MOISTURE EQUILIBRIA IN SEEDS

by

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INTRODUCTION

Moisture equilibria in seeds are problems of considerable practical importance because of their direct relationship to storage and drying problems. They are also of theoretical interest because of the mechanisms and forces involved.

The overall problem has been considered from the aspects of moisture movement and moisture sorption. The two are closely interrelated in that the same factors affect both. Drying curves were obtained for whole soybeans, and graded size fractions of beans at four temperatures. An attempt has been made to describe the drying of seeds in terms of the mechanisms involved.

Adsorption and desorption isotherms were obtained at 20° and 30°C. The interpretation of the isotherms has been approached in two ways. First, the Brunauer, Emmett, and Teller theory has been used to describe the isotherms, and secondly, the thermodynamic functions of free energy, enthalpy, and entropy have been calculated. These functions may indicate the mode of sorption of the water molecules and can be related to the theoretical interpretations of the isotherms.

REVIEW OF LITERATURE

Drying

The drying of seeds is similar in many respects to the drying of inert porous solids, such as clay pellets. In some aspects, however, it differs markedly.

The classical analysis of the drying of porous solids is due largely to Lewis (17), Sherwood (24, 25, 26, 27, 28) and Newman (19, 20). They have divided the drying process into constant rate and falling rate periods, the junction of these two being termed the critical point. The falling rate period has frequently been further subdivided into two portions, spoken of as the first and second falling rate periods.

During the constant rate period the surface remains completely wet. The rate of drying during this period is very nearly equivalent to the rate of evaporation of water from a free water surface.

The first falling rate period is characterized by a continuously decreasing liquid concentration at the surface, and the drying rate is postulated to be proportional to the fraction of the surface which is wet. This period continues until the liquid concentration at the surface has reached equilibrium with that of the air.

During the second falling rate period the moisture concentration at the surface remains constant and the drying rate is controlled by the rate of internal diffusion.

Many materials fail to exhibit a constant rate period because the initial moisture content is less than the critical moisture content. Furthermore, some of these materials, as they dry, pass so quickly into the second falling rate period, that for all practical purposes the first falling rate period is negligible. Such is the case in the drying of seeds. During this phase the rate of internal liquid flow controls the rate of drying, and the mechanism of liquid flow is diffusion (15, 29).

Numerous attempts have been made to describe mathematically the drying of seeds; these efforts have met with varying degrees of success. Some workers (3, 4) have used the diffusion equation based on Fick's laws of diffusion. The two familiar differential forms of Fick's laws of diffusion are

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

and

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (2)$$

where P = rate of permeation per unit area
C = concentration of diffusing substance
x = space coordinate
D = diffusion coefficient
t = time.

Equation (1) gives the rate of permeation, in terms of the concentration gradient, while Equation (2) is the fundamental differential equation of diffusion. Equation (2) is readily derived from Equation (1) by considering the rate of accumulation of matter within an element of volume dx of a rectangular parallelepiped of unit cross section. This is simply the difference between the rate of flow into the volume and the rate of flow out of the volume. In three dimensions Equation (2) becomes

$$\frac{\partial c}{\partial t} = D\left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right] . \qquad (3)$$

If Equation (3) is expressed in terms of spherical coordinates it becomes

$$\frac{\partial c}{\partial t} = \frac{D}{r^2}\left[\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial c}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 c}{\partial\phi^2}\right] . \qquad (4)$$

For spherically symmetrical diffusion, Equation (4) reduces to

$$\frac{\partial c}{\partial t} = D\left[\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right] . \qquad (5)$$

Babbitt (3), working with wheat, used the non-steady state diffusion equation for diffusion out of spheres to describe his drying curves. The solution he used is of the form

$$m = m_o-(m_o-m_2) \left[1- \frac{6}{\pi^2} \sum_{1}^{\infty} \frac{1}{n^2} \exp(-D \frac{n^2 \pi^2 t}{r^2}) \right] \qquad (6)$$

where m = average moisture content, %

m_o = initial moisture content, %

m_2 = final moisture content, %

D = diffusion coefficient

r = kernel radius

t = drying time, hours.

He evaluated D by making the calculated values fit the experimental values at $t = 100$. When the calculated drying curve was plotted and compared with the experimental curve there was a rather large discrepancy, particularly in the lower range. He worked in the moisture range of 0-16%, and concluded that the diffusion coefficient decreases witn falling moisture content.

Becker and Sallans (4), also working with wheat, used the non-steady state diffusion equation for diffusion out of spheres to describe their drying curves. The solution they used was of the form

$$\frac{\bar{m} - m_s}{m_o - m_s} = \frac{6}{\pi^2} \sum_{1}^{\infty} \frac{1}{n^2} \exp\left(\frac{n^2 \pi^2 D_c t}{r_o^2}\right) \qquad (7)$$

where $\bar{m}$ = average moisture content, %

m_o = uniform initial moisture content, %

m_s = surface moisture content, %

D_c = diffusion coefficient

r_o = kernel radius

t = drying time, sec.

Becker and Sallans used a different procedure to evaluate the diffusion coefficient, D_c. They plotted moisture loss per 19.7 minute drying period against initial content. By rearranging the left hand side of Ecuation (7) into the form $1 - \frac{m_o - \bar{m}}{m_o - m_s}$ and designating this as $\overline{M}$, they stated that $\overline{M}$ is equal to unity minus the slope of the regression of moisture loss for a 19.7 minute drying period on initial moisture content. By use of Equation (7) they were then able to determine D_c for a fixed value of $\overline{M}$. In order to determine a value for m_s, they extrapolated the plot of moisture loss per 19.7 minute drying period against initial moisture content, to the point where it crossed the horizontal axis. That is, the initial moisture content at which the seeds would lose no moisture in a 19.7 minute drying interval.

Other workers (12, 21) have attempted to describe the drying of seeds by means of the relationship

$$\frac{dm}{dt} = k\ (m - m_e) \qquad (8)$$

where m = average moisture content at time t

m_e = equilibrium moisture content

k = a constant

t = drying time.

This equation states that the rate of drying is proportional to the "free"moisture content $m - m_e$. It is analogous to Newton's law of cooling. Upon integration it becomes

$$\frac{m - m_e}{m_o - m_e} = e^{-kt} \quad . \tag{9}$$

The applicability of this equation can be tested, and the constant k evaluated, by plotting $\ln(m - m_e)$ against time. If the relationship holds this semilogarithmic plot should give a straight line, the slope of which represents k.

It may be noted that Equation (9) is very similar in form to the first term of the Fourier series in Equation (7) and might, therefore, be expected to approximate the series. This approximation is relatively close for large values of t but is poor for small values, where it becomes necessary to use a large number of terms of the series.

While Equation (9) describes the rate of drying only approximately, and is sometimes a poor approximation, it is nevertheless useful because of its simplicity and ease of handling.

Sorption

It is a well known fact that seeds are hygroscopic and that their moisture content will vary with the relative humidity and temperature of the air. The moisture value approached at any fixed relative humidity and temperature is known as the equilibrium moisture content. If, at a constant temperature, the equilibrium relationship between the amount of water vapor sorbed by the seed and the relative humidity or vapor pressure of the atmosphere is represented graphically, the curve obtained is known as an isotherm. Depending on whether moisture is taken up or given off by the seed as it approaches equilibrium, the isotherm is classed as either an adsorption or a desorption isotherm.

In general, the isotherm characteristic of seeds is an S-shaped or sigmoid type curve. In the low vapor pressure range it is concave to the vapor pressure axis; in the mid-range it is approximately linear and has an inflection point; and in the high vapor pressure range it is convex to the vapor pressure axis.

Freundlich (10) was one of the first to attempt to describe the isotherm with a mathematical expression. The Freundlich isotherm may be expressed by the equation

$$x = ap^{1/n} \tag{11}$$

where x = amount adsorbed

p = equilibrium pressure

a and n = constants.

The Freundlich equation holds for only a very narrow range of vapor pressures and has no theoretical basis. It is, therefore, of little value in elucidating the mechanism of moisture sorption by seeds.

Langmuir (16) advanced a theory that probably represents the first theoretical approach to adsorption. He developed an adsorption equation based on theoretical considerations by equating the rate of evaporation to the rate of condensation. The isotherm equation proposed by Langmuir may be expressed in the form

$$x = \frac{abp}{1 + bp} \qquad (12)$$

where x = amount adsorbed

p = equilibrium pressure

a and b = constants.

Langmuir's equation is based on the theory of monomolecular adsorption and may be represented as a hyperbola, the curvature of which is concave to the pressure axis. It is, therefore, able to account for only the initial portion of the S-shaped isotherm.

Brunauer, Emmett, and Teller (6) extended the Langmuir derivation to include multimolecular adsorption, and thus developed an equation to describe the S-shaped isotherm. The Brunauer, Emmett, and Teller (BET) theory is based on the assumption that the same forces which produce condensation are chiefly responsible for the binding energy of multimolecular adsorption. That is, that the heats of adsorption in the second and subsequent layers are equal to the heat of liquefaction. By equating condensation and evaporation rates between the layers of adsorbate they derived the equation

$$X = \frac{X_m Cp}{(p_o - p)\left[1 + (C-1)p/p_o\right]} \qquad (13)$$

where X = amount adsorbed

X_m = amount required to cover a complete monomolecular layer

p = equilibrium pressure

p_o = saturation pressure

C = a constant which is very closely approximated by the relationship

$$C = \exp(E_1 - E_L)/RT \qquad (14)$$

where E_1 = average heat of adsorption for the first layer

E_L = heat of liquefaction

R = gas constant

T = absolute temperature.

To examine the applicability of the BET theory, Equation (13) is transformed into the form

$$\frac{p}{X(p_o - p)} = \frac{1}{X_m C} + \frac{(C - 1)}{X_m C} \frac{p}{p_o} \quad . \qquad (15)$$

Thus if the BET theory does apply, a plot of $p/X(p_o - p)$ against p/p_o should result in a straight line with $(C-1)/X_m C$ as the slope and $1/X_m C$ as the intercept. This gives a method for determining the constants X_m and C from experimental data. If the surface area occupied by a single water molecule is known, it is possible to calculate the specific surface of the seed. The heat of adsorption for the first layer, E_1, can be calculated from Equation (14).

The BET theory given by Equation (13) assumes that the number of layers adsorbed at saturation is infinite. This is not always true, particularly with an adsorbent such as a seed where structural features definitely limit the number of adsorbed layers to some finite value. BET (6) provide an extended equation to describe such isotherms. This modified equation is

$$X = \frac{X_m \, Cp}{(p_o - p)} \quad \frac{1-(n + 1)(p/p_o)^n + n(p/p_o)^{n + 1}}{1+(C - 1)p/p_o - C(p/p_o)^{n + 1}} \qquad (16)$$

where X, X_m, p, p_o, and C are defined as in Equation (13), and n is the number of adsorbed layers. In order to evaluate the constants in Equation (16), Equation (15) is plotted as before and the constants X_m and C determined from the linear portion. These constants are then substituted in Equation (16) along with the experimental data and the best value for n is determined by trial and error.

Recent theories in the field of adsorption may be classified in two general categories: those which modify and extend the BET theory, and those which are completely different from the BET theory. An excellent review of these various theories is given by McLaren and Rowen (18).

In a large number of sorbent-sorbate systems the adsorption and desorption isotherms do not coincide. The desorption isotherm shows a marked displacement to the left of the adsorption isotherm. This corresponds to a larger quantity of moisture present at a given pressure, or what amounts to the same thing, a lower pressure for a given amount of moisture. This phenomenon is known as the hysteresis effect.

Numerous attempts have been made to explain hysteresis. Coolidge (9) offers as an explanation the effect of permanent gases. According to his explanation the vapor being absorbed displaces from the surface small quantities of previously adsorbed permanent gases. These remain in the gas phase during adsorption and thus raise the pressure. Since desorption involves the removal of gas, these permanent gases are removed along with the adsorbate so that the extra pressure they exert is less than during the adsorption process. According to this explanation the desorption isotherm will more nearly correspond to the true values.

Hougen et al. (13) offer an explanation for hysteresis without reference to permanent gas. They explain the phenomenon by assuming a particular geometric shape of the pore space within the solid. They picture the pore spaces as shaped like ink bottles with narrow necks and wide bodies tapering at the bottom. Starting with an adsorbate-saturated solid, desorption continues until the curvature attained in the capillary of the "neck" corresponds to the equilibrium vapor pressure. Starting with an adsorbate-free solid, adsorption continues until the liquid level in the "body" has reached the point where the curvature, and hence the vapor pressure, is the same as that in the neck upon desorption. Thus equilibrium is attained in desorption with a high liquid content, and in adsorption with a low liquid content.

Urquhart (31) suggested a mechanism for hysteresis based on swelling-shrinking phenomena which cause a distortion of the surface. Smith (30) proposed an analogous mechanism for hysteresis in sorption of water vapor by proteins. Pierce and Smith (23) demonstrated that plane surfaces with no capillary structure may also show hysteresis. They suggest that hysteresis results from the energy changes which take place in the system when adsorption occurs. It would appear, therefore, that perhaps no single mechanism is adequate to explain hysteresis, and that it is probably the combination of several factors acting simultaneously.

The isotherm provides a useful tool for the study of the sorption of water by seeds. Starting with the classical work of Coleman and Fellows (8), a great many purely descriptive data have been accumulated relating equilibrium moisture content to the relative humidity and temperature of the air. A discussion of these may be found in Hlynka and Robinson (11). The main object of the majority of these studies was to get some indication of the comparative moisture contents under different storage conditions. Little effort was made to interpret the results in terms of the mechanisms involved.

Many of the earlier workers failed to appreciate the differences between adsorption equilibria and desorption equilibria and the magnitude of the hysteresis effect. Babbitt (1) was among the first to distinguish clearly between the two. He studied hysteresis in both wheat and flour, and found that the isotherms for wheat showed considerably more hysteresis than those for flour.

Babbitt (2) was also one of the first workers to present a unified picture of the sorption process. He applied the BET treatment to the adsorption isotherms for spruce wood and cotton. In addition, he studied the thermodynamics of adsorption in an effort to describe more clearly the actual mechanisms involved.

More recently, isotherm studies have been reported by Becker and Sallans (5), and Bushuk and Winkler (7). Becker and Sallans studied desorption isotherms of wheat at 25° and 50°C. Rather than apply the BET equation to the overall isotherm by varying the value of n, they divided the isotherm into three portions and applied a different equation to each. They found that the simplified BET equation applied between 0.04 and 0.30 relative vapor pressure. From 0.12 to 0.65 the linear equation $m-m_o = a\ p/p_o$, where m_o and a are constants, applied. Between 0.50 and 0.95 the semi-logarithmic equation given by Smith (30) applied. Smith's equation is of the form $m = m_b - M' \ln(1 - p/p_o)$, where m is the moisture content g/g wet basis, m_b is the intercept of the plot of m vs. $\ln(1 - p/p_o)$ and M' is the slope. Becker and Sallans also evaluated the differential heat of desorption.

Bushuk and Winkler (7) studied both adsorption and desorption of water vapor on wheat flour, starch, and gluten at four temperatures: 20.2°, 30.1°, 40.8°, and 50.2°C. They applied the modified BET equation to the entire flour-water isotherm and obtained a reasonably good fit if they assumed the number of adsorbed layers at saturation to be five or six. In addition, they calculated the heat of adsorption.

MATERIALS AND METHODS

The seeds used in this investigation were locally grown soybeans of the variety Hawkeye.

Drying Methods

The seeds used in the drying studies were first rewet to approximately 40% moisture, dry weight basis, by suspending them in a screen wire basket above water in a closed container for a period of three months. They were kept at a temperature of 1°C to retard mold growth. This procedure was thought to be more desirable, in terms of insuring uniform moisture distribution, than soaking the seeds. As the samples were used for drying studies they were warmed from 1°C by allowing them to stand at room temperature for 12 hours in sealed mason jars.

The seeds used for particle size studies were broken into approximately 1/2, 1/4, and 1/8 fractions. Volume measurements of each of the particle sizes were made by the method of toluene displacement, using a burette with a large bulb blown on one end. The average volume was used to compute the radius of a sphere of equal volume.

The drying apparatus consisted of a specially constructed drying chamber. This was designed to maintain a constant, rapid flow of dry, heated air over the seeds. The chamber was placed in a constant temperature cabinet.

The seeds were weighed at fifteen minute intervals for the first two hours and then at thirty minute intervals until the weight loss per unit time became very small compared with the total weight loss. The weighings were made to one-tenth of a milligram on an analytical balance.

Sorption Methods

Desorption equilibria between vapor pressure of water and moisture content of seeds were studied using both naturally wet and rewet seeds. The naturally wet seeds were harvested when they had a moisture content of approximately 40%, dry weight basis. The rewet seeds were prepared by the method described above. They also had a moisture content of approximately 40%.

Adsorption equilibria were studied using seeds previously dried at 100°C for 48 hours, the standard drying procedure used for moisture determination; seeds dried at 50°C for four days, and seeds dried at 30°C for nine days. Vacuum drying was used at the two lower temperatures.

Sulfuric acid solutions were used to produce the desired relative vapor pressures, which ranged from 0.0 to 0.7. These were prepared from tables given by Perry (22). The seeds, in wire baskets, were suspended above the acid solutions in sealed glass jars. The jars were kept in constant temperature cabinets. The seeds were weighed periodically to determine moisture equilibria. Equilibrium was established when the seeds showed no further weight change in a two week interval. The moisture content at equilibrium was determined by drying the seeds at 100°C for 48 hours.

EXPERIMENTAL RESULTS

The research on this problem consisted primarily of the establishment of drying curves and sorption isotherms under varying conditions.

Drying Studies

Drying data were obtained for whole beans and 1/2, 1/4, and 1/8 size fractions of beans at 40°, 50°, 60°, and 70°C. These data have been plotted as drying curves expressing the percentage of moisture on a dry weight basis as a function of time. The data are given in Table 1 and the drying curves in Figures 1 through 8.

Examination of the curves shows that the rate of drying decreases constantly, and that it is influenced by both temperature and the size of the particle.

