COMPARISON OF THE RATES OF ABSORPTION OF WATER BY CORN KERNELS WITH AND WITHOUT DISSOLVED SULFUR DIOXIDE[1]

LIANG-TSENG FAN,[2] HUAI-CHONG CHEN,[2]
JOHN A. SHELLENBERGER,[3] AND DO SUP CHUNG[3]

ABSTRACT

Diffusion of water into kernels of three varieties of corn steeped in both aqueous SO_2 solution and in water was investigated quantitatively at temperatures ranging from 10° to 71°C. Absorption rate of water in SO_2 solution as well as in water followed approximately the diffusion equation based on Fick's law.

Adding SO_2 in water has two extreme effects on absorption rate, a retarding effect at the onset of steeping and then an accelerating effect. For Gold Rush sweet corn the retarding effect was appreciable, for K-4 hybrid popcorn it was comparatively small, and for DeKalb dent corn it was almost negligible. On the other hand, the accelerating effect was small for Gold Rush sweet corn, but quite appreciable for K-4 hybrid popcorn and DeKalb dent corn. At all temperatures, absorption rate was slower in SO_2 solution than in water in the initial period of steeping, but this was reversed as absorption time increased. The higher the steeping temperature, the sooner the reversion took place. The acceleration in absorption rate increased with increasing temperature; but at about the gelatinization temperature of starch the difference decreased after a certain period of absorption.

Some results of continuing studies on the diffusion process of cereal grains are reported here. Previous work dealt with rates of mass and volume increases in various cereal grains during steeping in water (1,2,3,4,5). In the wet-milling processes, however, grains are almost invariably steeped in warm water containing 0.10 to 0.20% of sulfur dioxide rather than in plain water (6). Therefore, absorption rates of water by corn kernels in the steeping solutions with and without dissolved SO_2 were investigated.

Function of SO_2 as a steeping agent has been investigated by Cox and MacMasters (7), who found starch embedded in and tightly held by a protein network. During steeping the network swells and tends to form tiny globules of hydrated protein. With time, the protein loses its birefringence and finally disperses. SO_2 greatly accelerates this process and hence increases starch recovery.

Adding SO_2 in steeping water also is known to inhibit microorganism activity as well as to soften the endosperm. However, a

[1] Manuscript received July 1, 1963. Contribution No. 523, Department of Flour and Feed Milling Industries, Kansas State University, Manhattan.
[2] Department of Chemical Engineering.
[3] Department of Flour and Feed Milling Industries.

strictly quantitative comparison of the absorption rate of water by grain kernels in sulfurous acid solution and in water has not been reported. Therefore, differences between diffusion rates of water into corn kernels steeped in water containing sulfur dioxide and in plain water were recorded.

This paper may provide not only practical information of weight increase of corn grain during steeping but also some basic information which may reveal the mechanism of SO_2 as it affects the diffusion rate of water during steeping.

The diffusion equation derived by Becker and tested by others was used as the model to correlate the data (2,3,5,8,9).

Theoretical Aspects

Becker (8,9) demonstrated that Fick's second law equation can be integrated approximately for the particle of arbitrary shape, assuming that the surface-to-volume ratio, A/V, remains constant and that the steeping time is short, as:

$$\overline{C} = 1 - \frac{2}{\sqrt{\pi}} X + BX^2 \qquad (1)$$

where $\overline{C} = \frac{\overline{c} - c_s}{c_0 - c_s}$ in which $\overline{c}$ is the average concentration, c_0 the initial concentration, and c_s the concentration at bounding surface, $X = (A/V)\sqrt{Dt}$, and B is a dimensionless constant. If the concentration term is represented by the moisture content on a weight basis:

$$\overline{C} = \overline{M} = \frac{\overline{m} - m_s}{m_o - m_s} \qquad (2)$$

where $\overline{m}$ is the average moisture content at the given absorption time, m_s is the effective surface moisture content, and m_o is the initial moisture content (moisture contents expressed in g. per g. dry basis). Equation 1, then, can be written:

$$\overline{M} = 1 - \frac{2}{\sqrt{\pi}} X + BX^2. \qquad (3)$$

With the first-order approximation, or when X is small, equation 3 is approximated to:

$$1 - \overline{M} = \frac{2}{\sqrt{\pi}} X \qquad (4)$$

or, in terms of experimental variables:

$$\overline{m} - m_o = K_1 \sqrt{t} \qquad (5)$$

where $K_1 = 2/\sqrt{\pi}\,(m_s - m_o)\,(A/V)\,\sqrt{D}$.

