 C_{i, j+1}} \right\}
$$

$$
\lambda_2 = \gamma \left\{ \frac{C_{i+1/2, j+1}}{k_1 + k_2 C_{i+1/2, j+1}} \right\} \quad (A-14)
$$

$$
\lambda_3 = \gamma \left\{ \frac{C_{i+1, j+1}}{k_1 + k_2 C_{i+1, j+1}} \right\}
$$

successively and gives the final result

$$
H_{i+1, j+1} = H_i, j+1 + \frac{1}{6} \left( \lambda_1 + 4\lambda_2 + \lambda_3 \right) \quad (A-15)
$$

where

$$
\gamma = \frac{C_0(1-\varepsilon)AL}{M_f} \Delta \gamma
$$

The process repeats itself sequentially to yield the accumulated quantity, \( H_{N+1, \tau} \), of the diffusing substance sorbed in time \( \tau \).
APPENDIX B. LEAST SQUARES FIT OF THE SORPTION ISOTHERMS

The Fortran program used in this work consisted of a main program for performing the least squares fit of a function having M unknown coefficients to N points, and a subroutine program for solving the system of linear equations by the Grauss-Seidel iteration. Pennington's approach (77) was followed in programing this routine computation. Obviously, it is feasible to handle more terms by adding the desired number of functions, $F_U$, in the main program and a corresponding number of function subprograms. The symbol NCASE is equivalent to the number of cases or lines which have to be fit.

The program is shown on the following pages.
PLEASE NOTE:
Not original copy. Several pages have very small print. Filmed as received.

University Microfilms, Inc.
SUBROUTINE GAUSS(A, N, B, ERR, XI)

SOLVING A SYSTEM
OF
LINEAR EQUATIONS
BY
GAUSS-SEIDEL METHOD

DIMENSION A(20,20), B(20), CI20), X(20)

DO 12 I = 1, N
   IF (A(I,I)) LT 1.0
      12 X(I) = 1.0
      C(I,NN) = B(I) / A(I,I)
      DO 15 J = 1, N
         15 C(I,J) = A(I,J) / A(I,I)
   CONTINUE
   E = 0.0
   DO 3 J = 1, N
      P = C(I,J)
      DO 2 J = 1, N
         P = P - C(I,J) * X(J)
      2 CONTINUE
      X(I) = P
      E = E + ABS(P)
      IF (E > ERR) GO TO 4
      4 RETURN
      5 K = K + 1
      IF (K = N) GO TO 4
      6 RETURN
   END

END OF COMPILATION GAUSS

Compilation time was 0002.38 seconds

SIZE OF COMMON 00000
PROGRAM 02460

END OF COMPILATION FU2
Compilation time was 0001.10 seconds
APPENDIX C. COMPUTER PROGRAM FOR THE SIMULATION PROCESS

Two different computer programs are presented on the following pages. The first is for the case where the initial surface concentration was taken to be one-half the steady-state concentration. The second is for the case where an analytical solution of the simple diffusion equation was used to predict the first few values of the concentration. A common subroutine subprogram titled RUNKUT was included in both main programs. An additional subroutine subprogram named ERFC was used in the second program for starting the computation with an exact solution.

For studying the effects of variable effective diffusivity, higher order nonlinear isotherms and variable surface concentrations, the main program was slightly modified to include the different conditions respectively. Since the changes are obvious and easy to make, they are not included here.

Some of the less obvious notation which is not explained in the programs is listed below.

\[
\begin{align*}
D & = \text{normal diffusivity} \\
\text{EXTWSO} & = \text{experimental value of total weight sorbed at equilibrium} \\
\text{DEITA} & = \frac{\Delta \gamma}{2} \\
\gamma & = \Delta \gamma \\
T & = L \\
\text{DEINIT} & = \text{initial } D_e \text{ assigned} \\
\text{RUNOM} & = \text{lumped constant in Runge-Kutta integration process}
\end{align*}
\]
DDTAN = \Delta \tau
DTCN = \tau
Begin the calculation for a flour sample with a certain moisture content

Begin the calculation for a certain HCl concentration in gas phase

Set an effective diffusivity

Set a fine increment of dimensionless time

Write out the initial conditions

Assigned a mean value to the point of discontinuity

Start iteration process

Enter to Do loop

Define the boundary values for predictor

Estimate the coefficients defined in the Thomas Algorithm

Calculate the HCl concentration in gas phase

Are we computing the approximate values for predictor?

Use the computed value as input data

Are we starting to compute the solutions for collector?

Define the boundary values for collector

(continued)
Call subroutine RUNKUT

End of Do loop

Calculate the sorption times

Write out the answer

Use the last computed values as input for new iteration process

Have we reached the end of the small sorption time defined?

Set a coarse increment of dimensionless time

Have we reached the equilibrium amount of sorption?

Have we reached the maximum or minimum values of $D_e$ defined?

Have we computed all the cases of the different HCl conc. in gas phase at certain moisture content?

Have we computed all the cases of the samples with different moisture contents?