Sorption Studies

Desorption isotherms were obtained at 20° and 30°C for both naturally wet and rewet seeds. The data are given in Table 2 and the isotherms in Figures 9 through 12. These are of a sigmoid shape characteristic of many types of biological materials. It may be noted that the isotherm for the naturally wet seeds lies above the isotherm for the rewet seeds, thus indicating a larger percentage of water

Table 1. Drying data for soybeans of four relative particle sizes at four temperatures showing percentage moisture on a dry weight basis as a function of time

Time	Particle sizes at 40°C				Time	Particle sizes at 50°C			
(Min.)	1	1/2	1/4	1/8	(Min.)	1	1/2	1/4	1/8
0	40.60*	40.82	40.40	40.44	0	41.29	40.83	40.81	40.98
15	34.20	32.50	31.00	29.75	15	33.20	31.50	28.50	27.55
30	31.14	27.80	26.76	25.06	30	30.40	26.36	24.19	22.42
45	29.25	25.28	24.10	22.15	45	28.22	23.38	21.31	19.37
60	27.90	23.57	22.42	20.40	60	26.44	21.38	19.39	17.28
75	26.82	22.18	20.88	18.72	75	24.90	19.73	17.76	15.63
90	25.71	20.98	19.80	17.61	90	23.58	18.50	16.78	14.58
105	24.88	19.72	18.51	16.58	105	22.50	17.44	15.61	13.55
120	24.18	18.98	17.98	15.92	120	21.60	16.43	14.89	12.67
150	23.00	17.50	16.50	14.60	150	20.00	14.78	13.41	11.49
180	21.85	16.08	15.28	13.52	180	18.60	13.50	12.10	10.50
200	20.80	15.03	14.25	12.57	210	17.50	12.50	11.12	9.57
265	19.18	13.76	12.72	11.36	270	15.52	10.91	9.58	8.43
320	17.58	12.34	11.36	10.14	315	14.32	9.98	8.86	7.81
380	16.30	11.16	10.32	9.36	385	13.12	9.02	8.04	7.13
490	14.36	9.70	9.09	8.30	445	12.02	8.28	7.46	6.56
775	11.21	7.47	7.14	6.70	1005	6.79	4.99	4.77	4.60
835	10.68	7.14	6.88	6.52	1085	6.45	4.77	4.61	4.39
1300	7.97	5.64	5.58	5.46					
1470	7.27	5.28	5.38	5.23					
2190	5.50	4.60	4.74	4.66					

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*Each entry represents the average of two closely agreeing replications.

Table 1. (Continued)

Time	Particle sizes at 60°C				Time	Particle sizes at 70°C			
(Min.)	1	1/2	1/4	1/8	(Min.)	1	1/2	1/4	1/8
0	40.24	41.73	39.70	38.60	0	41.45	40.68	40.86	39.72
15	32.04	30.80	27.48	25.00	15	31.40	29.50	27.30	23.58
30	28.35	25.32	22.19	20.65	30	28.03	23.78	21.32	18.54
45	25.84	22.21	19.14	17.38	45	25.24	20.03	17.62	15.16
60	23.94	19.77	16.90	15.25	60	23.12	17.40	15.08	12.74
75	22.26	17.80	15.23	13.72	75	21.43	15.37	13.37	11.20
90	20.92	16.29	13.85	12.60	90	19.92	13.82	12.00	10.04
105	19.80	15.01	12.78	11.58	105	18.60	12.48	10.64	9.01
120	18.64	14.10	11.98	10.82	120	17.30	11.24	9.58	8.48
150	16.92	12.54	10.22	9.63	135	16.81	10.36	8.90	7.64
180	15.48	11.24	9.46	8.82	165	14.22	8.55	7.53	6.83
210	14.25	10.08	8.60	8.07	195	12.58	7.43	6.62	6.08
240	13.17	9.36	8.00	7.53	255	10.39	6.05	5.46	5.10
360	10.20	6.92	6.12	6.08	315	8.79	4.91	4.30	4.48
420	9.06	6.25	5.52	5.55	495	5.69	3.39	3.37	3.49
550	7.30	5.08	4.82	4.43	945	2.99	2.36	2.50	2.43
900	4.62	3.60	3.57	3.62					
1050	4.19	3.40	3.30	3.23					

