

WEIGHT AND VOLUME CHANGES IN WHEAT DURING SORPTION AND DESORPTION OF MOISTURE¹

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ABSTRACT

The toluene-displacement pycnometric method was applied to measure the change in volume of whole wheat with gain or loss of moisture after equilibration at various relative pressures of water vapor. The corresponding weight changes were determined also. A plot of the volume changes against the equilibrium relative pressure gave a *volume* isotherm with hysteresis between the sorption and the desorption branches similar to that in the *weight* isotherm.

A definite hysteresis also exists between the sorption and the desorption branches of the plots of change in volume against change in weight. The sorption branch seems to be curvilinear. At low moistures, the weight changes faster than the volume; at intermediate moisture the change in volume varies directly with the change in weight; and, at moistures above about 15% (dry basis) the volume changes faster than the weight. There seems to be a net decrease in total volume for low sorption and a net increase for high sorptions. For the desorption branch the change in volume varies directly with the change in weight. The dry grain shows a net increase in volume after a complete sorption-desorption cycle in the relative pressure range 0 to 0.94.

Wheat density changes approximately linearly with moisture for both branches of the isotherm. The densities during desorption are lower than the values during sorption at equivalent relative pressures. Wheat which was put through a sorption-desorption cycle in the moisture range 0 to 26.4% showed a net decrease in density of 0.014 g. per ml.

The standard method in sorption studies is to measure the increase or decrease in weight of the sorbent equilibrated to various pressures of the sorbate. Such data give a *weight* isotherm, the shape of which gives some indication of the mechanism of the sorption process. A less common approach is to measure the volume changes of the sorbent during uptake or loss of sorbate. These data can be used to construct a *volume* isotherm. This isotherm may yield information

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on the sorption process additional to that obtainable from the weight isotherm.

This paper reports the results of a study in which the weight and volume isotherms were obtained under identical conditions for the sorption and desorption of water vapor by wheat. The variations in density of the wheat used, with moisture content, during sorption and desorption, which can be derived from the weight-volume data are reported and discussed also.

Materials and Methods

The wheat used in this study was a high-grade sample of hard spring wheat from which all small and broken kernels were removed by hand picking. Its protein content ($N \times 5.7$) was 15.7% on a 14% moisture basis.

The following method was used: Two approximately 4-g. samples of wheat, one for volume determination and the other for moisture content determination, were equilibrated above constant humidity solutions of sulfuric acid in vacuum desiccator chambers from which the air was removed by evacuation. Under such conditions equilibration periods of 3 to 4 days were sufficient to establish moisture equilibrium (2). The vapor pressures of the sulfuric acid solutions were obtained from reference tables, using the densities of the solutions which were determined pycnometrically.

To ensure that the changes in moisture content and volume were unidirectional during sorption and desorption, the samples for the sorption experiments were initially vacuum-dried at room temperature to 1.5% moisture; the samples for the desorption experiments were equilibrated to 26.4% moisture.

The entire experiment was carried out in a temperature-controlled room set at 22.2°C. All weighings were made in air.

Moisture contents (weight changes) of the wheat samples were determined from the loss in weight after drying in a vacuum oven for 24 hours at 22.2°C., 48 hours at 40°C., and finally at 100°C. until the weight changed by less than 0.001 g. after an evacuation period of 1 hour at this temperature. The final drying step usually required about 4 hours. This method was adopted instead of the standard AACC method (1) for wheat to eliminate possible moisture interchange during grinding, particularly for the low- and high-moisture samples. However, moisture data obtained by the two methods were comparable for check samples containing from 8 to 14% moisture.

Volumes were determined from the amount of toluene displaced from calibrated, Weld-type pycnometers, using the density of toluene

at the temperature of the experiment. The filled pycnometers were equilibrated in a water bath at $22.20^\circ \pm 0.02^\circ\text{C}$.

All weight and volume changes given in this paper are on a dry matter basis. The wheat was assumed dry when dried by the procedure used to determine moisture content. Densities were calculated as outlined by Sharp (12).

