

DIFFUSION OF CARBON DIOXIDE THROUGH DOUGH

by

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INTRODUCTION

Wheat is our most important cereal crop. To-day, more acreage is devoted to the cultivation of this crop than to any other of the cereals. Much of the popularity of wheat is due to the fact that an easily palatable, fine-textured bread may be baked from a yeasted, wheaten flour dough. The mechanism by which these familiar characteristics of wheaten bread are attained, is largely accounted for by two factors. One of these is gas production; yeast enzymes ferment certain sugars in dough and thus produce the gas. The second factor is called gas retention; this term defines the capacity of the bubbles or envelopes formed in the distensible elastic dough to retain some of the gas produced. Acting together, the factors change the yeasted dough from a heavy mass, to a light and spongy one which, when baked, yields the well-known bread loaf.

Gas production and retention then, are two important factors influencing the quality of bread. Gas production has been extensively investigated. Initial rates of gas production as well as continuous rates over long periods of time have been measured accurately. On the other hand, gas retention has not been as fully studied. To date, indirect measurements have been made, usually in systems where the first concern was measurement of gas production. Some qualitative data on gas retention are also available.

It was thought that more fundamental knowledge of gas retention might be gained, if it were possible to study it in a simple experimentally isolated system of non-yeasted dough. In such a system, a non-yeasted dough membrane would divide an enclosure in half. To one surface of the

membrane could be applied carbon dioxide gas; a device for estimating the amount of gas diffusing could be connected with the part of the enclosure containing the other membrane surface. In such a system, the effect of a wide range of variables such as temperature, pressure, and membrane thickness could be examined. In order to carry out such a study, special apparatus had to be designed and constructed. With suitable apparatus available, it was desirable to study the effects on gas retention of changes in some of the more important variables affecting retention. This would make it possible to understand the fundamental relationships between retention and these important physical factors. That knowledge could then be used, in an attempt to piece together the complex picture of the intricate interdependencies of gas retention on the one hand, and the many variables involved in the fermentation and baking processes, on the other. Such a preliminary but fundamental study has been undertaken and is described in this dissertation.

An outline of the thesis will give an overall picture of the investigation. The various parts mentioned here, will be elaborated in the body of the thesis. Following the introduction, the available literature on gas retention in doughs, is reviewed. There follows a brief review of apparatuses and methods used previously in measurements of carbon dioxide gas retention in doughs. Then, a detailed description of the apparatus developed for this investigation is presented. There is also a description of procedure attending use of the new apparatus. A section is next devoted to a concise treatment of the basic theoretical background involved in this study. The materials used are next listed. A full description of experiments, designed to study the fundamental relationships between carbon dioxide retention and a number of variables, is presented. Included are studies of the effects on gas retention of changes in:

- (1) pressure differential across membranes,
- (2) membrane thickness,
- (3) time of diffusion,
- (4) temperature,
- (5) water content in membranes,

Also described is a study of the retention properties in doughs mixed from flour of a wide variety of wheats. All results are fully discussed, with the aid of plots and diagrams. The dissertation ends with the usual bibliography.

LITERATURE REVIEW

That gas retention and production are very important factors in determining the final quality of bread, was recognized late in the 19th century. A survey of literature shows that in the past three or four decades many investigations on gas retention and production have been made. This survey, which forms a necessary background for the present study, is divided into two parts. One is a discussion of investigations on the characteristics of gas retention and production, the other a short discussion of studies in which apparatuses and methods for determining gas retention and production have been presented. At this stage only the former part will be given, while the review of apparatuses and methods may be found in a later section where the apparatus and method used in this study is described.

At the outset, it will be well to define certain terms which are frequently encountered in studies dealing with gas retention and production. The danger of confusing certain terms, similar in meaning, will thus be minimized.

Diastatic Activity.—Diastatic activity is the total amount of reducing sugar, expressed as maltose, obtained from a quantity of 10 gm. of flour after an autolytic digestion period of one hour under specified conditions. The sugar is produced solely due to the action on available starch of amylases inherently present in the flour. It is therefore a measure of the amylases naturally occurring in flour. For exactness, the free sugar originally present in the flour is determined and subtracted from the above result. Diastatic activity must not be confused with gassing power of which it is an indirect measure.

Gassing Power.—Gassing power is a measure of the total amount of gas produced in six hours of fermentation of a specified amount of yeasted dough under defined conditions. It is characteristic of a flour, since the total amount and rate of fermentation depend on the amount of fermentable sugars present in the flour, and on the rate of action by the amylases on the flour starch. Since the pH of the gassing power determinations is about five to six, diastasis is not complete after six hours, and the determination is a comparative one. Gassing power is expressed as total pressure in mm. Hg.

Gas Production.—Gas production is the general term applied to the production of carbon dioxide gas in a fermenting dough. Gas production is controllable by the addition to the dough of yeast, sugar or enzyme or a combination of all three.

Gas Retention.—Gas retention is the property of a dough of restraining produced gas from escaping from a fermenting dough. The retention may be due to physical retention in the bubbles of the dough, adsorption, emulsification or to chemical combination with the dough. The relationship: $\text{gas retention} = \text{gas production} - \text{gas diffusion}$, holds true.

Diffusion.—Diffusion is a purely physical concept and is applied to the property of gases of escaping from their confining spaces through the walls of the confining media. Applied to fermenting doughs, diffusion is the flow of produced gas through the dough. In fermenting doughs diffusion must be dependent on gas production and gas retention. In this project, diffusion will be used to describe the passage of carbon dioxide through specific thicknesses of non-yeasted doughs.

Late in the last century, the various factors acting during the fermentation period to determine the final bread quality, were being investigated. Among these factors were gas production and retention.

Thus, according to E. Elion (15), H. Elion in 1893 expressed his belief that gas production and retention influence the quality of bread. He thought, however, the effects of these two factors were minor ones, compared to the composite effect of all the factors acting during the fermentation period. However, as a result of subsequent investigations, cereal chemists have placed more and more importance on gas production and retention, and today, these are considered among the key factors that determine the final quality of the bread loaf.

C. H. Bailey was among the first investigators to undertake extensive study of the retention and production factors. He drew attention to and supports Wood's statement of 1907, that it appears certain that the gas retention factor is the most important single factor determining the quality of bread. Bailey and Weigley (7) suggest that carbon dioxide is for some time chemically adsorbed or combined in the dough surface, thus providing a time lag between gas production and release, during which a gas bubble is formed and the dough expands. Thus germinated Bailey's belief that flour strength can be determined through retention measurements. Bailey and Johnson (5), state that "at maximum volume a dough loses carbon dioxide most rapidly. This is probably due to the rupturing of vesicles at the surface, filled with gas". Later the same investigators state that when the percentage of gluten in a flour is reduced by the addition of starch, the gas retaining capacity of the flour is impaired, the producing capacity enhanced. An important concept introduced here was that the gas retention was due chiefly to the gluten part of the dough, and that amount of retention was dependent on gluten quality. Subsequently, Bailey and Johnson (6), carried on this line of research and found that rye flour doughs were characterized by poor gas retaining properties. Also, alcohol treated flours yielded doughs with poor gas retaining capacities. This was

explained in that the "gluten" of a rye flour is inferior to that of a wheat flour and that alcohol damages the gluten. Thus, the conclusion was that the superior gluten had higher gas retention and yielded the better bread loaf. Karacsonyi and Bailey (24), supported the view that higher diffusion is due to a weak gluten or a greater proportion of starch in the gluten network. They studied the effect of overgrinding of flour and found that overgrinding causes increased gas production but a decreased retention value. This decrease in retention, they thought was due possibly to a weakening of the gluten through overgrinding. The gas production increase was also explicable. Large granules of starch are attacked by water with difficulty whereas smaller particles gelatinize readily. Overgrinding provided a greater number of small "damaged" starch particles, which gelatinize readily and produce a greater quantity of fermentable sugar. Karacsonyi and Bailey also suggested that the ratio rate of production of carbon dioxide to the rate of loss of carbon dioxide from a fermenting dough be accepted as index of flour strength.

Sherwood and Bailey (36), applied gas retention measurements to yet another related problem. Studying the effects of wheat germination on produced bread, the investigators stated that the gas retaining power of gluten is hampered by the admixture of germinated wheat. They found that when wheat, germinated for five days, was added to pure grain in 5% proportion, poorer loaves were obtained, because the increased protease activity caused impairment of the gas retaining properties of the gluten.

The work of several other investigators calls for attention. Geddes (17), carried out intensive research on the effect of heat treatment of flour on bread quality. He found, that in all cases, heating the flour resulted in poorer gluten quality, as evidenced by reduced gas retention capacity. Martin and Whitcomb (32), carried out investigations which

extended the work of Bailey. They showed that ether extracted flour doughs yielded finer textured bread, and that gas retention in such doughs was much greater than in untreated doughs. They also found that addition of fats reduced the gas retaining capacity somewhat. Hence, the dough surface becomes more permeable on fat additions, and similarly the presence of ether soluble materials reduces the gas retention property of a dough.

A paper by Heald (21), is of considerable interest because for the first time it links experimentally gas retention and the baking formula. Heald, using various types of flours, studied the effect on gas retention and loaf volume of adding shortening to the baking formula. In general he found, in confirmation of Martin and Whitcomb's work, that shortening increased loaf volume somewhat, but slightly lowered gas retention. Earlier Heald (20), presented an interesting paper, listing the effects of numerous factors on gas production, during the fermentation period. Larmour and Brockington (28) mention the beneficial effects on gas retention in dough of added punching of the dough during the fermentation period and of the addition to the baking formula of the bromate ion in the form of potassium bromate. The view that addition of bromate ion increases gas retention was supported by Geddes and Larmour (18).

The effect of chemical flour improvers on proteolytic activity as related to gas retention in doughs was studied by Flohil (16). He states, "whereas the gas producing capacity (of a dough) depends on the availability of fermentable sugars, the gas retaining ability is determined by the quantity and physical condition of the gluten, though perhaps the starch complex of the dough may influence retention to some extent". He goes on to state that chemical flour improvers of the "non-yeast food type", owe their properties to their positive action on the gas retaining capacity of the dough. And so, yet another facet of the retention factor has been disclosed.

Several papers by Baker are noteworthy. In his works the primary aim seems to be to show the magnitude of the effect of gas retention in doughs by attempting to evaluate the quality of bread itself. In one paper, Baker (8), describes his investigation on the permeability of bread by air. This was an attempt to demonstrate the relation between bread texture and gas retention. He showed that the change in permeability from sample to sample is nearly proportional to the change in cell size. He also found that permeability was increased by semi-solid shortening, higher yeast content, and higher water content; and decreased by oxidation, fermentation, higher protein content, twisting of dough and baking in a closed pan. Next Baker attempted to get at the basis of gas retention (9). He found that in dough development, the bubbles acquire a thin gluten lining, with a characteristic shiny appearance, thus accounting for some of their gas retaining capacity. As the bubbles expand, the amounts of gluten required to satisfy their surface needs are drawn from the starch-gluten matrix of the endosperm material. When the matrix is exhausted, further bubble expansion causes ruptures. This information is of great interest and as such stands as a reasonable retention theory.

The work of Kneen and Sandstedt (26) and Kneen, Sandstedt and Hollenbeck (27), on the effect of alpha and beta amylase supplements on the dough in the baking oven is of much interest. It is a known fact that the amylases increase gas production but the theory is put forward here that oven loaf volume increases on the addition of amylases due to enhanced retention. It is known that when the sugar level is low, malt addition increases gas production. These workers maintained gas production constant, and found that alpha amylase supplements increased loaf volume by modifying the gas retention capacity of a dough during the baking process. It is, however, not clear what the mechanism of the process might be.

Johnson and Miller (23), elaborate on the Kneen and Sandstedt work

and confirm it. According to them, gas retention in fermenting doughs is unaltered by additions of alpha amylase, but it is enhanced in the baking process. These experimenters further believe that proteinase addition also increased the retention. This was first suggested by Read and Haas (34).

Finally, the work of Swanson must be recorded. Swanson and Swanson (37) carried out a detailed study of the effects on gas production and retention of choice of flour type, baking formula and mixing time. The paper is of added interest, since here for the first time an attempt was made to ascribe certain effects to the retention factor alone. The data were treated in a complex statistical manner which allowed the investigators to separate effects due to production from effects due to gas retention. The results showed that spring wheat flour, the malt-phosphate-bromate formula and two minute mixing time, all contributed to maximum retention results. The same investigators carried out a study of the effects on gas retention and production of surface active oxidizing and reducing agents (38). Their work indicated that adequate dough structure is a prerequisite for adequate gas retention. Thus chemicals altering the physical structure of the dough would also alter its gas retaining properties. Surface active agents such as "aerosol" and "santomerse" have a detrimental effect on gas retention, whilst "tergitol" has no effect at all. The reducing agent glutathione is detrimental as are cysteine and sodium sulfite. Peroxides are very harmful to gas retention whereas the bromate ion has a beneficial effect.

This completes the review of available literature. It is evident that the importance of the gas retention factor has been recognized. Many of its facets have been brought to light. The studies undertaken have pointed out some factors influencing gas retention, and are indeed an important advance toward the evaluation of the true importance of gas

retention. However, one basic shortcoming is applicable to all but one of the studies mentioned. The results cannot be attributed to changes in the gas retention factor alone. Only in the Swanson experiments, and in an indirect manner, was an attempt made to ascribe certain results to changes in gas retention alone. The experiments of this investigation are designed to overcome this shortcoming. It is believed that they constitute a positive contribution to the chosen field of study, because they make possible a quantitative measurement of the retention factor and a quantitative evaluation of the effect on retention of variations in some of the factors influencing retention.

APPARATUS

The success of the proposed study depended greatly on the newly developed apparatus. This section presents a detailed description of its various parts and of the procedure attending its use. Preceding this description is a review of apparatuses used by other investigators in retention studies. It was thought more logical to describe these in this section rather than in the literature review.

Review of Previous Apparatus

The same principle was employed in nearly all of the earlier gas retention measuring devices. In essence this is the measurement of the changes in volume of fermenting doughs and the measurement of the amount of gas evolved from fermenting doughs. The earlier apparatuses may roughly be divided into three groups, according to the actual measurement made. One group may thus be classified "volumetric", another group may be termed "manometric", and the third "gravimetric" type of apparatus.

1. "Volumetric" Type of Apparatus.— These apparatuses are the earliest of the gas retention ones to be used extensively. The general principle involved is measurement of the volume of a yeasted dough. E. Elion states (15) that to his knowledge, Maurizio in 1902 was the first investigator to differentiate clearly between gas production and gas retention measurements. In his experiments he employed a simple gas burette which, according to Elion, was developed earlier by Hayduck, Kusserow and Kunis.

As early as 1916, C. H. Bailey (3), stressed the importance of gas retention measurements during the fermentation period. He was largely responsible for the development of a popular apparatus which could measure gas retention. A simple form of the apparatus was first described in a paper with Weigley (7). Fermenting doughs were used and the gas escaping

from the dough was absorbed in standard barium hydroxide the excess base being titrated with standard hydrochloric acid. The apparatus was improved by Bailey and Johnson (5, 6). Samples of yeasted dough were put into shallow beakers and placed in perforated wax cylinders, which in turn were placed in a Mason jar. A solution of 23 per cent potassium hydroxide was in the jar. A gas burette filled with saturated sodium chloride was inverted into the jar. The gas escaping from the dough was absorbed in the potassium hydroxide and the change in volume due to the expansion of the dough was registered. This was a measure of gas retention. More recently, C. H. Bailey (4), has presented an automatic, continuously recording version of this apparatus.

Various other "volumetric" type of apparatuses have been used from time to time. Most of these were used to measure gas production. Among the more popular were devices introduced by Markley and Bailey (30), Glabe (19) and E. Elion (13).

2. "Manometric" Type of Apparatus.—These apparatuses register pressure differences in gas production and gassing power determinations. They have not been used in gas retention measurements, but are included here, for most of them could be used for such measurements upon slight modification. Among the more popular of these is the one of Blish, Sandstedt and Astleford (11). In this the mercury manometer is introduced to fermenting dough systems. Another apparatus worthy of mention is that of Sandstedt and Blish (35). That of Malloch (29) is also of some interest.