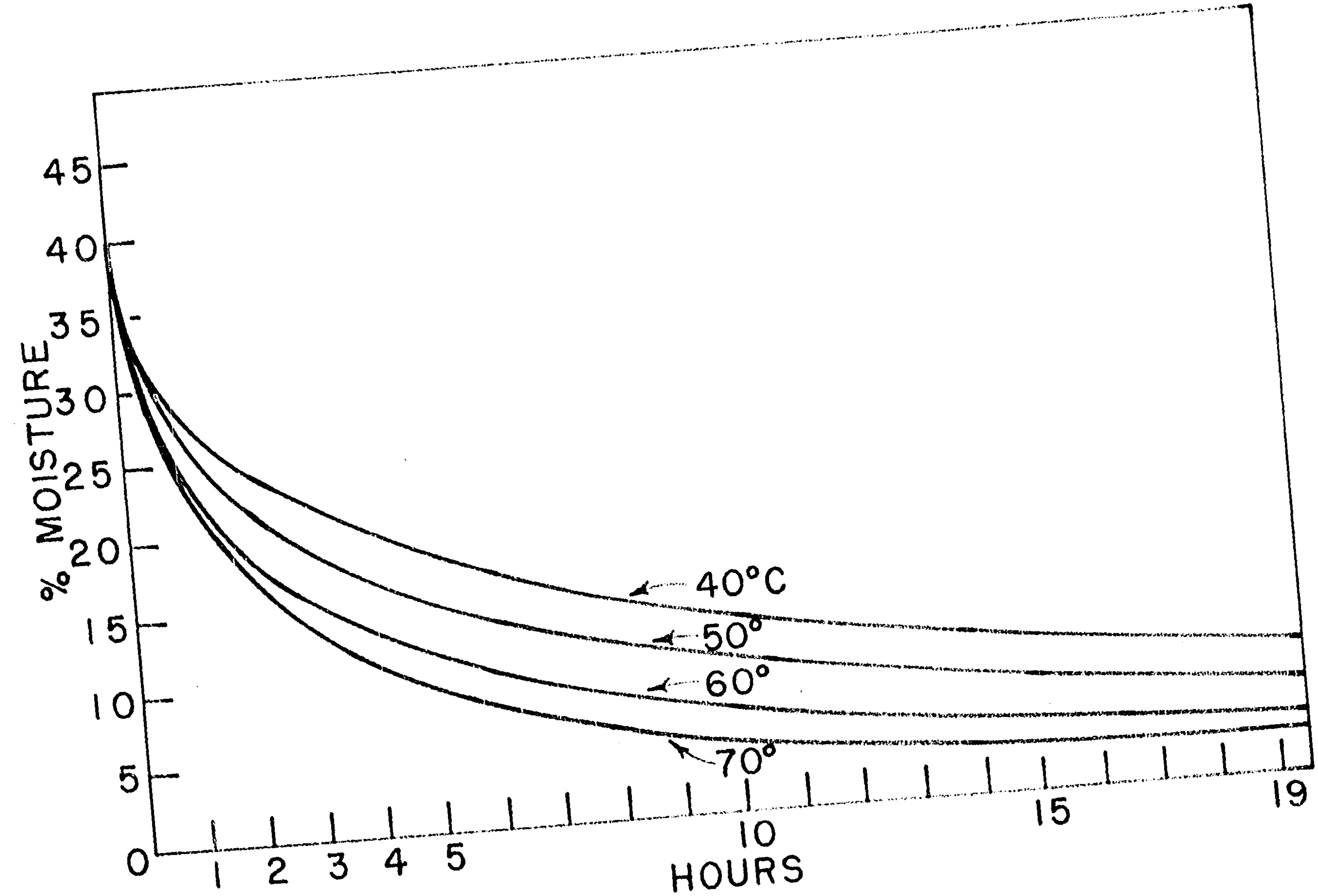

Figure 1. Drying curves for soybeans at four temperatures

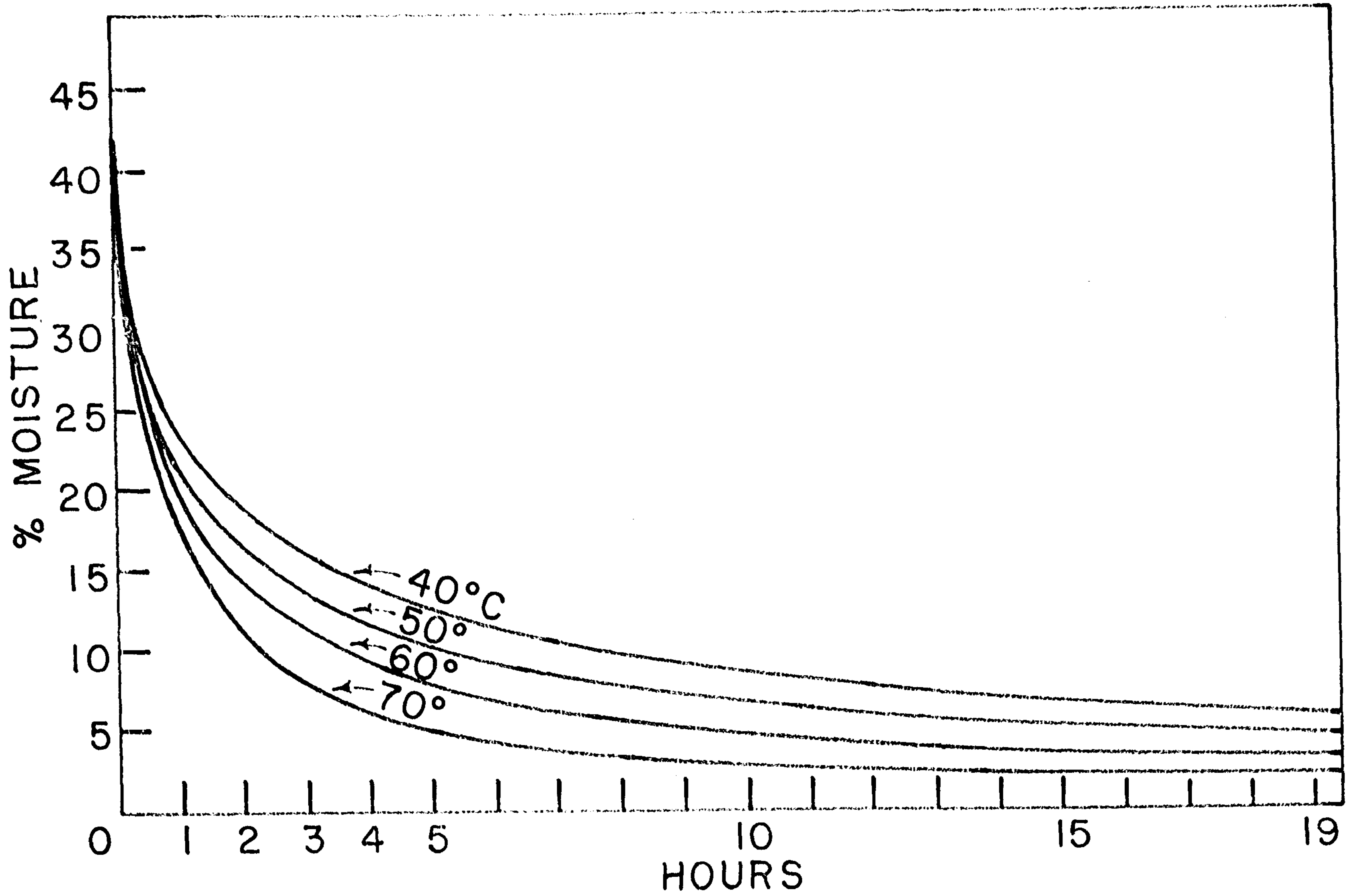

Figure 2. Drying curves for 1/2 size fractions at four temperatures

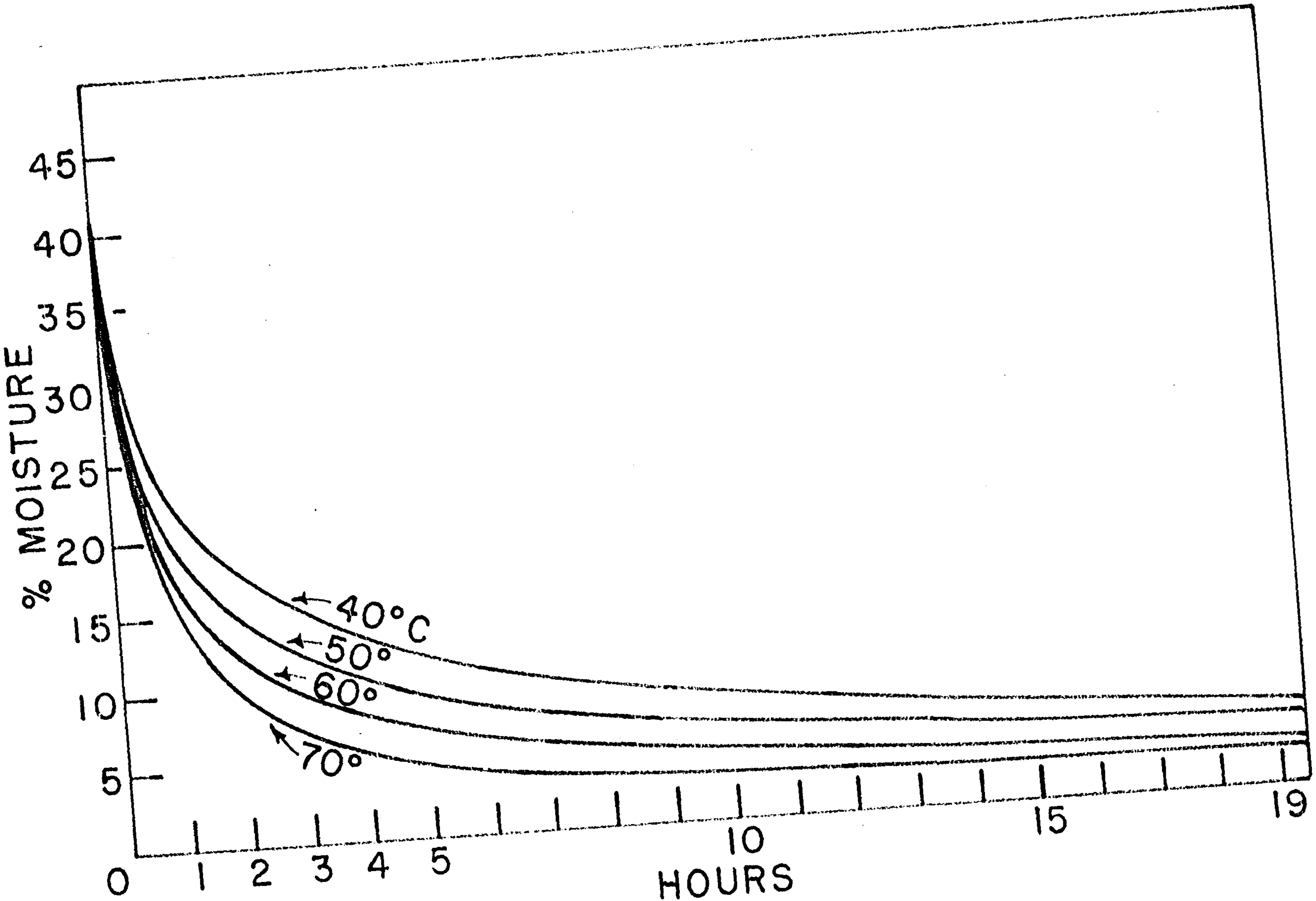

Figure 3. Drying curves for 1/4 size fractions at four temperatures

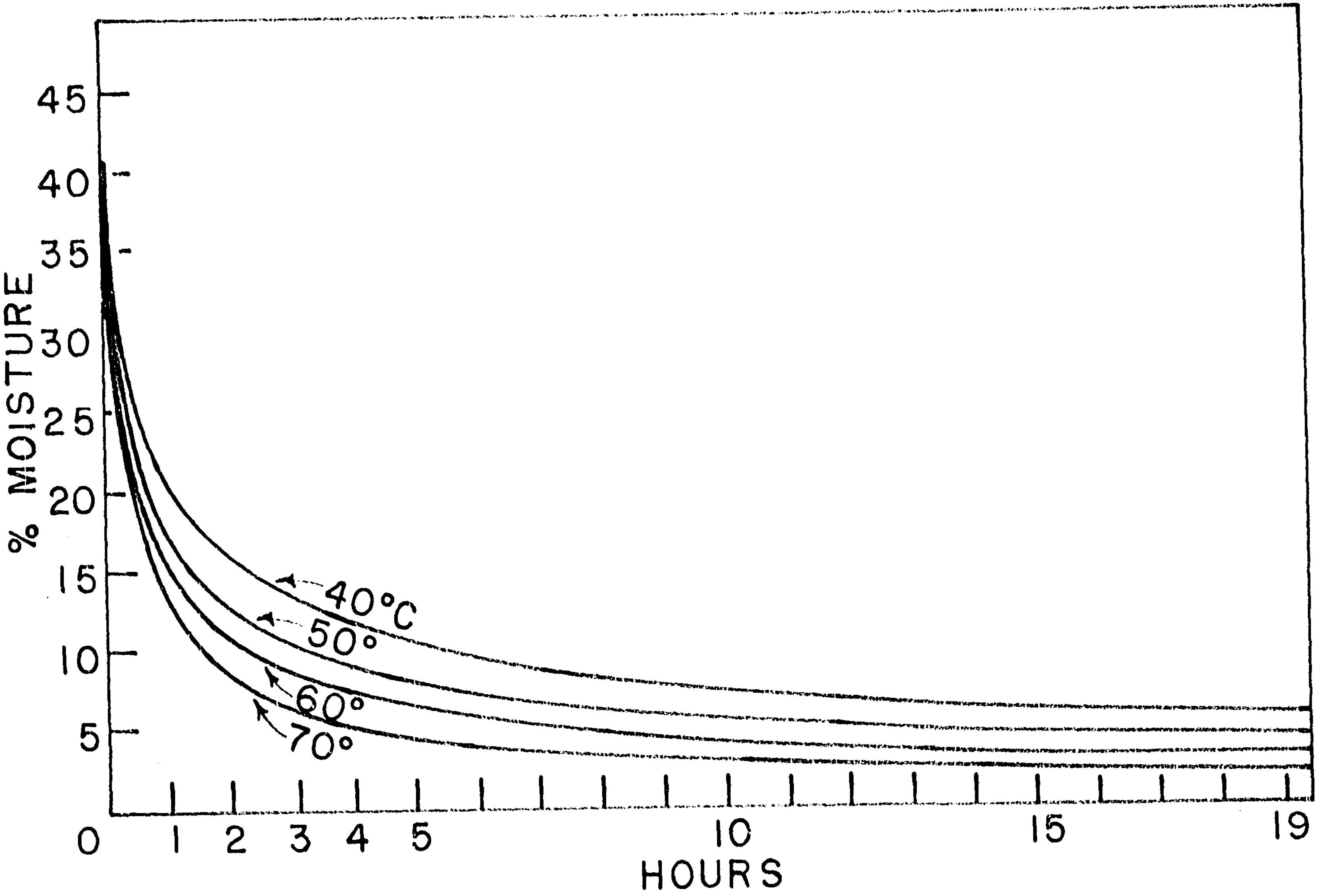

Figure 4. Drying curves for 1/8 size fractions at four temperatures

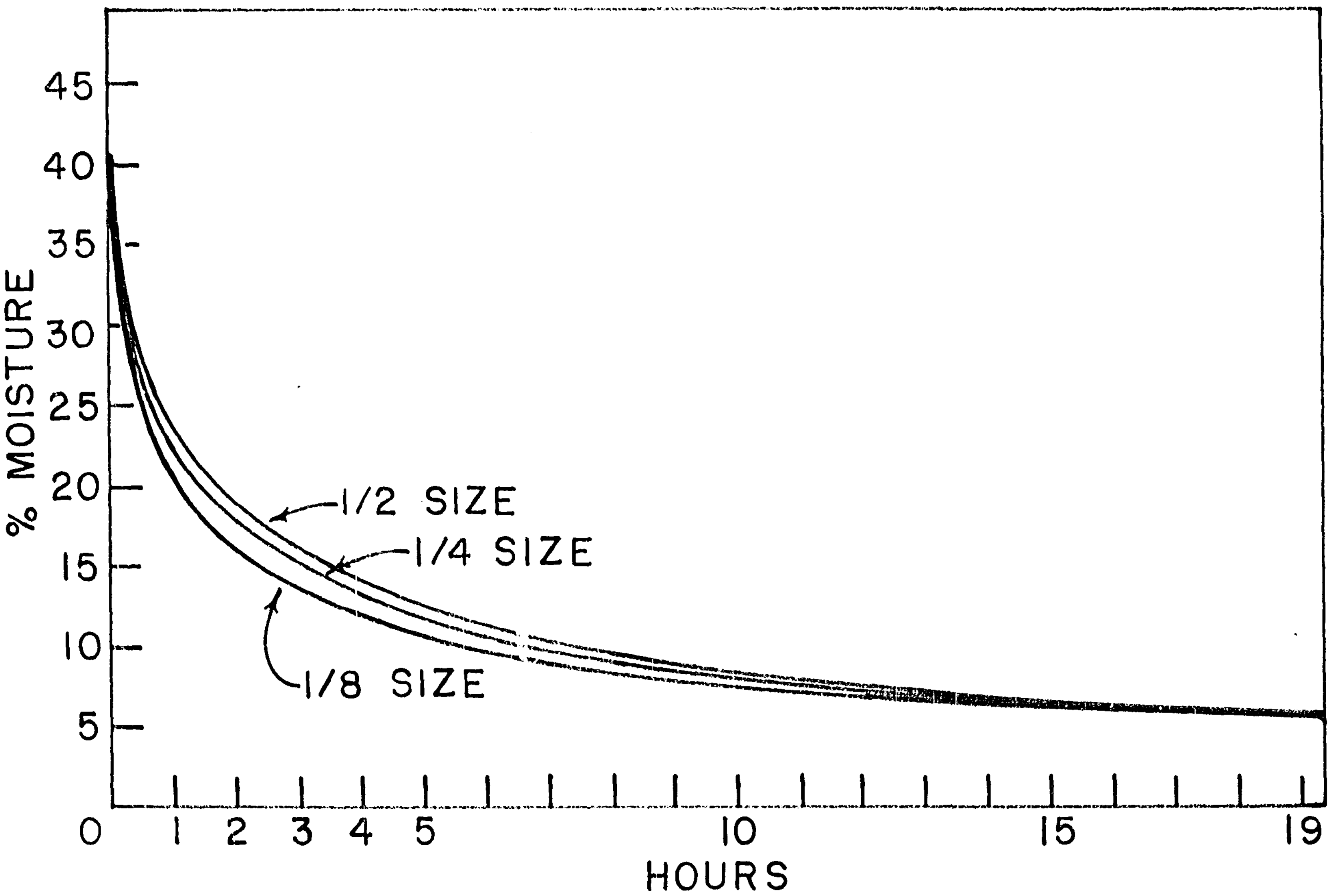

Figure 5. Drying curves for three fractions at 40°C

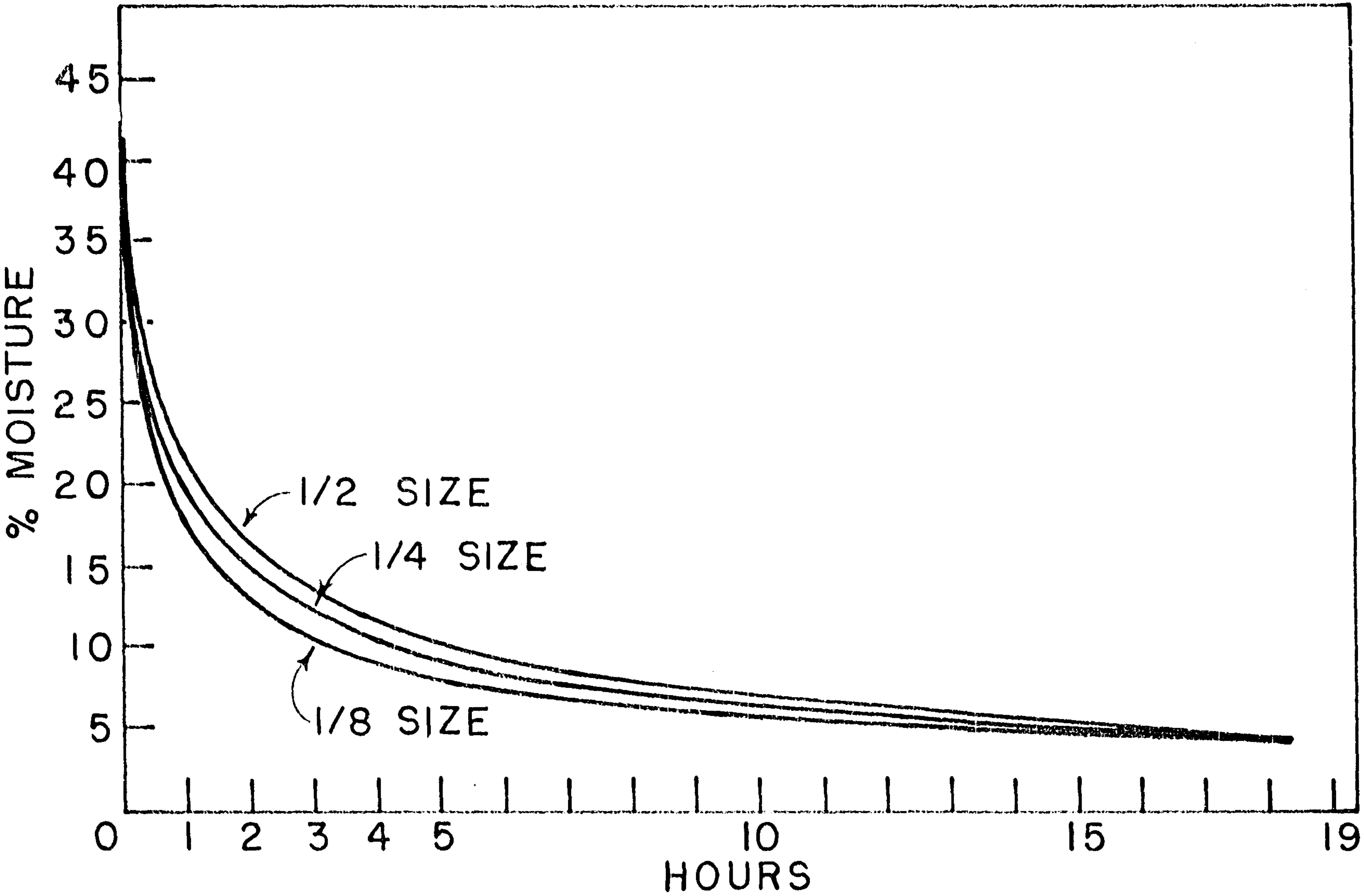

Figure 6. Drying curves for three fractions at 50°C

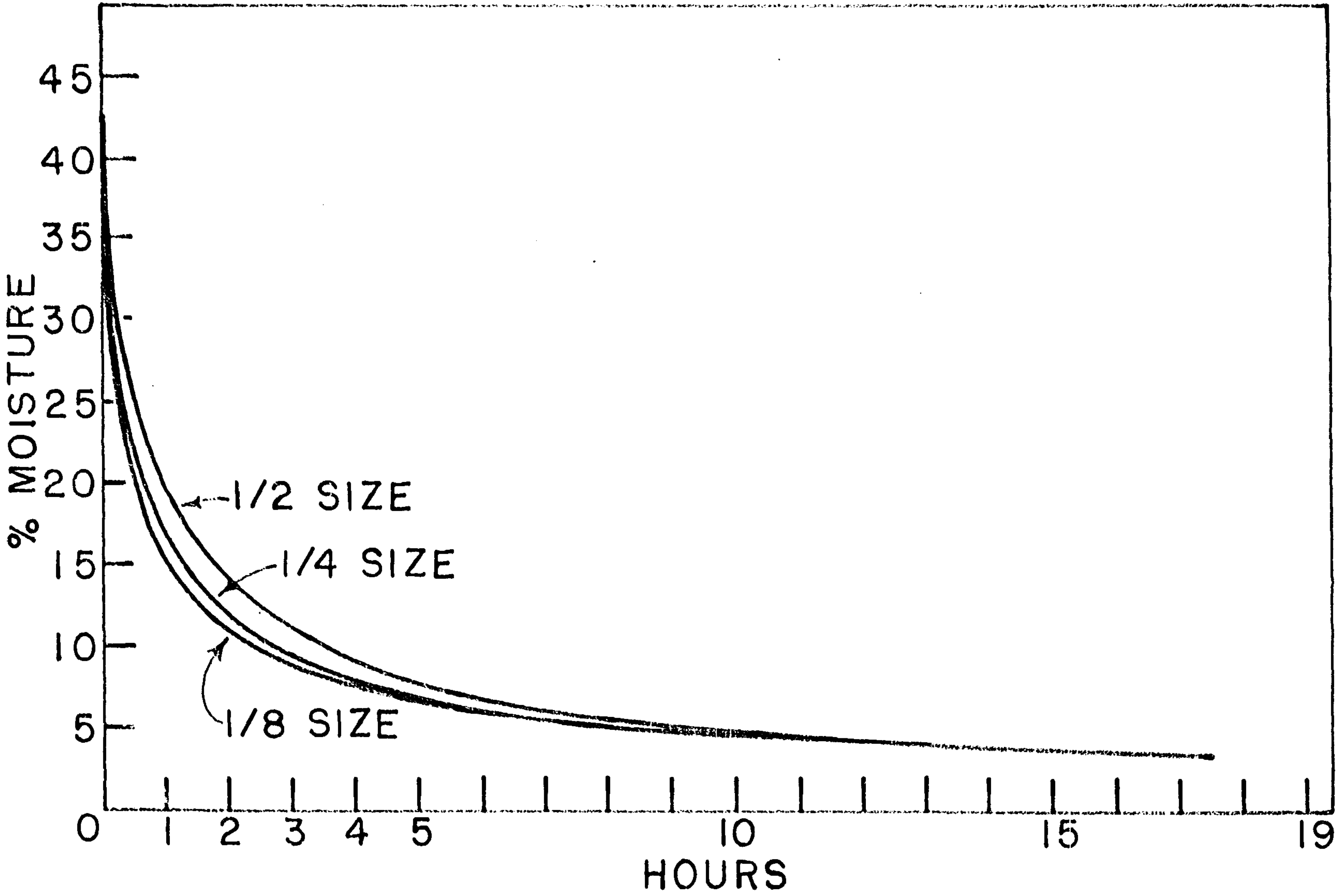

Figure 7. Drying curves for three fractions at 60°C

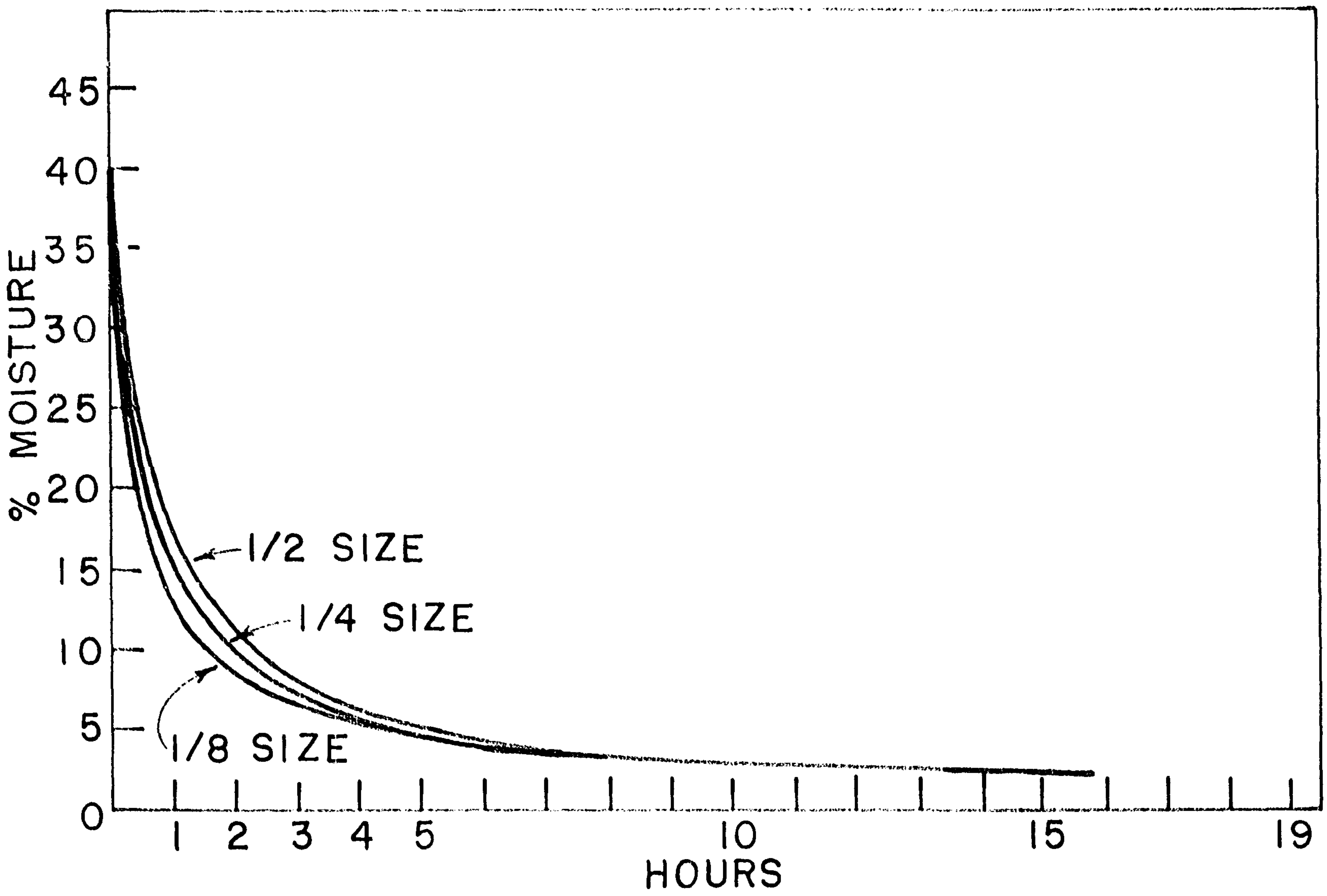

Figure 8. Drying curves for three fractions at 70°C

Table 2. Adsorption and desorption data for soybeans at two temperatures showing the equilibrium moisture percentage on a dry weight basis as a function of relative vapor pressure

	Equilibrated at 30°C					Equilibrated at 20°C		
p/p_0	Naturally wet	Rewet	Predried at 30°C	Predried at 50°C	Predried at 100°C	Naturally wet	Rewet	Predried at 50°C
0	1.26*	.74		.68	.12	1.86	1.49	1.07
.0003	1.50	.96		.78	.18	2.02	1.60	1.18
.0015	1.49	.90		.92	.26	2.08	1.82	1.27
.005	1.64	1.44		.90	.24	2.48	2.06	1.45
.015	2.10	2.18		1.28	.60	2.80	2.56	1.66
.03	3.00	2.80		1.49	.92	3.80	3.14	2.02
.05	3.70	3.36		1.80	1.30	4.65	3.75	2.38
.07	4.20	3.81		2.19	1.61	5.10	4.20	2.66
.10	4.80	4.28	4.20	3.00	2.19	5.50	4.68	3.39
.20	5.67	5.22	5.45	4.78	3.95	6.40	5.62	5.38
.30	6.62	6.24	6.54	6.00	5.39	7.38	6.59	6.54
.40	8.16	7.60	8.06	7.41	6.98	8.80	8.07	7.98
.50	10.00	9.37	10.00	9.30	8.92	10.36	9.60	9.65
.60	12.16	11.53	12.18	11.65	11.43	12.28	11.58	11.81
.70	15.01	14.28	15.09	14.83	14.59	15.00	14.32	14.98

*Each entry represents the average of two closely agreeing replications.

