

## A Study of Diffusion in Solids of Arbitrary Shape, with Application to the Drying of the Wheat Kernel

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### INTRODUCTION

A previous paper<sup>1</sup> reported a study of the basic variables involved in the drying of wheat kernels in a stream of dry, isothermal air. It was shown that the gross conditions for application of an integral diffusion equation existed, and a conventional correlation of the data was therefore formulated by assuming the applicability of the equation for diffusion in spheres (the standard integral which most nearly corresponds to the geometry of the wheat kernel).

While this approach at once afforded a practical solution, it is a theoretically unsatisfying substitute for a general approach to the rigorous treatment of nonstationary-state diffusion in solids of geometry too complex to allow analytical integration of the differential diffusion equation, and leads to an indeterminate error in the calculation of the diffusion coefficient. The present research was therefore undertaken to develop mathematical methods for the general solution of problems on nonstationary-state diffusion in solids of arbitrary shape, and, in particular, to obtain an improved solution to the drying of the fully exposed wheat kernel. In the experimental work, drying of wheat was studied under the simplest conditions at constant temperature and zero external resistance to mass transfer. The latter condition was assured by the use of high vacuum. Analysis of the data led, finally, to an integral diffusion equation which shows that the decrease in drying rate with time is slightly smaller than that predicted by the equation for spheres.

### THEORETICAL

The object of this section is to formulate a method for general evaluation of the diffusion coefficient from data on the nonstationary state

and to examine methods for the subsequent correlation of data.

#### A. Derivation of a General Diffusion Equation

Consider the diffusion of a substance through an elemental volume  $dx \cdot dy \cdot dz$  arbitrarily located within a solid. Diffusive flow from the surface  $x$  to the surface  $x + dx$  is caused by a difference between the thermodynamic potentials at these surfaces. When this is due to a difference in concentration, the proportionality between the diffusion current and the potential gradient is conventionally expressed by Fick's first law of diffusion:

$$J_x = -D_x \frac{\partial c}{\partial x} \quad (1)$$

where the proportionality factor  $D$ , the Fickian diffusion coefficient, is, in the general case, a function of concentration, position, and direction. In the stationary state the concentration at a given point is invariant; hence the sum  $J_x + J_y + J_z$  is constant and

$$D_x \frac{\partial c}{\partial x} + D_y \frac{\partial c}{\partial y} + D_z \frac{\partial c}{\partial z} = \text{constant} \quad (2)$$

In the nonstationary state, the diffusion current is a function of time. Suppose that the amount of substance diffusing across the elemental area  $dy \cdot dz$  at  $x$  in a differential time  $dt$  is  $J_x \cdot dy \cdot dz \cdot dt$ , while at  $x + dx$  it is  $[J_x + (\partial J_x / \partial x) dx] dy \cdot dz \cdot dt$ , etc. The differences in input and output of the substance result in an accumulation in the element equal to  $(\partial c / \partial t) dt \cdot dx \cdot dy \cdot dz$ . On equating the total difference between input and output to the accumulation, and putting  $J_x = -D_x \partial c / \partial x$ , etc., we obtain the nonstationary-state differential diffusion equation in Cartesian coordinates:

$$\frac{\partial}{\partial x} \left( D_x \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_y \frac{\partial c}{\partial y} \right) + \frac{\partial}{\partial z} \left( D_z \frac{\partial c}{\partial z} \right) = \frac{\partial c}{\partial t} \quad (3)$$

Solution of the differential equation, or its equivalent in cylindrical or spherical coordinates, is not difficult if the diffusion coefficient is constant and if adequate initial and boundary conditions are given. Simplest are those cases in which symmetry exists about a point, line, or plane; the differential equations for a constant diffusion coefficient are of the general form:

$$D \left( \frac{\partial^2 c}{\partial r^2} + \frac{n}{r} \frac{\partial c}{\partial r} \right) = \frac{\partial c}{\partial t} \quad (4)$$

where  $r$  is a coordinate whose axes are everywhere perpendicular to the bounding surface and whose origin is at the center of symmetry, and  $n$  has the value zero for planar symmetry, unity for axial symmetry, and two for spherical symmetry.

However, to approach solution from a general viewpoint, let us consider diffusion in a solid of arbitrary shape. The initial and boundary conditions of present interest are:

$$\begin{aligned} c &= c_0 & \text{at } t = 0 \\ c &= c_s & \text{at } s = 0 \text{ and } t > 0 \end{aligned} \quad (5)$$

where  $s$  is a general coordinate whose origin is at the bounding surface and whose axes are everywhere perpendicular to the surface (in eq. (4),  $s = r_0 - r$ , where  $r_0$  is the distance from the center of symmetry to the surface). We shall examine the general form of solutions—for a constant diffusion coefficient—from the neighborhood of  $t = 0$  to  $t = \infty$ .

It is evident that, near  $t = 0$ , concentration changes in the solid, under the stated conditions, will be confined to the neighborhood of the surface. Therefore, in the first instant of time, the state of affairs near the surface approximates the case of a semi-infinite, plane-faced solid. The solution of eq. (4) for this case takes the form of the Gauss error integral:<sup>2</sup>

$$1 - C = \frac{2}{\sqrt{\pi}} \int_c^Z \exp \{-Z^2\} dZ \quad (6)$$

which gives the concentration as a function of the distance from the surface; where

$$C = \frac{c - c_s}{c_0 - c_s}$$

and

$$Z = \frac{s}{2\sqrt{Dt}} \quad (7)$$

To obtain the average concentration in a finite solid as a function of time near  $t = 0$ , we make a material balance about the bounding surface:

$$(c_0 - \bar{c})V = \int_0^t JS dt \quad (8)$$

where, by Fick's first law;

$$J = -D \left( \frac{\partial c}{\partial s} \right)_{s=0} \quad (9)$$

(Note that for a constant diffusion coefficient  $J$  approaches constancy over the surface as the time  $t$  approaches zero.) The concentration gradient at the surface,  $(\partial c / \partial s)_{s=0}$ , is obtained by differentiating eq. (6). Putting  $\partial C = \partial c / (c_0 - c_s)$  and  $\partial Z = \partial s / 2\sqrt{Dt}$ , and noting that  $\exp \{-Z^2\}$  approaches unity as  $t$  and  $s$  approach zero, we find that

$$- \left( \frac{\partial c}{\partial s} \right)_{s=0} \rightarrow \frac{c_0 - c_s}{\sqrt{\pi Dt}} \text{ as } t \rightarrow 0 \quad (10)$$

On substituting for  $J$  and integrating, we obtain, from eq. (8),

$$\begin{aligned} \bar{C} &\rightarrow 1 - \frac{2}{\sqrt{\pi}} X \text{ as } X \rightarrow 0, \text{ or} \\ \frac{1 - \bar{C}}{X} &= \frac{2}{\sqrt{\pi}} \text{ at } X = 0 \end{aligned} \quad (11)$$

where

$$\bar{C} = \frac{c - c_s}{c_0 - c_s}, X = \frac{S}{V} \sqrt{Dt} \quad (12)$$

This result provides a first approximation to a general solution, valid in the neighborhood of  $t = 0$ , of the nonstationary-state differential diffusion equation. Note that the prescribed form of the solution for  $t \geq 0$  is

$$\bar{C} = f(X) \quad (13)$$

To obtain a more accurate approximation, we assume that  $f(X)$  can be represented, in the neighborhood of  $X = 0$ , as a power series in  $X$ ; we find, (Maclaurin's series):

$$\begin{aligned} f(X) &= f(0) + f'(0)X + \frac{f''(0)}{2!} X^2 \\ &+ \dots + \frac{f^n(0)}{n!} X^n + \dots \end{aligned} \quad (14)$$

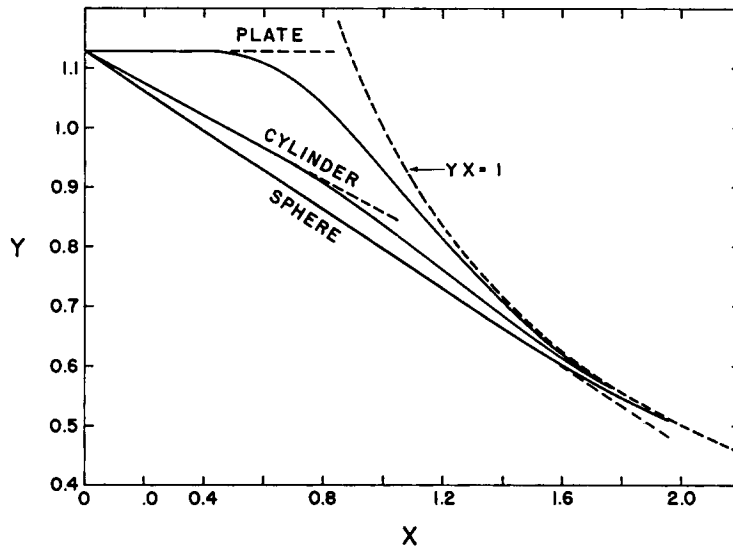


Fig. 1.  $Y = (1 - \bar{C})/X$  as a function of  $X$ , showing the analytical solutions for a plate of infinite area, a cylinder of infinite length, and a sphere.  $YX = 1$  is the trivial solution for the neighborhood of  $t = \infty$ .