Results and Discussion

Representative data from approximately 20 determinations for each of the sorption and the desorption cycles are summarized in Table I. These points were selected to give a good distribution of points over the relative pressure range investigated. The first and second columns give the relative water-vapor pressures and the corresponding equilibrium weight changes. The volume changes in column 3 are the net changes per g. of dry matter obtained by subtracting the specific volume at 0% moisture from the volumes, per g. of dry matter, at the other moistures.² The densities in column 4 are for 22.2°C . and were calculated using the density of toluene at the same temperature.

Figure 1 gives the standard sorption-desorption isotherm (weight) as well as the volume isotherm which relates the change in volume of

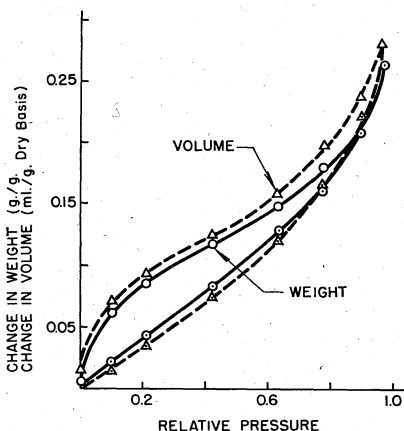


Fig. 1. Sorption isotherms for water vapor and wheat. Lower curves, sorption; upper curves, desorption.

² Sample calculation of the volume change at 0.77 relative pressure for the desorption cycle:
 Weight of wheat (wet), 4.5413 g.
 Volume of wheat (wet), 3.456 ml.
 Moisture content (dry basis), 18.0%
 Dry matter in 4.5413 g. of wet wheat = $4.5413/1.18 = 3.8486$
 Volume per g. of dry matter = $3.456/3.8486 \times 1 = 0.898$ ml.
 Volume per g. of dry matter at 0% moisture = 0.701 ml.
 Change in volume per g. = $0.898 - 0.701 = 0.197$ ml. per g. of dry matter.

TABLE I
WEIGHT, VOLUME, AND DENSITY CHANGES IN WHEAT DURING SORPTION AND
DESORPTION OF WATER VAPOR

RELATIVE VAPOR PRESSURE	WEIGHT CHANGE	VOLUME CHANGE	DENSITY
	<i>g/g, dry basis</i>	<i>ml/g, dry basis</i>	<i>g/ml</i>
Sorption: Initial moisture = 1.5%, dry basis			
0 ^a	0	0	1.426
0.10	0.022	0.016	1.423
0.21	0.043	0.035	1.417
0.42	0.083	0.075	1.396
0.63	0.128	0.120	1.374
0.77	0.162	0.165	1.342
0.89	0.207	0.220	1.311
0.94	0.264	0.285	1.282
Desorption: Initial moisture = 26.4%, dry basis			
0.94	0.264	0.285	1.282
0.89	0.207	0.235	1.290
0.77	0.180	0.197	1.314
0.63	0.147	0.157	1.337
0.42	0.118	0.127	1.350
0.21	0.086	0.094	1.366
0.10	0.063	0.070	1.379
0 (Drierite)	0.005	0.014	1.406
0 (Oven-dried)	0.0	0.008	1.412

^a Dried in oven after vacuum-drying to 1.5% moisture.

1 g. of dry wheat during gain or loss of moisture as a function of the equilibrium relative pressure.

The two branches of the weight isotherm are of sigmoid shape and essentially the same as those published by Babbitt (2) and Becker and Sallans (5). This isotherm is included here for the purpose of comparison with the volume isotherm. The sorption branch of the volume isotherm appears to be convex to the pressure axis over the entire range investigated. The desorption branch is of sigmoid shape similar to the corresponding branch of the weight isotherm.

Figure 1 shows two interesting features that might be emphasized. First is the much greater hysteresis effect in the volume isotherm than in the weight isotherm and the definite indication that after desorption from 26.4% moisture there is a residual increase in volume of the wheat, indicating that a portion of the volume hysteresis is irreversible. This is probably due to micro cracks, the formation of which has been demonstrated in moistened and dried wheat (7), in naturally and artificially weathered wheat (10), and in conditioned wheat (8). Practical implications of this observation will be discussed later.