3. "Gravimetric" Type of Apparatus.—This class of apparatus records gas evolved or retained in terms of weight difference of doughs. The designs are complex, their accuracy is less than that of the first two types, but they are useful where measurements on great dough masses are required.

Most important is the adaptation of an accurate balance to the measurement of gas production and retention. The apparatus known as the Chefaro balance is described by E. Elion (14). Quantities of gas produced and retained are measured on sensitive balances, and the results automatically and continuously recorded. The results are, however, subject to a number of errors. The principle of the Chefaro balance has been used at least twice to design models for the measurement of gas production and retention. The more important application has been made by Working and Swanson (39), the other by Miller, Edgar and Whiteside (33). The former really utilizes "manometric" measurements in that the evolved gas is registered as pressure increase and the results are automatically and continuously recorded by electric sparks burning holes in the chart paper.

Two additional apparatuses deserve mention, which do not belong to either of the broad groups designated. One is the novel device of Edelman and Cathcart (12) which measures the oven spring of bread as indication of gas retention. The obtained results were however unreliable, for too many complex reactions occur in the baking process which tend to obscure the retention factor. The other apparatus is the Chopin Alveograph. It is usually classified as a dough testing device (25), but it may perhaps measure among other factors, gas diffusion through dough membranes. Again the usefulness of the device is limited for it cannot be used to measure diffusion alone.

It is seen from this survey that the described apparatuses were designed primarily to measure gas production or gassing power and that the measurement of gas retention was merely an adaptation of their use. Moreover, they measured only some gross changes associated with gas retention. None could be used in a study of the diffusion of carbon dioxide gas through

dough membranes of specified type and dimension, under specific physical conditions. Such a fundamental study of the gas retention factor in a simple system had to await the development of a special apparatus.

Description of New Apparatus

The apparatus which made possible the study of gas diffusion as a measure of gas retention in doughs, in a simple isolated system of non-yeasted doughs, is now described. To clarify the description, sketches of the apparatus are presented. The apparatus is in the main a device which holds a dough membrane of known dimensions in an enclosed gas-tight unit in such a way as to divide the enclosed unit into two parts. Carbon dioxide from a suitable source may be led to one part of the enclosure and thus suitable gas pressure may be applied to one surface of the membrane. To the other part of the enclosed unit may be attached a suitable apparatus which traps the diffused gas. Other parts of the apparatus include a membrane pressing assembly, a source of carbon dioxide, and a means of trapping and estimating the diffused gas. The entire apparatus may be considered a carbon dioxide supply-diffusion-absorption train. For the purpose of exposition, one may conveniently consider it in three sections, one for each of the three links in the train. The diffusion unit, characteristic feature and the most important part of the apparatus, will be dealt with first. Description of the other parts will follow. Where necessary functional and constructional detail will be appended.

1. Diffusion Unit.--The importance of this unit has already been stressed. The description will be more clearly understood by referring to Figure 1, which shows the diffusion unit as it appears when it is assembled. From the section cut in Figure 1, it is seen that the diffusion unit consists of four parts. There is a lower diffusion chamber, a dough holding unit, an upper diffusion chamber and a unit coupling ring.

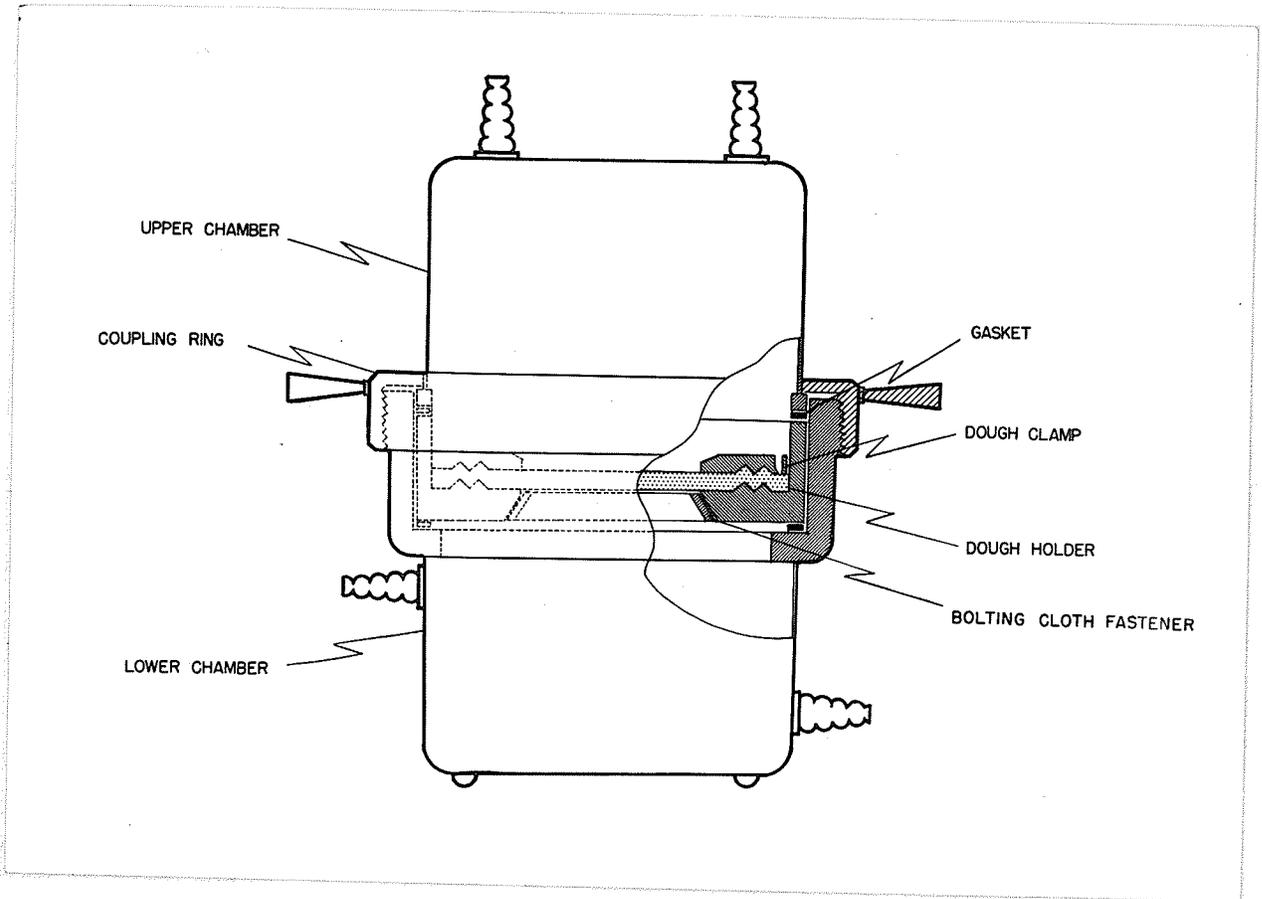


Figure 1.—Diffusion unit when assembled.

The lower diffusion chamber serves a double purpose. It provides an enclosure for the gas diffusing through the dough membrane to enter and also, as is shown in the section of Figure 1, it serves as a dough holder seat. The dough holder seat is the wider portion at the top of the lower diffusion chamber. It is noted in Figure 1, that the topmost portion of the dough holder seat is threaded so as to lock with the thread of the unit coupling ring. A neoprene gasket rests on the base of the dough holder seat. This permits a gas tight seal to be made between the upper and the lower diffusion chamber. Two inlets are welded to the lower diffusion chamber. Figure 1 shows that these are diametrically opposite each other but at different levels. The lower chamber stands on three feet, two of which may be seen in Figure 1. A small hole is drilled in the centre of each of the feet; this construction allows the lower chamber to rest on a special diffusion unit vice, not shown in the diagram. This vice is simply a metal plate with three pegs protruding from it. The pegs fit into the drilled holes in the feet of the lower chamber. Thus secured, the diffusion unit may be easily assembled and disassembled. The vice is secured to a laboratory table by means of clamps.

The dough holding unit fits snugly into the dough holder seat and rests on the gasket. The section of Figure 1 shows the dough holding unit, which consists of three pieces of apparatus. However, a detailed description of the unit will be more logically presented when the membrane pressing assembly is considered. Suffice it to say now, that the dough holding unit is the carrier of a dough membrane of known dimension, and that it forms a gas tight barrier between the upper and lower diffusion chambers. Figure 1 shows that a second membrane gasket rests on the top edge of the dough holding unit. This assures a gas tight seal between the diffusion unit and the outside.

The upper chamber confines the carbon dioxide which exerts pressure on the dough membrane. This piece of apparatus, Figure 1 shows, rests on the gasket of the top edge of the dough holder. Two inlets are soldered to the roof of the upper diffusion chamber.

The unit coupling ring, as seen in the section of Figure 1, locks the various parts of the diffusion unit into a gas tight system. To facilitate operation of the ring three handles are soldered to it.

2. Membrane Pressing Assembly.—Almost as important as the diffusion unit as an apparatus section is the membrane pressing assembly, an exploded diagram of which is seen in Figure 2. The assembly makes it possible to press and then hold firmly a dough membrane 6.4 cm. in diameter and of predetermined thickness. This membrane may then be loaded into the diffusion unit. The assembly then consists of the dough holding unit, also shown in the section of Figure 1, and two flat pressing surfaces. Figure 1 shows, that the dough holding unit rests in the diffusion unit in such a way that it forms a partition between the upper and the lower diffusion chamber.

The principal part of the pressing assembly is the dough holding unit which consists of three pieces, the dough holder, the bolting cloth retaining ring and the dough clamp.

The dough holder and the bolting cloth fastener, shown in Figure 2, may be considered simultaneously. The bolting cloth fastener holds a piece of fine mesh bolting cloth tightly stretched over the orifice of the dough holder. The bolting cloth is a support for the dough membrane. The bolting cloth fastener is secured in place by three screws. The floor of the dough holder has teeth and grooves machined into it which run concentrically with the two inch orifice. These grooves and teeth lock with similar ones in the dough clamp and help form a good dough seal in the dough holding unit. A second piece of coarser bolting cloth rests on the

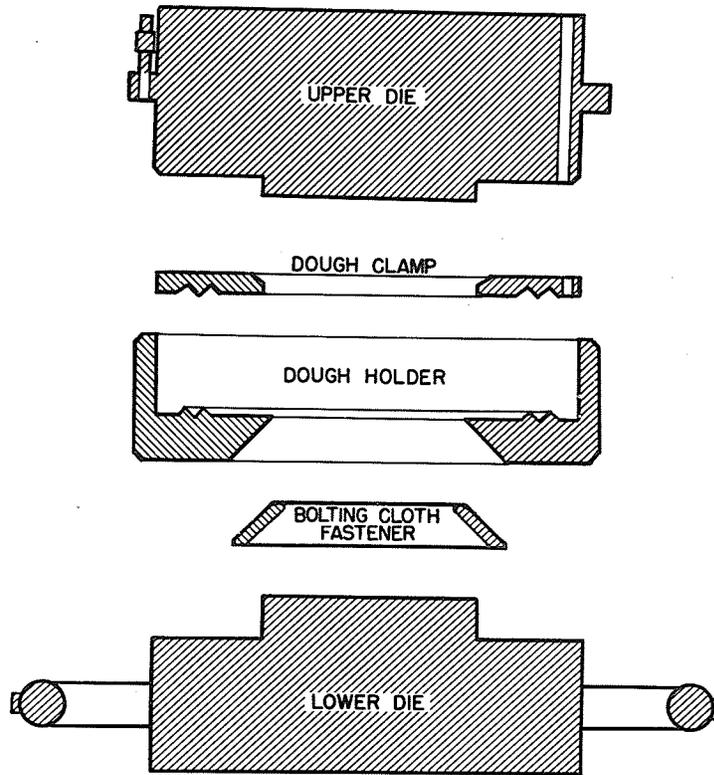


Figure 2.—Exploded diagram of the pressing assembly.

top surface of the dough membrane. This piece of cloth prevents the dough from sticking against the upper pressing surface.

The lower pressing die shown in Figure 2, serves as a false bottom against which a mass of dough may be pressed into a membrane. The die is so constructed as to form a flush surface with the floor of the dough holder. To facilitate handling of the die, two handles are attached.

The upper pressing die is a heavy unit which flattens a mass of dough into a membrane of required thickness. It is shown in Figure 2. The rim encircling the upper die has in it three large set screws. When the set screws are removed the rim of the upper die and the upper edge of the dough holder just touch when the two pressing surfaces meet. Thus a membrane of desired thickness may be pressed by adjusting the position of the setting screws. The key shaft in the upper die, seen in Figure 2, is a seat for an Allen screw in the dough clamp. Also, an Allen key fitting this screw may be inserted here, and thus the dough clamp may be released from the upper die and locked against the dough holder at will.

The dough clamp, also shown in Figure 2 and in the section of Figure 1, is a flexible ring, for it has three slits machined into it. The two partial slits give the clamp its spring or elasticity. The full slit, has a tapered threaded hole (see Figure 2 or Section Figure 1) which is a seat for an Allen screw. The dough clamp is in its normal state when the screw just barely engages in the thread or is removed, as in Figure 2. In this state the clamp fits very tightly against the upper pressing die. The Allen screw fits into the key shaft of the upper die and the lower surface of the clamp is flush with the pressing surface of the die. The clamp is in the expanded state when the screw is well inserted. In this state, the clamp fits tightly against the walls of the dough holder.

3. Carbon Dioxide Supply Section.—The purpose of this section of the apparatus is to deliver carbon dioxide to the upper surface of the dough membrane. The chief member of this section is the source of the gas - a carbon dioxide cylinder. The cylinder is fitted with a reducing valve and two auxiliary fine-control valves. Gas escapes from the cylinder into the reducing valve, at the pressure in the cylinder, by opening the cylinder's needle valve. In the reducing valve, the gas is reduced to a desired lower pressure. The actual rate of flow of the gas into the apparatus train and the pressure it exerts on the dough membrane is controlled by appropriate use of the two auxiliary fine control valves.
4. Absorption Section.—This section of the apparatus is concerned with trapping the diffused carbon dioxide gas. The most essential part of the section is a Brady-Meyer absorption unit. It is a long glass tube which has nine bulbs. This tube fits into a 500 ml. suction flask and dips into a known volume of standard barium hydroxide solution in the flask. When air is drawn through the absorption unit, the base is drawn into the Brady-Meyer tube so that eight of the bulbs are filled. The diffused carbon dioxide is absorbed in the barium hydroxide and deposited as the sparingly soluble carbonate.
5. The Train Assembly.—The apparatus units just described are the most essential parts of the apparatus train. A number of other pieces, which fulfil specific functions are also included in the apparatus assembly. They may be best accounted for by describing briefly the train as it appears when it is completely assembled in a diffusion experiment. Figure 3, shows a diagram of the entire train under such conditions.