Equation (11) immediately gives  $f(0) = 1$  and  $f'(0) = -2/\sqrt{\pi}$ . The higher derivatives,  $f''(0)$ , etc., are clearly dependent on solid shape. However, since the series should converge rapidly near  $X = 0$ , terms higher than  $f''(0)$  will be neglected, giving for our final approximation

$$\bar{C} = 1 - \frac{2}{\sqrt{\pi}} X + \frac{f''(0)}{2!} X^2 \quad (15)$$

The range of validity of this equation may be tested by comparing it with some specific solutions of the differential equation, eq. (4). The solutions\* of interest, subject to the conditions of eq. (5), are as follows.<sup>2</sup>

The solution for a plate of infinite area is given by:

$$\bar{C} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} \exp \left\{ - \frac{(2n + 1)^2 \pi^2}{4} X^2 \right\} \quad (16)$$

The solution for an infinitely long cylinder is given by:

$$\bar{C} = \sum_{n=1}^{\infty} \frac{4}{\lambda_n^2} \exp \left\{ - \frac{\lambda_n^2}{4} X^2 \right\} \quad (17)$$

where  $J_0(x)$  is the Bessel function of zero order

\* Note that in  $X$  the volume-to-surface ratio,  $V/S$ , replaces the center of symmetry to surface distance,  $r_0$ , usually appearing in these solutions; i.e., the radius of the sphere and cylinder and the half-thickness of the plate. For the plate  $V/S = r_0$ ; for the cylinder,  $V/S = r_0/2$ ; and for the sphere,  $V/S = r_0/3$ .

and  $\lambda_n$  are the roots (2.405, 5.520, 8.654, . . .) of  $J_0(x) = 0$ .

The solution for a sphere is given by:

$$\bar{C} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left\{ - \frac{n^2 \pi^2}{9} X^2 \right\} \quad (18)$$

To test eq. (15), we determine  $(1 - \bar{C})/X$  as a function of  $X$  (Fig. 1). It is seen that, in the neighborhood of  $X = 0$ , the slope,  $f''(0)/2$ , is essentially constant. For the plate,  $f''(0) = 0$  to approximately  $X = 0.5$  ( $\bar{C} = 0.45$ ); for the cylinder,  $f''(0) = 0.538$  to  $X = 0.8$  ( $\bar{C} = 0.3$ ); and for the sphere,  $f''(0) = 0.661$  to  $X = 1.0$  ( $\bar{C} = 0.2$ ); where the limits of validity are quoted for an error in  $1 - \bar{C}$  of less than 1%. It can be concluded, therefore, that eq. (15) accurately represents the solution in the neighborhood of  $X = 0$ .

We turn now to the general solution in the neighborhood of  $X = \infty$ . Here the examples, eqs. (16)-(18), indicate that

$$\bar{C} = \frac{\alpha}{\beta^2} \exp \{ -\beta^2 X^2 \} \quad (19)$$

where  $\alpha$  and  $\beta$  are constants for a given solid shape. Table I gives the values of  $\alpha$ ,  $\beta$ , and  $f''(0)$  for the examples, and shows that the difference  $\beta^2 - \alpha$  is nearly constant and has the maximum value  $(\pi^2 - 8)/4$ . The limits of validity of eq. (19) for an error in  $C$  smaller than 1% are: for the plate,  $X > 0.35$  ( $\bar{C} < 0.6$ ); for the cylinder,  $X > 0.4$  ( $\bar{C} < 0.4$ ); and for the sphere,  $X > 0.8$  ( $\bar{C} < 0.3$ ).

These limits overlap with those of eq. (15); hence it appears that eqs. (15) and (19) provide a general solution for all values of  $X$  from zero to infinity. Note that the examples leading to this deduction represent the very extremes of the shapes that can be produced by flattening, elongation, and compaction of a solid.

TABLE I  
Constants in the Diffusion Equations

Solid	$\alpha$	$\beta^2$	$\alpha/\beta^2$	$\phi =$	
				$\frac{\beta^2 - \alpha}{\pi^2 - 8}$	$f''(0)$
Plate of infinite area	2.000	2.467	0.810	1.000	0
Cylinder of infinite length	1.000	1.446	0.691	0.953	0.538
Wheat	0.862	1.300	0.663	0.940	0.588
Sphere	0.667	1.097	0.608	0.918	0.661

**B. Interpretation of Experimental Data**

(i) **Treatment of data in the neighborhood of  $t = 0$ .** Equation (15) can be written, in terms of the experimentally measured variables,

$$k = k_0 - b\sqrt{t} \tag{20}$$

where

$$k = \frac{c_0 - c}{\sqrt{t}} \tag{21}$$

$$k_0 = \frac{2}{\sqrt{\pi}} \frac{S}{V} \sqrt{D} (c_0 - c_s) \tag{22}$$

$$b = \frac{f''(0)}{2} \left(\frac{S}{V}\right)^2 D (c_0 - c_s) \tag{23}$$

Hence, if the equation is applicable, the ratio,  $k$ , of the decrease in the average concentration to the square root of the time should be a linear function of the square root of the time, with a slope  $-b$  and an intercept  $k_0$  at  $t = 0$ .

(ii) **Evaluation of the surface concentration,  $c_s$ .** Equations (20)–(23) show that, if the diffusion coefficient is independent of concentration,  $k_0$ ,  $b$ ,  $k$ , and  $(c_0 - \bar{c})$  should all be linear functions of the initial concentration,  $c_0$ , with identical intercepts  $c_0 = c_s$  at  $k_0$ ,  $b$ ,  $k$ , and  $c_0 - \bar{c}$  equal to zero ( $k$  and  $c_0 - \bar{c}$  being evaluated at a constant exposure time  $t$ ).

(iii) **Calculation of the diffusion coefficient.** Equation (22) gives, for the diffusion coefficient,

$$D = \left(\frac{\sqrt{\pi}}{2} \frac{V}{S} \frac{k_0}{c_0 - c_s}\right)^2$$

(iv) **The solution for the neighborhood of  $t = 0$ .** When the surface concentration and the diffusion coefficient have been calculated, eq. (23) gives the value of the coefficient  $f''(0)$ . Equation (15) then gives the solution of the neighborhood of  $t = 0$ .

(v) **Treatment of data in the neighborhood of  $t = \infty$ .** The surface concentration, as noted under section (ii), is generally obtainable from the linear regression of  $c_0 - \bar{c}$  on  $c_0$ ; hence  $\bar{C}$  can be calculated from data confined to the neighborhood of  $t = \infty$ . Equation (19) shows that  $\ln \bar{C}$  should be a linear function of time, extrapolating to  $\ln \alpha/\beta^2$  at  $t = 0$  and having a slope  $-\beta^2(S/V)^2D$ . Rigorous evaluation of  $\alpha$ ,  $\beta$ , and  $D$  is not possible, unless one of them is determined independently. However, Table I indicates that  $\beta^2 - \alpha = \phi(\pi^2 - 8)/4$ , where  $\phi$  lies between 0.918 and unity. Since  $\phi$  is so nearly constant, it may be assumed that  $\phi = 1$  for plate-like solids, while for bluff-shaped solids  $\phi = 0.92$ . Remembering that  $\alpha/\beta^2$  is directly obtainable from the data,  $\beta$  is given by

$$\frac{\alpha}{\beta^2} = \frac{\beta^2 - \phi(\pi^2 - 8)/4}{\beta^2} \tag{24}$$

A similar method can be used to approximate the values of  $\alpha$  and  $\beta$  from the solution for the neighborhood of  $t = 0$ . Since  $\alpha$  and  $\beta$  are so closely related, it may be assumed that  $\beta^2$  and  $\phi$  are unique functions of  $f''(0)$ , as given by the data for the plate, the cylinder, and the sphere (Table I and Fig. 2). The constant  $\alpha$  then follows from eq. (24).