The second interesting feature is the relation of the volume chang-

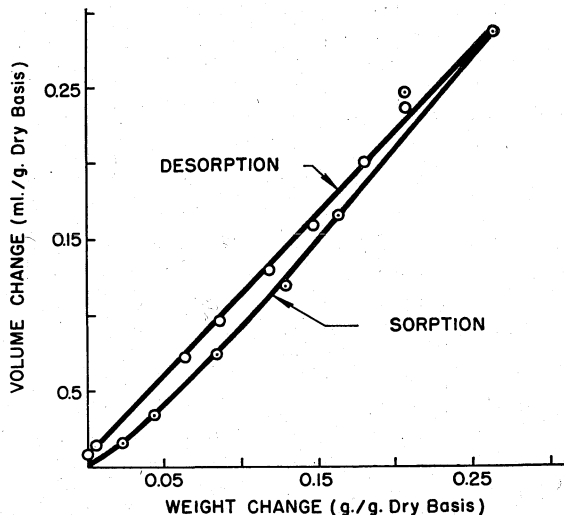


Fig. 2. The change in volume as a function of the change in weight at the same relative pressures for water vapor and wheat.

es to the weight changes. Figure 2, which gives the relation between volume change and weight change at the same relative pressure for the two branches of the isotherm, is included to facilitate discussion of this feature. Since there is no theoretical reason at present to believe that there should be a crossover of the sorption and desorption curves for the volume change versus weight change at 0.89 relative vapor pressure, it was assumed that deviation of the one point for sorption was due to a combination of experimental error. (See discussion of errors below.)

For the sorption portion of the cycle, the plot of volume increase against weight increase is curvilinear, whereas the corresponding plot for the desorption branch appears to be linear. There is a definite hysteresis between the sorption and the desorption branches and also a residual volume change in the wheat after the sorption-desorption cycle is completed. A similar volume hysteresis was observed by Barkas (3) in the volume changes of wood fibers during sorption-desorption of moisture.

In a study of this type where significance is attached to relatively small differences in the quantities measured, it is necessary to ensure that the differences are not invalidated by the magnitude of the experimental errors. The largest source of error in working with wheat is the sampling error. An attempt was made to reduce this as much as possible in this study by using a large sample of sound kernels. An-

other source of error in the volume determination is the entrapment of air in the creases and larger cracks that would otherwise be accessible to toluene. Most of such air was generally removed by tapping the filled pycnometer until no more bubbles could be removed. The subsequent replicability of the method was checked by determining the volume and weight changes in six replicate samples of wheat conditioned at the same time in a single desiccator. The specific volume changes calculated from the measured volumes of wheat samples which varied in weight from 4.433 to 4.654 g. were (0.121 ± 0.002) ml. per g. The corresponding densities were (1.372 ± 0.003) g. per ml. Six replicate moisture determinations by the method outlined above gave values that were within $\pm 0.2\%$ from the average value, that is, the weight change was reproducible to ± 0.002 mg. per g. at a moisture level of 12%. No comprehensive statistical study was made of the errors at low and high moisture contents. Experience indicates that the errors in these regions would be slightly higher. At high relative pressures, development of mold was occasionally a source of difficulty. Samples that showed evidence of moldiness were discarded. On the basis of this semiquantitative appraisal of the experimental errors involved, it was concluded that the relative trends of the results shown in Table I are definitely significant.

The curvilinear plot for volume change against weight change for the sorption branch (see Fig. 2) can be explained as follows. Initially, the weight change is much greater than the corresponding volume change. Consequently, there is a net decrease in the total volume of the system. This physical effect is probably a direct manifestation of the high energy attraction forces between the sorption sites and the water molecules. The high heat of sorption for the low moisture levels (6) supports this hypothesis. This region of negative volume change (based on total volume) is followed by a region where the volume change seems to be directly proportional to the weight change. At moisture above about 15%, the volume seems to change much faster than the weight change so that there is actually a crossover of the sorption branches of the isotherms (see Fig. 1). It is postulated that this relation arises from the rapid swelling of the wheat that occurs at high moistures. This seems to be accompanied by a permanent, physical change in the kernel which probably is responsible for some of the hysteresis between the sorption and the desorption branches of the isotherm (2), the change of vitreous to starchy of the wheat-endsperm appearance (13), and the appearance of fissures (8,10). The consequence of this physical change is a net change in density which has been measured previously (10) to a limited extent and determined

over a relatively wide moisture range for both branches of the isotherm in the present study.