The carbon dioxide supply section consists chiefly of the carbon dioxide cylinder, marked C, in Figure 3 and a humidifier (H in Figure 3). The carbon dioxide gas is allowed to enter the train by operating the

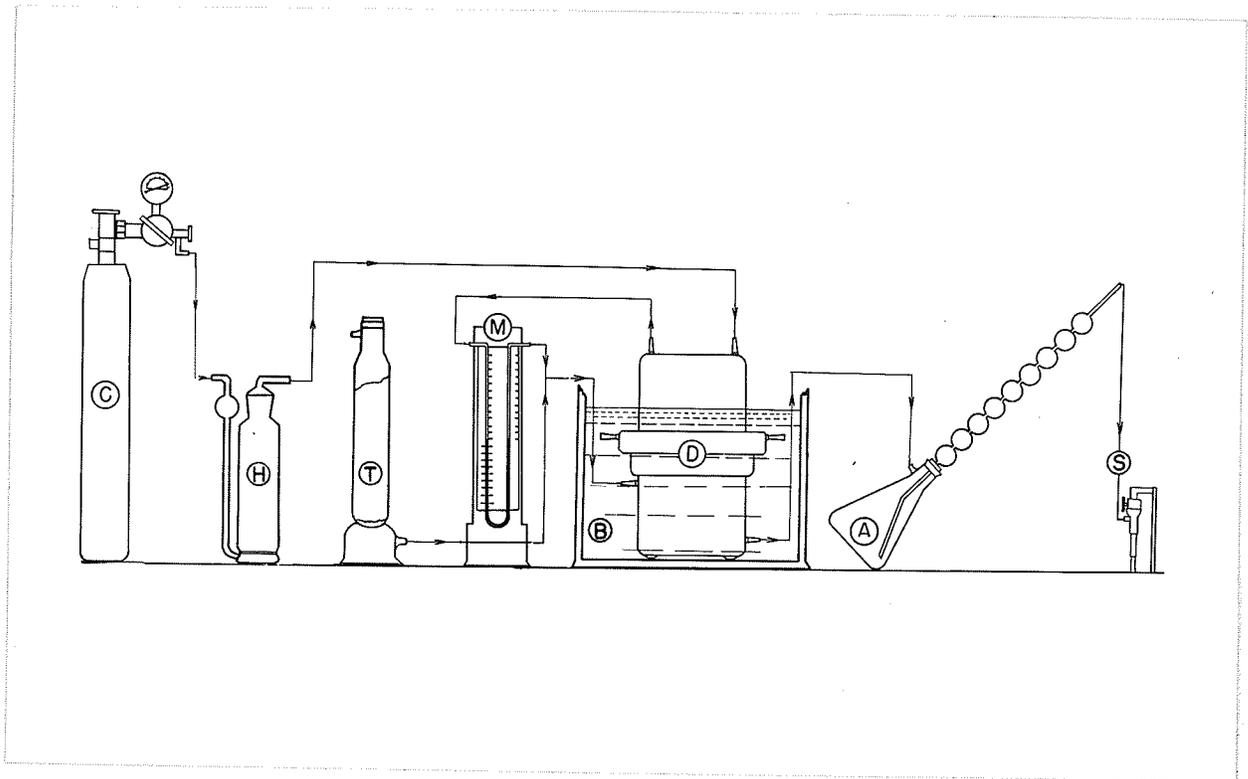


Figure 3.—Diffusion train showing various parts:
C - carbon dioxide cylinder, H - humidifier, T - ascarite tower,
M - manometer, B - water bath, D - diffusion unit, A - Brady-Meyer
absorption unit, S - suction pump. Arrows indicate direction of gas flow.

valves on the cylinder as described. The gas is led through rubber tubing into the humidifier H, filled to a height of four inches with saturated sodium chloride solution. This is done to keep the humidity of the atmosphere in the diffusion unit high. From the bubbler the gas is led into the upper chamber of the diffusion unit. A glass T tube (not shown in Figure 3) is included in the line so that if in a diffusion experiment, the pressure on the membrane inadvertently rises, the excess gas may be eliminated by providing an outlet to the atmosphere. Under ordinary circumstances this "leak" is not used however.

On entering the upper diffusion chamber, the gas can pass into the lower chamber only by diffusing through the dough membrane. Once it has done so, it is swept by a stream of air into the absorption section. The lower inlet of the lower diffusion chamber is connected by means of a three-way stopcock to the Brady-Meyer absorption unit, A in Figure 3, and the latter is in turn connected to a suction pump. The other outlet of the three-way stopcock, not shown in Figure 3, is connected to suction directly, so that the lower diffusion chamber may be swept without pulling the air through the absorption unit.

Figure 3 shows that the lower diffusion chamber is connected through a T tube from the upper inlet to an ascarite scrubbing tower. Ascarite is a good carbon dioxide absorbent, so that the laboratory air pulled into the lower chamber by suction contains little of this gas.

The upper inlet of the lower diffusion chamber is also connected to one arm of a mercury manometer M, as shown in Figure 3. The other arm of the manometer is connected to an inlet of the upper diffusion chamber. Thus, the manometer measures the pressure difference across the dough membrane.

A final piece of apparatus is the water bath B, shown in

Figure 3. The diffusion unit D rests in the thermostat controlled water bath during a diffusion experiment, so that the experiments may be carried out at constant temperatures.

Procedure for Carrying Out Diffusion Experiments

With the apparatus now familiar, the method used in carrying out diffusion experiments may be described. All the steps in the experimental procedure will be listed in chronological order, and, where necessary, attention will be drawn to some errors common to this procedure.

1. Membrane Thickness Setting.—It must be decided what membrane thickness is wanted. The procedure will be more easily followed by constantly referring to Figure 2. It is assumed that the membrane pressing assembly is completely disassembled.

The dough holder is first inverted and a piece of 72 GG bolting cloth, about 5 inches square, is placed over the bottom of the holder. The bolting cloth fastening ring is inserted in position and is firmly secured by fastening the three screws fully. It should be made certain that the cloth forms a smooth surface over the dough holder orifice. The excess bolting cloth is trimmed away, so that the bottom surface of the dough holder is smooth.

The dough holder is now placed onto the lower pressing die. Three pieces of standard shim stock, one piece .025 inches, one .010 inches, and the third .004 inches in thickness are placed onto the bolting cloth in the dough holder. These pieces add up to a thickness of .039 inches which corresponds to 1 mm. A circular piece of 36 GG bolting cloth is also placed here.

The dough clamp in the normal state, that is with the Allen screw just barely engaged is attached to the upper die. The upper die is allowed to fall gently into the dough holder. It must be made certain that the

three setting screws in the rim of the upper die are either removed or do not protrude from the rim. Pressure is applied to the upper die, so that the shim stock is properly flattened out and the upper die enters the dough holder as far as possible. A convenient method is to put the pressing assembly under pressure of approximately 500 pounds in the Carver hydraulic press. The setting screws are now inserted into the rim of the upper die, until they just touch the upper edge of the dough holder. The screws are secured in place by locknuts which are tightened with pliers.

The assembly is now removed from the source of pressure application. It is set to press membranes one mm. thick. By inserting suitable shim stock thicknesses, the assembly may be set to press membranes of other thicknesses. Shim stock .025, .020, .010, .005, .004, and .003 inches thick is available. Suitable combinations of these various thicknesses allow membranes of 0.5 mm., 1 mm., 1.5 mm., 2.0 mm., and 3.0 mm. to be pressed.

2. Membrane Pressing Procedure.—One hundred grams of suitable flour is weighed and placed in a dough mixing bowl. In this case, a Hobart mixer equipped with a small bowl was used. Enough water is added to mix a dough to baking absorption as determined by the Farinograph - or to any other desired consistency. The dough is mixed for three minutes in the Hobart mixer. For other types of mixers, corresponding standard mixing times are used.

The dough holder prepared as described above is placed on the lower pressing die. About 30 grams of the mixed dough is shaped into a ball and placed in the centre of the bolting cloth in the dough holder. The coarser piece of bolting cloth is placed on top of the dough ball. The upper pressing die is prepared by forcing the dough clamp into position on the upper die. The upper die is allowed to fall into the dough holder;

pressure is applied to the upper die. This may be done conveniently by standing on the upper die for one minute. The Allen key is inserted into the key shaft of the upper die and the Allen screw of the dough clamp is turned to expand the clamp and lock it against the dough holder. The upper die is then removed. The dough holding unit is removed from the lower pressing die. The unit containing the one millimeter membrane is placed for 15 minutes into a constant humidity chamber operating at 30°C., prior to loading into the diffusion unit.

3. Loading and Assembling the Diffusion Unit.— It is assumed that the diffusion unit is completely disassembled. The procedure will be more easily understood by referring to Figure 1.

The lower diffusion chamber is placed on the special vice so that the pegs in the vice fit into the holes in the feet of the lower chamber. Next, glycerol is applied to the outside edge of the bottom of the dough holder. Glycerol is used to assure a good seal between the gasket and the lower chamber. The dough holding unit is placed onto the neoprene gasket in the lower diffusion chamber. Figure 1 shows the position of the dough holding unit in the diffusion unit. Glycerol is applied to the upper rim of the dough holder and another neoprene gasket is placed on this rim.

Glycerol is applied to the lower rim of the upper diffusion chamber. Also, a piece of wetted cheese cloth, pinned on a strip of steel wire, is pressed against an inside wall of the upper diffusion chamber. This helps maintain high humidity in the chamber. The upper chamber is placed on the gasket on the upper rim of the dough holder. The unit coupling ring is placed over the upper diffusion chamber, as shown in Figure 1, and tightened well. The unit is now ready to be connected into the apparatus train.

4. Assembling the Diffusion Train.— It is assumed that all the parts of the apparatus are disconnected. The following account will show what connections must be made to have the apparatus set up as it is in a diffusion experiment.

The cylinder C in Figure 3 is connected with rubber tubing to the inlet tube of the humidifier H. The outlet tube of the humidifier H is connected to one of the inlets of the upper diffusion chamber in the unit D. For this connection rubber tubing and a glass T tube is used. The remaining outlet of the T tube is clamped off by a pinch clamp and may be used to allow excess gas to escape, if pressure on the dough membrane inadvertently rises during an experiment. The second inlet of the upper diffusion chamber of unit D is attached with rubber tubing to the left arm of the manometer M. The right arm of the manometer M, is connected through a T tube to the lower connecting arm of the ascarite-filled tower T and to the upper inlet of the lower diffusion chamber of the unit D. The lower inlet of the lower diffusion chamber is connected to an arm of a three-way stopcock. The second arm of the three-way stopcock is connected directly to the water suction pump S. The third arm of the stopcock is connected to the inlet of the suction flask A, in which the Brady-Meyer absorption tube rests. The upper end of the absorption tube is connected through a stopcock to the suction pump S. The absorption unit, suction flask and absorption tube, are inclined and fastened by a clamp so that the height between the table top and the last bulb of the absorption tube is about ten inches.

5. Procedure in a Diffusion Experiment.— The diffusion unit is loaded as previously described and all the connections, with one exception, are made, as described. The exception is that the left arm of the manometer M is not attached to an inlet of the upper diffusion chamber of the unit D. This inlet is left free. When the connections have been made, the

diffusion unit D is placed in the water bath B, as seen in Figure 3.

6. Establishing a Carbon Dioxide Atmosphere in the Upper Chamber and Dough Saturation Period.—The needle valve on cylinder C is opened. The handle of the pressure reducing valve is turned until a pressure of 30 pounds per square inch is indicated. The outlet of the reducing valve is opened slightly. The auxiliary fine-control valve is opened fully. Carbon dioxide is swept freely through the upper diffusion chamber for 5 minutes. After this sweeping period, the dough saturation period is allowed for by attaching the outlet of the upper diffusion chamber to the left arm of the manometer M. The pressure of gas on the dough membrane is allowed to rise to the pressure selected for the particular experiment, e.g. 6 cm. Hg. The auxiliary fine-control valve is closed slightly; only enough gas is allowed to escape to maintain constant pressure. This state of conditions obtains for 10 minutes.

7. Sweeping the Lower Chamber.—The three-way stopcock connected to the lower inlet of the lower diffusion chamber is turned so that connection is made directly to suction. The suction pump S is turned on, both arms of the ascarite tower T, are unclamped. Ascarite scrubbed air is pulled through the lower diffusion chamber for 15 minutes. This sweeping period proceeds simultaneously with the upper dome sweeping period and the membrane saturation period.

Meanwhile, the Brady-Meyer tube is temporarily withdrawn from the suction flask, and the latter is charged with 75 ml. standard alkali solution, which is approximately 0.1N to barium hydroxide and 0.2N to barium chloride. Fifty ml. distilled water are also run into the suction flask. Such a solution is an efficient carbon dioxide absorbent according to Martin and Green (31).

8. The Diffusion Period.—After the fifteen minute sweeping period, the three-way stopcock at the lower inlet of the lower diffusion chamber is turned so as to connect the absorption unit A into the train. The base solution is sucked up into the Brady-Meyer tube, so that eight bulbs are filled. Then the tube is twisted so that the stem just touches the remaining base in the flask. The rate of aspiration is controlled and kept slow by regulating the opening of the stopcock at the top of the Brady-Meyer tube. The pressure on the dough membrane is kept constant by allowing a trickle of gas to flow in the train. The diffusion experiment continues for any required length of time.

9. Final Sweeping Period.—After the experimental time has elapsed, the valve of the cylinder C is closed; the connections to the upper diffusion chamber are broken. Suction is allowed to pull air through the lower chamber and the absorption unit for an additional ten minutes. Then suction is stopped and the diffusion unit removed from the bath.

10. Estimation of the Amount of Gas Diffused.—The absorption unit is taken out of the train; the Brady-Meyer tube is washed with a stream of distilled water. The washings are allowed to fall into the suction flask. The base in the flask is titrated with 0.045N hydrochloric acid, using phenolphthalein as indicator. Knowing the initial acid equivalent of the base, the amount of carbon dioxide is calculated from the expression

$$\text{Vol. carbon dioxide absorbed} = \left(\frac{\text{Initial acid equiv.} - \text{Final acid equiv.}}{1000} \right) \times 509$$

The apparatus is disassembled. The dough holder and dough clamp must be cleaned after each diffusion experiment. When not in use, the cylinder C should be shut off, the handle on the pressure gauge should be released and both the fine control valves closed. Both outlets of the ascarite-filled tower T should be clamped off. In a diffusion experiment the membrane

thickness, the pressure, and the time of experiment are at the experimenter's choice.

11. Blank Determination.—The blank accounts for the amount of carbon dioxide introduced through aspiration of the lower chamber-absorption unit-system. The ascarite tower T is connected to the Brady-Meyer absorption unit in which 25 cc. standard alkali solution and 100 cc. distilled water is placed. The absorption unit is attached to suction. Both arms of the ascarite tower are unclamped and suction is turned on for 30 minutes. Level of the base in the Brady-Meyer tube and the rate of aspiration are the same as in a diffusion experiment. At the end of the half hour, the base is titrated and the volume of gas absorbed calculated as before. The value thus obtained is always corrected to apply to the particular diffusion period used and subtracted from the experimental value of carbon dioxide absorbed during a diffusion trial.

THEORY OF DIFFUSION

The passage of gas from one point to another within a medium is a process of diffusion. If boundaries be placed on the medium, we speak of diffusion of gas through the medium or permeation. A dough membrane is such a confined medium. It will be desirable to present a suitable solution of Fick's law of diffusion, and parts of the theory applicable to the particular case of diffusion under study. A monograph by Barrer (10) on diffusion has been used as a basic reference.

Two common types of diffusion are (a) stationary flow and (b) non-stationary flow. In stationary flow, gas under pressure diffuses through a barrier in such a way that no accumulation of matter occurs on the other side of the barrier. This discussion will be concerned with this type of diffusion. In study of non-stationary flow, similar conditions obtain initially, but matter does accumulate at the outgoing surface of the barrier. Thus, continued diffusion is opposed and eventually an equilibrium is set up.

Two familiar differential forms of Fick's law correspond to the stationary and non-stationary flow respectively:

$$P = - D \frac{\partial P}{\partial x} \dots\dots\dots(1)$$

$$\text{and } \frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} \dots\dots\dots(2)$$

where P is the permeability constant in cc. of gas diffusing at N.T.P. in unit time, through unit area of barrier 1 mm. thick, when a pressure differential of 1 cm. Hg. exists across the barrier; and D is the diffusion constant, in cc. of gas, diffusing in unit time at N.T.P. through a 1 cm. cube within the barrier when a pressure gradient of 1 cm. Hg. exists across the

cube.

$\partial p / \partial x$ is the pressure gradient across the medium.

$\partial p / \partial t$ is the change in the pressure across the medium with time, and

$\partial^2 p / \partial x^2$ refers to the accumulation of material at any point within the medium.

Thus equation 1 gives the rate of permeation in terms of pressure gradient and the diffusion constant, equation 2, refers to the accumulation of matter as a function of time.

An equation pertaining to steady states of flow may be derived by solving either of the equations. Barrer solves equation 2 by considering steady state diffusion through a plate. Now, there is no accumulation of matter, that is, as much solute leaves a given volume element as enters it; whence the term $\partial p / \partial t = 0$

Then also $D \partial^2 p / \partial x^2 = 0$ (3)

Suppose the plate has thickness l . If at the plate boundaries

$$p = p_1 \text{ at } x = 0 \text{ for all values of } t$$

$$\text{and } p = p_2 \text{ at } x = l \text{ for all values of } t$$

A general solution of equation 3 follows,

$$p = Ax + B \text{(4)}$$

If $x = 0$ and $x = l$, A and B may be eliminated and

$$\frac{p - p_1}{p_2 - p_1} = \frac{x}{l} \text{(5)}$$

where p is the steady state pressure at any value x .