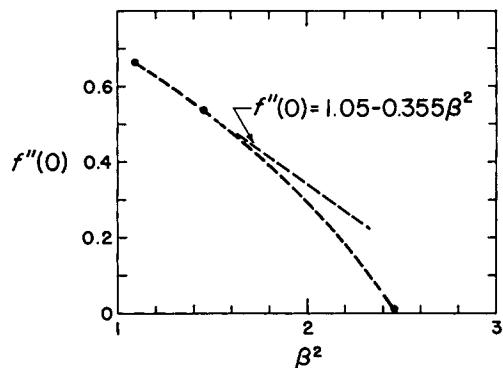


Fig. 2. The apparent relation between the coefficients  $f''(0)$  and  $\beta^2$ . The points represent, left to right, the sphere, the cylinder of infinite length, and the plate of infinite area.

(vi) **Evaluation of  $\bar{C}$  in the case of moisture diffusion.** Equations (15)–(19) were derived for a solid of constant dimensions. For such a solid,  $\bar{C}$  is exactly equal to  $\bar{M}$ , where

$$\bar{M} = (\bar{m} - m_s)/(m_0 - m_s) \quad (25)$$

However, in most natural and synthetic polymers, moisture adds its volume (as liquid water) to the volume of the solid. Since it is not practicable to account for the resulting swelling, it must be assumed that  $\bar{C} = \bar{M}$  in these cases also. The resulting error should not be serious so long as  $m_0 - m_s$  is reasonably small compared with the specific volume of the solid (in cm.<sup>3</sup>/g.).

**(vii) Evaluation of the volume-to-surface ratio in moisture diffusion.** It is not practicable to account for swelling in evaluating the volume-to-surface ratio,  $V/S$ . If  $m_0 - \bar{m}$  is very much smaller than  $m_0 = m_s$ ,  $V/S$  may be evaluated at the initial moisture,  $m_0$ . When  $m_0 - \bar{m}$  is comparable with  $m_0 - m_s$ ,  $V/S$  is best evaluated at the surface moisture,  $m_s$ .

Rearrangement of the ratio  $V/S$  gives

$$\frac{V}{S} = \frac{r_s}{3} \frac{4\pi r_s^2}{S} \quad (26)$$

The factor  $4\pi r_s^2/S$  is the ratio of the surface area of a sphere of equal volume to the surface area of the solid, and is a shape factor commonly known as the sphericity and denoted by  $\psi$ . It can be assumed that the sphericity of a swelling solid is constant, unless swelling is unusually anisotropic.

**(viii) Static and dynamic equilibrium relations.**

The methods described under section (ii) give dynamic (extrapolated) values of the surface concentration,  $c_s$ . Static methods, such as adsorption-desorption equilibrium studies, give the true surface concentration at  $t = \infty$ , when  $c = c_s$ . It might appear that both methods should give the same value of  $c_s$  for a given boundary condition in the surroundings. In actuality, three, and probably more, sources of divergence may be anticipated; (a) adsorption-desorption hysteresis; (b) swelling; and (c) the manifestation of dynamic pseudo-equilibria when the static equilibrium concentration is outside the range of concentration independence of the diffusion coefficient. Generally, dynamic values of  $c_s$  can be expected to be equal to or greater than static values determined under similar conditions.

**(ix) Sources of experimental deviations from the diffusion equations.** Failure of experimental data to follow eqs. (15)–(19) may be due to any of the following factors.

(a) The diffusion coefficient varied with time because the temperature of the solid was not constant.

(b) The surface concentration varied with time because the concentration of the diffusing species in the surroundings was not constant.

(c) The diffusion coefficient is dependent on concentration in the range studied. (Equation 20 may still be followed, but  $k_0$ ,  $k$ , and  $b$  will usually be curvilinear functions of the initial concentration. At a given concentration,  $k_0^2$  should show approximately the same temperature dependency as the diffusion coefficient at that concentration. The relation between  $k_0$  and the initial concentration at constant temperature may provide the basis for an empirical correlation.)

(d) The diffusion coefficient is dependent on position within the solid. (Empirical correlations may be formulated as in the preceding case. However, the net effect may be simply equivalent to a distortion of the solid geometry, accomplished without affecting the apparent applicability of the diffusion equations, but leading to an indeterminately weighed diffusion coefficient.)

(e) The process occurring is not diffusion. (This may be suspected if  $f''(0)$  falls outside the range enclosed by the sphere and the plate (Table I) or if the relation with the  $S/V$  ratio required by the diffusion equations is not obeyed.)

## MATERIALS AND METHODS

### Wheat

The Thatcher wheat selected for study was of No. 2, first generation, registered seed grade. Samples at moisture levels from 7.6 to 28%, dry basis, were prepared and stored as previously reported,<sup>1</sup> except that 0.1% each of candidin and neomycin was added to the water used in conditioning to suppress the growth of fungi.

### Kernel Density

The kernel density was determined pycnometrically with toluene. Table II summarizes the results for moistures from 7.6 to 20.2%, dry basis. The calculated density of moisture-free wheat,  $\rho_s$ , is seen to be constant, showing that the volume of moisture, which is calculated as liquid water, is added directly to the volume of the moisture-free wheat. The formula relating density to moisture content is

$$\rho = \rho_s \frac{1 + m}{1 + \rho_s m} \quad (27)$$

where  $\rho$  is the density (in g./cm.<sup>3</sup>) at a moisture content  $m$  (in g./g.) dry basis.

TABLE II  
 Density of Wheat

$m_0$ , g./g.	$\rho$ , g./cm. <sup>3</sup>	$\rho_s$ , g./cm. <sup>3</sup>
0.0761	1.400	1.444
0.0907	1.406	1.460
0.1078	1.393	1.455
0.1311	1.370	1.440
0.145	1.379	1.459
0.174	1.369	1.463
0.202	1.350	1.453
		1.453 ± 0.006

### Volume-to-Surface Ratio

It has been indicated in the theoretical section that, when the moisture loss  $m_0 - \bar{m}$  is comparable to the limiting moisture loss  $m_0 - m_s$ , the volume-to-surface ratio of a solid,  $V/S$ , may be calculated at the surface moisture content,  $m_s$ . Surface moistures in the present study were in the range 9.9–10.6%, dry basis. Kernel dimensions were measured on a sample of wheat at 10.8% and required no correction.

The mean kernel volume was calculated from the weight of a sample of 2000 kernels, according to the formula:

$$\bar{V} = \frac{\Sigma w}{\rho n} \quad (28)$$

where  $w$  is the weight of a kernel and  $n$  is the number of kernels. The value found was  $\bar{V} = 0.0205$  cm.<sup>3</sup>/kernel.

To determine the mean surface area per kernel, measurements of the maximum diameter,  $d_{max}$ , the minimum diameter,  $d_{min}$ , and the length,  $l$ , were made in a sample of 120 kernels; (the location of the diameters is shown in Fig. 3). The mean surface area is correctly calculated as

$$\bar{S} = \frac{\Sigma S}{n} \quad (29)$$

However, because the kernel size distribution (Fig. 3) was narrow and the diameters  $d_{max}$  and  $d_{min}$  are nearly the same, it was estimated that there is less than 1% error in calculating  $\bar{S}$  as

$$\bar{S} = K \left( \frac{\Sigma l}{n} \right) \left( \frac{\Sigma d_m}{n} \right) \quad (30)$$

where  $K$  is a constant and  $d_m = (d_{max} + d_{min})/2$ . The mean visible surface area was therefore esti-

ated by the formula for an ellipsoid:

$$\bar{S} = \frac{\pi}{2} \bar{l} \bar{d}_m \left[ \frac{\bar{d}_m}{\bar{l}} + \frac{1}{e} \sin^{-1} e \right] \quad (31)$$

where  $e = \sqrt{\bar{l}^2 + \bar{d}_m^2}/\bar{l}$ . The mean values of length and diameter where  $\bar{l} = 0.522$  cm.;  $\bar{d}_{max} = 0.296$  cm.;  $\bar{d}_{min} = 0.266$  cm. Hence  $\bar{d}_m = 0.281$  and  $\bar{S} = 0.398$  cm.<sup>2</sup>.