Equation 5 shows that, if this mathematical model is applicable, a linear relationship exists between $(\overline{m} - m_o)$ and $\sqrt{t}$. According to the first-order approximation, the diffusivity, D, can be obtained from

$$D = \left[\frac{K_1}{\frac{2}{\sqrt{\pi}} \quad \frac{A}{V} \quad (m_s - m_o)} \right]^2 \tag{6}$$

using experimentally determined values of K_1, (A/V), and $(m_s - m_o)$.

Materials and Methods

The varieties of corn investigated in this work were Gold Rush sweet corn, K-4 popcorn, DeKalb 3 × 1 dent corn, and K1830 hybrid dent corn. Their characteristics are summarized in Table 1.

TABLE I
CHARACTERISTICS OF THE MATERIAL INVESTIGATED

	Gold Rush Sweet Corn	K-4 Hybrid Popcorn	DeKalb 3×1 Dent Corn	K1830 Hybrid Yellow Dent Corn
Protein, %	10.88	10.69	8.31	8.06
Ether extract, %	8.18	3.69	3.90	3.94
Crude fiber, %	1.99	3.25	1.74	2.09
Moisture, %	10.10	9.78	11.46	10.12
Ash, %	1.83	1.45	1.18	1.40
N-free extract, %	67.02	72.14	73.41	74.39
Average initial surface area per grain, $cm.^2$	2.334	1.0655	2.1196	2.0830
Average initial volume per grain, $cm.^3$	0.1874	0.1038	0.2441	0.2291
A/V, $cm.^2/cm.^3$	12.984	10.277	8.684	9.110
Density, $g./cm.^3$	1.3228	1.3333	1.2500	1.2490
Initial moisture content, m_o, g./g.	0.1028	0.1300	0.1331	0.1040
Moisture gain by capillary action, m_i, g./g.	0.0208	0.0216	0.0113	0.029
Surface moisture content, m_s, g./g.[a]	0.730	0.515	0.599	0.450

[a] Values of m_s were found to be practically independent of temperature.

Experiments were carried out with temperatures ranging from 10° to 71°C. and for immersion periods from several min. to 10 hr. For each run, two weighed samples were placed in 500-ml. flasks. One contained 0.3% aqueous SO_2 solution and was sealed to prevent escape of SO_2 gas; the other contained distilled water. Both were immersed in a stirred water bath controlled within 0.1°C. of the testing temperature. At the end of each immersion, both samples were quickly removed from the water bath and superficially dried on a large filter paper. After the surface water on the kernels was removed, the samples were weighed. Moisture gain was calculated from the weight of the water absorbed by the samples.

Quantities of m_i, m_o, m_s, and (A/V) were determined by using methods suggested by previous investigators (2,3,5,9,10).

Results and Discussion

As shown in equation 5, the moisture increase should be proportional to the square root of the absorption time if the diffusion model is applicable. Since the initial moisture pick-up, m_i, was due to a phenomenon other than diffusion (2,9), the experimental data for each sample ($\bar{m}$-m_o-m_i) were plotted as a function of $\sqrt{t}$ at all the temperature levels as shown in Figs. 1, 2, and 3.