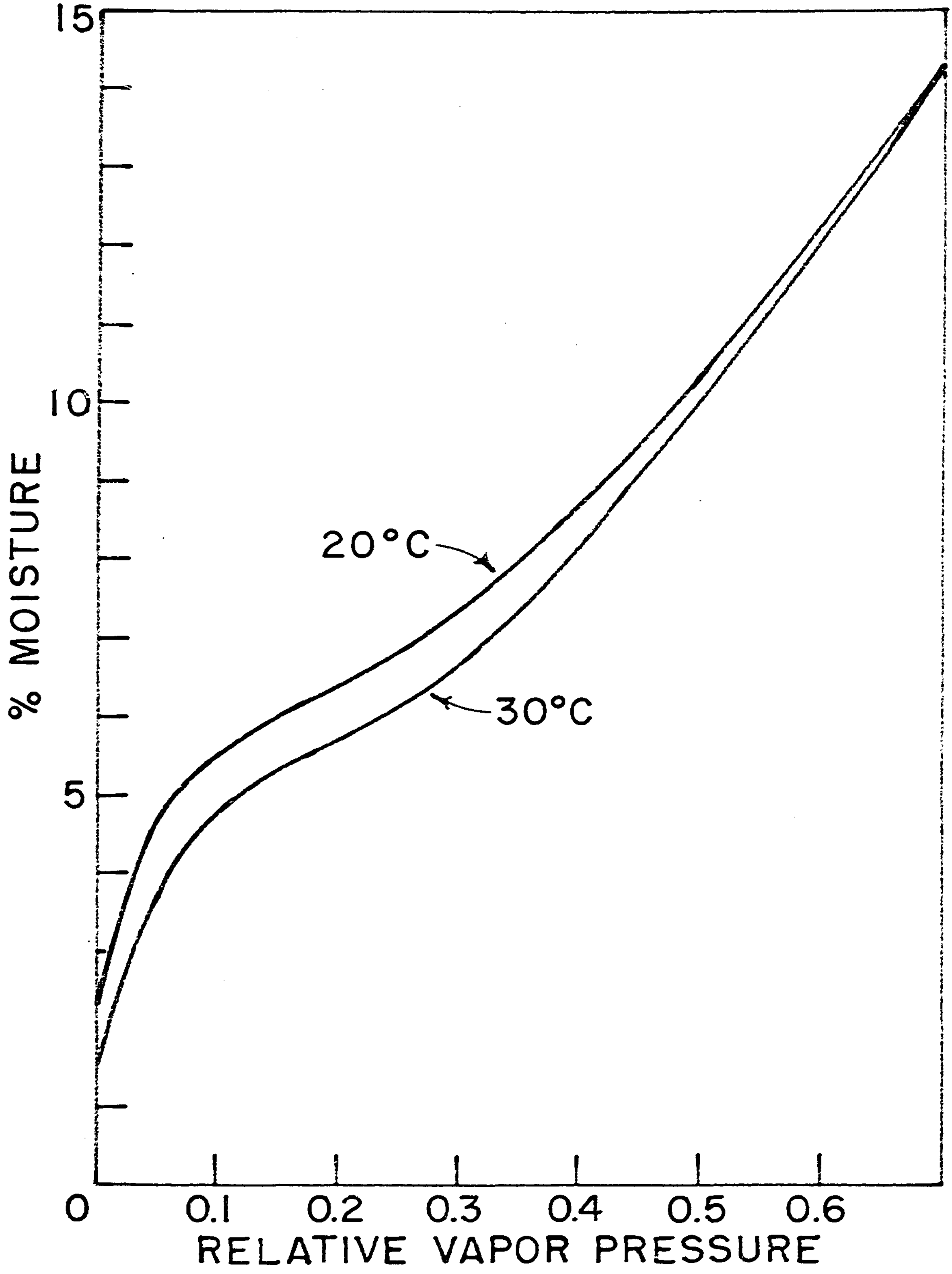

Figure 9. Desorption of naturally wet or fresh seeds

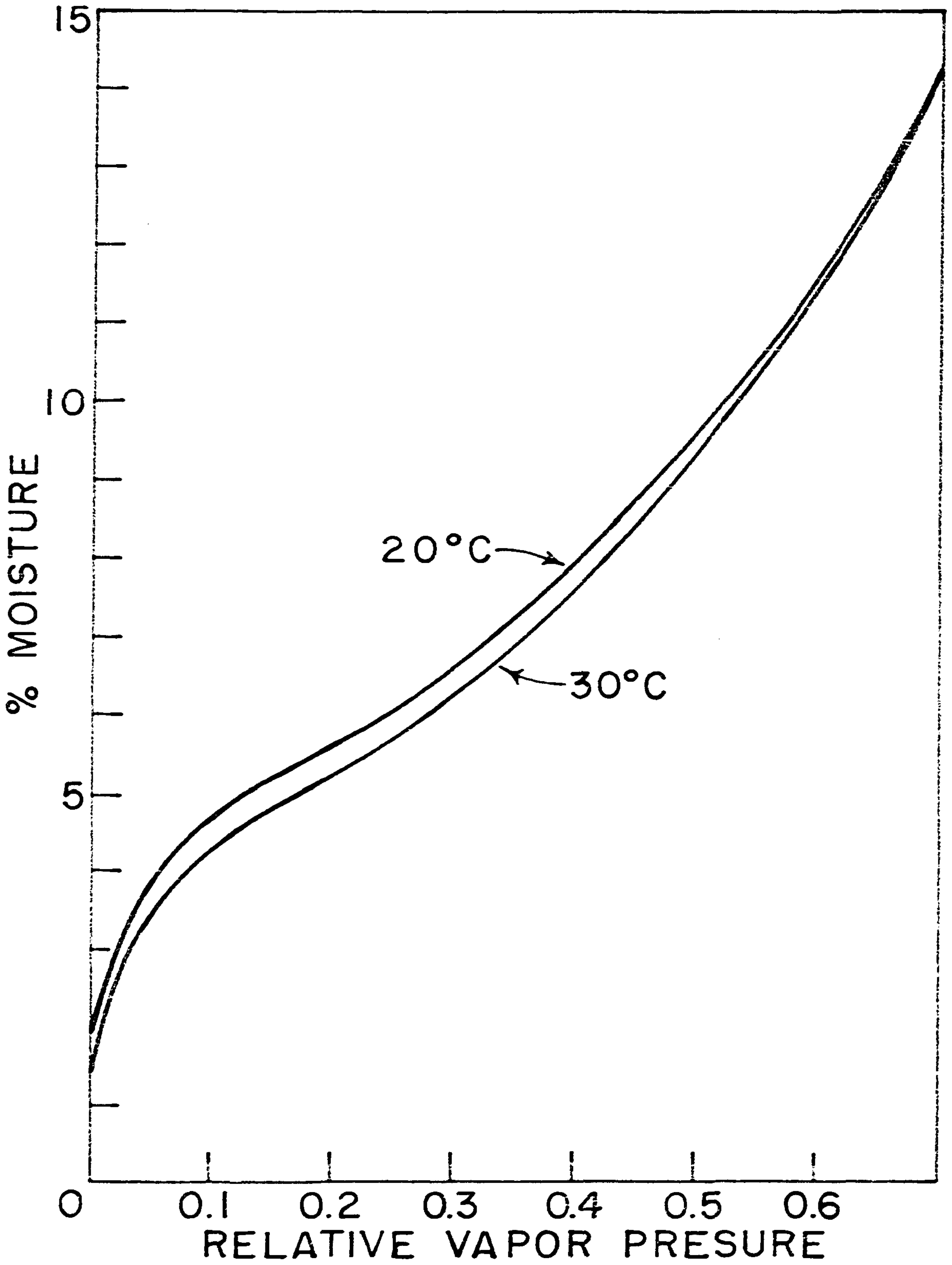

Figure 10. Desorption of rewet seeds

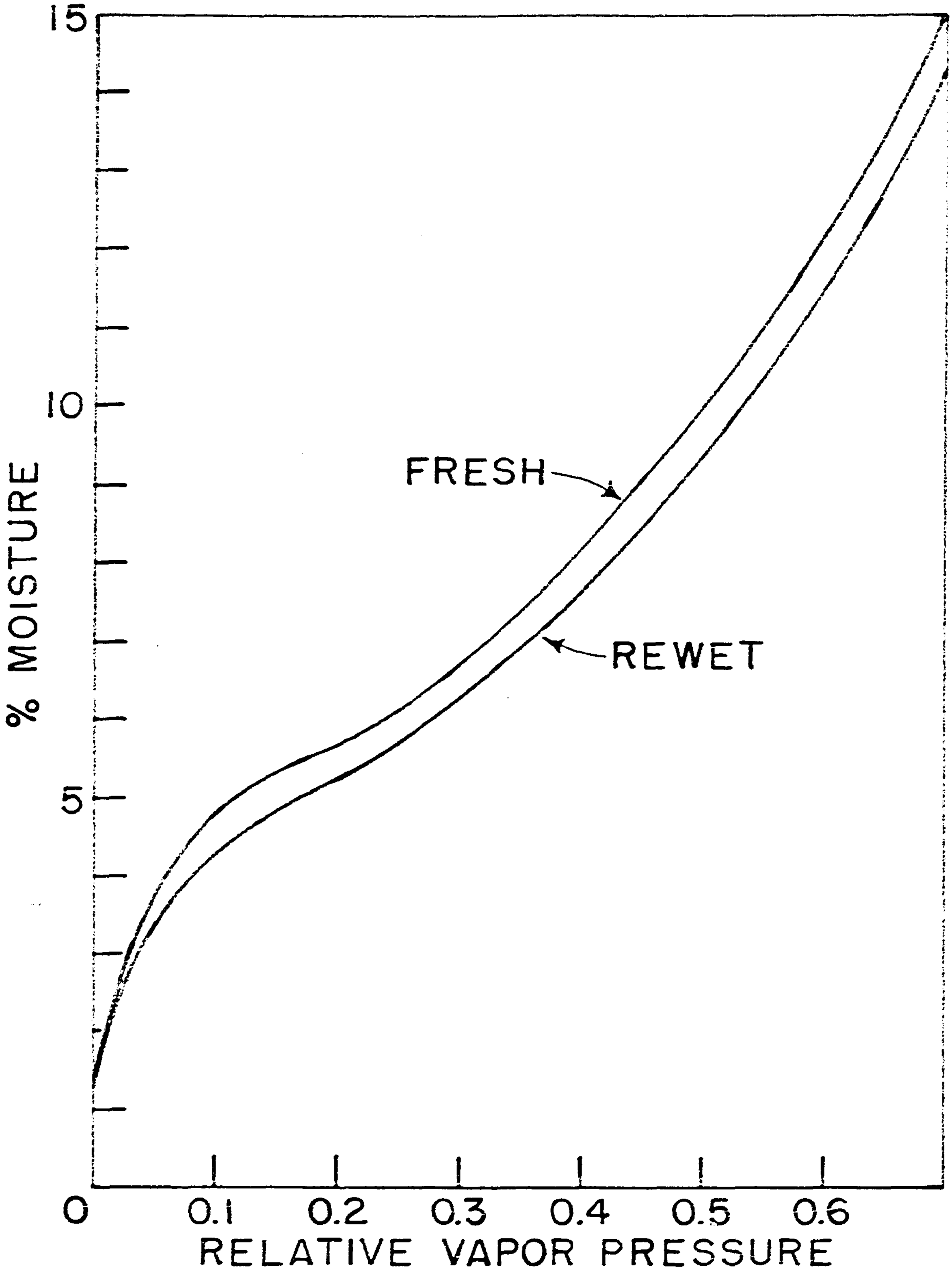

Figure 11. Desorption of fresh and rewet seeds at 30°C

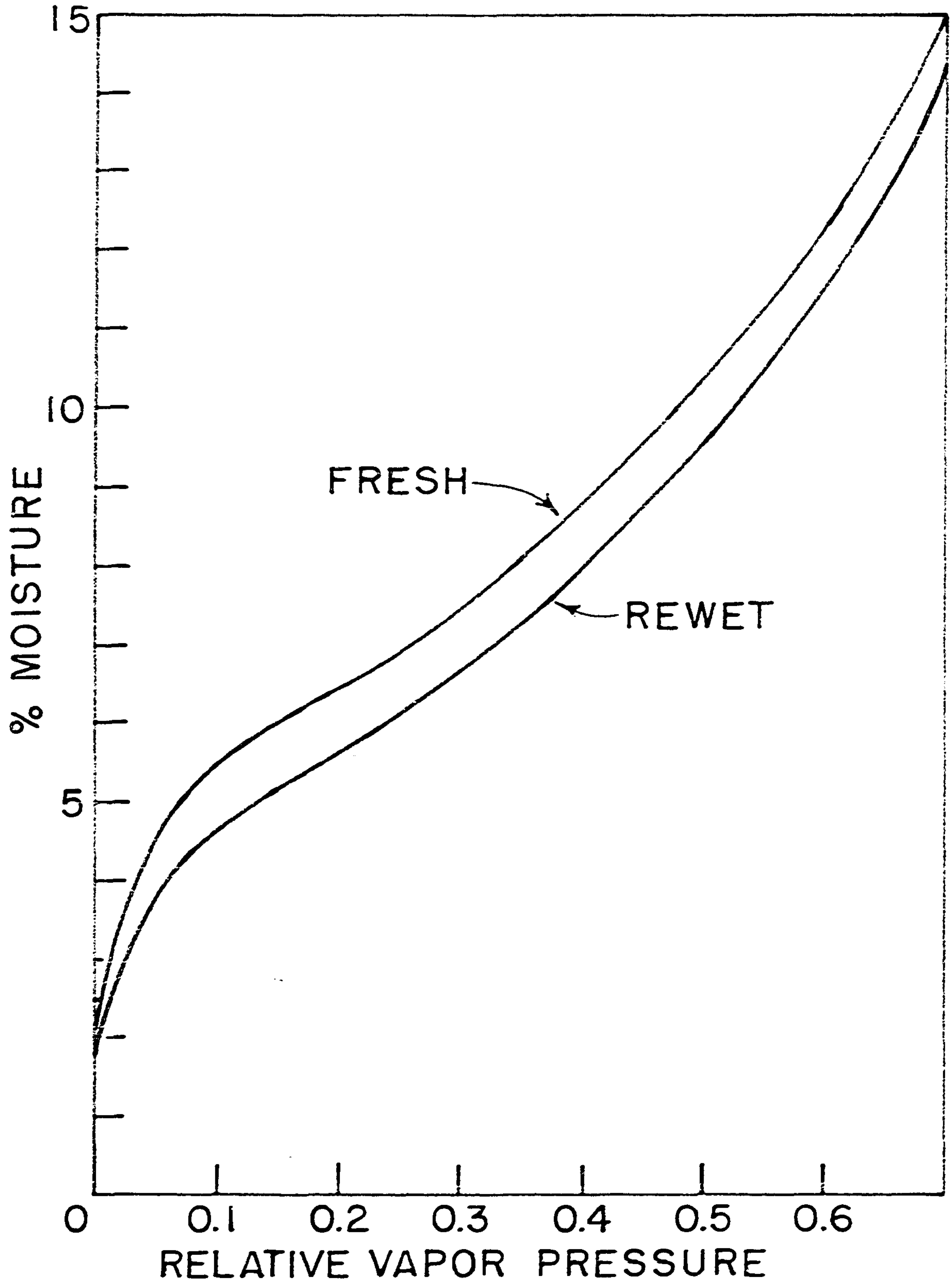

Figure 12. Desorption of fresh and rewet seeds at 20°C

present in the fresh seeds at the same relative vapor pressure, or what amounts to the same thing, a lower vapor pressure for a given percentage of moisture. It may also be noted that the isotherms at 20° lie above those at 30°C. This is to be expected inasmuch as desorption is endothermic.

Adsorption isotherms were obtained using seeds previously dried at 30°, 50°, and 100°C. These data are given in Table 2 and the isotherms in Figures 13 and 14. Figure 14 shows a definite hysteresis effect; that is, the adsorption curves for the predried seeds do not retrace the desorption curve. The discrepancy was small in the seeds predried at 30° and increased markedly with predrying at 50° and 100°C. These results indicate that the higher temperatures had changed the chemical or physical properties of the seed materials. Drying at 30° was so slow that data for the lower end of the desorption curve were not obtained.