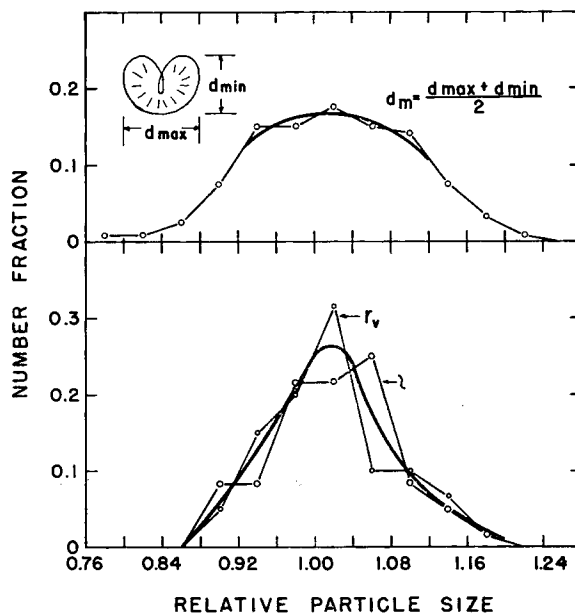


Fig. 3. The size distribution in the dimensions of the wheat kernel, based on measurement of 120 kernels. Shown is the number fraction of kernels within 0.04 unit brackets of relative particle size, where relative particle size is defined as the ratio between a given dimension and its arithmetic-average value.

However, it appears that, in vacuum drying, the area enclosed by the cheeks of the kernel, within the crease, is fully exposed and should be added to the visible area. This area was estimated as one half of the elliptical area  $\pi \bar{l} \bar{d}_{min}/4$ , or 0.055 cm.<sup>2</sup>/kernel. The total surface area is thus 0.453 cm.<sup>2</sup>/kernel, and the volume-to-surface ratio is  $\bar{V}/\bar{S} = 0.0453$  cm. The equivalent spherical radius is  $r_s = 0.170$  cm. and the sphericity is  $\psi = 0.80$ .

When the area within the crease is omitted,  $\bar{V}/\bar{S} = 0.0515$  cm. and  $\psi = 0.91$ .

### Moisture Analysis

Initial moistures were determined by drying samples of ground wheat four hours at 110°C. under high vacuum. Moistures so determined agreed within 0.001 g./g. with moistures found by drying sixteen hours at 30°C. at high vacuum,

followed by four hours at 110°C. The method was chosen to give results closely approximating the "true" moisture content.<sup>3</sup>

### High Vacuum Drying Technique

Samples of 70–100 kernels were dried in thin-walled brass tubes 0.8 cm. in inside diameter and 10 cm. in length. The tubes were attached by rubber tubing to a vacuum manifold and were immersed in a constant temperature bath controlled within  $\pm 0.1^\circ\text{C}$ . An initial warming period of 20–30 minutes allowed the samples to reach the temperature of the bath before drying was begun. The difference between the initial and final weights of a sample gave the moisture lost during the drying period. Drying times ranged from three minutes to sixteen hours. Experiments were carried out at temperatures of 25, 30, 35, 40, and 50°C.

The large ratio between the kernel diameter,  $d_m = 0.28$  cm., and the drying tube diameter, 0.8 cm., assured that each kernel was in direct contact with the tube wall, facilitating rapid conduction of heat into the kernel. The degree of temperature control effected by this method was checked by comparing it with a more efficient method: single layers of kernels were dried afloat a pool of mercury in a pycnometer bottle. Moisture losses by the two methods were found to be identical.

### CORRELATION AND DISCUSSION OF RESULTS

The experimental data were first plotted to show  $k = (m_0 - \bar{m})/\sqrt{t}$  as a function of  $\sqrt{t}$  to determine the applicability of eq. (20). The relation, exemplified by the data for 40°C. (Fig. 4), was found to be essentially linear in the neighbor-

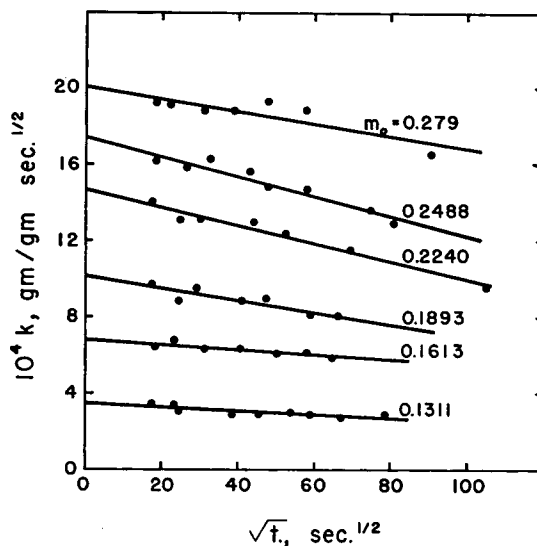


Fig. 4.  $k = (m_0 - \bar{m})/\sqrt{t}$  as a function of  $\sqrt{t}$  and  $m_0$  for the vacuum drying of wheat at 40°C.

hood of  $t = 0$ , and the slope  $-b$  and the intercept  $k_0$  were therefore calculated statistically. Table III shows the results for 40°C. (In this and in the following discussion, the moisture content,  $m$ , replaces the concentration,  $c$ , in the diffusion equations.)

The dynamic surface moisture content, given by eqs. (20)–(23), was next evaluated at each temperature. The intercept  $k_0$  was found to be essentially a linear function of the initial moisture in the range of initial moistures 0.13–0.25 g./g. (Fig. 5). Statistical calculation of the intercepts at  $k_0 = 0$  gave surface moistures (Table IV) of 0.0989–0.1069 g./g. The slope  $-b$  was also found to be a linear function of the initial moisture (Fig. 6). Statistical calculation of the intercepts at  $b = 0$  gave nearly constant surface moistures averaging 0.1157 g./g. (Table IV). The apparent disagree-

TABLE III  
Intermediate Data on the Vacuum Drying of Wheat at 40°C.

$m_0$ , g./g.	$\sqrt{t}$ , sec. <sup>1/2</sup>	$10^4 k$ , sec. <sup>-1/2</sup>	$10^5 k$ ( $\sqrt{t} = 50$ ), sec. <sup>-1/2</sup>	$10^4 k_0$ , sec. <sup>-1/2</sup>	$10^5 b$ , sec. <sup>-1</sup>	$10^3 k_0$	$10^5 b$
						$m_0 - m_s$ ( $m_s = 0.1034$ ), sec. <sup>-1/2</sup>	$m_0 - m_s$ ( $m_s = 0.1157$ ), sec. <sup>-1</sup>
0.1311	45.0	3.01	2.96	3.43	0.093	1.238	(6.02) <sup>a</sup>
0.1613	40.6	6.29	6.16	6.85	0.139	1.183	3.06
0.1893	40.7	8.84	8.55	10.12	0.315	1.178	4.28
0.202	38.9	10.90	10.55	12.07	0.304	1.224	3.53
0.224	49.0	12.36	12.31	14.69	0.477	1.218	4.41
0.249	47.7	15.0	14.88	17.46	0.515	1.200	3.87
0.279	43.7	18.67	18.46	20.09	0.326	1.144	(2.05) <sup>a</sup>
						$1.198 \pm 0.030$	$3.83 \pm 0.50$

<sup>a</sup> These values were omitted in calculating the mean.

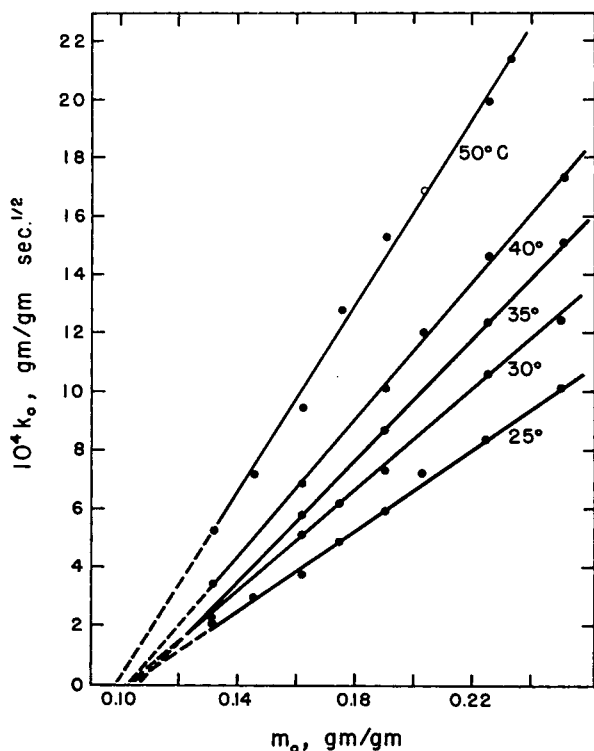


Fig. 5. The intercept  $k_0$  as a function of initial moisture content and temperature.

ment here with the values obtained from  $k_0$  is not serious in its practical consequences, as is seen when the surface moisture is calculated from the regression of  $k$  on the initial moisture at an intermediate value of  $\sqrt{t}$  (Fig. 7 and Table IV).