The flow through unit area of plate then is

$$V \frac{\partial p_g}{\partial t} = -D \left(\frac{\partial p}{\partial x} \right)_{x=l} = D \frac{p_1 - p_2}{l} \text{(6)}$$

where p_g is the pressure of gas that has diffused into a volume V in time t .

If p_g be unity (atmospheric), equation 6 further simplifies; and the volume

of gas diffusing, in time t through unit area of barrier of unit thickness when unit pressure difference exists across the barrier is

$$V = D \frac{(p_1 - p_2)}{l} t \dots\dots\dots (7)$$

A similar solution may be obtained from equation 1. The pressure gradient $\frac{\partial p}{\partial x}$ may be solved for, if the pressures p_1 and p_2 at the ingoing and outgoing surfaces of the plate, and the total thickness l are known.

Integrating equation 1 with respect to x

$$Px = -Dp + k \dots\dots\dots (8)$$

P at any x is constant for all values of t

D and P are the same for all values of x

and when $x = 0, p = p_1$

$$\therefore 0 = -Dp_1 + k \dots\dots\dots (9a)$$

$$\text{or } Dp_1 = k \dots\dots\dots (9b)$$

when $x = l, p = p_2$

$$\therefore P_1 = -Dp_2 + k = -Dp_2 + Dp_1 \dots\dots\dots (10)$$

$$\therefore P = -D \frac{p_2 - p_1}{l} \dots\dots\dots (11)$$

$$\text{and } Vp_g = Pt = D \frac{p_1 - p_2}{l} t \dots\dots\dots (12a)$$

or, if $p_g = 1$

$$V = Ft = D \frac{p_1 - p_2}{l} t \dots\dots\dots (12b)$$

The deductions from equations 7 or 12b may be listed.

- (1) The rate of permeation or the volume of gas diffused in any period t, increases linearly with pressure difference.
- (2) The rate of permeation or the volume of gas diffused in time t is inversely proportional to the barrier thickness.
- (3) If the rate of permeation be constant, then the volume of gas diffusing is a linear function of the time.

From equation 11 it is apparent that the permeability constant is

proportional to the diffusion constant, and numerically equal to it in the special case when $\frac{(p_1 - p_2)}{1} = 1$.

Equations 7 and 12b hold only at constant temperature. A temperature change results in a change in the constant of diffusion, according to the expression,

$$D = D_0 e^{-E/RT} \dots\dots\dots(13)$$

where D_0 is the temperature independent factor

e is the Napierian constant

E is the activation energy of the diffusion process

R is the gas constant

T is the absolute temperature.

Analogously $P = P_0 e^{-E_1/RT} \dots\dots\dots(14)$

where P_0 is the temperature independent factor

E_1 is the activation energy of the overall permeation process.

The actual values of the activation energies of the diffusion or the overall permeation processes may be found, if two values of the diffusion or permeation constants are known at two different temperatures.

Then, $\log D_2/D_1 = E/2.303R \cdot T_2 - T_1/T_2 T_1 \dots\dots\dots(15)$

where D_1 and D_2 are the diffusion constants at temperatures T_1 and T_2 respectively.

The analogous expression, using values of P , yields E_1 , the activation energy of the overall permeation process. Once E and E_1 are known, equation 13 and 14 may be used to find the temperature independent components of the diffusion and permeation constants.

The evaluation of the activation energies E or E_1 is helpful in indicating the nature of the diffusion process. Diffusion systems may be broadly classified as

- (1) Inert
- (2) Adsorptive
- (3) Chemisorptive

In inert diffusion systems, where no physical or chemical interaction takes place between diffusing material and medium, the values of the activation energy are very low. In adsorptive diffusion systems, where physical adsorption occurs between diffusing agent and medium, the activation energy is of greater magnitude.

In chemisorptive diffusion systems, where actual chemical bonds are set up between diffusing agent and medium, the activation energy is of greater value still.

The diffusion process may involve more than one mechanism. For example, the mechanism of permeation in organic solids may be partially at least, (and in some systems, of which the system dough - carbon dioxide may be an example, to a great extent) solution of gas in the solid. The diffusion constant D consists of components each of which is characteristic of a particular mechanism of diffusion. Hence, to represent these constants in the Fick's law equation, the constant D must be split into two parts. Thus, equation 12b becomes

$$Pt = V = D \frac{\Delta p}{l} t.K \dots\dots\dots(16)$$

where K is the solubility constant in ml. of gas dissolving at N.T.P. in unit volume of membrane at atmospheric pressure and

D is the diffusion constant pertaining to the passage of gas through the medium by means other than solution in the medium.

Depending on the diffusion mechanism, either D or K may be negligibly small and may thus be eliminated from the equation. It is further possible that in some cases, the solubility constant K may be again divided to include, as an example, factors representing free and bound water.

The solubility constant, analogously to the diffusion and permeation constants, is temperature dependent, according to the equation

$$K = K_0 e^{-\Delta H/RT} \dots\dots\dots(17)$$

where K_0 is the temperature independent factor and

ΔH the heat of solution of gas in the medium.

Values of ΔH may be obtained in a way analogous to that in which the activation energies E and E_1 are found in equation 15. The values thus obtained, may be used in estimating the importance of the diffusion mechanism to which each pertains, in the particular permeation process under consideration.

Each system of diffusion must be studied individually and suitable theory adapted to the problem at hand.

MATERIALS AND METHODS

In the investigation of gas retention in doughs, a total of ten flour samples was used from which doughs were prepared. Table I, shows the particulars for the various flours used.

Table I—Particulars on Flours used in the Investigation of Carbon Dioxide Retention in Doughs

Sample No.	Type of Wheat	Crop Year	Flour Protein, % (14% Moisture)	Absorption, % (14% Moisture)	Flour Moisture, %	Remarks
1	Composite of 1 and 2 H.R.S. Wheat	1949	13.1	63.8	13.5	used in investigations of single factors or variables
2	Comp. 1 and 2 H.R.S. Wheat	1948	12.9	62.6	13.8	
3	Comp. 1 and 2 H.R.S. Wheat	1945	12.8	62.0	13.4	
4	2 C.W. Garnet	1948	11.3	62.2	13.7	
5	2 A. Durum	1948	10.8	60.6	13.2	used in investigations of miscellaneous flour series
6	Soft white Spring Wheat	1947	7.2	50.0	13.2	
7	1 A.R. Winter (Lethbridge)	1945	9.9	62.6	13.2	
8	3 Northern Low protein (Edmonton)	1946	7.5	58.4	13.5	
9	English	1948	9.1	56.8	13.1	
10	Australian	1948	8.1	55.2	12.7	

Sample 1, the composite 1 and 2 grade Hard Red Spring Wheat, was used in studies of the effects on carbon dioxide retention of variations in

1. pressure differential across dough membranes
2. membrane thickness
3. time of diffusion

4. temperature
5. water content of membranes

It was deemed desirable to use the same flour throughout this series of experiments and hence the flour was milled in some bulk and stored at ordinary laboratory temperatures. When used, the flour ranged in age from two weeks to five months.

In order to test the experimental method with a wide variety of material, a second series of experiments was carried out in which the gas retention property of doughs prepared from miscellaneous flour samples was studied. Flour samples 2 to 10 include the 1948 and 1945 composites, the 2 Canada Western Garnet, 2 Amber Durum, A Soft White Spring Wheat, 1 Alberta Red Winter, a 3 Northern low protein sample, English and Australian wheats.

All wheat samples were milled on an Allis Chalmers Experimental Mill. The protein contents of the milled flours were determined by the official Kjeldahl method (1). The designation, absorption per cent on 14 per cent moisture basis, needs some explanation. Absorptions were determined on the Farinograph, and were taken to 540 Farinograph units. This corresponds to baking absorption for the flour. That is, baking absorption by the Farinograph gives the amount of water that must be added to 100 g. of flour on a 14 per cent moisture basis. If the flour has a moisture content other than 14 per cent, a correction must be made. In the present case, the amount of water added was adjusted. Thus, for sample 1 the absorption is 63.8 on 14 per cent moisture basis. Since the flour has a moisture content of 13.5 per cent, it is necessary to add 64.1 ml. water to 100 g. of that flour to give a dough of baking absorption. The moistures were determined by the standard air oven method (2). All the flour samples were untreated, that is neither bleaching nor improving

agents were added, nor was the flour in any way physically treated.

In all cases the mixing was done in a Hobart mixer fitted with a small mixing bowl. Three minute mixing periods were employed. All doughs were mixed to baking absorption, corresponding to 540 Farinograph units, except where otherwise indicated. All other procedures such as membrane pressing, diffusion experiment and diffusion assay etc. have already been described in the section dealing with procedure for diffusion experiments.

RESULTS AND DISCUSSION

The experimental parts of the investigation of the diffusion of carbon dioxide through doughs may now be presented. The experiments may be said to fall into four phases. First, it was necessary to develop and test the details of the procedure for diffusion experiments, using the newly developed apparatus. Next, experiments had to be carried out to determine suitable working ranges in which the dependence of retention with a number of variables could be studied. The third phase of the investigation was a detailed study of the effect on the amounts of gas diffused of changes in pressure difference across membranes, membrane thickness, time of diffusion, temperature and water content of membranes. Finally, the developed method was applied in a study of the retention in doughs mixed from a wide variety of flour.

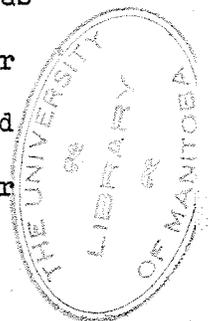
Only the more essential features of the first experimental part, the development and testing of the procedure, will be mentioned here. The second series of experiments, the delimiting of the working ranges will not be discussed separately, because its accomplishments are the basis of later experiments and are thus incorporated in them. The major portion of this section of the thesis will therefore be devoted to a presentation and discussion of results obtained in the latter two experimental parts and to a description of these experiments.

The development of the experimental procedure to the stage which is described in the section on "Procedure for Carrying Out Diffusion Experiments" involved a considerable amount of experimental work. The details of these experiments need not be labored; suffice it to say all steps incorporated in the procedure were the result of experimental findings.

Throughout the experiments, the measured amounts of diffused

carbon dioxide were small and therefore it was necessary to reduce the error to a minimum. Thus, rigid procedures for sweeping out the atmosphere in the diffusion unit both before and after diffusion trials had to be adopted. First, it was necessary to establish an atmosphere of carbon dioxide in the upper chamber prior to the experiment. It was found that this could be done in five minutes of rapid sweeping of the upper chamber with carbon dioxide, as described in the section on "Procedure". It was then found in the experiments that dough membranes required some time to become saturated with carbon dioxide gas. Therefore, prior to an experiment, a saturation period long enough to saturate the membranes at both high and low pressures, had to be allowed. For this reason dough membranes are subjected to the pressure differential to be used in the actual experiment for a period of ten minutes. The total "sweeping" period of the upper chamber of fifteen minutes has been found adequate for the type of investigations which were made in this study.

Because the amount of gas diffusing is small, it was found necessary to ensure that all atmospheric carbon dioxide be swept out of the lower diffusion chamber before the diffusion experiment. When this precaution was not taken, a large error was introduced in the result. A fifteen minute period was adopted; in this time the atmosphere in the lower chamber is replaced by ascarite-scrubbed laboratory air. A blank determination accounts for the atmospheric carbon dioxide sucked through the absorption unit during a diffusion experiment. The final sweeping out of the lower chamber after completion of the diffusion experiment, was set at ten minutes. It was desirable to sweep the lower chamber to clear all the diffused gas into the absorption unit, although a lengthy period of sweeping was not advisable because the dough membrane, no longer under



carbon dioxide pressure, began to desaturate. Thus, the longer the sweeping period, the greater the error due to carbon dioxide released by the desaturating of the dough. The ten minute period was thought to be a satisfactory compromise. While the preliminary experiments failed to show any change in diffusion with aging of dough, it was decided to use only membranes pressed from freshly mixed doughs; the membranes were given a fifteen minute rest period in addition to the reaction time of the experiment. Thus each step of the procedure was based on the results of suitable experiments. The method, as finally adopted, gave results precise to 0.1 ml. of carbon dioxide.

Attention may now be focussed on the two major experimental parts; the study of the effect on diffusion of a change in the five variables already outlined and a study of retention in doughs mixed from a wide variety of flour. As will become apparent, the good reproducibility of the results, and their logical significance, testify that the pains taken in the development of the procedure were well advised.

It is pointed out, that in the following presentation of the data, the amounts of carbon dioxide diffused will be expressed in terms of total volume of gas diffusing across a dough membrane 32 cm^2 in area and under specified conditions of thickness, time and pressure difference. This total volume is not the same as the value V defined in Fick's law of diffusion (see equation 7) but is, in all cases, proportional to it. Hence all conclusions drawn from the data, may be also interpreted from the point of view of Fick's law. In all cases the value V may be calculated from the value of the total volume of diffusion as actually measured.

Effect of Pressure Variation on Diffusion

A series of experiments was conducted to study in detail the relationship between volume of carbon dioxide diffused and the pressure difference across the membrane. A suitable range for this investigation was established in the preliminary experiments. In this series of experiments, pressure differences across the membranes of 0, 2, 6, 10 and 14 cm. Hg. were used. Pressure could be maintained to within 1 mm., by the method previously described. In all cases the atmosphere in the upper diffusion chamber was entirely carbon dioxide, in the lower chamber ascarite-scrubbed laboratory air. In the zero pressure difference trials, the pressure on both sides of the membrane was atmospheric. No attempt was made to study diffusion with carbon dioxide pressures in the upper chamber less than atmospheric, that is, using mixtures of air and carbon dioxide. The upper limit was set at 14 cm. Hg; beyond this pressure difference, membrane ruptures became a frequent hazard. Membrane thickness was $1 \pm .05$ mm; membranes were pressed from doughs mixed from flour sample 1, Table I; the temperature was thermostatically controlled at $30 \pm 0.1^\circ\text{C}$., the time of diffusion 60 min.; doughs were mixed to baking absorption. In the 2, 6, 10 and 14 cm. Hg. pressure difference trials, standard rest and sweeping period procedures were used as described in the section on "Procedure for Carrying Out Diffusion Experiments". The zero pressure difference trial was a special case and will be considered shortly. All experiments were done in triplicate. The data are presented in Table II.

Table II- Amounts of Carbon Dioxide Diffused Through Dough Membranes Under Varying Conditions of Pressure

Pressure Difference Across Membrane (cm. Hg.)	Amount of Carbon Dioxide Diffused (ml.)	Average (ml.)
0 ¹	6.4	6.4
0 ²	6.1	
0	6.5	6.2
0	6.1	
0 ³	6.4	
0	6.6	6.5
0	6.5	
2	6.8	
2	7.1	7.0
2	7.2	
6	8.1	
6	7.9	8.1
6	8.2	
10	9.5	
10	9.1	9.3
10	9.2	
14	10.5	
14	10.4	10.5
14	10.6	

¹ extrapolated

² standard procedure

³ amended procedure

The data are shown graphically in Figure 4, where the average of three diffusion values is plotted as ordinate against the pressure difference. A good straight line is obtained which shows that in the investigated range, the amount of gas diffused under specified conditions varies directly as the pressure difference across the membrane.