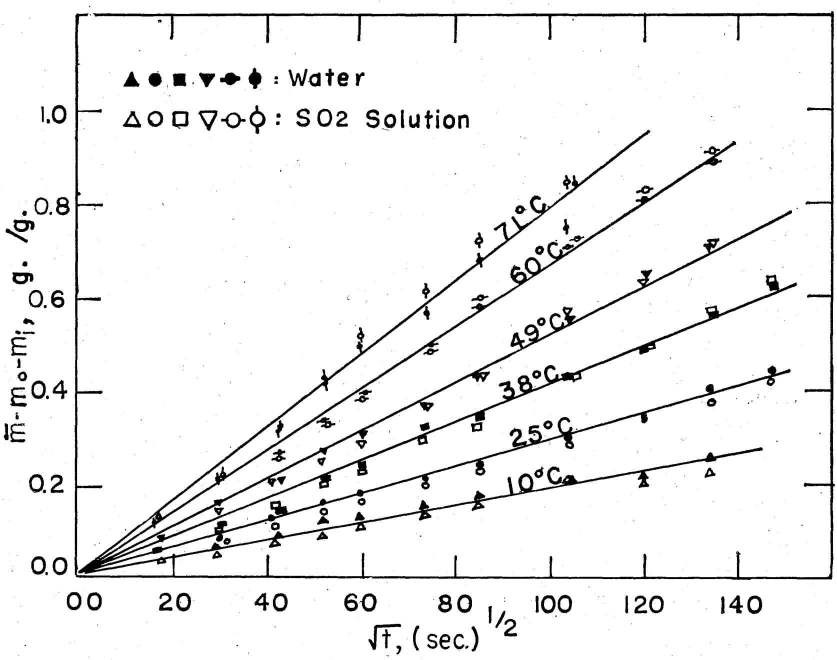

Fig. 1. Linear relation between moisture gain and the square root of absorption time for Gold Rush sweet corn.

Average slopes of lines in the figures were determined by the method of least squares, using all the data included.

The diffusivities calculated from equation 6 by using average slopes of the lines in Figs. 1, 2, and 3 were plotted against the reciprocal of the absolute temperatures on a semilogarithmic scale in Figs. 4, 5, and 6 for sweet corn, popcorn, and dent corn, respectively. The results show that the relation between diffusivity and absolute tem-

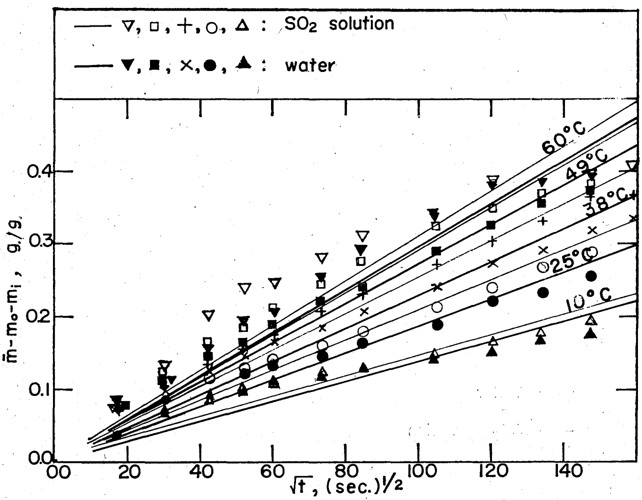

Fig. 2. Linear relation between moisture gain and the square root of absorption time for K-4 hybrid popcorn.

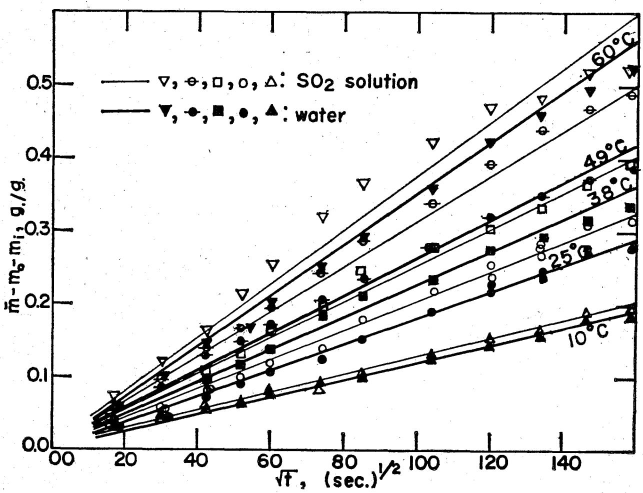

Fig. 3. Linear relation between moisture gain and the square root of absorption time for DeKalb 3 × 1 dent corn.

perature followed the Arrhenius-type equation in both plain water and SO_2 solution:

$$D = D_0 \exp\left[-\frac{E}{RT}\right] \qquad (7)$$

where E is the activation energy, R is the universal gas constant, and T is the absolute temperature.