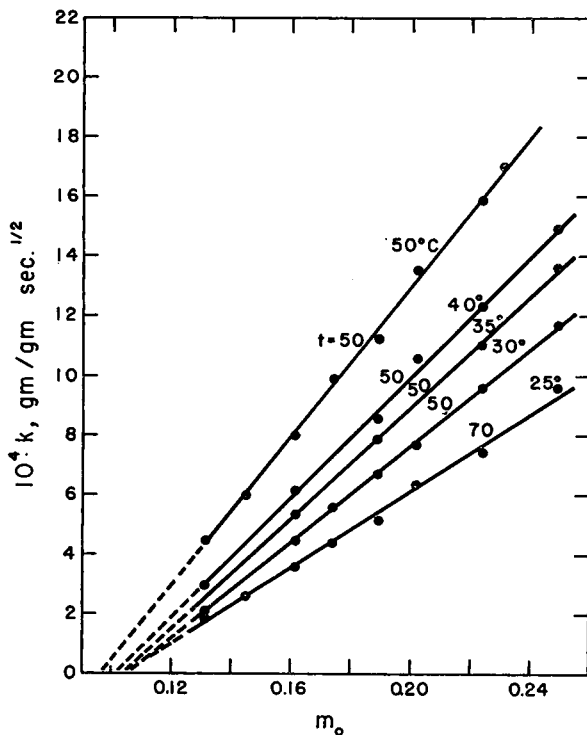


Fig. 7.  $k = (m_0 - \bar{m})/\sqrt{t}$  as a function of initial moisture content and temperature at values at  $\sqrt{t}$  intermediate between zero and infinity.

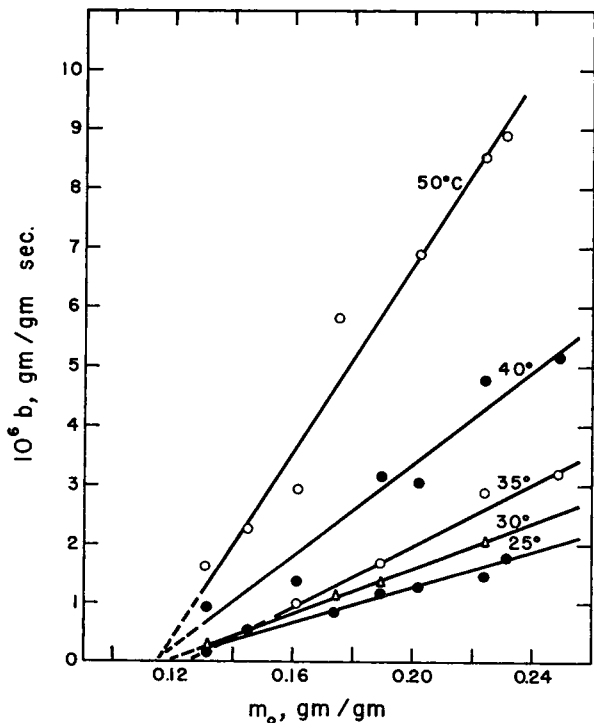


Fig. 6. The slope  $b$  as a function of initial moisture content and temperature.

Comparison with the values for  $\sqrt{t} = 0$ , i.e.,  $k = k_0$ , shows that the actual drift in the dynamic value of  $m_s$  with time is practically negligible at drying times of ordinary interest.

TABLE IV  
Dynamic Surface Moisture Contents in the Vacuum Drying of Wheat

Temperature, °C.	$m_s$ , g./g.		
	$k_0 = 0$	$k = 0$	$b = 0$
25	0.1044	0.1045 <sup>a</sup>	0.1159
30	0.1037	0.1057 <sup>b</sup>	0.1173
35	0.1069	0.1044 <sup>b</sup>	(0.1247) <sup>c</sup>
40	0.1034	0.1013 <sup>b</sup>	0.1142
50	0.0989	0.0965 <sup>b</sup>	0.1153
			0.1157

<sup>a</sup>  $k$  evaluated at  $\sqrt{t} = 70 \text{ sec.}^{1/2}$ .

<sup>b</sup>  $k$  evaluated at  $\sqrt{t} = 50 \text{ sec.}^{1/2}$ .

<sup>c</sup> This value was omitted in calculating the mean.



The above-calculated surface moisture contents have been given theoretical significance by the authors' recent analysis<sup>4</sup> of the moisture desorption isotherm of wheat. It is therein remarked that the surface moisture, 0.1157 g./g., intercepted by the regression of  $b$  on  $m_0$  is quantitatively identifiable with the number of primary (low energy) sites available for sorption, while the surface moisture intercepted by the regression of  $k_0$  on  $m_0$  is quantitatively identifiable with the number of primary sites actually occupied at saturation equilibrium at a given temperature. These surface moistures are thus correlated (inferentially) by the theoretical equation:

$$(m_s)_{t=0} = 0.1157 \frac{K}{1 + K}$$

where  $K = 3.05 \times 10^{-4} \exp \{6270/RT\}$ . This equation gives a good, theoretically plausible description of the presently observed properties of the dynamic surface moisture content.

The values of the surface moisture finally chosen for the correlation of the drying data were taken from the regression of  $k_0$  on the initial moisture, for the following reasons: (1) theoretically, because the diffusion coefficient is calculated from  $k_0$ , and (2) practically, because the drift in the surface moisture with time among the present data is practically negligible, and it is least arbitrary to evaluate it at time zero.

To evaluate the diffusion coefficient, the mean value of  $k_0/(m_0 - m_s)$  was first calculated for each temperature, as exemplified by the data for 40°C. (Table III). Diffusion coefficients were

TABLE V  
Diffusion Constants in the Vacuum Drying of Wheat

Temperature, °C.	$m_s$ , g./g. <sup>a</sup>	$10^3/T$ , °K. <sup>-1</sup>	$10^7 D$ , cm. <sup>2</sup> /sec.	$f''(0)/2$	
				(Method 1)	(Method 2)
25	0.1045	3.356	0.869	0.300	0.340
30	0.1045	3.300	1.223	0.273	0.306
35	0.1045	3.247	1.700	0.253	0.287
40	0.1034	3.195	2.314	0.312	0.338
50	0.0989	3.096	4.229	0.329	0.360
				0.294	0.326

<sup>a</sup> Average value of  $m_s$  was used at 25, 30, and 35°C., since departures from this average (Table IV) are insignificant both theoretically<sup>4</sup> and practically.

then calculated from eq. (22) and are given in Table V. The relation between the diffusion coefficient and the absolute temperature (Fig. 8)

follows the Arrhenius-type equation:

$$D = D_0 \exp \{-E/RT\} \quad (32)$$

where  $D_0 = 76.8$  cm.<sup>2</sup>/sec. and  $E = 12.20$  kcal./mole.

The shape-dependent coefficient in eq. (15),  $f''(0)$ , was then evaluated by the following two methods. In the first, the mean value of  $b/(m_s - m_s)$  in the moisture range 0.15–0.25 (values too near  $b = 0$  being eliminated), was calculated

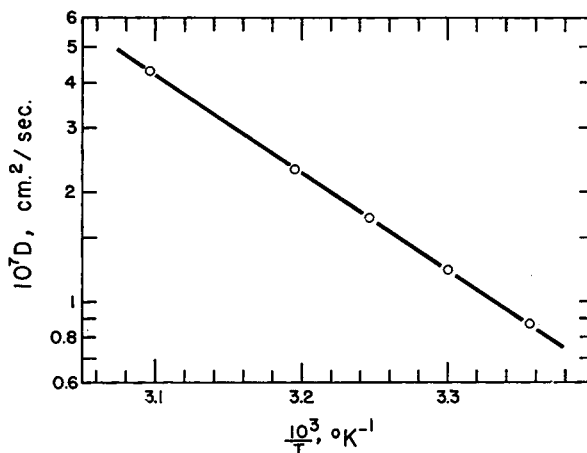


Fig. 8. The diffusion coefficient as a function of the reciprocal of the absolute temperature.

for each temperature, whereupon  $f''(0)$  was calculated from eq. (23). The results (Table V) give a mean value  $f''(0) = 0.588$ . The diffusion equation for vacuum drying of the wheat kernel in the neighborhood of  $t = 0$  is therefore

$$\bar{M} = 1 - \frac{2}{\sqrt{\pi}} X + 0.294 X^2 \quad (33)$$

where  $0.294 = f''(0)/2$ . The second method of calculating  $f''(0)$  led to a small, empirical correction of this equation. Mean values of  $b/(m_0 - m_s^*)$  were calculated (see example in Table III), and gave  $f''(0) = 0.652$ , (where  $m_s^*$  is the value of the surface given by the regression of  $b$  on the initial moisture). The corrected diffusion equation thus becomes

$$\bar{M} = 1 - \frac{2}{\sqrt{\pi}} X + 0.326 \frac{m_0 - 0.1157}{m_0 - m_s} X^2 \quad (34)$$

where  $0.326 = f''(0)/2$  and  $0.1157 = m_s^*$ . This equation describes exactly the results of statistical analysis of the data in the neighborhood of  $t = 0$ . However, in practice, eq. (33) is nearly as accurate and has the advantage of greater simplicity.