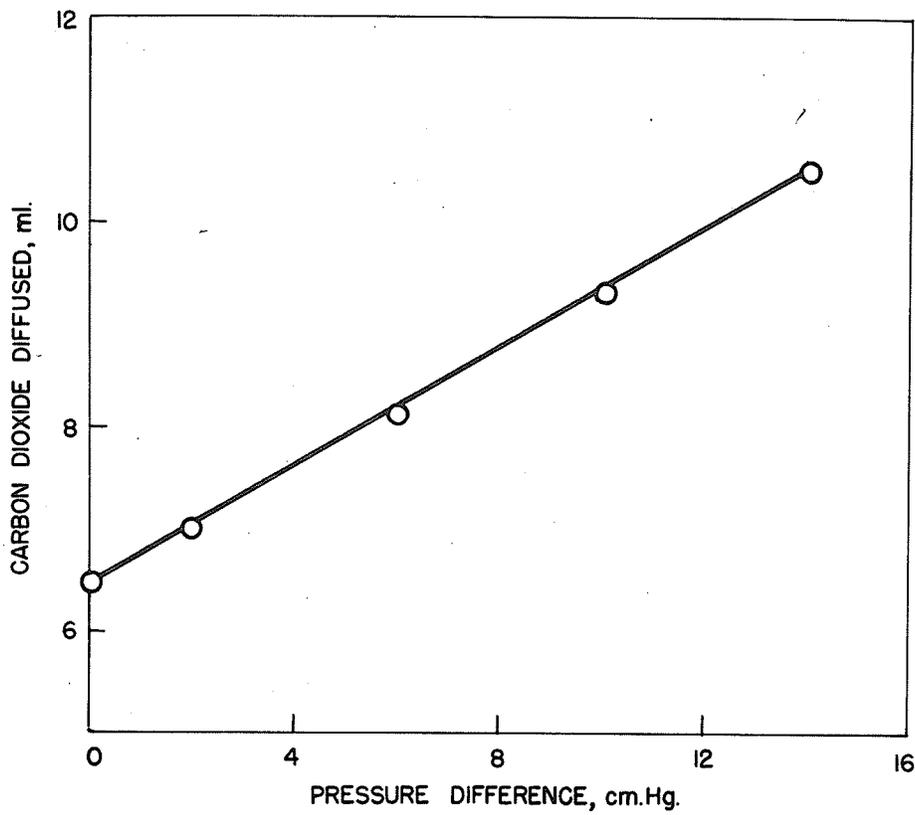


Figure 4.- Effect of change in pressure difference across dough membranes on amount of carbon dioxide diffused.

It will be recalled from the section on "Theory of Diffusion" that Fick's law of diffusion predicts that the volume of carbon dioxide diffusing across a membrane should be directly proportional to the pressure applied, i.e.

$$V \propto \Delta p \text{ where}$$

V = volume of gas diffused in given time as defined in the section on Theory

Δp = pressure differential across the barrier.

The experimental data presented thus substantiate the prediction of the law for the range of pressures studied.

The way in which the zero pressure difference value was obtained merits special attention. The 2, 6, 10 and 14 cm. trials were conducted first, and the zero value extrapolated from a plot of the four known values. Extrapolation gave a value of 6.4 ml. carbon dioxide diffused. In order to check on this value the zero pressure difference trials were done, using the regular experimental procedure. The obtained value of 6.2 ml. was somewhat low, though likely within the experimental error. To determine, however, whether the low result was not due to an inadequate upper chamber sweeping period, an experiment using an extended thirty minute sweeping period of the upper chamber was conducted. This gave a value of 6.4 ml. in good agreement with the extrapolated value.

The ordinate intercept value is of some interest. As has been pointed out, at zero pressure differential, the pressure in both diffusion chambers is atmospheric. However, the partial pressure of carbon dioxide is unity in the upper chamber and nearly zero in the lower, thus in terms of carbon dioxide, a pressure difference of approximately 760 mm. Hg. still exists across the membrane. We may use the intercept value to characterize the line shown in Figure 4, by a slope of + 0.29. The uninvestigated

portion of the plot of pressure difference against amount of gas diffused, is characterized by a slope of 0.084. Thus, it seems that the pressure vs. diffusion relationship is not consistently linear when such a long range of pressure variation is considered, although in the investigated region it assuredly is.

Effect of Membrane Thickness Variation

A series of experiments was conducted to study, in detail, the effect of changes in membrane thickness on amounts of carbon dioxide diffused. Preliminary experiments had outlined a suitable range for this study and consequently 3.0 mm.; 2.0 mm.; 1.0 mm. and 0.5 mm. membranes were used. The precision of setting the thickness was within .05 mm. An upper limit of 3.0 mm. was chosen, because beyond that thickness, diffusion was so slight as to make difficult accurate estimation of the amount of carbon dioxide diffused. Membranes thinner than 0.5 mm. could not be pressed with any degree of precision, hence this thickness is a lower limit for the membrane pressing method as developed. All membranes were pressed from freshly mixed doughs, made up to baking absorption. Flour sample 1, designated in Table I was used. The temperature was thermostatically maintained at $30 \pm 0.1^\circ\text{C}$.; the pressure was 6 ± 0.1 cm. Hg; the time of diffusion was 60 minutes. Standard rest period and sweeping period procedures were followed. All trials were done in triplicate and the data are presented in Table III.

Table III—Amounts of Carbon Dioxide Diffused Through Dough Membranes of Varying Thickness

Membrane Thickness (mm.)	Membrane Thickness (1/mm.)	Amt. Carbon Dioxide Diffused (ml.)	Average (ml.)
3.0		1.0	
3.0	.33	0.7	0.8
3.0		0.8	
2.0		2.5	
2.0	.5	2.3	2.5
2.0		2.5	
1.0	1	8.1	
1.0		8.0	8.1
1.0		8.2	
0.5		15.4	
0.5	2	15.9	
0.5		15.4	15.6

The diffusion values, each point representing an average of three determinations, were plotted on the ordinate against membrane thickness and a hyperbolic type of curve was obtained. This suggested an inverse relationship between membrane thickness and amount of gas diffusing. Thus, the mean diffusion values were plotted against reciprocal membrane thickness, as shown in Figure 5. A good experimental straight line was obtained indicating that

$$\text{Total } V \propto l^{-1}$$

where V = volume of gas diffusing in given time,
under specified conditions,

l = membrane thickness

It will be recalled, that this result is in agreement with the prediction of Fick's law of diffusion, which states that volume of gas diffusing varies inversely as the membrane thickness.

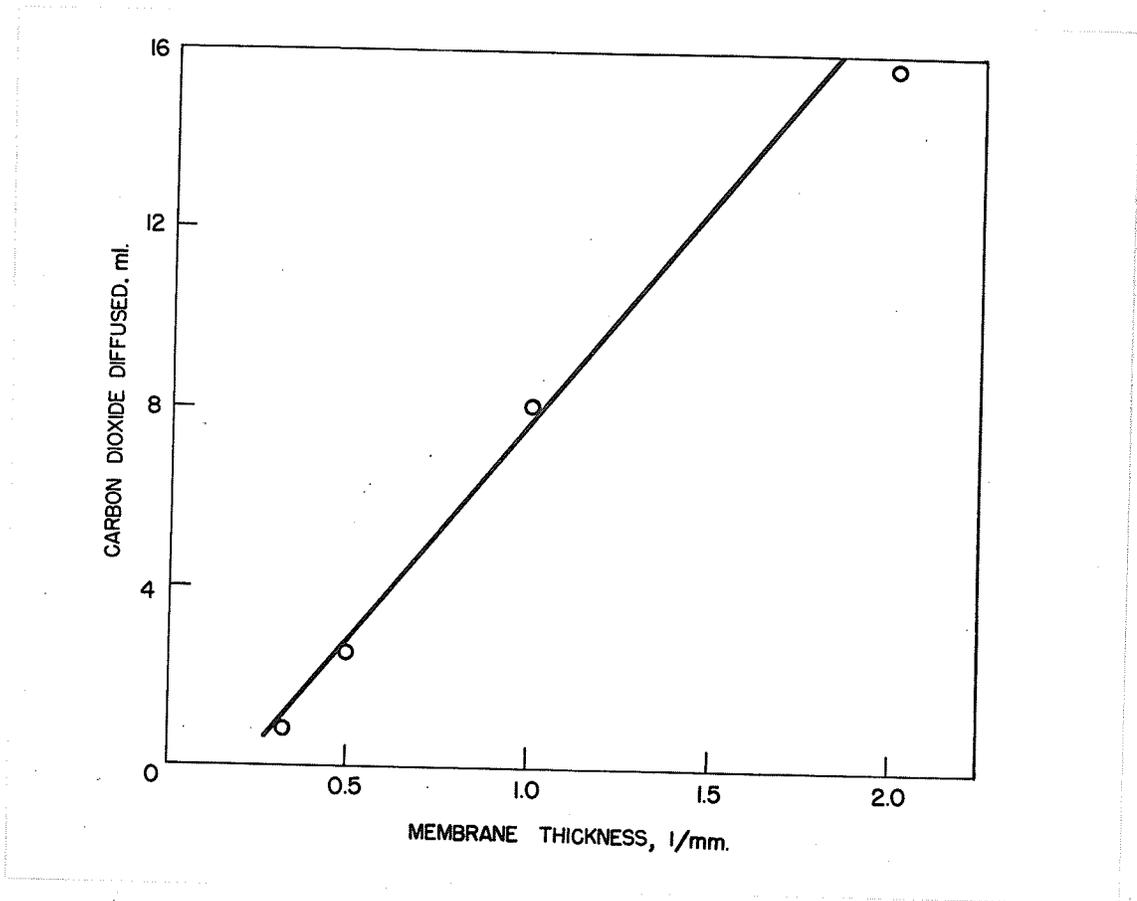


Figure 5.—Effect of change in dough membrane thickness on amount of carbon dioxide diffused.

Further inspection of Figure 5, reveals that less importance is attached to the result obtained for diffusion through membranes 0.5 mm. thick, than to the other results. This is done, because the likelihood of error in this result is considerably greater. The error in pressing membranes 0.5 mm. thick may be as great as 10 per cent. Finally, it is pointed out that the dough membranes are bounded on either surface by a piece of bolting cloth. This is done to support the membranes and also to prevent them from sticking to the pressing dies in the pressing process. In setting the apparatus for the "membrane pressing procedure", allowance is made for these pieces of cloth, so that the stated thickness is that of the dough membrane itself. However, although in membrane pressing the cloths are pressed well into the surfaces of membranes, it is possible that the bolting cloths add to the effective thickness of the barrier through which carbon dioxide must pass. This error would naturally be most evident in the 0.5 mm. thickness experiments. Since no significant deviation from the prediction of the diffusion law was shown in the experiments with membranes of greater thickness than 0.5 mm., it is assumed that the error due to the bolting cloths is slight. Also, from first principles, it would not be expected that at such low rates of permeation, the bolting cloth should offer appreciable resistance to gas flow.

Effect of Varying Time of Diffusion

A series of investigations was carried out to study, in some detail, the effect of a variation in the time of diffusion on amounts of carbon dioxide diffusing. The diffusion periods used in this investigation were those found most useful in the preliminary set of experiments and included, 10, 20, 30, 60, 120 and 180 minute periods. It was thought

desirable to investigate the initial stages of diffusion thoroughly, hence the three short period trials were included. The upper limit was set at 180 minutes; longer trials seemed unnecessary and were inconvenient. All membranes were pressed to 1 ± 0.05 mm. thickness from doughs, freshly mixed to baking absorption from flour sample 1, as described in Table I. Pressure difference was 6 ± 0.1 cm. Hg.; the temperature $30 \pm 0.1^\circ\text{C}$. Standard rest period and sweeping procedures were used and all trials were done in triplicate. The data are presented in Table IV in the columns headed "usual conditions". The "higher humidity" trials will be discussed later.

Table IV—Amounts of Carbon Dioxide Diffused in Various Diffusion Periods

Time of Diffusion min.	Amount of Carbon Dioxide Diffused		Averages, ml.	
	Usual Conditions ml.	Higher Humidity ml.	Usual Conditions	Higher Humidity
10	2.0	2.0		
10	2.0	2.0	2.0	2.0
10	2.1	2.1		
20	3.3	3.2		
20	3.3	3.3	3.4	3.4
20	3.7	3.7		
30	5.2	5.3		
30	5.4	5.2	5.2	5.2
30	5.1	-		
60	8.2	7.6		
60	8.0	8.5	8.1	8.3
60	8.1	8.6		
120	11.3	12.7		
120	10.9	13.0	11.3	12.9
120	11.5	13.1		
180	14.5	16.7		
180	18.4	16.6	15.0	16.5
180	15.3	16.2		

The two sets of results are shown graphically in Figure 6. For the moment, attention may be focussed on the "usual conditions" curve. In Figure 6, diffusion values, each an average of three determinations, are

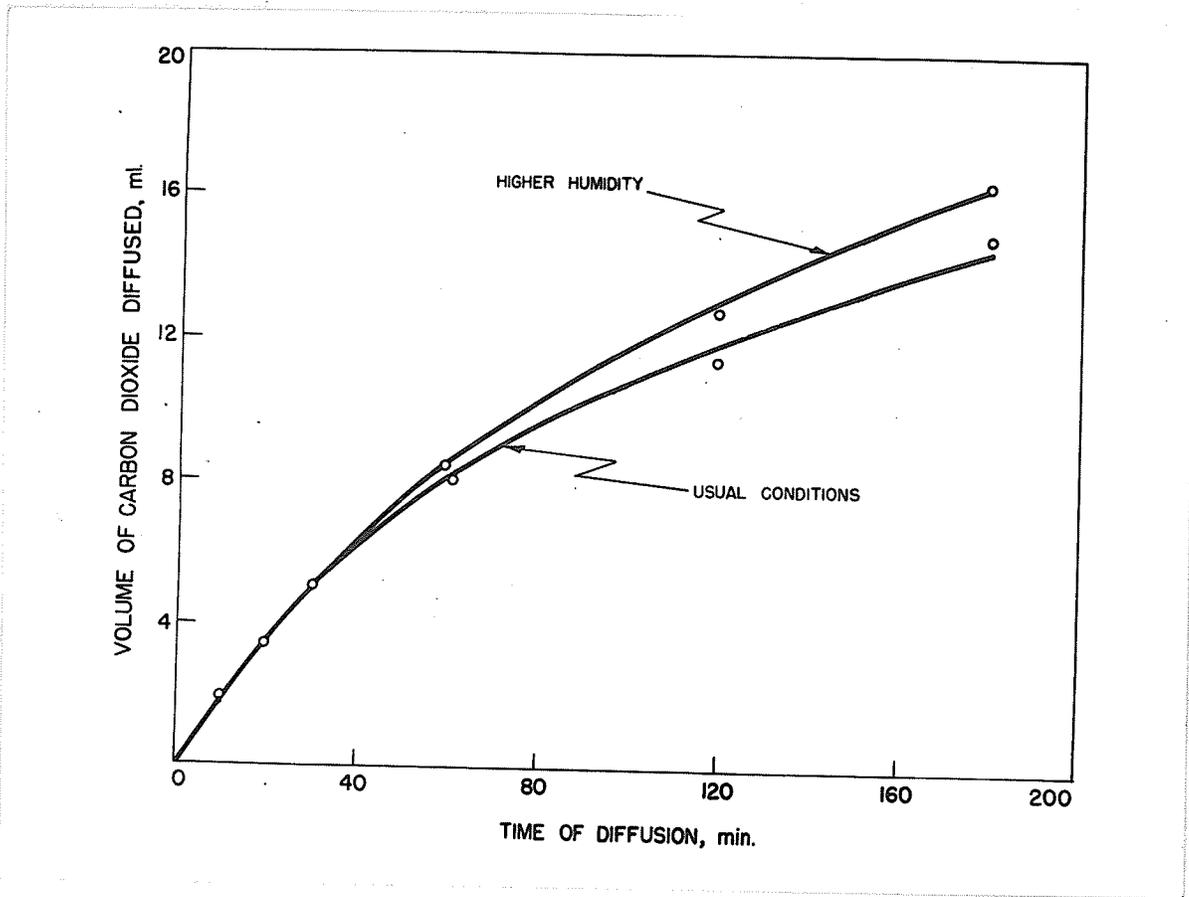


Figure 6.- Effect of change in time of diffusion on amount of carbon dioxide diffused.

plotted against the time of diffusion and a smooth curve is obtained. The interpretation of such a curve presents some difficulty. It is noted that the curve is markedly flat in the initial portion, indicating that a linear relationship between time of diffusion and amount of gas diffusing exists. Thereafter, the rate of diffusion seems to decrease with increase in time of diffusion, as indicated by the falling off the curve. Toward the outer extreme of the curve, a gradual flattening seems to appear.

It will be remembered, that Fick's law of diffusion, formulated in equation 12b, predicted that the time of diffusion should be directly proportional to the volume of gas diffusing, that is $V \propto t$. The experimental results show that this is so in the initial stages of diffusion, but that a subsequent deviation from linearity occurs. Thus the results present a limitation to Fick's law characteristic of the diffusion system dough-carbon dioxide.