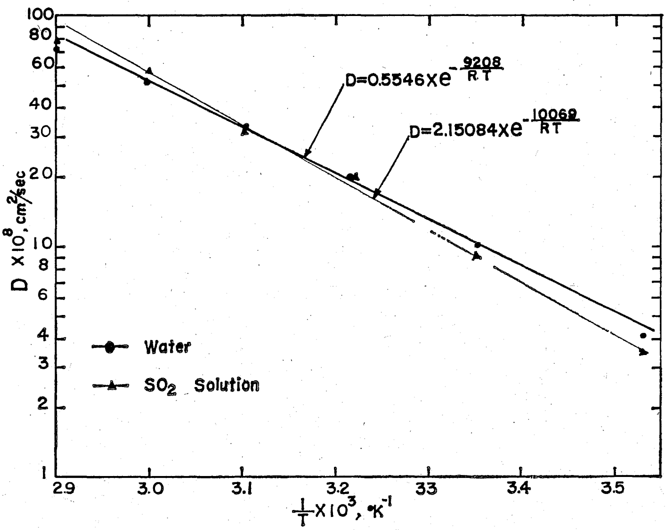

Fig. 4. Diffusion coefficient calculated from equation 6, as a function of reciprocal of temperature for Gold Rush sweet corn.

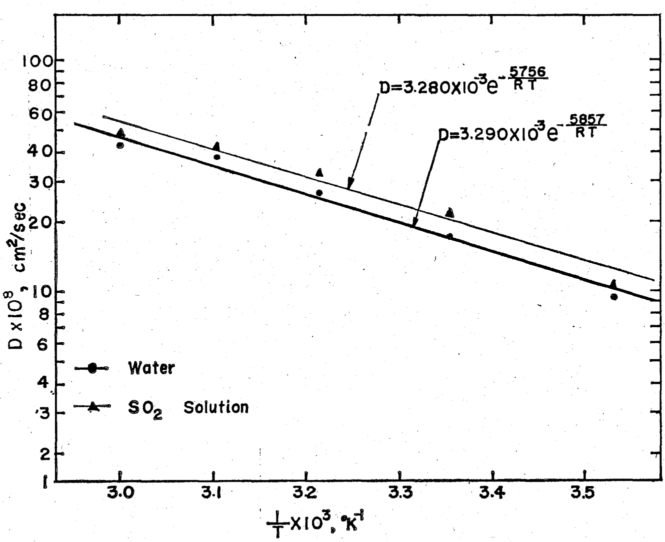

Fig. 5. Diffusion coefficient calculated from equation 6, as a function of reciprocal of temperature for K-4 hybrid popcorn.

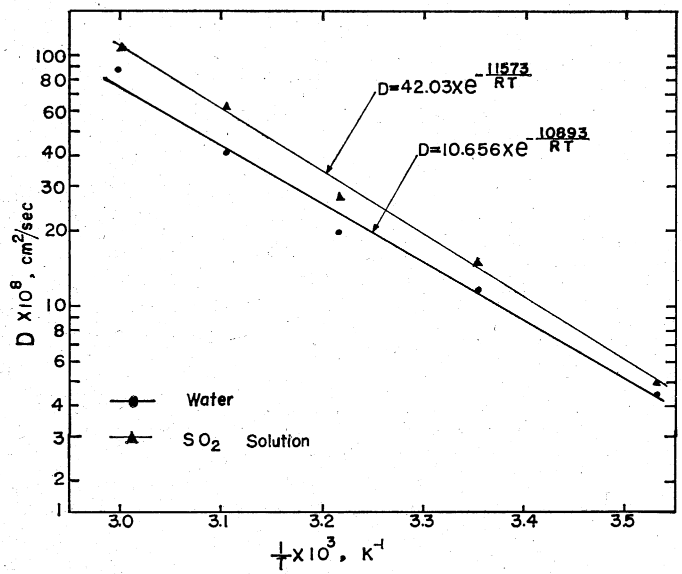

Fig. 6. Diffusion coefficient calculated from equation 6, as a function of reciprocal of temperature for DeKalb dent corn.

The difference in moisture increase of corn kernels in water and in aqueous SO_2 solution was plotted as a function of the steeping time for sweet corn, popcorn, and dent corn, as shown respectively in Figs. 7, 8, and 9.