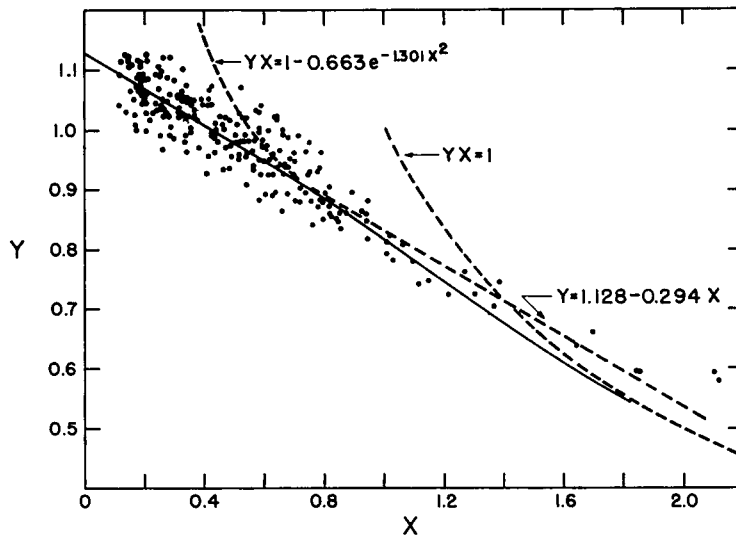


Fig. 9. General correlation of data on the vacuum drying of wheat at initial moistures of 0.14–0.25 g./g., dry basis.

It has been suggested in the theoretical section that eq. (33) can be used to deduce a solution for the neighborhood of  $t = \infty$ . The value  $f''(0) = 0.588$  for the wheat kernel is intermediate between the values for the sphere and the infinitely long cylinder (Table I). With the assumption that, in this region, the relations between  $f''(0)$  and the constants  $\phi$  and  $\beta^2$  are linear (see Table I and Fig. 2), these values for wheat are found to be  $\phi = 0.94$  and  $\beta^2 = 1.301$ . Equation (24) then gives  $\alpha = 0.862$ , whence  $\alpha/\beta^2 = 0.663$ . (For a comparison with the plate, cylinder, and sphere, see Table I.) The diffusion equation for the vacuum

drying of wheat in the neighborhood of  $t = \infty$  is, therefore,

$$\bar{M} = 0.663 \exp \{-1.301X^2\} \quad (35)$$

Figure 9 shows the agreement between the experimental data for initial moistures of 0.14–0.25 g./g. (the values of  $m_s$  and  $D$  in Table V being used), and values calculated from eqs. (33) and (35). The residual scatter is attributable in part, to the effects of abnormal size distributions in the seventy to one hundred kernels comprising a drying sample. The standard deviation in the value of  $1 - \bar{M}$  of the 233 points in

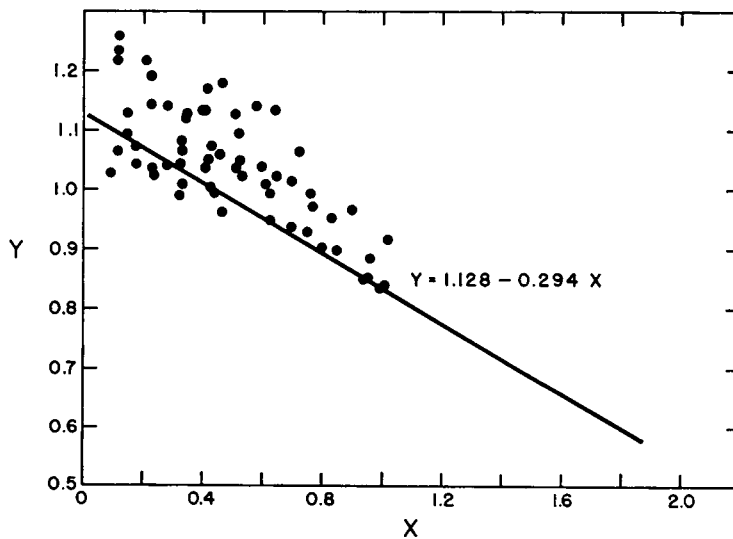


Fig. 10. General correlation of data on the vacuum drying of wheat at initial moistures of 0.26 and 0.279 g./g.

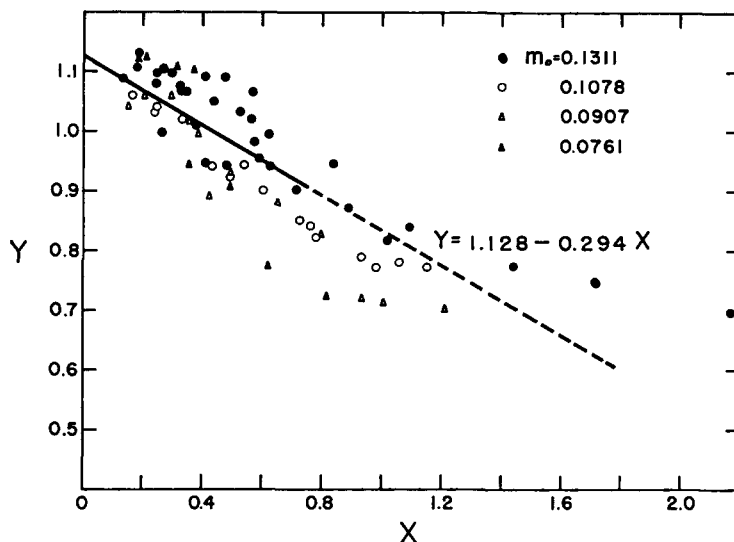


Fig. 11. General correlation of data on the vacuum drying of wheat at low initial moisture contents.

the range  $0 < X < 1.2$ , ( $0 < 1 - \bar{M} < 0.9$ ), is  $\pm 3.9\%$ . Because of the distribution in the value of  $f''(0)$  (Table V), the distribution of the individual deviations is not normal, but is bimodal with sharp peaks at  $\pm 2\%$ . One half of the data fall between these peaks. At  $X = 1.4$ ,  $1 - \bar{M}$  exceeds unity, and thereafter continues to increase with increasing value of  $X$ . This is because the value of the dynamic surface moisture prevailing at low and intermediate values of  $X$  becomes meaningless when  $X$  closely approaches infinity; under vacuum conditions the true, static equilibrium condition at the surface is  $m_s = 0$ , and drying continues until all moisture has been removed, i.e.,  $\bar{m} = 0$ .

Figure 10 shows that the relative moisture losses  $1 - \bar{M}$  (based on the values of  $m_s$  and  $D$  in Table V) for initial moistures of 0.26 and 0.279 g./g.

were slightly higher than those in the range of 0.14–0.25, to which eqs. (33) and (35) apply. In addition, the slopes  $b$  for these data were frequently subnormal (see Table III). While this behavior may be due to an increase in the diffusion coefficient, it may also be that in this region, in which equilibrium water vapor pressures approach the saturation point,<sup>5</sup> capillary effects augment the purely diffusive flow.

Figure 11 shows a correlation of data for initial moistures of 0.0761, 0.0907, 0.1078, and 0.1311 g./g. The value of  $X$  is based on the diffusion coefficients in Table V, and the ratio  $Y = (1 - \bar{M})/X$  was calculated from the relation

$$\frac{1 - \bar{M}}{X} = \frac{2}{\sqrt{\pi}} \frac{k}{k_0} \quad (36)$$

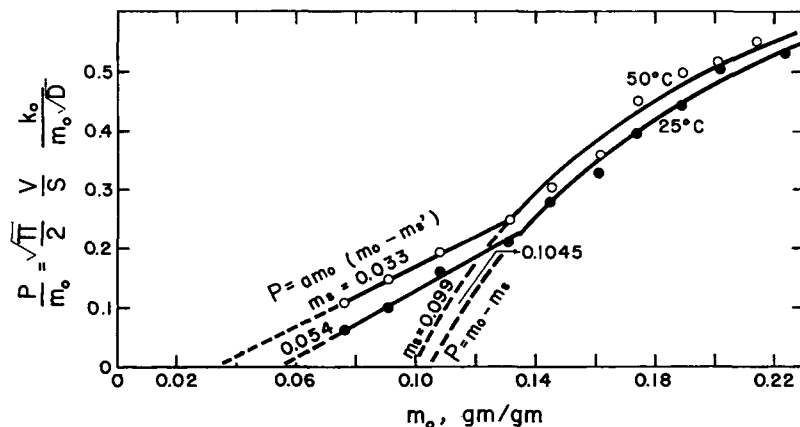


Fig. 12. A correlation of apparent values of the driving potential  $P$  in the vacuum drying of wheat at low initial moisture contents.