The deviation from linearity and thus the limitation to Fick's law may be due to a number of physical or chemical changes in the dough itself. The action of atmospheric oxygen on the dough may give rise to some reaction cutting down the diffusion rate; or the deviation might be due to the change in pH of the dough as the diffusion experiment proceeds. Another cause of the deviation might be the interaction of carbon dioxide with amino groups of the dough protein giving rise to carbamino type of compounds. Otherwise gluten layer formation on the membrane surface, might account for the deviation, on the analogy of surface active agents. Available data are insufficient to allow conclusions to be made as to the true cause of the deviation. One possible cause of the observed deviation was investigated to some extent.

It was noted that in diffusion trials exceeding 30 minutes, a dry "skin" or crust formed on the membrane surfaces. It was postulated

that this crust formation resulted from a desiccation of the membrane due to water evaporation. The crust was less permeable to carbon dioxide than fresh dough, thus as the crust was formed a gradual decrease in the rate of diffusion was noted.

In order to test this hypothesis "higher humidity" trials were done. It was thought that if the humidity in the diffusion unit were raised, desiccation would be retarded and thus the deviation from linearity in the V vs. t plot should occur only after a lengthier diffusion period and would be less drastic. Two additional humidifiers were introduced into the apparatus assembly (see Figure 3). One humidifier was inserted between the cylinder C and the diffusion unit, so that incoming gas was humidified thoroughly; the second was inserted between the ascarite tower T and the diffusion unit, so that air used to sweep out the lower diffusion chamber was also humidified. Using the additional humidifiers, the entire time of diffusion series of experiments was repeated. The results are tabulated in Table IV and presented graphically in the "higher humidity" curve of Figure 6. The new curve is very similar to the previous one from the origin to about the 60 minute mark. Thereafter higher humidity has caused a discernible increase in the amount of gas diffused, showing that to some extent at least, membrane desiccation causes deviation from an essentially linear V - t relationship. The change in the amount of carbon dioxide diffused is not great enough to verify an hypothesis that deviation from linearity is due to desiccation alone. A broader viewpoint must be adopted. In all likelihood the relationship between time of diffusion and amount of gas diffused is dependent on this, the forementioned other factors, and additional factors not mentioned here.

It appears evident, however, that the diffusion constant D is some function of the time of diffusion.

In the experiments described above, the time of diffusion was always sixty minutes. Figure 6 shows that over the period of diffusion from zero to about sixty minutes only little deviation from a linear relationship occurs. Hence for the time of diffusion range of practical interest in this case, the relationship $V \propto t$ may be said to hold approximately.

The Effect of Temperature Change

A detailed study of the effect of temperature change on the amount of gas diffusing through dough membranes was carried out. In the study, temperatures used were 15, 20, 25, 30, 32.5 and 35°C. From preliminary experiments, it was apparent that this range of temperatures was wide enough to give the study adequate scope. In all trials, doughs were mixed to baking absorption and pressed to $1_{-0.05}^{+}$ mm. thickness; flour sample 1, designated in Table I, was used; the pressure difference was $6_{-0.1}^{+}$ cm. Hg.; time of diffusion 60 minutes; standard rest and sweeping period procedures were employed. All trials were done in triplicate and the results are tabulated in Table V.

The results are shown graphically in Figure 7. There, diffusion values, each point representing the mean of three trials, are plotted on the ordinate against temperature. Evidently as the temperature increases, the volume of gas diffusing decreases. The rate of decrease in the diffusion seems fairly uniform in the temperature range 15 - 30°C., but from the appearance of the curve, it is judged that above 30°C., some change in the dough occurs which complicates the diffusion mechanism to a marked extent. It is also rather startling to observe a decrease in diffusion with temperature rise, since on first consideration of gas kinetics it might be predicted that the rate of diffusion should increase with temperature rise.

Table V- Amounts of Carbon Dioxide Diffused at Various Temperatures

Temperature, °C.	Amount of Gas Diffused (ml.)	Average (ml.)
15.0	11.0	11.2
15.0	11.2	
15.0	11.3	
20.0	10.6	10.5
20.0	10.3	
20.0	10.4	
25.0	9.0	9.2
25.0	8.4	
25.0	9.1	
30.0	8.2	8.1
30.0	8.0	
30.0	8.1	
32.5	4.8	4.8
32.5	4.7	
32.5	5.0	
35.0	4.1	4.0
35.0	4.2	
35.0	3.8	

The decrease in diffusion with temperature increase suggests that the mechanism of the diffusion of carbon dioxide through doughs involves the solution of carbon dioxide in water. A major portion of dough is of course water, and it is well known that the solubility of carbon dioxide in water decreases with a temperature rise. The decrease in diffusion with temperature rise may then be accounted for, if it is postulated that in diffusion, carbon dioxide dissolves in the water of the dough, is transported across the membrane and subsequently released. A comparison of the curve shown in Figure 7 with the curve shown in Figure 8 proves instructive. Figure 8 shows a curve obtained when the volume of carbon dioxide dissolving per unit volume of water (22) is plotted against temperature. The temperatures are the same as those used in the experiments on diffusion. The two curves resemble each other

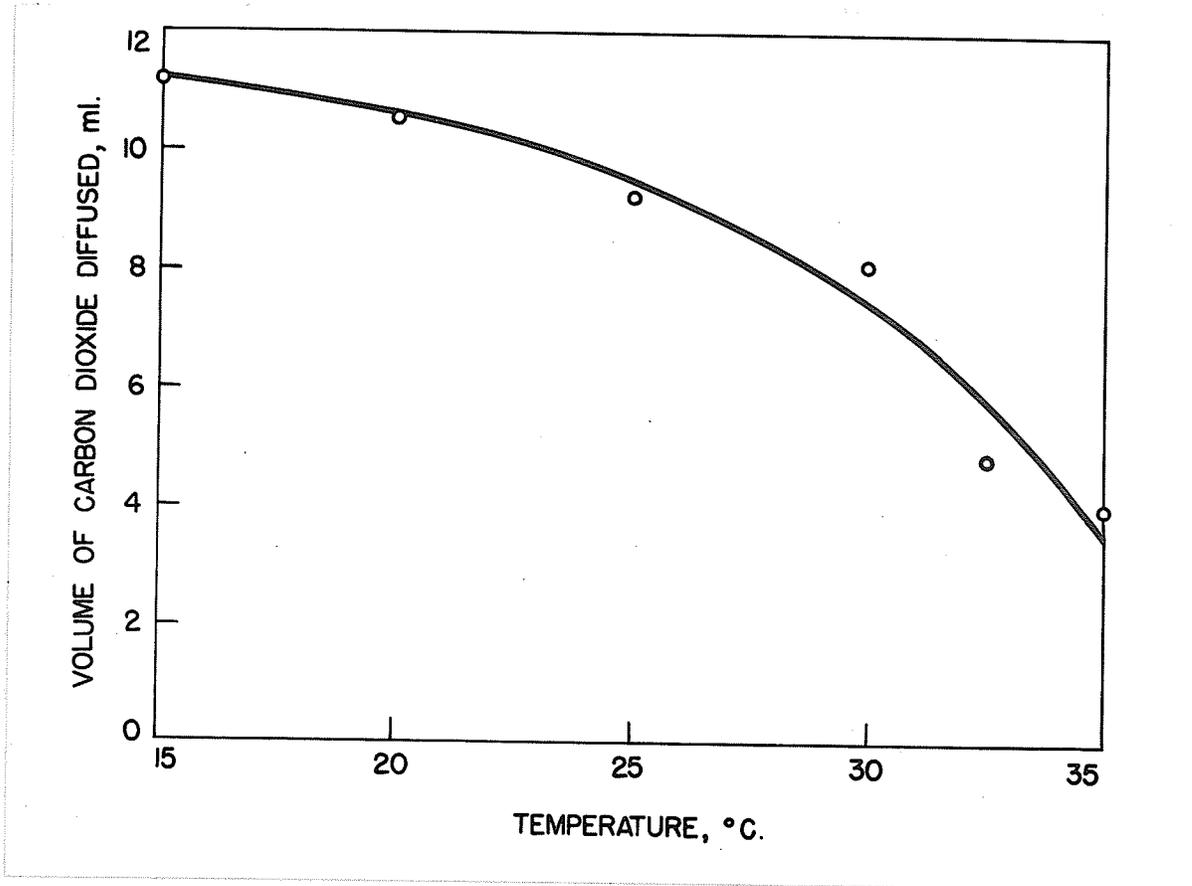


Figure 7.—Effect of change in temperature on amount of carbon dioxide diffused.

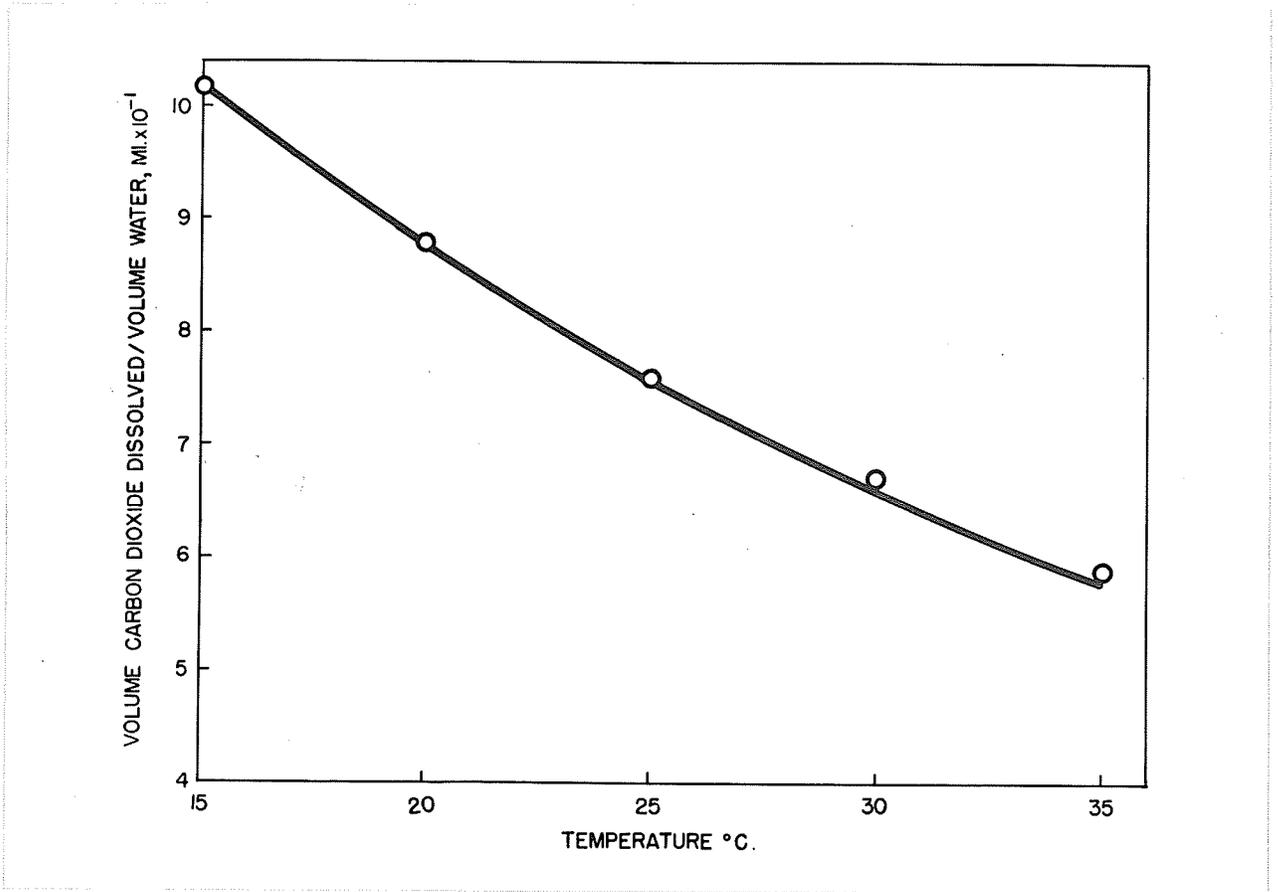


Figure 8.— Solubility of carbon dioxide in water at varying temperatures.

closely in the temperature range 15 - 30°C. In other words, in this range, the decrease in diffusion seems paralleled by the decrease in the solubility of carbon dioxide in water. Above 30°C., the two curves become discrepant. Thus in the range 15 - 30°C., it appears that the decrease in diffusion might be due to the decreased solubility of carbon dioxide in the water component of dough. Above 30°C., it can only be assumed that the solution of carbon dioxide in water is not the dominant mechanism of diffusion.

The interpretation of the observed result from the point of view of the theory of diffusion is most interesting; a full exposition of this interpretation will be presented in the section on General Discussion. Suffice it to say, at this point, that although Fick's law is isothermal as shown in equation 12b, the temperature variation is accounted for by the temperature dependence of either the permeability constant P or the diffusion constant D . Attention to the dependence which is entirely analogous for the two constants, has been drawn by Barrer (10); it may be expressed in the equation

$$P = P_0 e^{-E_1/RT} \quad (14)$$

The equation indicates that the overall process of permeation of carbon dioxide through dough requires energy. A calculation of this energy will indicate the mechanism involved in the diffusion process. In order to support the postulated mechanism of solution of carbon dioxide in water, the calculated value of E_1 should approximate the heat of solution of carbon dioxide in water.

Finally, more direct evidence of the importance of water in the diffusion of carbon dioxide through dough membranes will be presented in

the following section with a discussion of the effect of varying water content of membranes on amounts of gas diffusing.

The Effect of Variable Water Content

In this, the last of the studies showing the relationship between diffusion and a number of the important physical factors influencing diffusion, the effect of changing the water content on amount of gas diffusing through a dough membrane was studied in more detail. In this study, doughs were mixed by adding varying amounts of water to 100 g. of flour sample 1, described in Table I. Thus, the absorption values of the doughs were 45.0, 48.0, 51.0, 54.0, 56.0, 58.0, 60.0, 62.0 and 64.1 ml. water. However, it is perhaps more fundamental to consider the overall water content of the dough membranes. Since flour sample 1 had a moisture content of 13.5 per cent, the water contents of the membranes used in this study were 58.5, 61.5, 64.5, 67.5, 69.5, 71.5, 73.5, 75.5 and 77.6 per cent. Doughs of higher water content than 77.6 per cent were not used, for such doughs became very sticky and could not be pressed into good membranes by the standard procedure. The water content of 77.6 per cent yields doughs of baking absorption for flour sample 1, and such doughs were used in the previously described studies. A convenient lower limit of 58.5 per cent water content was adopted, because below this value doughs became too stiff to be pressed into membranes in the usual way. In all trials the pressure difference was 6 ± 0.1 cm. Hg.; the time of diffusion 60 minutes; temperature $30 \pm 0.1^\circ\text{C}$; the membrane thickness 1 ± 0.05 mm. Standard rest and sweeping period procedures were used. The experiments were carried out in triplicate and the data are presented in Table VI.

Table VI—Effect of Change in Water Content of Doughs
on Amount of Carbon Dioxide Diffused

Water Content, %	Amount of Carbon Dioxide Diffused, ml.	Average, ml.
77.6	8.1	
77.6	8.0	8.1
77.6	8.2	
75.5	6.9	
75.5	6.6	6.9
75.5	7.1	
73.5	5.8	
73.5	5.5	5.8
73.5	6.0	
71.5	5.5	
71.5	5.1	5.2
71.5	5.0	
69.5	5.0	
69.5	5.0	5.1
69.5	5.3	
67.5	3.6	
67.5	4.1	3.9
67.5	3.8	
64.5	3.1	
64.5	2.6	2.8
64.5	2.7	
61.5	1.9	
61.5	2.3	2.2
61.5	2.4	
58.5	2.5	
58.5	2.1	2.2
58.5	2.2	

The results are shown graphically in Figure 9. Here diffusion values, each point being a mean of three trials, are plotted as ordinates against water content. A smooth curve is obtained which shows that the amount of gas diffusing through dough membranes is greatly reduced as the water content of the membranes is decreased. An interesting feature of Figure 9, is the apparent levelling out of the curve in the extreme lower ranges of water content--from 61.5 per cent downward.