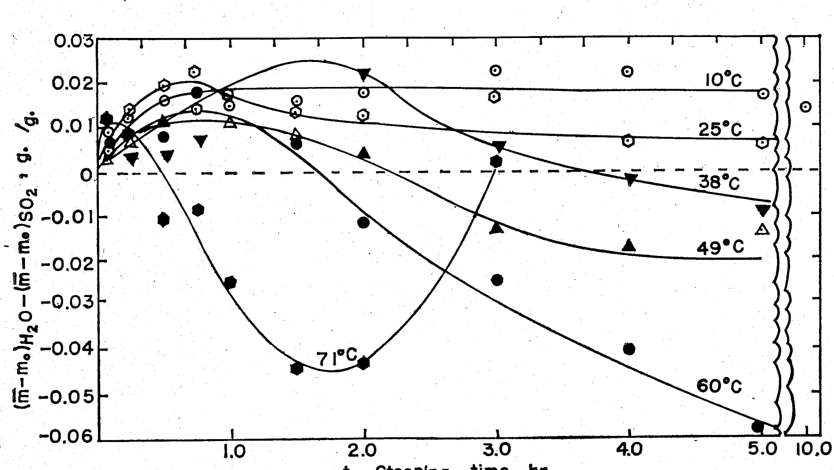

Fig. 7. Difference in moisture increase as a function of absorption time for Gold Rush sweet corn in water and in aqueous SO_2 solution.

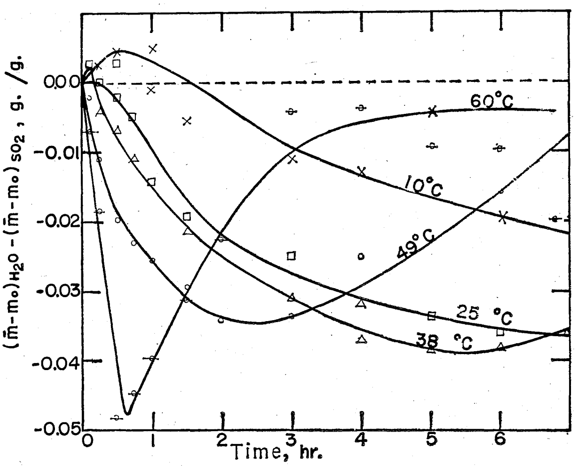

Fig. 8. Difference in moisture increase as a function of absorption time for K-4 hybrid popcorn in water and in aqueous SO_2 solution.

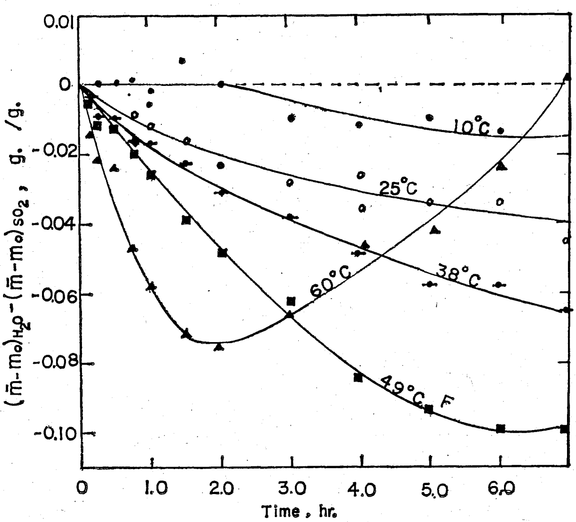

Fig. 9. Difference in moisture increase as a function of absorption time for DeKalb 3 × 1 dent corn in water and aqueous SO_2 solution.

The intuitively accepted idea that corn kernels absorb water faster in aqueous SO_2 solutions than in water is not always true. As seen in Fig. 7, kernels of Gold Rush sweet corn absorb water in aqueous SO_2 solutions more slowly than in water at any particular temperature in the initial period; but, as steeping was prolonged, differences in the rates of moisture gain first increased and then reversed that trend, and eventually they switched. The higher the temperature, the sooner the change occurred. For example, it took approximately 30 min. at 71°C., 100 min. at 60°C., and 130 min. at 49°C., but at 10°C. it did not occur after 10 hr. of steeping. After such change occurred, differences in moisture content increased with increasing temperature. At 71°C. the difference reached the maximum at approximately 110 min. after immersion and then diminished again. This phenomenon might result from both samples being completely swollen by denaturization of protein and gelatinization of starch.