Although the dynamic surface moistures prevailing in the moisture range 0.14–0.25 g./g. are meaningless here, empirical driving potentials,  $P$ , can nevertheless be calculated from the relation, based on eq. (22):

$$P = \frac{\sqrt{\pi}}{2} \frac{V}{S} \frac{k_0}{\sqrt{D}} \quad (37)$$

where  $P = (m_0 - \bar{m})/(1 - \bar{M})$  in eq. (36). Figure 12 shows these potentials (obtained on the basis of the diffusion coefficients in Table V) as a function of the initial moisture content at 25 and 50°C. The figure indicates that, in the moisture range of 0.076–0.13 g./g.,

$$P = am_0(m_0 - m_s') \quad (38)$$

where  $a = 2.83$  and  $m_s' = 0.054$  at 25°C., and  $a = 2.53$  and  $m_s' = 0.033$  at 50°C. While the meaning of this equation is not immediately clear, the simplest interpretation suggests that the diffusion coefficient here is actually proportional to the square of the moisture content and that  $m_s'$  is a dynamic surface moisture. Equation (37) thus becomes

$$k_0 = \frac{2}{\sqrt{\pi}} \frac{S}{V} (m_0 - m_s') \sqrt{D'} \quad (39)$$

where  $\sqrt{D'} = am_0\sqrt{D}$ ; and  $D$  is the value of the diffusion coefficient in the range of its constancy, 0.14–0.25 g./g. (Table V). This interpretation is supported qualitatively by the fact that, in Figure 11,  $f''(0)$  becomes increasingly abnormal as the moisture content decreases below 0.13 g./g. (indicating that the diffusion coefficient decreases with decreasing moisture content),  $f''(0)$  being approximately proportional to  $1 + 7(0.13 - m_0)$ . An alternative but qualitatively similar explanation would make the diffusion coefficient proportional to  $(m_0 - m_s')^2$  and the dynamic surface moisture equal to zero:

$$k_0 = \frac{2}{\sqrt{\pi}} \frac{S}{V} m_0 \sqrt{D'} \quad (40)$$

where  $\sqrt{D'} = a(m_0 - m_s')\sqrt{D}$ . Generally, then, the diffusion coefficient appears to increase with increasing moisture content in the moisture range 0.076–0.13 g./g., and to be independent of moisture content in the range 0.13–0.25 g./g. Its behavior at moistures below 0.076 g./g. cannot be conjectured in the absence of experimental evidence, but it is clear that the drying rate must become very low indeed as the moisture content approaches zero.

### Data of Jones<sup>6</sup> on Vacuum Drying

Jones studied the drying of three different varieties of wheat at an absolute pressure of 7 mm. Hg. Table VI shows the results obtained on applying eq. (33) to his data. The only significant disagreement with the present results occurs in the case of mixed English Red wheat dried at 46°C., for which values of  $1 - \bar{M}$  are 11% higher than predicted. This behavior is not confirmed by the results for 30 and 40°C., and, generally, it appears from Jones' and the present data that the botanical variety of wheat has no significant effect on the coefficient for the diffusion of moisture, and that the effect of the volume-average kernel size is obedient to the diffusion equations. Dynamic surface moistures in Jones' experiments (Table VI) were slightly lower than in the present study (Table V), but this is probably due to the different method of moisture determination employed by him (Jones air-dried coarsely ground samples four hours at 120°C.).

TABLE VI  
Vacuum Drying of Wheat at 7 mm. Pressure.<sup>a</sup> Data of Jones.<sup>6</sup>

	$m_0$ , g./g.	$1 - \bar{M}$ (corrected to $V/S =$ 0.045 cm.), at		
		30°C.	40°C.	46°C.
B	0.220	0.275		
A	0.220	0.261	0.353	0.466
C	0.220	0.267	0.377	0.466
D	0.220	0.251	0.375	0.490
B	0.138	0.264	0.384	0.475
B	0.166	0.302	0.389	
D	0.228	0.276	0.407	0.496
D	0.245	0.263	0.372	0.500
C	0.299	0.275		0.469
Mean		0.270	0.379	0.481
Std. Dev., %		4.6	4.0	4.0
$m_s$ , g./g.		0.103	0.0955	0.092
$10^3/T$ , °K <sup>-1</sup>		3.300	3.194	3.134
$10^7D$ , cm. <sup>2</sup> sec.		1.10	2.31	4.00

Values calculated from present results:

$10^7D$ , cm. <sup>2</sup> /sec.	1.22	2.33	3.40
$1 - \bar{M}$	0.285	0.384	0.450

<sup>a</sup> A:  $r_v = 0.1713$  cm.; Manitoba "A"

B:  $r_v = 0.1693$  cm.; Manitoba "B"

C:  $r_v = 0.1800$  cm.; Atle

D:  $r_v = 0.1892$  cm.; English Red

where  $r_v$  is the radius of a sphere with the same volume as the wheat kernel, measured at 10% moisture content, dry basis. Diffusion coefficients are calculated on the assumption that the shape factor is  $\psi = 0.80$

### Data of Becker and Sallans<sup>1</sup> on Air Drying

In a previous study, samples of wheat were dried in a stream of dry, isothermal air. Table VII shows diffusion coefficients calculated from

TABLE VII  
Drying of Wheat in a Stream of Dry, Isothermal Air. Data  
of Becker and Sallans<sup>1</sup>  
(Series "B":  $r_v = 0.169$  cm.;  $m_s = 0.103$  g./g.)

Tem- pera- ture, °C.	$1 - \bar{M}$	$10^7 D$ , cm. <sup>2</sup> /sec.			Present data
		Eq. (33) $\psi =$ 0.80	Eq. (18) $\psi =$ 1.00	Eq. (18) $\psi =$ 0.91	
24.7	0.177	0.79	0.97	0.80	0.85
44.3	0.352	3.28	3.75	3.10	3.04
50.0	0.424	5.20	5.65	4.67	4.32
52.8	0.442	5.70	6.35	5.25	5.05
59.4	0.525	8.52	9.52	7.90	7.30
67.3	0.620	13.0	15.0	12.4	11.3
79.5	0.770	29.4	27.7	23.0	21.3

these data on the hypotheses that (1) eq. (33) is applicable with a shape factor of 0.80, as in the present study; (2) eq. (18) for spheres is applicable with a shape factor of unity, as previously assumed<sup>1</sup>; and (3) eq. (18) for spheres is applicable with a shape factor of 0.91 (with the assumption that the crease of the kernel is not exposed in air drying). The last hypothesis gives the best agreement with the present data. That this apparent applicability of the equation for spheres is not inconsistent with the present results is clear from eq. (34): except for the factor correcting for the drift in the dynamic surface moisture with drying time, which may quite conceivably be different in air drying, eq. (34) is practically identical with the equation for spheres in the neighborhood of  $X = 0$ ,  $f''(0) = 0.652$  in eq. (34), while for a sphere,  $f''(0) = 0.661$ . Thus, the assumption previously made<sup>1</sup> appears to be substantiated, that the only appreciable error in applying the equation for spheres to the air drying of wheat is in the multiplication of the diffusion coefficient by a constant shape factor. However, the suggestion<sup>1</sup> that the diffusion coefficient, after a sharp decrease as the moisture falls from 0.14 to 0.10 g./g., is constant in the moisture range 0.07–0.10 g./g. was based upon inconclusive evidence and must be discarded in view of the present results. While dynamic surface moistures in the air drying experiments, (at zero relative humidity), appeared to be constant at 0.103 g./g., it is probable that more extensive

investigation will show a slight variation with temperature, as in the present study.

### Data of Simmonds, Ward, and McEwen<sup>7</sup> on Air Drying

Simmonds et al. studied the drying of shallow layers of wheat kernels at constant inlet air temperature and humidity. While the air flows used by them were sufficient to nullify the effects of external resistance to mass transfer, they were not high enough to provide reasonable control over the grain temperature, which increased gradually with drying time and approached the air inlet temperature only after prolonged drying. Consequently, the semilogarithmic drying law advanced by them to correlate their data,

$$\bar{M} = \exp \{-\gamma t\}$$

is partly the result of a fortuitous path in grain temperature, and, in view of the temperature dependence of the diffusion coefficient, is applicable only under conditions duplicating those prevailing in their experiments. Since the "constant"  $\gamma$  is not, therefore, a point function, the inference of McEwen et al.<sup>8</sup> that the resistance to drying resides almost entirely in the thin aleurone layer, just beneath the pericarp, is clearly invalid. That  $\gamma$  is not independent of the path followed in drying has already been noted by Jones,<sup>9</sup> who pointed out that, at low air temperatures, at which the grain temperature was nearly constant,  $\gamma$  decreased markedly with time. This behavior is in accord with the present results. It is to be concluded, therefore, that no evidence has yet been found to indicate that variation of the diffusion coefficient with position in the wheat kernel is a factor of practical or theoretical consequence insofar as the overall phenomenon of drying is concerned.