The theoretical significance of the results presented in this paper concerns their relation to the mechanics of the sorption-desorption process. It appears that any explanation of the shape of the isotherm and the hysteresis effect must include the changes in the physical structure of the wheat kernel during moisture interchange. Barkas (4) has suggested that the structural changes (plastic deformation) of the gel-type sorbent is responsible for the hysteresis in the system comprising water vapor and wood fiber. The sorptive properties of wheat are quite similar to those of wood fiber. On the basis of the hypothesis of Barkas (4) it can be predicted that the degree of sorption hysteresis should decrease as the sorbent particle size decreases. The hysteresis loops for wheat (2), for farina³, for flour (6), and for ball-milled flour⁴ decrease in the order named and, accordingly, are in line with this prediction.

In addition, Barkas (3) actually developed a theory showing that systems which exhibit sorption hysteresis owing to plastic deformation will also show a marked volume hysteresis such as is shown for wheat and water vapor in Fig 2. It is probable that the plastic deformation in the sorbent not only relieves the swelling stresses but also uncovers sorption sites which are not available at the lower relative pressures where the stress is insufficient to overcome the structural strength. The additional sorption sites may be responsible for at least a part of the rapid increase in the amount of sorption at relative pressures above about 0.6. This rapid increase in sorption is generally attributed to capillary condensation.

The practical significance of the present study concerns the residual change in density of wheat when it is put through a complete sorption-desorption cycle. The variation of wheat density with moisture content is well established (9,12); however, there are only limited published data (11) of densities for both sorption and desorption over a wide range of moistures. Figure 3 gives the variation of kernel density with moisture for the two types of moisture interchange obtained in the present study. The divergence in density for the two isotherm branches is quite apparent; however, it should be emphasized that this divergence can only be readily demonstrated if the wheat that is used for the sorption experiments is equilibrated initially to a very low moisture content; and conversely, the wheat for the desorption study must initially be at the highest moisture level used.

^{3,4} Unpublished results.

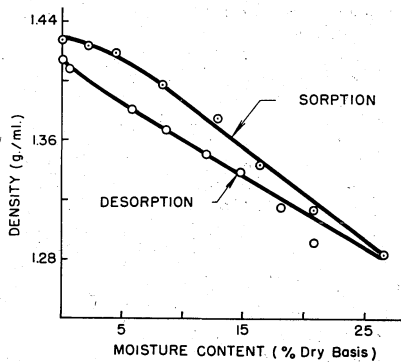


Fig. 3. Variation of gross kernel density with moisture content during sorption and desorption.

The net decrease in density of wheat that has been wetted and dried will give a decrease in the test weight and may actually change the grade of the wheat. For example, the change in bushel weight due to change in the density alone that will result when wheat of 7% moisture is wetted to 17% moisture and dried back to 7%, interpolated from Fig. 3, would be about 0.5 lb. This value will increase as the moisture range increases.

In conclusion, it is of interest to compare the density values obtained in this study with published values, particularly those of Sharp (12) and Jones and Campbell (9). The method used in this study is identical to that of Sharp (12), but the densities obtained in the present study for the sorption branch are slightly lower. The difference is probably due to the difference in the starch-protein ratio of the wheats used. The values of Jones and Campbell (9), obtained by flotation of small endosperm particles, are considerably higher than the values given in this paper. This difference can be due to two possible reasons in addition to the difference in protein content. First is that the density of the endosperm is higher than that of the other kernel components, and second is the difference in the methods used. The toluene-displacement method with whole kernels gives a gross kernel density, whereas the technique of Jones and Campbell (9), which uses small endosperm particles, is probably closer to the true density. If the wheat kernel has any internal cracks or fissures which are not accessible to toluene, then the gross density would tend to be lower than the true density.

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