For K-4 hybrid popcorn, the initial effect of SO_2 on retarding absorption rate was not so obvious as for Gold Rush sweet corn. When the temperature was low, however, the effect of SO_2 was still quite appreciable. Reversion to acceleration from retardation occurred in 80 min. at 10°C., whereas at room temperature or higher, the absorption rate was always higher in SO_2 solution. The higher the temperature, the greater the difference in rate of moisture gain. In most cases, the difference decreased again when steeping was extended to several hours. Again this was probably due to the near-saturation of corn kernels by water and, at high temperature, gelatinization in the corn kernels.

For DeKalb 3 × 1 dent corn, however, no detectable retarding effect of SO_2 on absorption rate was observed. If there was any, it must have disappeared quickly. Absorption rate of water in SO_2 solution was always higher than for water alone. Differences in rate of moisture increase for dent corn were about twice that for sweet corn and popcorn. It was surprising that moisture increase in SO_2 solution was 25% higher than in pure water after 7 hr. of steeping at 49°C. and that the isothermal curves did not appear to reverse themselves in the time range of the experiments, except that at the 60°C. line moisture differences reached their maximum after 2 hr. and diminished completely after 7 hr. of steeping. That was again due to saturation in the corn kernels.

In general, the retarding effect at the onset of steeping may be due to the creation of additional resistance by SO_2 molecules to the moisture transfer. The moisture should pass through several semipermeable membranes (pericarp, seed coat, and aleurone layer) before it reaches the endosperm. Since the size of SO_2 molecule is larger than that of H_2O molecule, some SO_2 molecules may completely or partially block micropores in semipermeable membranes and consequently create additional resistance to the moisture transfer and interfere with the path of moisture transfer.

The accelerating effect of SO_2 on absorption rate is probably due to disintegration of the protein network as described by Cox and MacMasters (7). The disintegration of the protein network will soften the endosperm and provide easy paths for moisture penetration.

Concentration of SO_2 in the steeping solution ranges from 0.10 to 0.20% for industrial processes. To study effects of concentration level of SO_2 on absorption rate of water by corn kernels, a sequence of experiments with K1830 yellow dent corn was conducted. Steeping was at 49°C. in solutions of four different concentration levels: 0, 0.1, 0.2, and 0.4%.

Differences between moisture increases in SO_2 solution and in plain water were as high as 20% after 8 hr. of steeping (Fig. 10). Note also

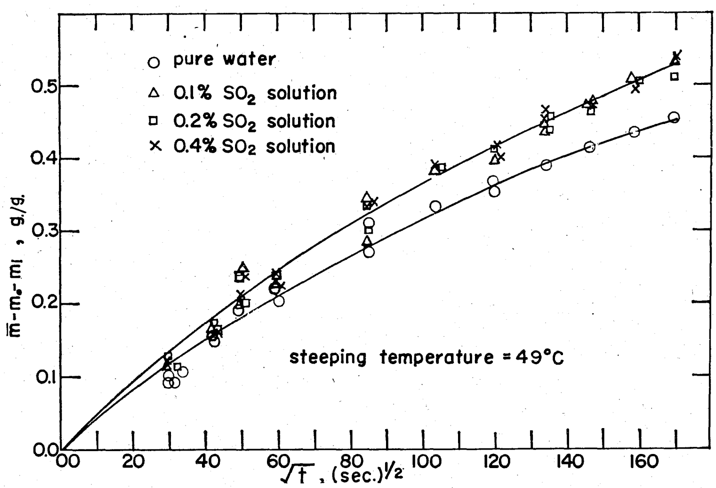

Fig. 10. Effect of concentration of SO_2 on moisture increase for K1830 hybrid yellow dent corn.

a very slight increase in rate of moisture gain with an increase of concentration levels from 0.1 to 0.4%. However, in many cases the moisture increase in 0.4% SO_2 solution showed slightly higher values than those at the lower concentration levels. Therefore, the optimum concentration of SO_2 in steeping water is around 0.2% or less from the standpoint of increasing diffusion rate.