Viewed positively, the data of Simmonds et al.<sup>7</sup> are obedient to the diffusion equations in the dependence of the drying rate on kernel size. Their equilibrium moistures extrapolate to a value of 0.085 g./g. at zero relative humidity, in rather good agreement with the present values of the dynamic surface moisture, considering that their drying rate curves were skewed by the variation of the grain temperature with drying time. It should be noted that the initial moistures in their experiments were very high, i.e., 0.4–0.65 g./g. (completely outside the range of 0.17–0.25 g./g. usually considered to be of practical importance in drying), and so their data are not directly comparable with the present results. The high value

of these initial moistures was the factor chiefly responsible for the exaggerated variation of kernel temperature with time.

### NOMENCLATURE

$c$	= concentration of diffusing substance at a point in a solid, g./cm. <sup>3</sup>
$c_0$	= initial, uniform concentration, g./cm. <sup>3</sup>
$c_s$	= concentration at the bounding surface, g./cm. <sup>3</sup>
$\bar{c}$	= average concentration, g./cm. <sup>3</sup>
$D$	= diffusion coefficient, cm. <sup>2</sup> /sec.
$D_0$	= diffusion constant (in Arrhenius equation), cm. <sup>2</sup> /sec.
$E$	= energy of activation, cal./mol.
$f$	= function
$f', f'', \dots$	= first, second, ..., derivatives of $f$
$J$	= diffusion current (i.e., the specific rate of mass transfer), g./cm. <sup>2</sup> sec.
$m_0$	= initial, uniform moisture content, dry basis, g./g.
$m_s$	= moisture content at the bounding surface, dry basis; g./g.
$\bar{m}$	= average moisture content, dry basis, g./g.
$n$	= an integer
$R$	= gas constant, cal./mol, °K.
$r, s$	= special coordinates, cm.
$r_0$	= radius of a sphere with the same volume as a given solid, cm.
$S$	= exposed surface area of a solid, cm. <sup>2</sup>
$T$	= absolute temperature, °K.
$t$	= time, sec.
$V$	= volume of a solid, cm. <sup>3</sup>
$x, y, z$	= Cartesian coordinates, cm.
$\rho$	= density, g./cm. <sup>3</sup>
$\psi$	= $4\pi r_v^2/S$ = surface sphericity

### Dimensionless Factors in the Diffusion Equation

$\bar{C}$	= $\frac{\bar{c} - c_s}{c_0 - c_s}$
$C$	= $\frac{c - c_s}{c_0 - c_s}$
$\bar{M}$	= $\frac{\bar{m} - m_s}{m_0 - m_s}$
$Z$	= $s/2\sqrt{Dt}$
$X$	= $\frac{S}{V}\sqrt{Dt}$
$Y$	= $(1 - \bar{M})/X$
$\alpha, \beta, \phi$	= constants

The author is indebted to Dr. C. R. Jones for information about the wheat used in his study.<sup>6</sup>

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### Synopsis

A general mathematical approach to the rigorous treatment of experimental data on nonstationary-state diffusion in solids of complex shape is developed. The general solution for a uniform initial concentration,  $c_0$ , and a constant surface concentration,  $c_s$ , at times greater than zero is shown to be of the form

$$\frac{\bar{c} - c_s}{c_0 - c_s} = 1 - \frac{2}{\sqrt{\pi}} \frac{S}{V} \sqrt{Dt} + \frac{f''(0)}{2} \left(\frac{S}{V}\right)^2 Dt$$

in the neighborhood of time zero, and

$$\frac{\bar{c} - c_s}{c_0 - c_s} = \frac{\alpha}{\beta^2} \exp \left\{ -\beta^2 \left(\frac{S}{V}\right)^2 Dt \right\}$$

in the neighborhood of time infinity, where  $\bar{c}$  is the average concentration at time  $t$ ;  $S$  and  $V$  are the surface area and volume of the solid, respectively;  $D$  is the diffusion coefficient; and  $f''(0)$ ,  $\alpha$ , and  $\beta$  are constants dependent on solid shape. The vacuum drying of wheat has been studied, and it is shown that, for the wheat kernel,  $f''(0) = 0.588$ ,  $\alpha = 0.862$ ; and  $\beta^2 = 1.301$ . The diffusion coefficient is an Arrhenius-type function of temperature given by  $D = D_0 \exp \{-E/RT\}$  where  $D_0 = 76.8$  cm.<sup>2</sup>/sec. and  $E = 12.20$  kcal./mole.

### Résumé

Une approximation mathématique générale de l'examen rigoureux des données expérimentales sur l'état non-stationnaire de la diffusion dans les solides de forme complexe est développée. La solution générale pour une concentration initiale uniforme,  $c_0$ , et une concentration constante en surface,  $c_s$ , à des temps plus grands que zéro semble être de la forme suivante

$$\frac{\bar{c} - c_s}{c_0 - c_s} = 1 - \frac{2}{\sqrt{\pi}} \frac{S}{V} \sqrt{Dt} + \frac{f''(0)}{2} \left(\frac{S}{V}\right)^2 Dt$$

aux environs du temps zéro, et

$$\frac{c - c_s}{c_0 - c_s} = \frac{\alpha}{\beta^2} \exp \left\{ -\beta^2 \left( \frac{S}{V} \right)^2 Dt \right\}$$

aux environs de l'infini, où  $c$  est la concentration moyenne au temps  $t$ ;  $S$  et  $V$  sont respectivement la surface et le volume du solide;  $D$  est le coefficient de diffusion; et  $f''(0)$ ,  $\alpha$ , et  $\beta$  sont des constantes dépendant de la forme du solide. Le séchage sous vide du blé a été étudiée et on montre que pour le grain de blé  $f''(0) = 0,588$ ,  $\alpha = 0,862$ , et  $\beta^2 = 1,301$ . Le coefficient de diffusion, fonction de la température, est du type Arrhenius et donné par  $D = D_0 \exp \{-E/RT\}$  où  $D_0 = 76,8 \text{ cm}^2/\text{sec}$  et  $E = 12,20 \text{ kcal/mol}$ .

### Zusammenfassung

Eine allgemeine mathematische Methode zur strengen Behandlung der experimentellen Ergebnisse bezüglich nichtstationärer Diffusionszustände in Festkörpern von komplexer Gestalt wird entwickelt. Es wird gezeigt, dass die allgemeine Lösung für einheitliche Anfangskonzentra-

tion,  $c_0$ , und konstante Oberflächenkonzentration,  $c_s$ , bei einer Diffusionsdauer grösser als Null von der Form

$$\frac{\bar{c} - c_s}{c_0 - c_s} = 1 - \frac{2}{\sqrt{\pi}} \frac{S}{V} \sqrt{Dt} + \frac{f''(0)}{2} \left( \frac{S}{V} \right)^2 Dt$$

in der Nachbarschaft der Zeit Null, und

$$\frac{\bar{c} - c_s}{c_0 - c_s} = \frac{\alpha}{\beta^2} \exp \left\{ -\beta^2 \left( \frac{S}{V} \right)^2 Dt \right\}$$

in der Nachbarschaft der Zeit unendlich ist, wo  $\bar{c}$  die mittlere Konzentration zur Zeit  $t$  ist;  $S$  und  $V$  sind Oberflächengröße bzw. Volumen des Festkörpers;  $D$  ist der Diffusionskoeffizient und  $f''(0)$ ,  $\alpha$  und  $\beta$  sind Konstante, die von der Gestalt des Festkörpers abhängen. Es wurde die Vakuumtrocknung von Weizen untersucht und es wird gezeigt, dass für das Weizenkorn  $f''(0) = 0,588$ ,  $\alpha = 0,862$  und  $\beta^2 = 1,301$  ist. Für die Temperaturabhängigkeit des Diffusionskoeffizienten gilt eine Arrheniusgleichung  $D = D_0 \exp \{-E/RT\}$  wo  $D_0 = 76,8 \text{ cm}^2/\text{sec}$  und  $E = 12,20 \text{ kcal/Mol}$ .

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