Stop
The sorption process

START TO SOLVE A MATRIX WITH A TRIDIAGONAL OF THE CRANK-NICOLSON METHOD ON A NON-LINEAR PARTIAL DIFFERENTIAL EQUATION OF PARABOLIC TYPE BY THE THOMAS ALGORITHM.

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START TO SOLVE A WATER WITH A TRIGONAL CRANK-NICOLSON PROCEDURE ON A NEW-EATED PARTIAL DIFFERENTIAL EQUATION BY THE THOMAS ALGORITHM

THE REMAINING PROGRAM IS SAME AS THE PART AFTER THE STATEMENT NUMBER S.008 IN THE FIRST MAIN PROGRAM INCLUDING SUBROUTINE RUNKUT.

(START OF THEN PROGRAM 5.0089 IN THE FIRST MAIN PROGRAM INCLUDING SUBROUTINE RUNKUT)
## APPENDIX D. COMPUTER INPUT DATA

<table>
<thead>
<tr>
<th>HCl conc. at</th>
<th>Moisture Content</th>
<th>Wet flour weight</th>
<th>Void fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gm. H₂O</td>
<td>Gm. dry flour</td>
<td>Gm. cm³</td>
<td>Gm.</td>
</tr>
</tbody>
</table>

| 0.2379       | 0.00000346       | 0.5840           | 0.558        |
| "            | 0.0000267        | 0.5880           | 0.540        |
| "            | 0.0000217        | 0.6040           | 0.527        |
| "            | 0.0000156        | 0.5530           | 0.567        |
| "            | 0.0000100        | 0.5960           | 0.557        |
| "            | 0.0000067        | 0.6150           | 0.509        |
| 0.2118       | 0.0000348        | 0.5680           | 0.558        |
| "            | 0.0000267        | 0.5880           | 0.543        |
| "            | 0.0000217        | 0.5480           | 0.574        |
| "            | 0.0000156        | 0.5530           | 0.570        |
| "            | 0.0000100        | 0.6090           | 0.526        |
| "            | 0.0000067        | 0.6010           | 0.526        |
| 0.1980       | 0.0000348        | 0.6240           | 0.517        |
| "            | 0.0000267        | 0.5980           | 0.537        |
| "            | 0.0000217        | 0.6150           | 0.525        |
| "            | 0.0000156        | 0.6010           | 0.535        |
| "            | 0.0000100        | 0.5970           | 0.538        |
| "            | 0.0000067        | 0.6795           | 0.467        |
| 0.1653       | 0.0000348        | 0.5740           | 0.560        |
| "            | 0.0000267        | 0.6150           | 0.528        |
| "            | 0.0000217        | 0.6240           | 0.521        |
| "            | 0.0000156        | 0.6250           | 0.521        |
| "            | 0.0000100        | 0.5880           | 0.512        |
| "            | 0.0000067        | 0.5900           | 0.548        |
| 0.1298       | 0.0000348        | 0.6240           | 0.565        |
| "            | 0.0000267        | 0.5970           | 0.547        |
| "            | 0.0000217        | 0.5890           | 0.553        |
| "            | 0.0000156        | 0.6220           | 0.528        |
| "            | 0.0000100        | 0.6050           | 0.541        |
| "            | 0.0000067        | 0.6000           | 0.542        |
| 0.0953       | 0.0000348        | 0.5950           | 0.554        |
| "            | 0.0000267        | 0.5870           | 0.560        |
| "            | 0.0000217        | 0.5650           | 0.576        |
| "            | 0.0000156        | 0.6060           | 0.546        |
| "            | 0.0000100        | 0.5750           | 0.569        |
| "            | 0.0000067        | 0.6140           | 0.538        |
| HCl conc. at Moisture Content surface of bed Wet flour weight Void fraction |
|-----------------|-----------------|-----------------|-----------------|
| Gm. H₂O         | Gm. dry flour   | Gm. cm³         | dimensionless   |
| 0.0879          | 0.0000348       | 0.6380          | 0.526           |
|                 | 0.0000267       | 0.6790          | 0.495           |
|                 | 0.0000217       | 0.5990          | 0.555           |
|                 | 0.0000156       | 0.6400          | 0.524           |
|                 | 0.0000100       | 0.6210          | 0.538           |
|                 | 0.0000067       | 0.6300          | 0.532           |
| 0.0334          | 0.0000348       | 0.6340          | 0.536           |
|                 | 0.0000267       | 0.5920          | 0.567           |
|                 | 0.0000217       | 0.6095          | 0.554           |
|                 | 0.0000156       | 0.5840          | 0.572           |
|                 | 0.0000100       | 0.5895          | 0.568           |
|                 | 0.0000067       | 0.5980          | 0.562           |
| 0.0071          | 0.0000348       | 0.6050          | 0.562           |
|                 | 0.0000267       | 0.6010          | 0.565           |
|                 | 0.0000217       | 0.5970          | 0.568           |
|                 | 0.0000156       | 0.6230          | 0.549           |
|                 | 0.0000100       | 0.5920          | 0.571           |
|                 | 0.0000067       | 0.6360          | 0.539           |