Average diffusivities were evaluated from all the data appearing in Figs. 1, 2, and 3. Those figures also show, in general, that slopes of $(\bar{m} - m_0)$ *vs.* $\sqrt{t}$ plots are slightly larger early in the initial period. To show such a trend, values of the so-called diffusivities were also calculated from the slope at the vicinity of origin (Table II). The linearity of $(\overline{m} - m_0)$ *vs.* $\sqrt{t}$ plots is quite good in the first 45 min. for the sweet corn and popcorn, and in the first 120 min. for the dent corn. Those periods were considered as the initial periods of steeping.

TABLE II

Diffusivities of Water in Corn Kernels

Corn Variety	Temperature	In Water		In SO_2 Solution	
		Initial	Average	Initial	Average
	°C.	$D \times 10^8$, cm.²/sec.			
Gold Rush sweet	10	5.2676	4.1422	3.2602	3.4762
	25	10.3333	10.1848	7.3919	9.0945
	38	15.578	20.005	14.925	19.862
	49	30.117	32.136	25.903	31.546
	60	46.593	52.771	44.684	58.347
	71	65.713	73.701	68.271	78.902
K-4 Popcorn	10	20.054	9.492	20.228	10.487
	25	32.675	17.466	33.510	21.678
	38	46.269	26.118	50.906	32.181
	49	57.018	37.645	71.442	42.302
	60	71.329	43.508	106.63	48.045
DeKalb 3 × 1 dent	10	4.941	4.502	4.896	4.967
	25	11.121	11.543	12.638	14.884
	38	33.722	19.725	42.886	27.618
	49	48.321	40.471	66.174	62.550
	60	89.681	89.275	141.23	109.682

Comparing data obtained in this work with those of previous work (1,2,3,4,5) demonstrated that, regardless of the varieties, almost all cereal grain had diffusivities of the same magnitude of 10^{-7} cm.²/sec. in the temperature range from 0° to 100°C. That could be expected because of the similarity in physical and chemical characteristics of cereal grains. Two varieties of corn – Gold Rush sweet corn and K-4 hybrid popcorn – used in a previous work were used again. Consistently lower values were obtained, but the order of magnitude was nearly identical. The difference in values was caused, in addition to human errors, by the change in bulk structure of the corn kernels during an additional year of storage.

Comparing values of activation energy for various varieties of cereal grain obtained by previous investigators (1,2,3,4,5) and in our work shows that the magnitudes of the activation energy are fairly close. This could also be expected because of the similarity in chemical and physical characteristics of cereal grains.

Acknowledgment

The authors are grateful for various suggestions by Majel M. MacMasters in conducting this project and for the Corn Industries Research Foundation's support.

Literature Cited

1. CHUNG, D. S., FAN, L. T., and SHELLENBERGER, J. A. Volume increase of wheat kernel accompanying absorption of liquid water. J. Biochem. Microbiol. Eng. **3:** 377–393 (1961).
2. FAN, L. T., CHUNG, D. S., and SHELLENBERGER, J. A. Diffusion coefficients of water in wheat kernels. Cereal Chem. **38:** 540–548 (1961).
3. CHU, P. S. Diffusion of water in kernels of corns and sorghums. M.S. Thesis, Kansas State University (1961).
4. FAN, L. T., CHU, P. S., and SHELLENBERGER, J. A. Volume increase of kernels of corn and sorghum accompanying absorption of liquid water. Biotech. Bioeng. **4:** 311–322 (1962).
5. FAN, L. T., CHU, P. S., and SHELLENBERGER, J. A. Diffusion of water in kernels of corn and sorghum. Cereal Chem. **40:** 303–313 (1963).
6. KERR, R. W. Chemistry and industry of starch (2nd ed.). Academic Press: New York (1950).
7. COX, M. J., MACMASTERS, MAJEL M., and HILBERT, G. E. Effect of the sulfurous acid steep in corn wet-milling. Cereal Chem. **21:** 447–465 (1944).
8. BECKER, H. A., and SALLANS, H. R. A study of diffusion in solids of arbitrary shape, with application to the drying of the wheat kernels. J. Appl. Polymer Sci. **1:** 212–226 (1959).
9. BECKER, H. A. On the absorption of liquid water by the wheat kernel. Cereal Chem. **37:** 309–323 (1960).
10. AMERICAN ASSOCIATION OF CEREAL CHEMISTS. Cereal laboratory methods (7th ed.). The Association: St. Paul, Minn. (1962).