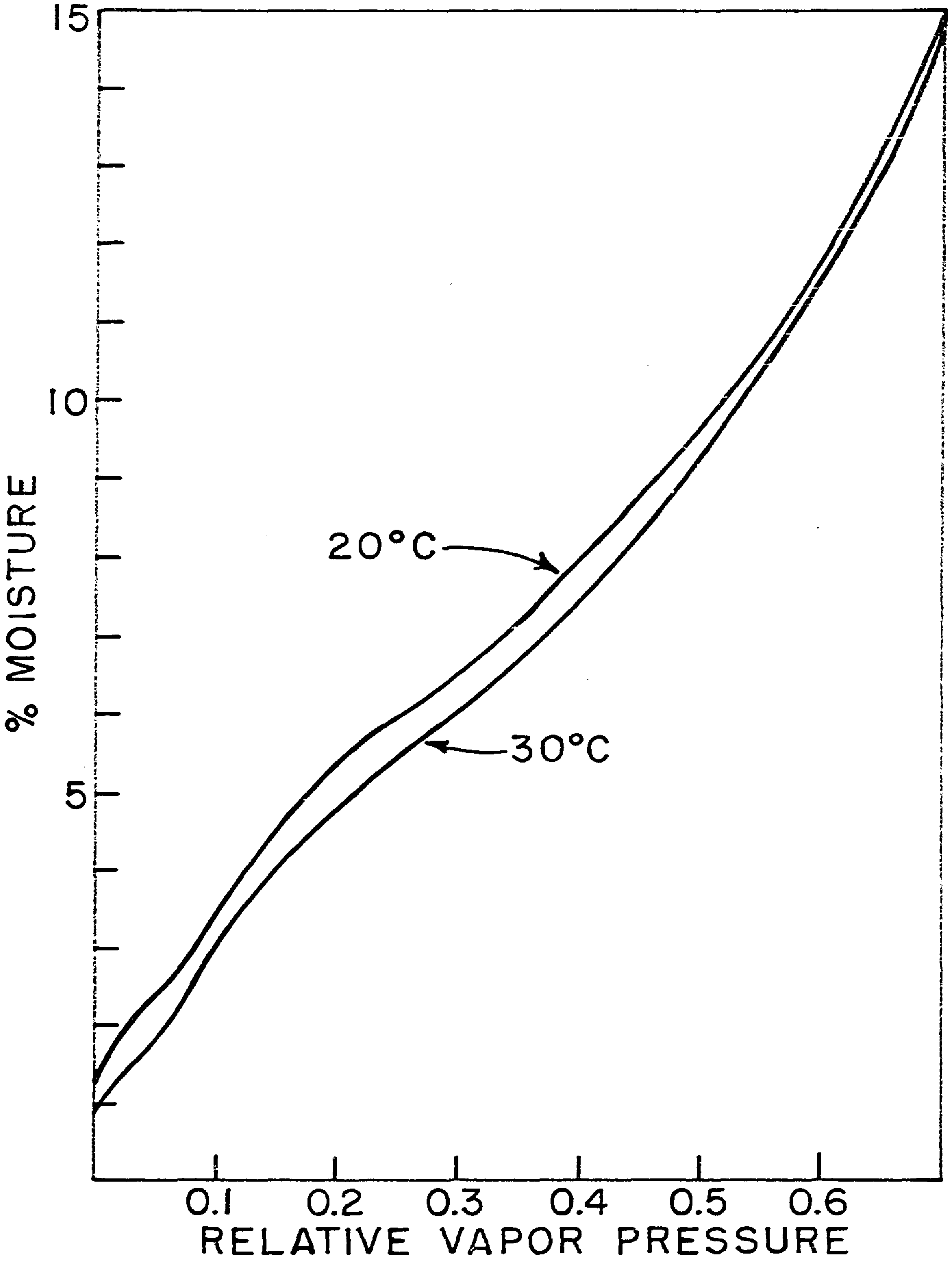

Figure 13. Adsorption by seeds dried at 50°C

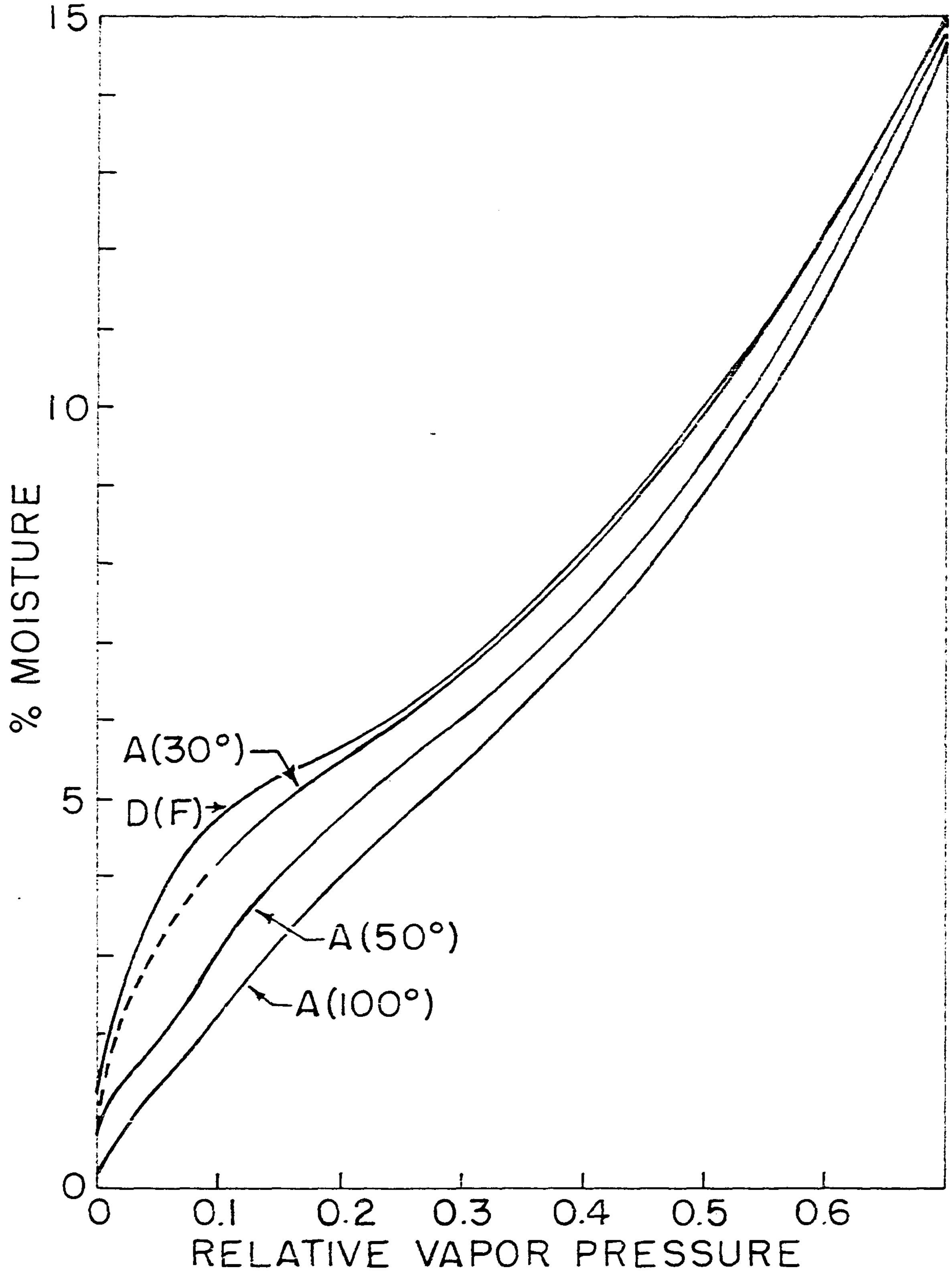

Figure 14. Desorption of fresh seeds (D(F)) compared to adsorption by seeds dried at three temperatures

ANALYSIS OF DATA

Drying

Experimental drying of seeds has revealed that the drying is all at a falling rate. Thus the rate of moisture loss is controlled by the rate of internal diffusion. Under these circumstances it should be possible to describe the drying of seeds by use of the fundamental equations of diffusion. The mathematical theory of diffusion in isotropic substances is based on Fick's laws of diffusion. These are of the form

$$P = - D \frac{\partial C}{\partial x} \qquad (17)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (18)$$

where P = rate of permeation

D = diffusion coefficient

C = concentration of diffusing substance

x = space coordinate

t = time.

Equation (17) gives the rate of transfer of the diffusing substance through a unit area, in terms of the concentration gradient. Equation (18) is the fundamental differential equation describing the non-steady state of diffusion. Equation (18) may be derived from Equation (17) by considering diffusion in a positive-x direction through a volume element (e.g., rectangular parallelepiped) bounded by two parallel planes of unit area at x and x + dx. Moisture accumulation in this element of volume is found by subtracting the flow out of the element from the flow into the element. Thus if P_1 = flow in and P_2 = flow out,

$$P_1 - P_2 = D\left[-\left(\frac{\partial C}{\partial x}\right)_x + \left(\frac{\partial C}{\partial x}\right)_{x + dx}\right], \text{ or} \qquad (19)$$

$$P_1 - P_2 = D\frac{\partial^2 C}{\partial x^2}dx \quad . \qquad (20)$$

The rate of moisture accumulation is also given by the expression

$$dx\frac{\partial C}{\partial t} \quad . \qquad (21)$$

Thus, by equating (20) and (21),

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \quad . \qquad (22)$$

The equation for diffusion in three dimensions may be derived by considering an element of volume in the form of a rectangular parallelepiped with sides of lengths dx, dy, and dz. The contributions to the rate of moisture accumulation in the element of volume may then be written:

$$\text{x-direction:}\quad P_1 - P_2 = dy\ dz\left[-D\left(\frac{\partial c}{\partial x}\right)_x + D\left(\frac{\partial c}{\partial x}\right)_{x+dx}\right]$$
$$= dx\ dy\ dz\ D\ \frac{\partial^2 c}{\partial x^2}$$

$$\text{y-direction:}\quad P_1 - P_2 = dx\ dz\left[-D\left(\frac{\partial c}{\partial y}\right)_y + D\left(\frac{\partial c}{\partial y}\right)_{y+dy}\right]$$
$$= dx\ dy\ dz\ D\ \frac{\partial^2 c}{\partial y^2}$$

$$\text{z-direction:}\quad P_1 - P_2 = dy\ dx\left[-D\left(\frac{\partial c}{\partial z}\right)_z + D\left(\frac{\partial c}{\partial z}\right)_{z+dz}\right]$$
$$= dx\ dy\ dz\ D\ \frac{\partial^2 c}{\partial z^2}\ .$$

The rate of moisture accumulation in this element of volume is also given by

$$dx\ dy\ dz\ \frac{\partial c}{\partial t}\ .$$

Thus

$$\frac{\partial c}{\partial t} = D\left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right]. \qquad (23)$$

Soybeans are best described as spherical particles of homogeneous composition. Equation (23) may be transformed into spherical polar coordinates r, θ, and ∅ by means of the transformation equations

$$x = r \cos \theta \sin \phi$$
$$y = r \sin \theta \sin \phi$$
$$z = r \cos \theta \; .$$

Equation (23) then becomes

$$\frac{\partial C}{\partial t} = \frac{D}{r^2}\left[\frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) + \frac{1}{\sin \theta}\frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial C}{\partial \theta}\right) + \frac{1}{\sin^2 \theta}\frac{\partial^2 C}{\partial \phi^2}\right] . \tag{24}$$

For spherically symmetrical diffusion, as may be assumed in the case of the soybean, Equation (24) reduces to

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right] \tag{25}$$

because $\frac{\partial C}{\partial \theta} = 0$ and $\frac{\partial^2 C}{\partial \phi^2} = 0$.

Equation (25) is, therefore, the general equation for diffusion out of a soybean. If it is assumed that the mass is proportional to the volume, then the moisture percentage, m, can be substituted for the moisture concentration C. If Equation (25) is now integrated with suitable boundary conditions, a solution will be obtained which will express the moisture, m, as a function of time, t, and location, r.

Suitable initial and boundary conditions consist of

$$m(r,0) = f(r) \; , \qquad 0 < r < r_o$$
$$m(r_o,t) = m_s \; , \qquad t > 0 \; .$$

Let $u = mr$.

It follows that

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2} \tag{26}$$

which is analogous to the equation for linear flow in one dimension. The initial and boundary conditions for Equation (26) are

$$u(r,0) = rf(r) , \qquad 0 < r < r_o$$

$$u(0,t) = 0$$

$$u(r_o,t) = r_o m_s .$$

Now let $w(r,t) = u(r,t) - m_s r$.

This function will satisfy the conditions

$$\frac{\partial w}{\partial t} = D \frac{\partial^2 w}{\partial r^2} \tag{27}$$

$$w(r,0) = rf(r) - rm_s , \qquad 0 < r < r_o$$

$$w(0,t) = 0$$

$$w(r_o,t) = 0 .$$

A standard method of obtaining a solution of a partial differential equation of the form of Equation (27) is to assume that the variables are separable. Thus a solution may be found of the type

$$w = R(r)\ T(t) \tag{28}$$

where R and T are functions of r and t respectively.

According to Equation (28)

$$\frac{\partial w}{\partial t} = RT'$$

and

$$\frac{\partial^2 w}{\partial r^2} = R''T \quad .$$

Substituting into Equation (27) yields

$$RT' = DR''T$$

which may be rewritten

$$\frac{R''}{R} = \frac{T'}{DT} \quad .$$

Since $\frac{R''}{R}$ is a function of r only, it cannot vary with t; however, since it is equal to a function of t only, it cannot vary with r. Therefore both sides of the equation must be equal to a constant, say a.

Thus

$$\frac{R''}{R} = a = \frac{T'}{DT}$$

or

$$R'' - aR = 0 \tag{29}$$

$$T' - aDT = 0 \; . \tag{30}$$

Both of these equations are linear homogeneous ordinary differential equations for which the solutions may be easily obtained. In order that the solution $w = R(r)\,T(t)$ satisfy the boundary conditions $w(0,t) = 0$ and $w(r_o,t) = 0$, $R(r)\,T(t)$ must vanish when $r = 0$ and when $r = r_o$, for all values of t.

Therefore $$R(0) = 0 \tag{31}$$

and $$R(r_o) = 0 \ . \tag{32}$$

The general solution of Equation (29) may be written

$$R = Ae^{\sqrt{a}r} + Be^{-\sqrt{a}r}$$

where A and B are arbitrary constants and the value of a must be determined so that conditions (31) and (32) will be satisfied. These conditions cannot be satisfied if a is positive. By assuming a to be negative:

$$a = -b^2$$

the general solution of Equation (29) can be written

$$R = G \sin br + H \cos br \tag{33}$$

where G and H are arbitrary constants and the value of b must be determined so that conditions (31) and (32) will be satisfied. Where $r = 0$, $H = 0$, and where $r = r_o$, $\sin br_o = 0$. Sin br_o is equal to zero when

$$b = \frac{n\pi}{r_o}, \qquad (n = 1,2,\ldots) \ .$$

Thus the general solution of Equation (29) has the form

$$R = G \sin \frac{n\pi r}{r_o} \ . \tag{34}$$

Consider next Equation (30)

$$T' - aDT = 0 \quad .$$

The general solution of this equation can be written

$$T = Q\ e^{aDt} \quad . \tag{35}$$

Since $a = -b^2 = -\dfrac{n^2\ \pi^2}{r_o^2}$, Equation (35) becomes

$$T = Qe^{-\dfrac{n^2\ \pi^2\ Dt}{r_o^2}}$$

or

$$T = Q\ \exp\left(-\ \frac{n^2\ \pi^2\ Dt}{r_o^2}\right) \quad .$$

Therefore all the functions

$$A_n\ \sin\left(\frac{n\pi r}{r_o}\right)\ \exp\left(-\ \frac{n^2\ \pi^2\ Dt}{r_o}\right) \qquad (n = 1,2,3,\ldots) \tag{36}$$

where the constants A_n are arbitrary, are solutions of Equation (27) and satisfy the homogeneous boundary conditions $w(0,t) = 0$, and $w(r_o,t) = 0$. There remains yet the nonhomogeneous boundary condition $w(r,0) = rf(r) - rm_s$, which must also be satisfied. Consider an infinite series of the functions (36),

$$w = \sum_{1}^{\infty}\ A_n\ \sin\left(\frac{n\pi r}{r_o}\right)\ \exp\left(-\ \frac{n^2\ \pi^2\ Dt}{r_o^2}\right) \tag{37}$$

This satisfies Equation (27) provided it converges and is termwise differentiable. It also satisfies the homogeneous boundary conditions. It will reduce to $rf(r) - rm_s$ when $t = 0$, provided the coefficients A_n are so determined that

$$rf(r) - rm_s = \sum_1^{\infty} A_n \sin\left(\frac{n\pi r}{r_o}\right) . \tag{38}$$

Assuming that the series can be integrated term by term, multiply both sides of Equation (38) by $\sin\left(\frac{n'\pi r}{r_o}\right)$ and integrate from zero to r_o:

$$\int_0^{r_o} \left[rf(r) - rm_s\right] \sin\left(\frac{n'\pi r}{r_o}\right) dr$$
$$= \sum_1^{\infty} A_n \int_0^{r_o} \sin\left(\frac{n\pi r}{r_o}\right) \sin\left(\frac{n'\pi r}{r_o}\right) dr .$$

It follows then that the coefficients A_n must have the values

$$A_n = \frac{2}{r_o} \int_0^{r_o} \left[rf(r) - rm_s\right] \sin\left(\frac{n\pi r}{r_o}\right) dr \tag{39}$$

since
$$\int_0^{r_o} \sin\left(\frac{n\pi r}{r_o}\right) \sin\left(\frac{n'\pi r}{r_o}\right) dr = 0 \quad \text{if } n' \neq n$$
$$= \frac{r_o}{2} \quad \text{if } n' = n .$$

Equation (37) can now be written

$$w = \frac{2}{r_o} \sum_{1}^{\infty} \sin\left(\frac{n\pi r}{r_o}\right) \exp\left(-\frac{n^2 \pi^2 Dt}{r_o^2}\right) \int_0^{r_o} \left[rf(r)-rm_s\right] \sin\left(\frac{n\pi r}{r_o}\right) dr \,. \tag{40}$$

Since $w = u-rm_s$,

it follows that

$$u = rm_s + \frac{2}{r_o} \sum_{1}^{\infty} \sin\left(\frac{n\pi r}{r_o}\right) \exp\left(-\frac{n^2 \pi^2 Dt}{r_o^2}\right) \int_0^{r_o} \left[rf(r)-rm_s\right] \sin\left(\frac{n\pi r}{r_o}\right) dr \,. \tag{41}$$

Likewise, since $u = mr$,

it follows that

$$mr = rm_s + \frac{2}{r_o} \sum_{1}^{\infty} \sin\left(\frac{n\pi r}{r_o}\right) \exp\left(-\frac{n^2 \pi^2 Dt}{r_o^2}\right) \int_0^{r_o} \left[rf(r)-rm_s\right] \sin\left(\frac{n\pi r}{r_o}\right) dr \tag{42}$$

or

$$m = m_s + \frac{2}{rr_o} \sum_{1}^{\infty} \sin\left(\frac{n\pi r}{r_o}\right) \exp\left(- \frac{n^2 \pi^2 Dt}{r_o^2}\right)$$

$$\int_0^{r_o} \left[rf(r)-rm_s\right] \sin\left(\frac{n\pi r}{r_o}\right) dr . \qquad (43)$$

which is the solution of the equation for diffusion out of a sphere with surface concentration maintained at m_s, and with an initial moisture distribution $f(r)$. If it is assumed that the initial distribution may be represented by an average initial moisture concentration, m_o, Equation (43) becomes

$$m = m_s + \frac{2}{rr_o} \sum_{1}^{\infty} \sin\left(\frac{n\pi r}{r_o}\right) \exp\left(- \frac{n^2 \pi^2 Dt}{r_o^2}\right)$$

$$\int_0^{r_o} \left[rm_o-rm_s\right] \sin\left(\frac{n\pi r}{r_o}\right) dr \qquad (44)$$

or

$$m = m_s + \frac{2}{rr_o} \sum_{1}^{\infty} \sin\left(\frac{n\pi r}{r_o}\right) \exp\left(- \frac{n^2 \pi^2 Dt}{r_o^2}\right) (m_o-m_s)$$

$$\int_0^{r_o} r \sin\left(\frac{n\pi r}{r_o}\right) dr . \qquad (45)$$

Since $\int_0^{r_o} r \sin\left(\frac{n\pi r}{r_o}\right) dr = (-1)^{n+1} \frac{r_o^{\,2}}{\pi n}$, Equation (45) can be written

$$m = m_s + \frac{2}{r r_o} \sum_1^{\infty} \sin\left(\frac{n\pi r}{r_o}\right) \exp\left(-\frac{n^2 \pi^2 Dt}{r_o^2}\right)$$

$$(m_o - m_s) \frac{r_o^2}{n\pi} (-1)^{n+1} ,$$

$$m = m_s + \frac{2(m_o - m_s) r_o}{r} \sum_1^{\infty} \frac{(-1)^{n+1}}{\pi n} \sin\left(\frac{n\pi r}{r_o}\right)$$

$$\exp\left(-\frac{n^2 \pi^2 Dt}{r_o^2}\right) ,$$

$$\frac{m - m_s}{m_o - m_s} = \frac{2 r_o}{\pi r} \sum_1^{\infty} \frac{(-1)^{n+1}}{n} \sin\left(\frac{n\pi r}{r_o}\right) \exp\left(-\frac{n^2 \pi^2 Dt}{r_o^2}\right). \quad (46)$$

This gives the moisture, m, as a function of both time and location. The value actually measured in a drying procedure is the average moisture, $\bar{m}$, and is a function of time only. An expression for the average moisture content, $\bar{m}$, at any time, t, may be obtained from Equation (46) by dividing the total moisture content at that time by the total volume. Consider a spherical shell within the solid sphere. The surface of the shell will be $4\pi r^2$ and its thickness dr, making its volume $4\pi r^2 dr$. The removable moisture content of the shell will be $(m-m_s)4\pi r^2 dr$, and the total removable moisture content of the solid sphere will be $(\bar{m}-m_s)\,\frac{4}{3}\,\pi r_o^{\,3}$. It follows that

$$(\bar{m}-m_s)\,\frac{4\pi r_o^{\,3}}{3} = \int_0^{r_o} (m-m_s)\;4\pi r^2 dr \;. \qquad (47)$$

From Equation (46)

$$m-m_s = (m_o-m_s)\,\frac{2r_o}{r}\sum_1^{\infty}\frac{(-1)^{n+1}}{n\pi}\,\sin\left(\frac{n\pi r}{r_o}\right)\,\exp\left(-\,\frac{n^2\,\pi^2\,Dt}{r_o^2}\right).$$

If this is substituted into Equation (47) the following is obtained:

$$(\bar{m}-m_s)\,\frac{4\pi r_o^{\,3}}{3} = \int_0^{r_o} (m-m_s)\,\frac{2r_o}{\pi r}\sum_1^{\infty}\frac{(-1)^{n+1}}{n}\left(\sin\frac{n\pi r}{r_o}\right)\exp\left(-\,\frac{n^2\,\pi^2\,Dt}{r_o^2}\right)4\pi r^2 dr \;. \qquad (48)$$

Simplification and integration of Equation (48) gives

$$\frac{\bar{m}-m_s}{m_o-m_s} = \frac{6}{\pi^2}\sum_1^{\infty}\frac{1}{n^2}\,\exp\left(-\,\frac{n^2\,\pi^2\,Dt}{r_o^2}\right). \qquad (49)$$

Equation (49) expresses the average moisture content, $\bar{m}$, as a function of time.