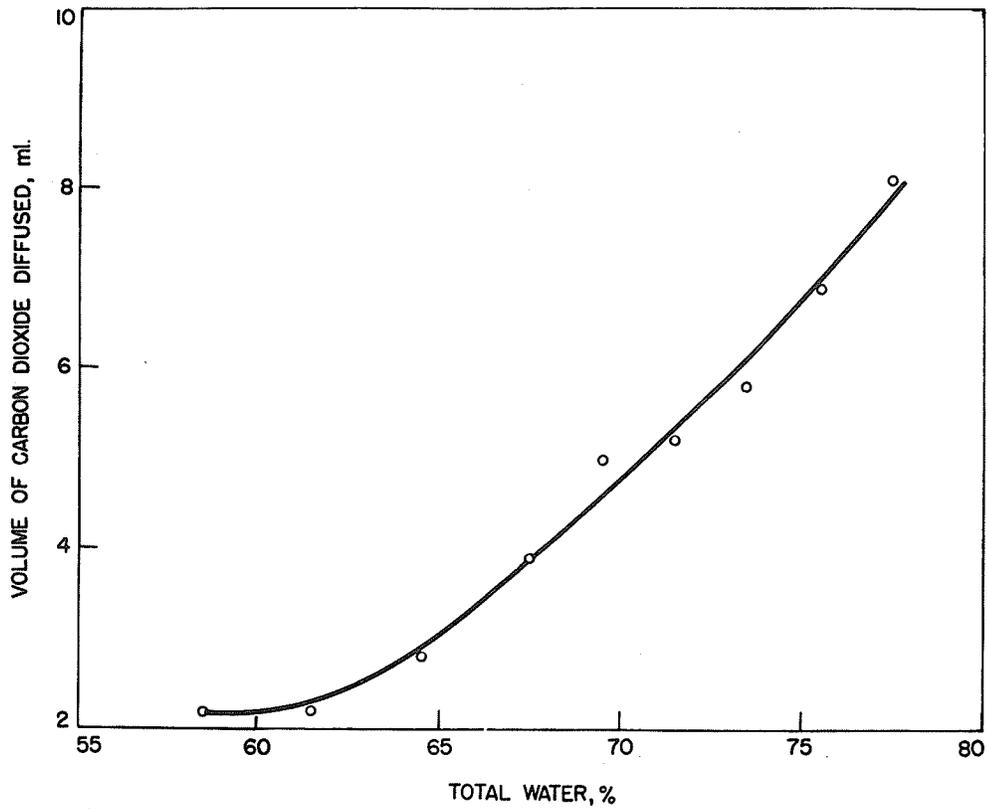


Figure 9.—Effect of change in total water content of doughs on amount of carbon dioxide diffused.

The study presents direct evidence of the important role that water plays in the transfer of carbon dioxide through dough. The results appear to support the diffusion mechanism hypothesis outlined in the study of the effect of temperature variation on diffusion, wherein carbon dioxide dissolves in the water of the dough membrane and thus diffuses. Clearly, the less water available in the dough, the smaller the volume of gas that can dissolve and hence the smaller the amount of gas diffused during a specific diffusion period. It must be pointed out that the shape of the curve in Figure 9, can be accounted for in hypothesis. A presentation and discussion of the hypothesis will follow in the section on General Discussion.

It will be remembered that Fick's law of diffusion makes no prediction of the dependence of rate of diffusion on water content. Since, however, this dependence has been demonstrated, it appears certain that the permeation constant P or the diffusion constant D is a function of the water content; if we designate the latter by the symbol C_w then

$$P = f (C_w) \dots\dots\dots(18)$$

In the section on General Discussion, this dependence will be discussed in more detail.

Carbon Dioxide Diffusion in a Wide Variety of Doughs

The final experimental section deals with the application of the developed method to a study of carbon dioxide diffusion through, and hence retention in, doughs mixed from a wide variety of flours. In the study, flour samples 2 to 10 inclusive, as characterized in Table I, were used. As that Table shows, these flours differed greatly in the type of wheat they were milled from, ranging from Hard Red Spring, Garnet and Durum wheats, to Winter and Soft Spring, English and Australian wheats.

The flours also differed in protein content and age, and were grown under diverse environmental conditions. Nothing is known of the dependence of the diffusibility of gas through dough with these variables. For this reason, this study was exploratory in nature, and designed to give only a broad view of the variation of carbon dioxide diffusion in these, randomly chosen flour types.

It was imperative that the experimental conditions be kept uniform throughout this study. A decision had to be made in choosing the water content to be used as a basis for comparison in these experiments. It will be remembered, that previous experiments have shown a great variation of diffusion with water content. There were two possibilities: from the point of view of the baker, it was most interesting to study the diffusion at the baking absorption of each of the flours. At such constant consistency the water content of the doughs would vary appreciably. On the other hand, more fundamental and easily comparable data would be obtained if a constant total water content were chosen as basis for comparison. To give this study somewhat broader scope, diffusion studies were made at both constant consistency (baking absorption) and constant water content, for each of the doughs. The baking absorption for each flour sample was determined by the Farinograph as previously described. It is here expressed in the more convenient terms of ml. water added to 100 g. of flour to give the desired dough consistency. The lowest of the absorption values, 50.5 ml. for sample No. 6, the soft white spring wheat (see Table I), was taken as a basis for choosing the constant water content of the doughs. Since the absorptions are calculated on a 14 per cent moisture basis, the constant water content was chosen at 64.5 per cent

(that is $50.5 + 14.0$). Thus, to 100 g. of flour sample 6, one would have to add $50.5 + (14 - \text{actual moisture of flour No. 6})$
 $= 50.5 + (14 - 13.2) = 51.3$ ml. water in order to arrive at the required 64.5 per cent water content. The time of diffusion was always 60 minutes; the temperature $30 \pm 0.1^\circ\text{C}$., the pressure differential 6 ± 0.1 cm. Hg.; membrane thickness 1 ± 0.05 mm. Standard rest and sweeping periods were employed. All experiments were done in triplicate, and the results are shown in Tables VII and VIII. In Table VII the results obtained with baking absorption as comparison basis are shown. Flour samples are arranged in order of increasing amounts of gas diffusing.

The amounts of gas passing through doughs mixed to baking absorption, follow no easily interpreted pattern. The order in which the flours fall is quite inconsistent and random. It must be assumed that the variable water content is largely responsible for the random distribution of the diffusion values.

The data obtained with constant water content as basis of comparison are presented in Table VIII. Again the flours are arranged in order of increasing amounts of gas diffused. Since the important water content variable was held constant in these experiments, it would be expected that the results presented in Table VIII should be the more easily interpretable. Such is indeed the case. The flours may be considered in a number of groups. Thus, the first group, including the 3 Northern low protein flour, the Hard Red Spring Wheat Composite (1948) and the 1 Alberta Red Winter wheat flours, yield doughs through which only small amounts of carbon dioxide will pass. These doughs, then, show a relatively high gas retaining capacity. The 2 Amber Durum wheat flour yields a dough with the somewhat higher amount of 2.9 ml. of gas diffusing. There follows the group of flours, including the Hard Red Spring Composite 1945, Australian and 2 Canada Western Garnet, which give doughs of moderate diffusibility of about 3.1 ml. These doughs show

Table VII- Amounts of Carbon Dioxide Diffusing Through
a Variety of Doughs Mixed to Baking Absorption

Flour Sample No.	Type of Wheat	Total Water Content, %		Amount of Carbon Dioxide Diffusing ml.	Average, ml.
		% Absorption on 14% Basis	Total Water Content, %		
7	1 A. R.	63.2	77.2	3.8	
7	Winter	63.2	77.2	4.0	4.0
7	1945	63.2	77.2	4.1	
10	Australian	56.0	70.0	4.6	
10	1948	56.0	70.0	4.7	4.7
10		56.0	70.0	4.7	
8	3 Northern	58.8	72.8	5.3	
8	Low Protein	58.8	72.8	5.2	5.3
8	1945	58.8	72.8	5.3	
3	1-2 H.R.S.	62.5	76.5	5.1	
3	Composite	62.5	76.5	5.5	5.5
3	1945	62.5	76.5	5.7	
6	Soft White	64.5	64.5	5.9	
6	Spring	64.5	64.5	5.8	5.8
6	1947	64.5	64.5	5.6	
2	1-2 H.R.S.	62.7	76.7	6.5	
2	Composite	62.7	76.7	5.8	6.3
2	1948	62.7	76.7	6.7	
4	2 C. W.	62.4	76.4	6.6	
4	Garnet	62.4	76.4	6.8	6.1
4	1948	62.4	76.4	6.7	
9	English	57.3	71.3	6.7	
9	1948	57.3	71.3	6.9	6.7
9		57.3	71.3	6.3	
5	2 A. Durum	61.2	75.2	8.4	
5	1948	61.2	75.2	7.5	7.5
5		61.2	75.2	7.3	

Table VIII—Amounts of Carbon Dioxide Diffusing Through
Variety of Doughs Mixed to Constant Water Content

Flour Sample No.	Type of Wheat	Total Water Content, %		Amount of Carbon Dioxide Diffusing ml.	Average, ml.
		% Absorption on 14% Basis	Total Water Content, %		
8	3 Northern	50.5	64.5	2.7	2.7
8	Low Protein	50.5	64.5	2.7	
8	1948	50.5	64.5	2.6	
2	1-2 H.R.S.	50.5	64.5	2.7	2.8
2	Composite	50.5	64.5	2.7	
2	1948	50.5	64.5	3.0	
7	1 A. R.	50.5	64.5	2.7	2.8
7	Winter Wheat	50.5	64.5	2.9	
7	1945	50.5	64.5	2.8	
5	2 A. Durum	50.5	64.5	3.1	2.9
5	1948	50.5	64.5	2.8	
5		50.5	64.5	2.9	
3	1-2 H.R.S.	50.5	64.5	3.4	3.1
3	1945	50.5	64.5	3.1	
3		50.5	64.5	3.0	
10	Australian	50.5	64.5	3.1	3.1
10	1948	50.5	64.5	3.1	
10		50.5	64.5	3.0	
4	2 G. W.	50.5	64.5	3.5	3.2
4	Garnet	50.5	64.5	3.2	
4	1948	50.5	64.5	3.1	
9	English	50.5	64.5	4.0	4.0
9	1948	50.5	64.5	3.7	
9		50.5	64.5	4.1	
6	Soft White	50.5	64.5	6.0	6.0
6	Spring	50.5	64.5	6.0	
6	1947	50.5	64.5	6.0	

intermediate retention capacity. Finally, there are two flours whose doughs show a large and a very large amount of gas diffused--the English and the Soft White Spring.

It might be expected on the basis of their performance that those flours, generally classified, as strong that is, the Hard Red Spring wheat composites, the Alberta Red Winter, the Durum and Garnet, should have greater retention capacities than such weak flours, as English, Australian and Soft White Spring. This is borne out reasonably well by the results shown in Table VIII. There are a number of puzzling features in the results; the excellent showing of the low protein flour (sample No. 8), the good showing of the Australian flour and the relatively poor showing of the 1945 composite (sample 3), and the Garnet. These apparently spurious results, must be attributed to the interfering effects of other factors, which cannot be determined at this time. In general, this set of results does show that with a full knowledge of the history of a flour sample, the developed method of diffusion measurement may contribute to the methods of assessing retention capacity, if the water content of the test doughs be controlled.

GENERAL DISCUSSION

All the experimental results have now been presented, and discussed to some extent. A number of broader and more general implications of these results, which could not be discussed in detail in the section dealing with the individual experimental studies, are presented now. Included here are calculations of activation energy for the process of diffusion, as added evidence for the postulated diffusion mechanism of the solution of carbon dioxide in the water component of dough. A more detailed analysis of the effect of water content variation on diffusion is presented here, and certain adaptations of Fick's law of diffusion to the present problem are made. Some attempt is also made to place dough into an appropriate permeability group. Finally, some remarks link this research to the problem of gas retention in fermenting doughs, and indicate further paths of investigation to be followed.

It will be remembered that in the study of the change in diffusion with temperature variation, it was found that the amounts of gas diffusing under set conditions, decreased with a rise in temperature. This indicated that the transfer of carbon dioxide across dough membranes was effected by the gas dissolving in the water component of dough, being transported in the liquid phase and eventually released again. Support for the hypothesis was drawn from the similarity of the temperature vs. diffusion plot (Figure 7) and the solubility of carbon dioxide in water vs. temperature plot (Figure 8). It was also noted that this mechanism of diffusion could account for the observed results only in the temperature range 15 - 30°C. Beyond 30°C., the plots shown in Figures 7 and 8 became discrepant.

Further evidence of the importance of water in diffusion was seen in the water content variation of diffusion (Figure 9).

Additional support for the postulated mechanism may be obtained from a calculation of the energy of activation for the process of diffusion of carbon dioxide across a dough membrane. This may be done by considering the temperature dependence of diffusion presented in the section on Theory of Diffusion. It is convenient to formulate, after Barrer (10), this dependence in terms of the permeability constant P

$$P = P_0 e^{-E_1/RT} \dots\dots\dots(14)$$

The activation energy is a summation of component activation energies, one for each step in the diffusion mechanism. If then, the proposed solution mechanism did indeed account for the major portion of diffusion in the temperature interval 15 - 30°C., then E_1 should be of the same order of magnitude as the heat of solution of carbon dioxide in water in the specified temperature range. The activation energy may be calculated from the integrated form of equation 14 which yields the expression

$$\log \frac{P_2}{P_1} = \frac{E_1}{2.303R} \cdot \frac{T_2 - T_1}{T_1 T_2} \dots\dots\dots(15b)$$

Where P_1 and P_2 are known values of the permeability constant at the temperatures T_1 and T_2 .

From the available data, it is not possible to calculate values for the permeability constant P, as defined in the section on Theory. However, certain changes can be made in the definition of the constant P, which make it possible to evaluate it and therefore to calculate the activation energy. It may be assumed that the measured volume of carbon

dioxide diffused is proportional to the permeability constant in the pressure difference range 76 to 90 cm. Hg. This approximation will, of course, cause E_1 to be of qualitative significance only. A further simplification results from the fact that only the ratio of P_2/P_1 is involved, whence it follows that provided P_2 and P_1 are expressed in the same units, the value of the activation energy is quite independent of the units of P . Caution must be exercised that the values of the permeability constant be calculated from data obtained in the temperature range 15 to 30°C.; also that the increment ($T_2 - T_1$) be small, for temperature independence of E_1 must be assumed.

The data presented in Table V, show the measured volume of diffused gas. This quantity may be symbolized as V' ml./hr./32 cm²/mm. thickness at 82.0 cm. Hg. pressure difference, at the stated temperature.

$$\text{But } \frac{V'}{A \times t} = P \text{ at the stated pressure difference}$$

(where A = area of membrane and
 t = diffusion time)

$$\text{and } \frac{V'}{A \times t} \propto P \text{ per cm. Hg. pressure difference in}$$

the range 76 to 90 cm. Hg.

Let $T_1 = 20^\circ\text{C.}$ and $T_2 = 30^\circ\text{C.}$

$$\text{Then } P_1 \propto \frac{V_1'}{32 \times 3600}$$

$$\propto \frac{10.5}{115,200}$$

$$\approx 9.1 \times 10^{-5} \text{ ml./sec./cm}^2\text{/mm./cm. Hg.}$$

in the range 76 to 90 cm. Hg.

$$\text{And } P_2 \propto \frac{V_2'}{32 \times 3600}$$

$$\propto \frac{8.1}{115,200}$$

$$\propto 7.0 \times 10^{-5} \text{ ml./sec./cm.}^2\text{/mm./cm. Hg.}$$

in the range 76 to 90 cm. Hg.

$$\text{Hence } \log \frac{7.0 \times 10^{-5}}{9.1 \times 10^{-5}} = \frac{E_1}{4.56} \frac{10}{393.1 \times 293.1}$$

$$\therefore \underline{E = -4.8 \times 10^3 \text{ cal.}}$$

This compares with the value of the heat of solution of carbon dioxide in water, calculated in the same temperature range by an analogous equation and using literature data (22) for the solubility of carbon dioxide in water.

$$\Delta H = -6.1 \times 10^3 \text{ cal.}$$

From the general agreement of the two values it appears that in the restricted range of temperature, the solution mechanism is of major importance. Above 30°C., the values of E_1 begin to vary widely from the relatively unchanged values of ΔH . Clearly, the diffusion mechanism becomes more complex at the higher temperatures. This is also indicated in Figures 7 and 8, by the great discrepancy between the temperature vs. diffusion and temperature vs. solubility of carbon dioxide in water curves, beyond 30°C.