It may be noted that Equation (49) is of the same form as that used by Becker and Sallans (see Equation 7) to describe the drying of wheat kernels. For the surface moisture content, they used the value 10.5%. If the seeds are dried with a current of dry, heated air, as was the case with both Becker and Sallans' work and also with the present study, it seems more logical because of continuity considerations, to assume a value of zero for the surface moisture content. In other words, it is assumed that the initial moisture concentration is uniform throughout the interior, but that at the surface the concentration drops to zero immediately at the beginning of the diffusional stage. If this assumption is valid, Equation (49) reduces to

$$\frac{\bar{m}}{m_o} = \frac{6}{\pi^2} \sum_{1}^{\infty} \frac{1}{n^2} \exp\left(- \frac{n^2 \pi^2 Dt}{r_o^2}\right). \qquad (50)$$

Likewise, Equation (46) reduces to

$$\frac{m}{m_o} = \frac{2r_o}{\pi r} \sum_{1}^{\infty} \frac{(-1)^{n+1}}{n} \sin\left(\frac{n\pi r}{r_o}\right) \exp\left(- \frac{n^2 \pi^2 Dt}{r_o^2}\right). \qquad (51)$$

Equations (50) and (51) are the ones which were used throughout this investigation. It might be mentioned in passing that Equations (50) and (51) can be more easily obtained by assuming an initial boundary condition $m(r_o,t) = 0$ at the very outset of the problem. It should be noted, however, that Equations (49) and (46) are more general than Equations (50) and (51) and are directly applicable in some cases. For example, in the study of desorption rates where the external atmosphere has a relative humidity greater than zero, m_s, must be larger than zero.

It may be noted that the series in Equation (50) contains the term $\frac{\pi^2 Dt}{r_o^2}$ in the exponent of e. Since π^2, D, and r_o^2 are assumed to be constant, this non-dimensional ratio may be denoted by D't. Inasmuch as the only variables in Equation (50) are the average moisture content and time, it is convenient to plot a curve of $\frac{\bar{m}}{m_o}$ vs. D't which may subsequently be used as a calibration curve.

The curve showing $\frac{\bar{m}}{m_o}$ as a function of D't was obtained by assigning arbitrary values to D't, and then solving the resulting series for the corresponding value of $\frac{\bar{m}}{m_o}$. The resulting values were then plotted on semi-logarithmic paper (Figure 15).

Values for $\frac{\bar{m}}{m_o}$ were calculated directly from the drying curves and the corresponding values of D't were then obtained from the calibration curve. By equating D't to $\frac{\pi^2 Dt}{r_o^2}$, the value of the diffusion coefficient, D, was calculated.

Figure 15. Calibration curve showing $\bar{m}/m$ as a function of D't

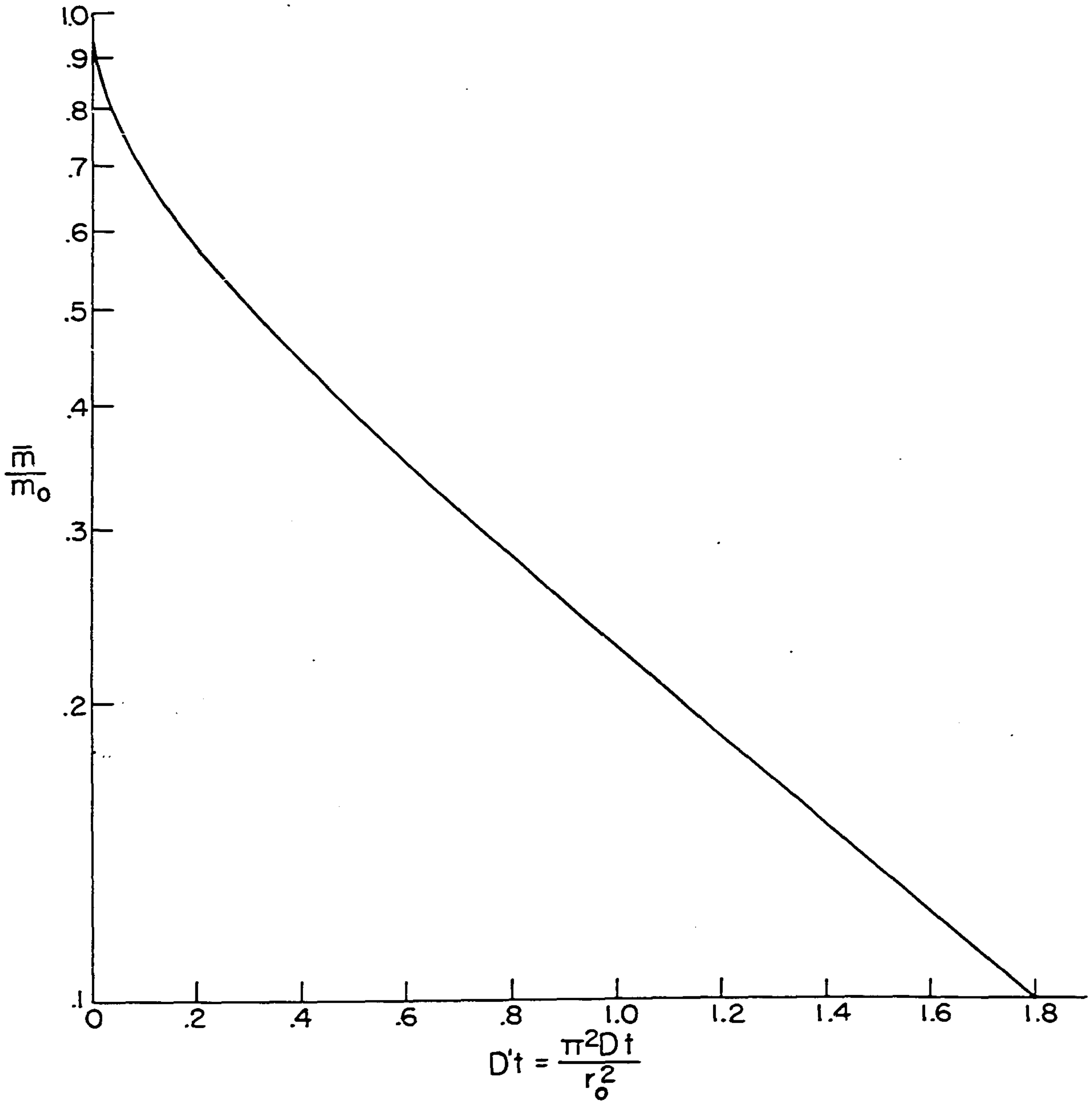
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
$\frac{\bar{m}}{\bar{m}_o}$
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
$D't = \frac{\pi^2 D t}{r_o^2}$

Table 3. Diffusion coefficients for four particle sizes at four temperatures

Temp.	Particle sizes			
	1	1/2	1/4	1/8
40°C	0.37*	0.43	0.28	0.25
50°C	0.53	0.60	0.45	0.37
60°C	0.70	0.80	0.58	0.43
70°C	0.87	0.97	0.75	0.60

*Data = $Dx10^6$

In this manner, the value of D was calculated for each point plotted, for each of the drying curves obtained. A summary of these results is shown in Table 3, and a typical set of data is shown in Table 4. The values shown in Table 3 are the average values of the diffusion coefficients in the range from 40% to 15% moisture content. The diffusion coefficient remained constant down to approximately 15% (slightly lower at 70°C), but below that point it dropped rather markedly, indicating non-conformity to Fick's law.

Measurements of the rate at which a diffusion process occurs are usually expressed in terms of the diffusion coefficient, which is defined as the rate of transfer of the diffusing substance across a unit area, divided by the concentration gradient. The effect of temperature on the

Table 4. Diffusion coefficients at 70°C with decreasing moisture contents and particle sizes

Particle sizes							
1		1/2		1/4		1/8	
$\bar{m}$	$D\times10^6$	$\bar{m}$	$D\times10^6$	$\bar{m}$	$D\times10^6$	$\bar{m}$	$D\times10^6$
41.45		40.68		40.86		39.72	
31.40	.88	29.50	.70	27.30	.64	23.58	.62
28.03	.87	23.78	.97	21.32	.73	18.54	.60
25.24	.87	20.03	.97	17.62	.77	15.16	.60
23.16	.87	17.40	.97	15.08	.75	12.74	.57
21.43	.87	15.37	.97	13.37	.72	11.20	.55
19.92	.87	13.82	.97	12.00	.68	10.04	.52
18.60	.87	12.48	.97	10.64	.68	9.01	.48
17.30	.87	11.24	.97	9.58	.67	8.48	.45
16.18	.87	10.36	.97	8.90	.62	7.64	.45
14.22	.87	8.55	.90	7.53	.60	6.83	.40
12.58	.87	7.43	.87	6.62	.55	6.08	.37
10.39	.50	6.05	.77	5.46	.45	5.10	.32
8.79	.48	4.91	.70	4.30	.45	4.48	.27
5.69	.42	3.39		3.27		3.49	

diffusion coefficient has been evaluated by means of the Arrhenius equation, which may be written

$$D = Ae^{-E_a/RT} \tag{52}$$

or

$$\log D = \log A - \frac{E_a}{2.3\ RT} \tag{53}$$

where D = diffusion coefficient

A = constant

E_a = heat of activation

R = gas constant

T = absolute temperature

Thus if the logarithm of the diffusion coefficient is plotted against the reciprocal of the absolute temperature, the slope of the resulting line is equal to $-E_a/2.3R$. Hence the energy of activation, E_a, may be obtained. Even if the plot of logD against 1/T exhibits a curvature, differentiation shows that

$$\frac{d(\log D)}{d\left(\frac{1}{T}\right)} = - \frac{E_a}{2.3R} \tag{54}$$

so that the tangent at any point is equal to $-E_a/2.3R$.

The data for whole soybeans have been plotted in Figure 16. The line drawn through all the points shows definite curvature. An average value of E_a = 8.2 Kcal/mole was obtained by considering the curve in three segments. By drawing a straight line (dashed), a value of E_a = 8.3 Kcal/mole was obtained.

The energy of activation is the energy that the molecules must acquire before they can react, or in other words, it is the difference between the average energy level of all the molecules that react and the average energy level of all the molecules. The values obtained here are of no particular significance in elucidating the problem of moisture sorption because they have been obtained in the range where the diffusion coefficient is constant (above 15% moisture). In this

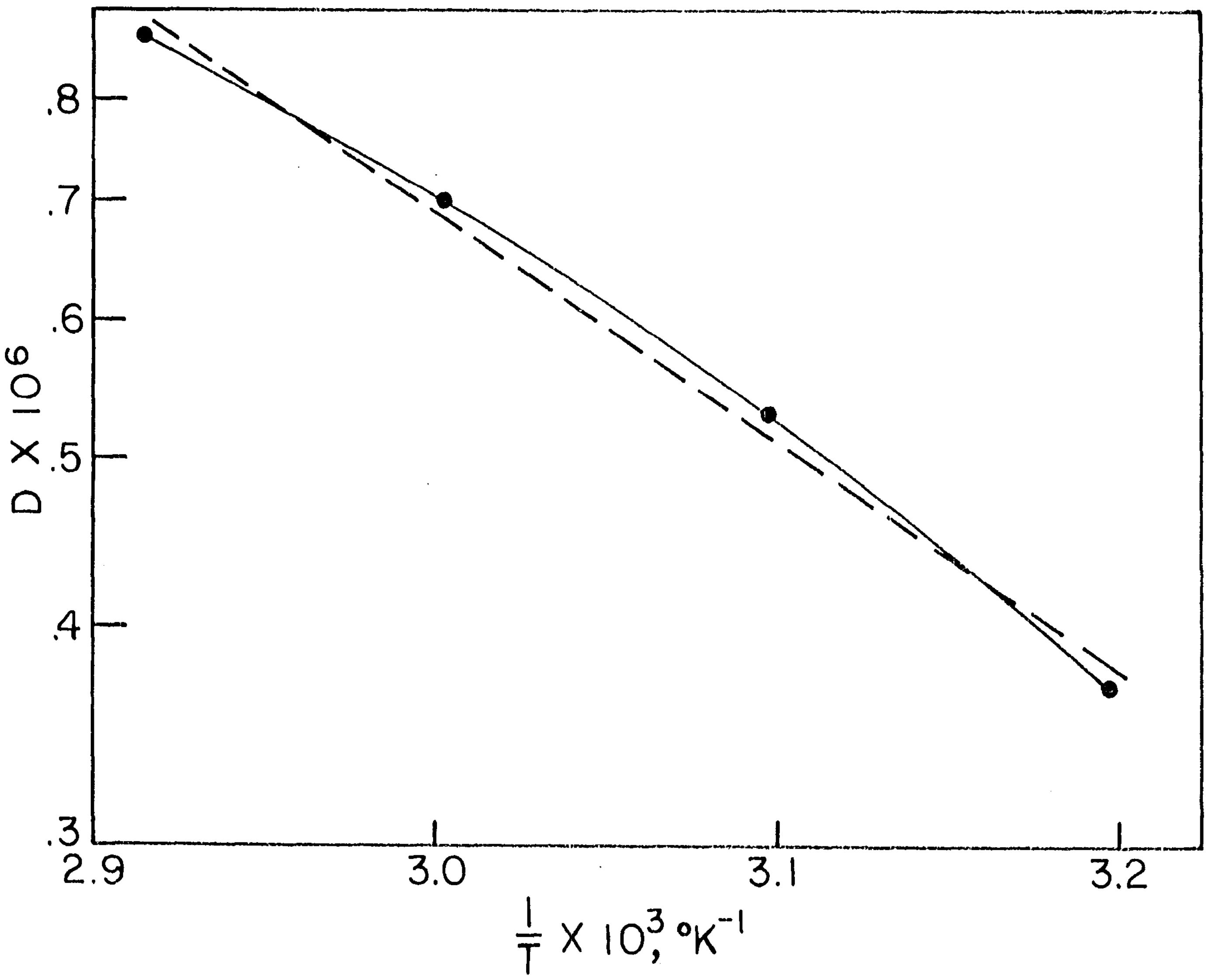

Figure 16. Arrhenius type temperature dependency

range the moisture is no more tightly bound to the seed than are water molecules to water molecules.

Table 3 shows that the particle size also had a definite effect on the diffusion coefficient. If the diffusion coefficient at uniform temperature is considered to be a function of the material only, it should be independent of particle size. This apparently is not the case. This variation of the diffusion coefficient with particle size can possibly be explained on the basis of a surface area to volume ratio. The volume can easily be determined by displacement, but the surface area can only be calculated and not accurately measured. Irregularities on the surface of the broken seeds would result in a surface area larger than that calculated. Hence it is difficult to interpret quantitatively the effect of particle size on the diffusion coefficient.

Equation (51) may be used to determine the moisture distribution within the drying seed. For a given value of $\frac{\bar{m}}{m_o}$, the corresponding value of D't can be obtained from the calibration curve. This value of D't can then be substituted into Equation (51) which thus gives $\frac{m}{m_o}$ as a function of r alone. Equation (51) was solved for several values of $\frac{\bar{m}}{m}$ and Figure 17 shows the resulting moisture gradients, where $\bar{M}$ is equal to $\frac{\bar{m}}{m_o}$.

Becker and Sallans (5) determined the moisture gradient in drying wheat kernels using the equation

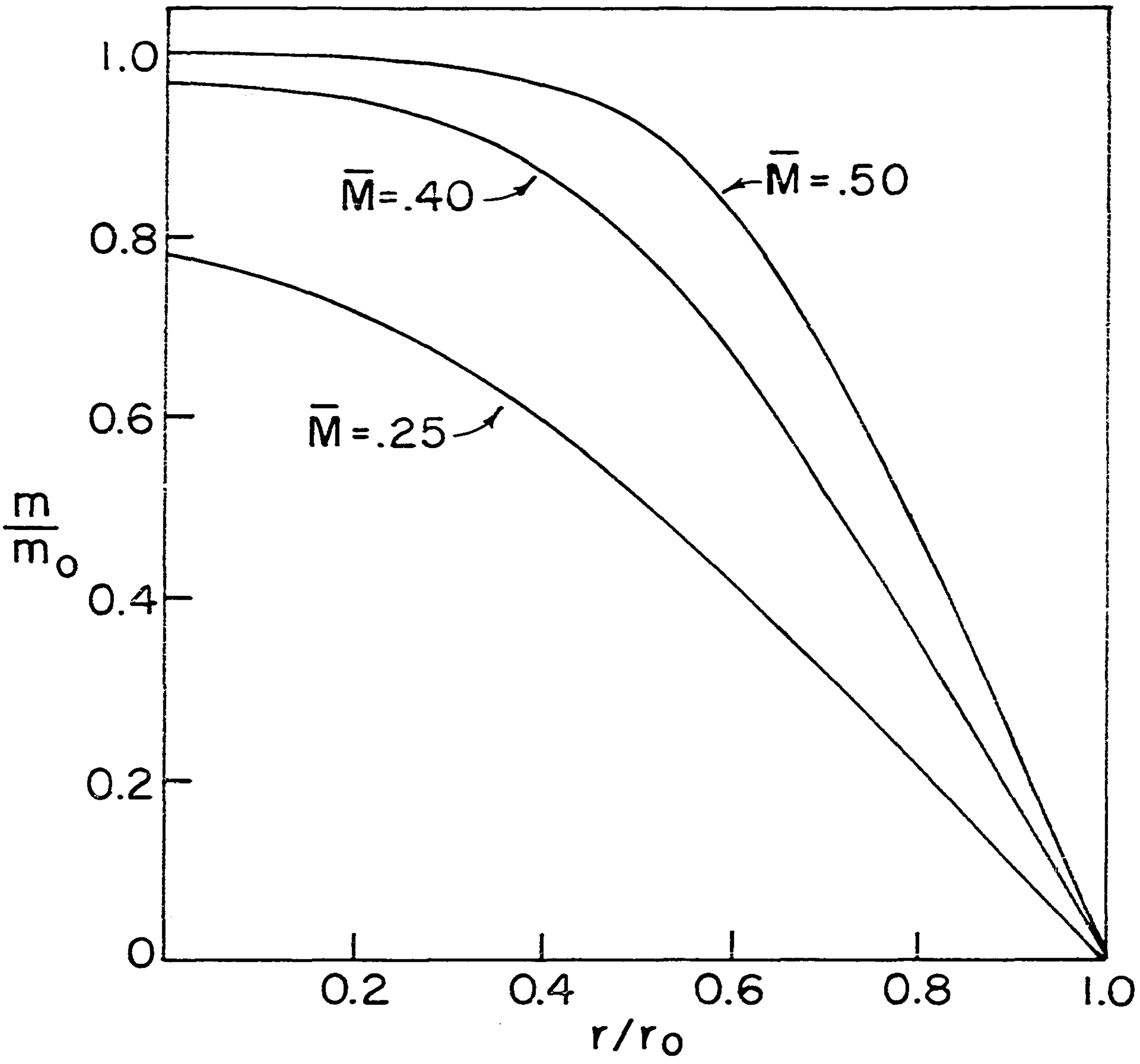

Figure 17. Moisture gradients in drying soybeans

($\overline{M}$ = .50, .40, .25, means that the average moisture content of the seed is equal to 50%, 40%, 25%, respectively, of the original moisture content)

$$\frac{m-m_s}{m_o-m_s} = \sum_{1}^{\infty} \frac{1}{n} (-1)^{n+1} \sin\left(\frac{n\pi r}{r_o}\right) \exp\left(-\frac{n^2 \pi^2 D_c t}{r_o^2}\right) \quad (55)$$

It may be noted, however, that when r is equal to zero, the series vanishes, and hence, $\frac{m-m_s}{m_o-m_s}$, which they denote as M, is also equal to zero. Furthermore, the equation which they use to describe the average moisture content as a function of time,

$$\frac{\bar{m}-m_s}{m_o-m_s} = \frac{6}{\pi^2} \sum_{1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_c t}{r_o^2}\right) \quad (56)$$

cannot be obtained from Equation (55).

Sorption

The BET equation was applied to each of the desorption isotherms. This equation is of the form

$$m = \frac{m_1 C p/p_o}{(1-p/p_o)\left[1+(C-1)p/p_o\right]} \quad (57)$$

where m = amount adsorbed

m_1 = amount required to cover a complete monomolecular layer

p = equilibrium vapor pressure

p_o = saturation pressure

C = a constant which is very closely approximated by the relationship

$$C = \exp(E_1 - E_L)/RT \tag{58}$$

where E_1 = average heat of adsorption for the first layer

E_L = heat of liquefaction

R = gas constant

T = absolute temperature.

To use the BET equation, it is first necessary to obtain values for the constants m_1 and C. These are obtained by transforming Equation (57) into the form

$$\frac{p}{m(p_o - p)} = \frac{1}{m_1 C} + \frac{(C-1)p}{m_1 C p_o} \quad . \tag{59}$$

Figure 18 shows that the plot of the BET equation for rewet seeds equilibrated at 30°C gave a rather good straight line in the relative vapor pressure range from 0.03 to 0.60. Below 0.03 the points fell below the straight line, and the point at 0.7 was above the line. BET (6) attributed the discrepancy in the lower range to a highly heterogeneous surface for which the approximation of an average heat of adsorption in the first layer does not hold. It is possible that the seeds at the lower relative humidities had not reached equilibrium. They were held for 14 months, however, and seeds held for two years gave even lower values. The deviation in the upper range is explained by the fact that Equation (57)

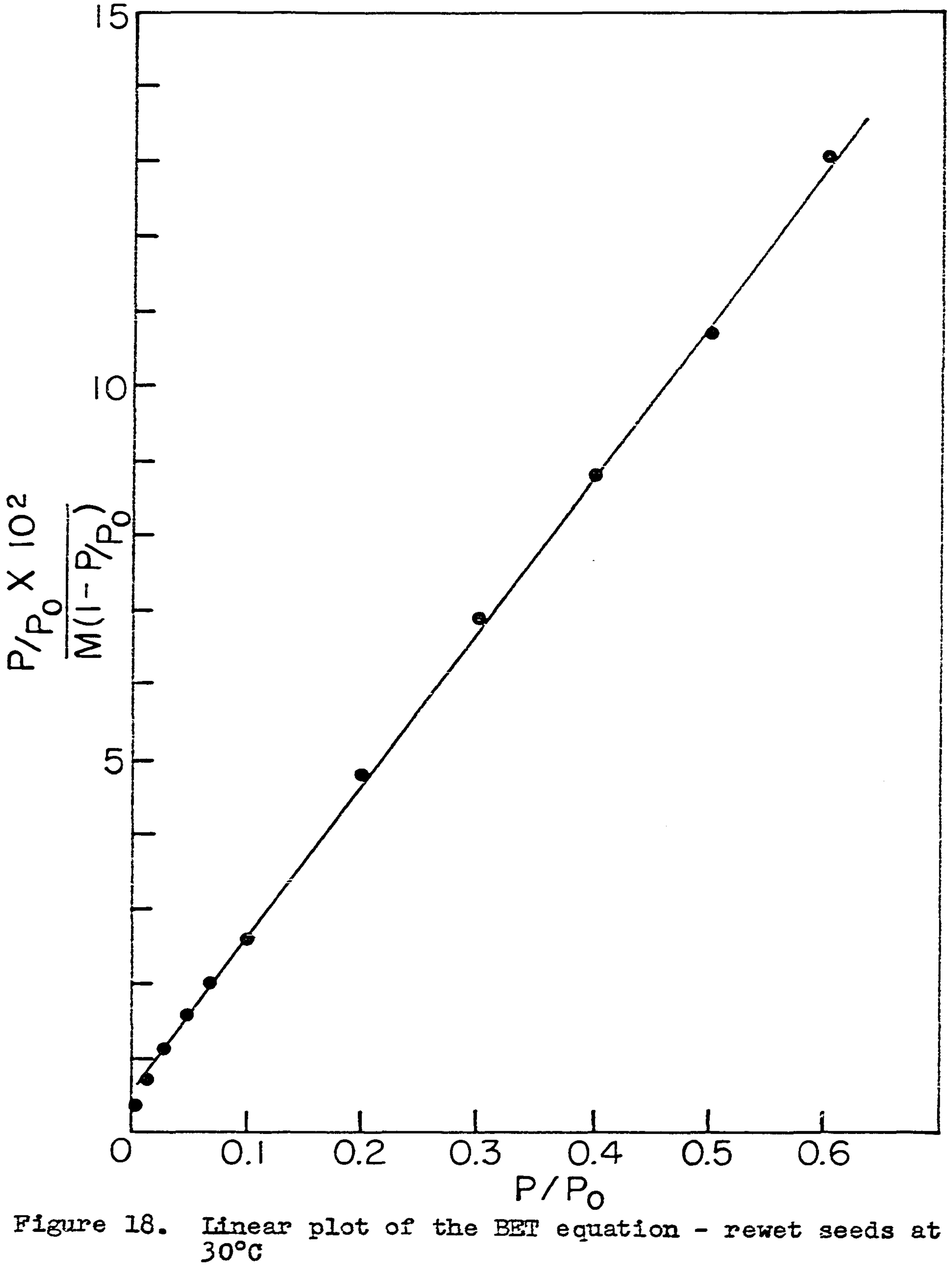

Figure 18. Linear plot of the BET equation - rewet seeds at 30°C

is derived on the assumption that adsorption occurs on a plane surface which does not limit the number of adsorbed layers. This is not true in seeds, and thus at higher relative vapor pressures less moisture is present than would be predicted by Equation (57).

The values of the constants m_1 and C were evaluated from the slope and the intercept of the straight line given in Figure 18.

$$\text{Slope} = \frac{C-1}{m_1 C} = .206$$

$$\text{Intercept} = \frac{1}{m_1 C} = 5.9 \times 10^{-3}$$

Hence $C = 35.9$

$m_1 = 4.72$.

Using these values for C and m_1, the average heat of adsorption of the first layer and also the specific surface area of the seed were calculated. These values are given in Table 5. The calculated BET isotherm is shown in Figure 19 along with the observed data points.

When water is adsorbed by the seed a quantity of heat is released which is known as the heat of adsorption. Likewise, when desorption occurs a quantity of heat known as the heat of desorption must be added to the water in order that it will possess sufficient energy to break away as vapor. The excess

Table 5. Heats of adsorption and specific surface of soybean seeds

Seed lot	Temperature	Heat of adsorption (E_1) (K cal)	Specific surface (m^2/g dry seed)
Rewet	30°C	12.6	167.4
Fresh	30°C	12.8	171.7
Rewet	20°C	12.7	169.6
Fresh	20°C	13.3	186.8

of the heat of desorption over the heat of vaporization is a measure of the strength of binding of the moisture to the seed.

Since the sorption (both adsorption and desorption) of water has been investigated at two temperatures (20°C and 30°C), it is possible, using the Clausius-Clapeyron equation, to calculate both the differential heat of adsorption and the differential heat of desorption. The Clausius-Clapeyron equation is of the form

$$\Delta H = \frac{RT_1T_2}{T_2-T_1} \ln \frac{(p'/p'_o)}{(p/p_o)} \qquad (60)$$

where p'/p'_o is the relative vapor pressure at the higher temperature, T_2, which corresponds to the same moisture content as the relative vapor pressure p/p_o at the lower

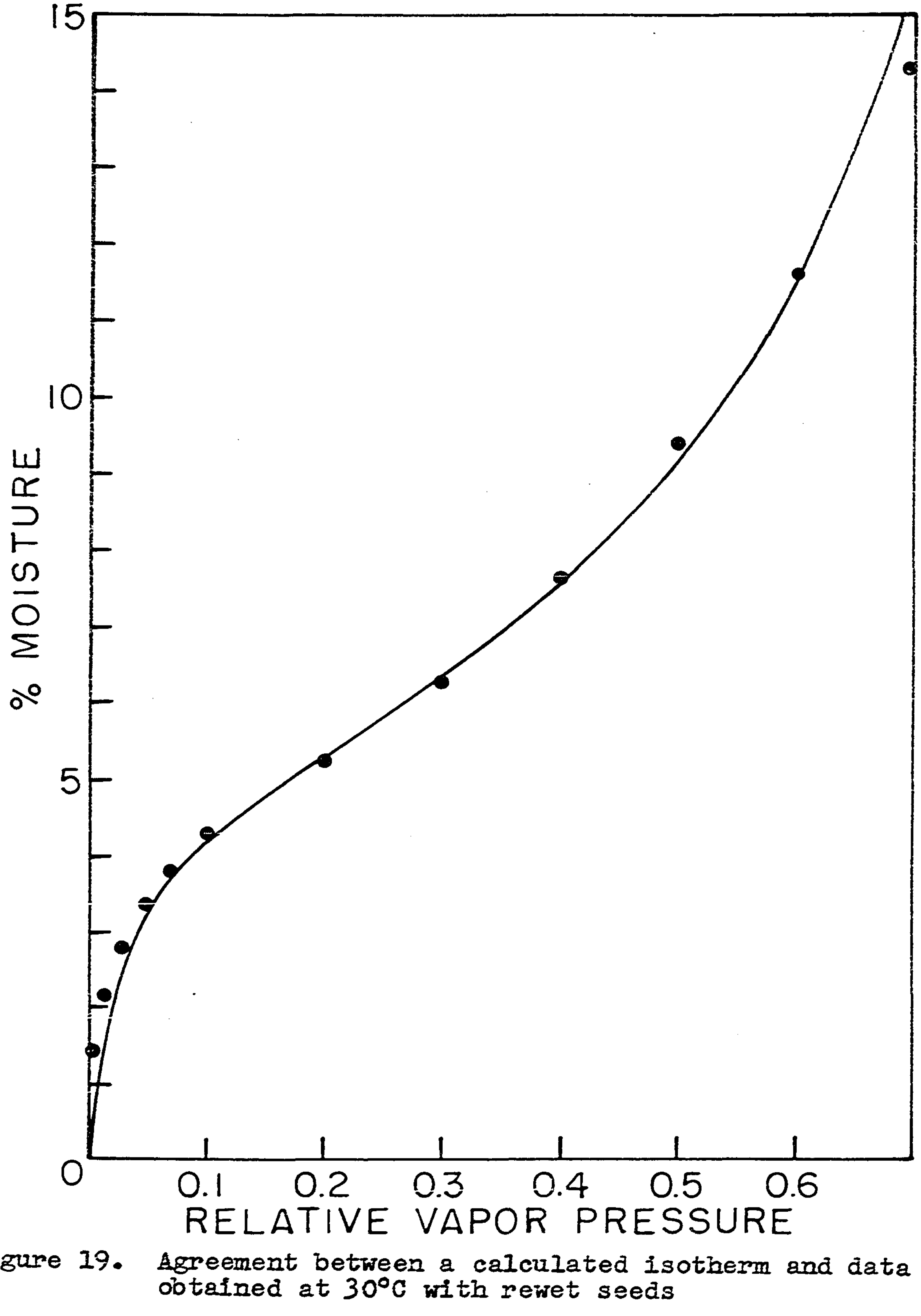

Figure 19. Agreement between a calculated isotherm and data obtained at 30°C with rewet seeds

temperature. The values of p/p_o and p'/p'_o at a given moisture concentration were obtained from the isotherms at the two temperatures.

Figure 20 shows the differential heat of adsorption and the differential heat of desorption for both naturally wet or fresh, and rewet seeds. To Equation (60) may be added the heat of vaporization, which is represented by the dashed line in Figure 20. The curves show a uniform decrease in degree of binding with increasing moisture content. The high initial portion probably represents chemisorption on specific active sites. It is of interest to note the breaks in the ΔH-curves. These coincide rather well with the values of the monolayer calculated from the BET equation.

The free energy change when one mole of water is added to the seed isothermally is given by

$$\Delta F = RT \ln p/p_o \quad .$$

This is known as the free energy of sorption and is a quantitative measure of the affinity of the seed for the water vapor. Figure 21 shows the free energy of adsorption and the free energy of desorption for both naturally wet and rewet seeds. The differential entropy of sorption is given by the relationship