Attention is now directed to the study of the variation of diffusion with changes in the water content of doughs. This study revealed the major dependence of diffusion on water content. From first considerations, it might be expected that the amount of carbon dioxide diffusing would be

directly proportional to the water content of doughs. In other words, $V \propto C_w$ where C_w is the water content. While this was found to be approximately so in the regions of high water content, it was observed in Figure 9 that as the water content became lower, the graph became curvilinear and reached a minimum near the value of 2.2 ml. for membranes with total water contents of 58 per cent and less.

This state of affairs may be accounted for, if it is remembered that not all the water in a dough is available to dissolve solute such as carbon dioxide. Kent-Jones (25) cites papers by Skovholt and Bailey, Vail and Bailey, Kuhlmann and Golossowa and others, in which the water component of doughs is divided into "free" and "bound" water. "Free" water is that fraction of water in a dough, which retains its capacity to act as solvent. "Bound" water on the other hand, is firmly held in the dough structure, and loses its property of dissolving solutes. It is generally thought that 35 to 50 per cent of the total water content of a dough is in the "bound" state.

Figure 9 may thus be clarified. Dough membranes prepared from flour sample 1 (see Table I), and having a water content of 58 per cent and less, contain little "free" water. Thus, the curvilinearity in this low water content range is the result of the interaction of two factors; one attributable to "free" water and the other to "bound" water. In regions where there is little "free" water, the graph will show pronounced curvilinearity toward the minimum. When the doughs have a water content greater than 58 per cent, "free" water is present in abundance and the major portion of diffusion takes place by the solution of the gas in this water. The linear relationship $V \propto C_w$ is then approximated.

It is now possible to make some changes in the equation representing Fick's law of diffusion,

$$V = D \cdot \frac{\Delta P}{l} \cdot t \quad \text{as developed in the Theory.}$$

The diffusion constant D is an overall constant and may be composed of a number of subsidiary constants each representing a step in the diffusion process. Evidence has been presented that in the range of temperature from 15 to 30°C., the solution of carbon dioxide in the water component of dough is the dominant diffusion mechanism. Hence, in the temperature interval 15 to 30°C. D may be replaced by K - the solubility constant for carbon dioxide in water. Thus,

$$V = K \frac{\Delta P}{l} \cdot t \quad \dots\dots\dots(19)$$

But K may be also composed of a number of subsidiary solubility constants. Thus it is possible to split the overall solubility constant K into further constituents, these to include a constant for the "bound" and one for the "free" water fractions of a dough. Hence,

$$K = k_b + k_f \quad \dots\dots\dots(20)$$

where k_b is the "bound" water solubility constant

and k_f is the "free" water solubility constant.

From the foregoing exposition it follows, that in regions of high water content where the "free" water fraction is large

$$K = k_f \quad \dots\dots\dots(21)$$

Therefore in such regions, the value K in equation 19 may be said to signify the "free" water solubility constant.

The modifications of Fick's law restrict its usefulness to a temperature range of 15 to 30° C. and its application to dough membranes with a considerable "free" water fraction; but the modified equation does account more satisfactorily for the observed results in the diffusion system carbon dioxide-dough.

It would be desirable to secure some information that the results obtained are compatible with general expectations of the permeability of such a medium as dough. This may be done if values of P as defined in the section on "Theory of Diffusion" are calculated and compared with those of Barrer, who has done extensive studies of the diffusion of gases through various solids (10). He introduces a "permeability spectrum", showing the permeability of a number of solids to air. The permeability constants of these solids to air are calculated and their logarithms arranged from low to high values. Substances are then grouped into various permeability classes. A rough approximation of the needed value of P for carbon dioxide in dough at 20°C. can be made, if it is assumed that The V vs. Δp relationship is continually linear; the assumption is, of course, untenable. For the sake of this presentation

$$\text{however, } \log P_{\text{CO}_2 - \text{dough}} = \log \frac{V^1}{A \times \Delta p \times t} = \frac{10.5}{32 \times 82 \times 3600} = -6.0$$

If, next, the not unreasonable assumption is made that the permeability of dough to carbon dioxide is of the same order of magnitude as that to air, then dough falls into the permeability classes A or B together with balloon fabrics, cellophane and rubbers on one hand and cellulose nitrate, acetate and vegetable parchments on the other. While certainly little importance can be attached to this result, it is at least a reasonable one.

The presentation and discussion of results is now complete. It is now advisable to point to the link between this investigation and its bearing on the yeasted doughs systems. The cereal chemist is greatly

interested in the retention factor in yeasted doughs, for reasons that are familiar. However, it would be impossible to study in detail the intricate interdependencies of retention with the numerous variables active in the fermentation and baking processes in a single research project in as complex a system as yeasted dough. Therefore, this study of the basic dependencies of the gas retention with a number of the more important variables was undertaken, in a simplified system of unyeasted dough. The information gained from this study should be applicable to systems of yeasted doughs, and may furthermore prove the stimulus for other and more detailed studies of retention in doughs. The results presented here may well make it possible to evaluate the retention factor in other than empirical and qualitative terms.

Finally, it is pertinent to point out several paths that might be followed in future research in this field. First of all, there are of course several problems that have arisen in this investigation which require further solution. Thus it would be most desirable to conduct a fuller investigation of the diffusion variation with pressure difference, which would make it possible to calculate the true permeability constant values, and thus yield a more exact picture of the permeability of dough. An investigation of the cause of the deviation from linearity in the diffusion vs. time relationship is in order; an explanation of the sudden drop of diffusion in the temperature range 30 to 35°C. is also called for. Further substantiation of the proposed solubility mechanism of diffusion and the suggested "free" and "bound" water explanation of the diffusion vs. water content relationship is also required. Next, it appears desirable that the effects on diffusion of changes in such important variables as protein

content of flour, and wheat variety, be investigated. Studies of the effects on diffusion of addition of bromate and salt to doughs would also prove of great interest. Finally, a detailed and exhaustive study might be carried out in which the various dependencies of gas retention on isolated variables would be pieced together to yield the entire complex picture of the interdependencies of gas retention and all other variables affecting retention of carbon dioxide in doughs.

This thesis is put forth, then, as a step toward the time when the question of the nature of the retention of carbon dioxide in doughs shall be answered in a fundamental way.

SUMMARY

1. Lively interest in gas retention in doughs has been maintained since the end of the last century. In previous studies, gas retention has been studied in systems of fermenting dough in which the effect of gas production was a complicating factor. Manometric, volumetric, and gravimetric methods of measurement were used.

2. A new apparatus has been developed which makes it possible to study diffusion of carbon dioxide, as a measure of retention, in unyeasted doughs. The main portion of the apparatus is a diffusion unit containing a dough membrane of known dimensions; to one surface of the membrane may be applied a known carbon dioxide pressure, and the gas diffusing through the membrane may be trapped and estimated.

3. A solution of Fick's law of diffusion, for stationary flow, applicable to systems of gas diffusion through barriers has been derived. The solution takes the form

$$V = D \cdot \frac{P_2 - P_1}{l} \cdot t$$

The temperature dependence of the diffusion constant may be expressed in the equation

$$D = D_0 e^{-E/RT}$$

from which the possibility of calculating the activation energy for the diffusion process is noted.

4. Doughs prepared from a composite of 1 and 2 Hard Red Spring wheat flour, have been used in the study of the effects of changes in a number of important variables in diffusion. Diffusion studies on doughs prepared from miscellaneous series of flours including a wide variety of types, have

also been carried out.

5. In the range of pressure difference across dough membranes from 76.0 to 90.0 cm. Hg. in terms of carbon dioxide, it has been found that the volume of gas diffusing in unit time is linearly proportional to pressure difference.

6. The volume of gas diffusing through dough in unit time has been found to be inversely proportional to the membrane thickness in membranes 0.5 to 3.0 mm.

7. The volume of gas diffusing through a dough membrane has been found to be linearly proportional to the time of diffusion, in the first 60 minutes of diffusion. Thereafter, a deviation from linearity has been observed. The relationships between volume of gas diffusing and pressure difference, membrane thickness and time of diffusion are in agreement with predictions of Fick's law of diffusion.

8. The volume of gas diffusing through a dough membrane in unit time has been found to decrease as the temperature rises. In the temperature range 15 to 30°C., the curve, temperature vs. carbon dioxide diffusing parallels the curve, temperature vs. volume of carbon dioxide dissolving in water.

9. The volume of carbon dioxide diffusing through a dough membrane has been found to decrease as the water content of the membrane is lowered. In regions of high water content the relationship is linear; in regions of low water content curvilinearity is noted.

10. Diffusion studies were made on doughs mixed to constant water content from a miscellaneous series of flours. When the results were arranged in terms of decreasing rates of diffusion the flours fell into groups approximately paralleling their baking strengths.

11. An approximate calculation of activation energy for the diffusion of carbon dioxide through dough gave a value -4.8×10^3 cal. This compares with -6.1×10^3 cal. for the heat of solution of carbon dioxide in water. The same order of magnitudes of these values together with the similarity of the temperature vs. volume of gas diffused curve with the temperature vs. volume of gas dissolved in water curve, in the temperature range 15 to 30°C., show that in that temperature range, the mechanism of diffusion of carbon dioxide through dough is the solution of the gas in the water of the dough transport in the liquid phase and eventual release.
12. The curvilinearity in the diffusion vs. water content curve may be explained as the interaction of two factors; one due to the "bound" water fraction of a dough, the other to the "free" water fraction of a dough.
13. An approximate calculation of the permeability constant for the diffusion system carbon dioxide - dough shows that dough is about as permeable a substance as rubber, cellophane and balloon fabrics, and somewhat less permeable than cellulose nitrate and acetate and vegetable parchments.

REFERENCES

1. Association of Official Agricultural Chemists. Official and tentative methods of analysis. 26-27 (6th ed.) A.O.A.C.: Washington (1945).
2. Association of Official Agricultural Chemists. Official and tentative methods of analysis. 237-238 (6th ed.) A.O.A.C.: Washington (1945).
3. BAILEY, C. H. A method for the determination of the strength and baking qualities of wheat flour. Ind. Eng. Chem. 8: 53-57 (1916).
4. BAILEY, C. H. Measuring fermentation rate and gas losses in dough. Cereal Chem. 16: 665-671 (1939).
5. BAILEY, C. H., and JOHNSON, A. H. Carbon dioxide diffusion ratio of wheat flour doughs as a measure of fermentation period. Cereal Chem. 1: 293-304 (1924).
6. BAILEY, C. H., and JOHNSON, A. H. Gluten of flour and gas retention of wheat flour doughs. Cereal Chem. 2: 95-106 (1925).
7. BAILEY, C. H., and WEIGLEY, M. Loss of carbon dioxide from dough as index of flour strength. Ind. Eng. Chem. 14: 147-150 (1922).
8. BAKER, J. C. The permeability of bread by air. Cereal Chem. 16: 730-733 (1939).
9. BAKER, J. C. The structure of the gas cell in bread dough. Cereal Chem. 18: 34-41 (1941).
10. BARRER, R. M. Diffusion in and through solids. Cambridge University Press (1941).
11. BLISH, M. J., SANDSTEDT, R. M., and ASTLEFORD, G. R. Sugars, diastatic activity and "gassing power" in flour. Cereal Chem. 9: 378-393 (1932).
12. EDELMANN, E. C., and CATHCART, W. H. The measurement of oven spring as an aid in controlling flour quality. Cereal Chem. 21: 385-388 (1944).
13. ELION, E. A simple volumetric method for measuring gas production during dough fermentation. Cereal Chem. 10: 245-249 (1933).
14. ELION, E. Some remarks on the varying influence of compressed yeasts of different industrial origin on the gas retention of dough, as recorded by a new instrument, the Chefaro balance. Cereal Chem. 16: 598-610 (1939).

15. ELION, E. The importance of gas production and gas-retention measurements during the fermentation of dough. *Cereal Chem.* 17: 573-579 (1940).
16. FLOHIL, J. T. The effect of chemical flour improvers on proteolytic action in relation to the gas-retaining capacity of fermenting doughs. *Cereal Chem.* 13: 675-689 (1936).
17. GEDDES, W. F. Chemical and physico-chemical changes in wheat and wheat products induced by elevated temperatures. *Can. J. Research.* 2: 195-213 (1930).
18. GEDDES, W. F., and LARMOUR, R. K. Some aspects of the bromate baking test. *Cereal Chem.* 10: 30-72 (1933).
19. GLAEBE, E. F. The fermentometer, a gas-production measuring device. *Cereal Chem.* 19: 230-234 (1942).
20. HEALD, W. L. Some factors affecting gas production during dough fermentation. *Cereal Chem.* 9: 603-616 (1932).
21. HEALD, W. L. Gas retention as affected by including shortening in the tentative A.A.C.C. basic test-bake formula. *Cereal Chem.* 16: 817-820 (1939).
22. HODGMAN, C. D. Editor, Handbook of chemistry and physics. 1360 (29th ed.) Chemical Rubber Publishing Co.: Cleveland (1945).
23. JOHNSON, J. A., and MILLER, B. S. Studies on the role of alpha-amylase and proteinase in breadmaking. *Cereal Chem.* 26: 371-383 (1949).
24. KARACSONYI, L. P., and BAILEY, C. H. Relation of the overgrinding of flour to dough fermentation. *Cereal Chem.* 7: 571-587 (1930).
25. KENT-JONES, D. W., and AMOS, A. J. Modern cereal chemistry. The Northern Publishing Co. Ltd. (4 ed.): 259-268 (1947).
26. KNEEN, E., and SANDSTEDT, R. M. The evaluation of malt for use as a flour supplement. *Cereal Chem.* 19: 181-195 (1942).
27. KNEEN, E., SANDSTEDT, R. M., and HOLLENBECK, C. M. The differential stability of the malt amylases - separation of the alpha and beta components. *Cereal Chem.* 20: 399-423 (1943).
28. LARMOUR, R. K., and BROCKINGTON, S. F. Studies on experimental baking tests. I. Effects of variation in baking formulas on gas production and loaf volume. II. The application of a high yeast-sugar formula in evaluating flour strength. *Cereal Chem.* 11: 451-470 and 420-486 (1934).
29. MALLOCH, J. G. A convenient apparatus for gas production determinations by the Blish method. *Cereal Chem.* 16: 178-182 (1939).
30. MARKLEY, M. C., and BAILEY, C. H. An automatic method for measuring gas production and expansion in doughs. *Cereal Chem.* 9: 591-594 (1932).

31. MARTIN, W. M., and GREEN, J. R. Determination of carbon dioxide in continuous gas streams. *Ind. Eng. Chem. (Anal. Ed.)* 5: 114-118 (1933).
32. MARTIN, W. M., and WHITCOMB, W. O. Physical and chemical properties of ether-soluble constituents of wheat flour in relation to baking quality. *Cereal Chem.* 9: 275-288 (1932).
33. MILLER, H., EDGAR, J., and WHITESIDE, A. G. O. An automatic gas recording apparatus. *Cereal Chem.* 20: 355-361 (1943).
34. READ, J. W., and HAAS, L. W. Further studies on the baking quality of flour as affected by certain enzyme action. Relative starch liquefying power of the diastatic agents investigated. *Cereal Chem.* 13: 14-37 (1936).
35. SANDSTEDT, R. M., and BLISH, M. J. Yeast variability and its control in flour gassing power tests. *Cereal Chem.* 11: 368-383 (1934).
36. SHERWOOD, R. C., and BAILEY, G. H. Control of diastatic activity in wheat flour. *Cereal Chem.* 3: 107-136 (1926).
37. SWANSON, E. C., and SWANSON, C. O. Gas production and gas retention of dough as affected by type of flour, baking formula, and amount of mixing. *Cereal Chem.* 23: 432-440 (1946).
38. SWANSON, E. C., and SWANSON, C. O. Modification of the gas production and gas retention properties of dough by some surface - active, reducing, and oxidizing agents. *Cereal Chem.* 23: 590-600 (1946).
39. WORKING, E. B., and SWANSON, E. C. An automatic device for the measurement of gas production and gas retention in doughs. *Cereal Chem.* 23: 210-216 (1946).