$$\Delta S = (\Delta H - \Delta F)/T \quad .$$

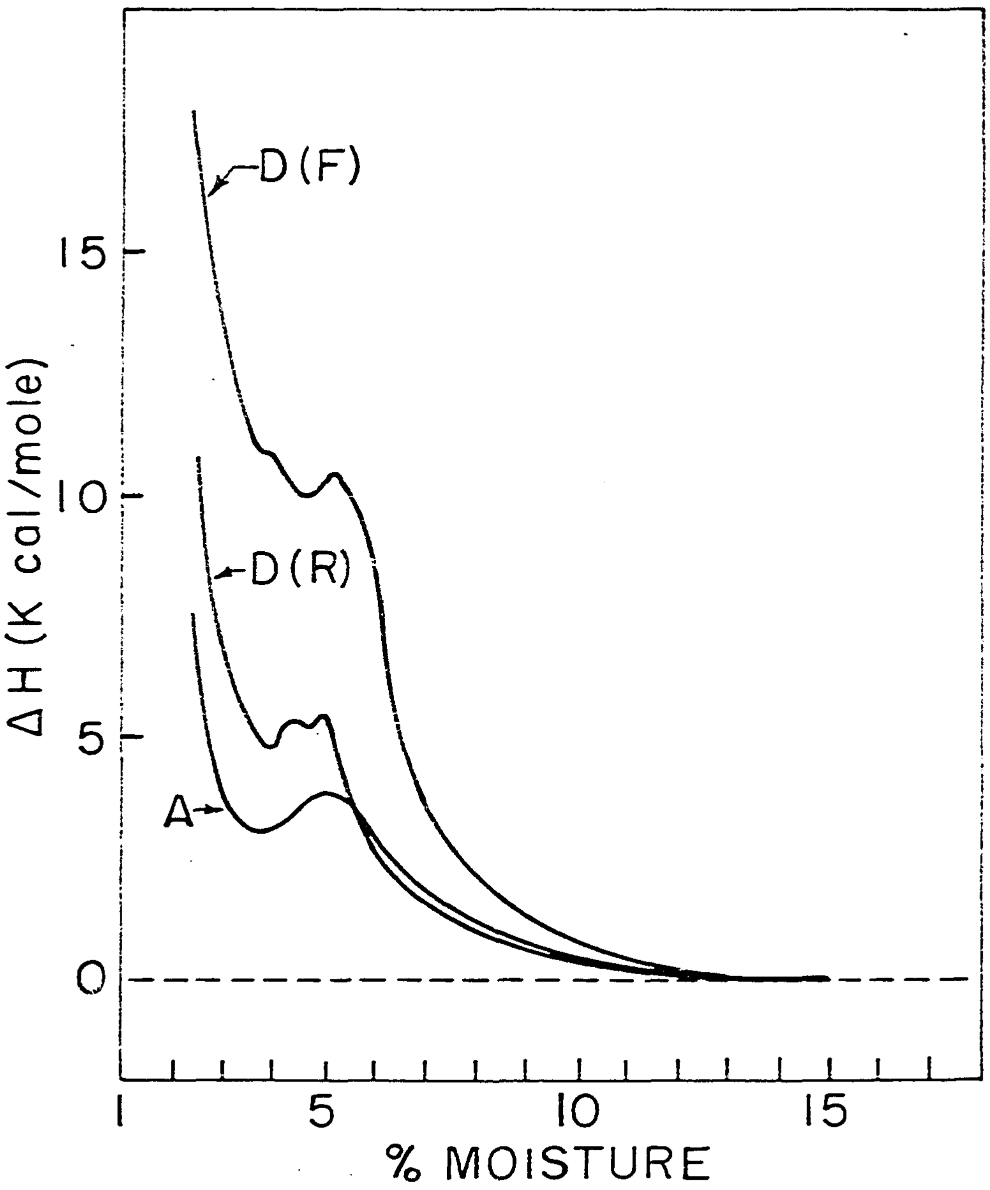

Figure 20. Differential heat of adsorption and desorption

D(F) = Desorption of fresh seeds
D(R) = Desorption of rewet seeds
A = Adsorption

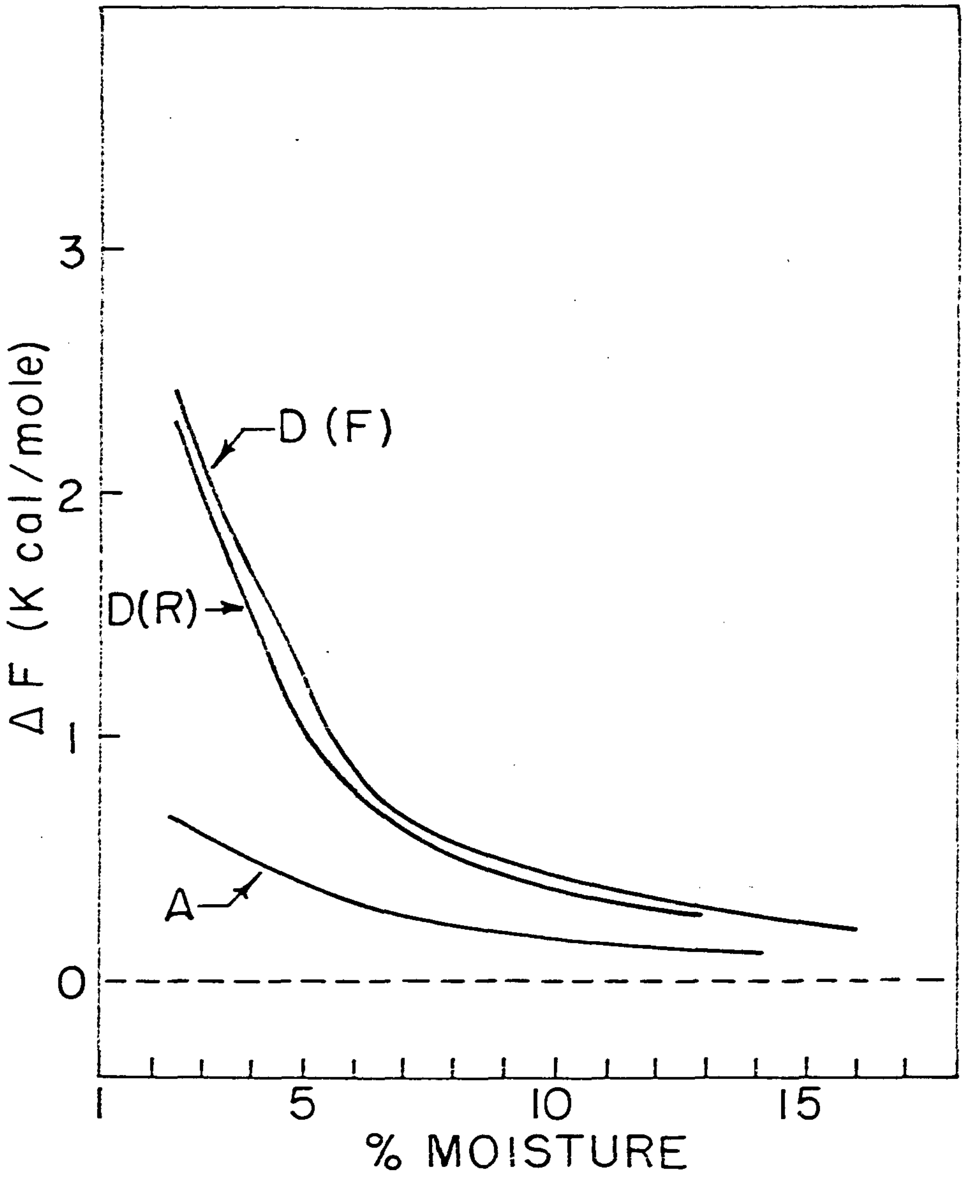

Figure 21. Differential free energy of adsorption and desorption

D(F) = Desorption of fresh seeds
D(R) = Desorption of rewet seeds
A = Adsorption

The differential entropy of adsorption and the differential entropy of desorption for both fresh and rewet seeds are shown in Figure 22. The magnitude of ΔS at each moisture content is a measure of the relative restriction of the motion of the water molecules. The high initial values indicate that the molecules are very restricted in motion, and suggest the possibility of orientation of the molecules such as would be expected to occur in the case of chemisorption on specific sites. The degree of restriction of the water molecules decreases with increasing moisture content.

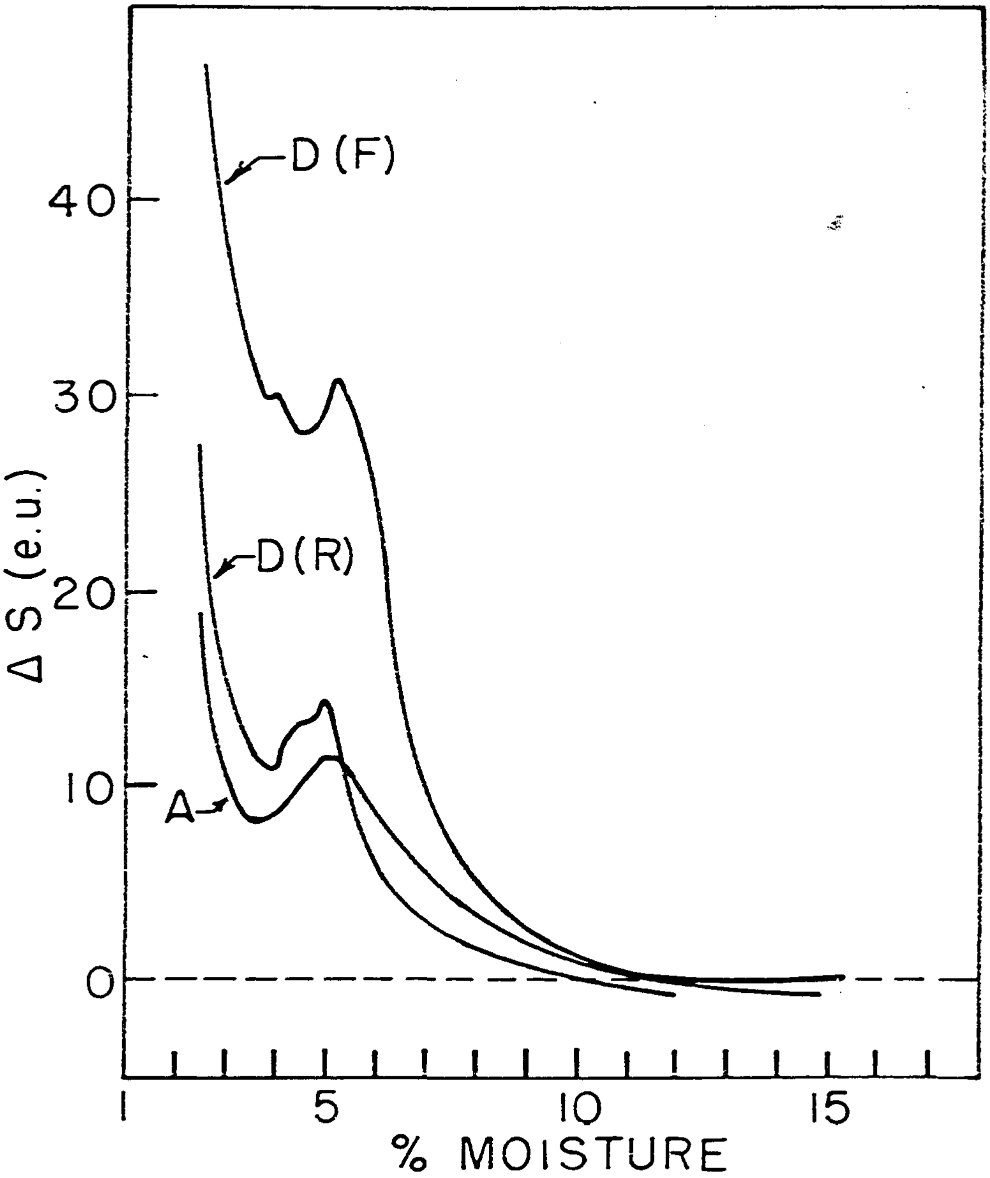

Figure 22. Differential entropy of adsorption and desorption

D(F) = Desorption of fresh seeds
D(R) = Desorption of rewet seeds
A = Adsorption

DISCUSSION

Diffusion of moisture in seeds is a complex process, thus making the mathematical description of the drying of seeds very difficult. Although the drying process is sometimes amenable to an empirical description, it is generally difficult to formulate a workable relationship based on theoretical interpretation of the diffusion mechanism. The deviations from what may be termed ideal behavior usually involve a variety of contributory factors. The mechanism of the diffusion of moisture may certainly be expected to depend on the physical and chemical properties of the seed and on the state of the adsorbed moisture. The sorption isotherm is of particular significance here. According to the Brunauer, Emmett, and Teller (BET) theory the initial, concave portion of the isotherm represents the sorption of a monomolecular layer of water on the adsorbing surface; the region of inflection represents the sorption of the second and third molecular layers; and the convex portion represents the adsorption of additional layers and finally capillary condensation. Sorption theories based on statistical thermodynamics have shown that the portion which BET consider as a monomolecular layer can be explained just as satisfactorily by sorption on specific sorption sites. This type of explanation has perhaps more merit than the BET theory if the heat of desorption curve is considered. One of the assumptions of the BET theory is that the heat of sorption is uniform throughout the monolayer. Considering the forces involved in adsorption and the chemical groups within the seed which are responsible for the binding of the moisture, it seems reasonable to expect not one but many types of binding, each with its own characteristic affinity between the moisture and the group on which the adsorption occurs. Thus there will be present, and represented by the sorption isotherm, a whole spectrum of types or degrees of moisture binding. The heat of desorption curves show uniform decrease of affinity with increasing moisture content, suggesting the presence of not one but numerous types and degrees of binding at the lower moisture levels. The entropy of desorption curves indicate the degree of restriction of motion of the water molecules adsorbed on the internal seed surface. This restriction suggests the possibility of the existence of a different type of moisture movement mechanism in the lower moisture range. If the water molecules in this lower range are considered as being tightly bound to the adsorbing surface so that their motion is restricted to two dimensions instead of three, then the moisture movement may be pictured as either a skating of the molecules along the internal surfaces or a site-to-site migration of activated molecules.

Fick's law of diffusion has been applied to the drying of soybeans. Satisfactory agreement between the theory and the data was obtained in the drying range from 40% to approximately 15% moisture. Below 15% the diffusion coefficient dropped markedly, indicating that the simple assumptions of Fick's law no longer applied. Sorption studies indicated that above approximately 15% moisture the heat of desorption is equal to the heat of vaporization, but below 15% it becomes considerably greater. Thus it seems reasonable to conclude that above 15%, the assumption of Fick's law that diffusion depends upon concentration is applicable. Below 15% moisture it is assumed that the surface forces of adsorption became significantly large in terms of the total, so that Fick's law is no longer applicable.

In the lower moisture range an empirical equation of the form

$$m = \frac{1}{a + bt} \tag{61}$$

where m = moisture percentage

t = drying time

a and b = constants

can be fitted to the drying data. Inasmuch as Equation (61) is empirical, it has little or no theoretical significance and hence, is of no particular value in elucidating the mechanism of moisture movement. In this lower range one of two alternative procedures is available. Fick's law with a variable diffusion coefficient may be applied. This can be written, for one dimension, in the form

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial m}{\partial x}\right) . \tag{62}$$

If D varies with the concentration, Equation (62) is non-linear. Thus a general solution cannot be found by addition of particular solutions. The alternative and more logical procedure is to consider some function other than concentration as responsible for the diffusive flow. The problem thus becomes one of determining, on the basis of theoretical considerations, the potential function to be used in place of concentration.

The free energy of water appears to be a considerably more attractive potential function than concentration. It is more general and at the same time more meaningful. It is worthwhile, therefore, to develop a diffusion equation in terms of free energy. If free energy is considered as the cause of diffusion, then the rate of flow is proportional to the negative of the free energy gradient. This may be written for one dimensional flow as

$$J = -D_F\,\frac{\partial \Delta F}{\partial x} . \tag{63}$$

To make Equation (63) more general a resistance factor may be included. Thus if G is the resistance factor, the general equation of flow may be written

$$J = -\frac{D_F}{G}\,\frac{\partial \Delta F}{\partial x} . \tag{64}$$

This is somewhat analogous to Ohm's law, the common characteristic being that the rate of flow is proportional to a certain potential difference divided by a resistance factor.

It may not be clear whether the resistance factor will be independent of the moisture content. It is apparent that the water molecules at the lower moisture content are more tightly held to the adsorbing surface and hence offer greater resistance to flow. Thus the resistance factor might be thought of as dependent upon the moisture content. On the other hand, this variation of the binding forces would cause a variation in the free energy of the water. Hence the resistance might be considered a constant. There should be considered, however, the resistance to the diffusive flow offered by the structural changes which occur within the adsorbing material. It is simplest in the derivation of the diffusion equation to consider G a constant and, for convenience, incorporate it into the diffusion coefficient. Thus Equation (63) is again obtained.

The fundamental differential equation of diffusion may be obtained from Equation (63) in a manner analogous to that described earlier. Thus the equation for non-steady state diffusion using free energy as the potential function is

$$\frac{\partial m}{\partial t} = D_F \frac{\partial^2 \Delta F}{\partial x^2} \quad . \qquad (65)$$

In a drying procedure the average moisture content is measured as a function of time. Therefore Equation (65) must be transformed into an expression which has moisture content as the only dependent variable. The free energy of the moisture is related to the vapor pressure by the expression

$$\Delta F = RT \ln p/p_o \, . \tag{66}$$

The vapor pressure is in turn related to the moisture content by the moisture desorption isotherm

$$m = \frac{m_1 \, C \, p/p_o}{(1-p/p_o)\,\left[1+(C-1)p/p_o\right]} \, . \tag{67}$$

Since ΔF is a function of p, p is a function of m, and m is a function of x

$$\frac{\partial \Delta F}{\partial x} = \frac{\partial \Delta F}{\partial p} \frac{\partial p}{\partial m} \frac{\partial m}{\partial x}$$

and

$$\frac{\partial^2 \Delta F}{\partial x^2} = \frac{\partial^2 m}{\partial x^2}\left[\frac{\partial \Delta F}{\partial p}\frac{\partial p}{\partial m}\right] + \left(\frac{\partial m}{\partial x}\right)^2\left[\frac{\partial \Delta F}{\partial p}\frac{\partial^2 p}{\partial m^2} + \frac{\partial^2 \Delta F}{\partial p^2}\left(\frac{\partial p}{\partial m}\right)^2\right] . \tag{68}$$

This may be substituted into Equation (65) giving

$$\frac{\partial m}{\partial t} = D_F \left\{ \frac{\partial^2 m}{\partial x^2}\left[\frac{\partial \Delta F}{\partial p}\frac{\partial p}{\partial m}\right] + \left(\frac{\partial m}{\partial x}\right)^2\left[\frac{\partial \Delta F}{\partial p}\frac{\partial^2 p}{\partial m^2} + \frac{\partial^2 \Delta F}{\partial p^2}\left(\frac{\partial p}{\partial m}\right)^2\right]\right\} . \tag{69}$$

$\frac{\partial \Delta F}{\partial p}$, $\frac{\partial^2 \Delta F}{\partial p^2}$, $\frac{\partial p}{\partial m}$, and $\frac{\partial^2 p}{\partial m^2}$ can be evaluated from Equations (66) and (67). The value obtained for $\partial^2 \Delta F / \partial x^2$ in Equation (69) may then be substituted into Equation (65). The resulting equation expresses moisture concentration as a function of time and location. It may be noted, however, that the equation is non-linear, and hence the general solution cannot be obtained by addition of particular solutions.

SUMMARY

Moisture equilibria in seeds have been investigated from the aspects of drying and moisture sorption.

It was found that the drying of seeds could be described by Fick's law of diffusion in the moisture range from 40% to 15%. Below 15% Fick's law was no longer applicable. An empirical equation of the form

$$m = \frac{1}{a + bt}$$

was found to give satisfactory agreement with the data below 15%, but, because of its empirical nature, is of no particular value in elucidating the mechanism of moisture movement. An equation for diffusion below 15% was developed in terms of free energy as the potential function. This equation may be written

$$\frac{\partial m}{\partial t} = D_F \frac{\partial^2 \Delta F}{\partial x^2} .$$

But when $\partial^2 \Delta F / \partial x^2$ was expressed in terms of the moisture content, the resulting equation was found to be a non-linear differential equation, and hence, not amenable to a general solution by addition of particular solutions.

Adsorption and desorption isotherms were obtained at 20° and 30°C. The Brunauer, Emmett, and Teller isotherm equation was applied to the desorption isotherms. The equation and the data showed close agreement, with the exception of those values in the very low relative vapor pressure range.

The thermodynamic functions of free energy, enthalpy, and entropy were calculated. The heat of desorption data showed very large values in the lower moisture content range, indicating the magnitude of the forces binding the moisture to the seed at the lower range. The heat of desorption curve showed further a uniform decrease of the binding energy with increasing moisture content, suggesting the presence of a multiplicity of types of water binding, and emphasizing the indefiniteness of the concept of bound water.

LITERATURE CITED

1. Babbitt, J. D. Hysteresis in the adsorption of water vapour by wheat. Nature 156: 265-266. 1945.

2. ________. Observations on the adsorption of water vapour by wheat. Can. J. Res. Sect. F. 27: 55-72. 1949.

3. ________. On the adsorption of water vapour by cellulose. Can. J. Res. Sect. A. 20: 143-172. 1942.

4. Becker, H. A. and Sallans, H. R. A study of internal moisture movement in the drying of the wheat kernel. Cereal Chem. 32: 212-226. 1955.

5. ________ and ________. A study of the desorption isotherms of wheat at 25°C and 50°C. Cereal Chem. 33: 79-91. 1956.

6. Brunauer, S., Emmett, P. H., and Teller, E. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60: 309-319. 1938.

7. Bushuk, W. and Winkler, C. A. Sorption of water vapor on wheat flour, starch, and gluten. Cereal Chem. 34: 73-86. 1957.

8. Coleman, D. A. and Fellows, H. C. Hygroscopic moisture of cereals, grains, and flaxseed exposed to atmospheres of different relative humidity. Cereal Chem. 2: 275-287. 1925.

9. Coolidge, A. S. The adsorption of vapors by charcoal, J. Am. Chem. Soc. 46: 596-627. 1924.

10. Freundlich, H. Colloid and capillary chemistry. London, Methuen and Co., Ltd. 1926.

11. Hlynka, I. and Robinson, A. D. Moisture and its measurement. In Anderson, J. A. and Alcock, A. W., eds. Storage of cereal grains and their products. pp. 1-45. St. Paul, Minnesota, American Association of Cereal Chemists. 1954.

12. Holman, L. E. Basic drying rates of different grains. Paper presented at Am. Soc. Ag. Eng. annual meeting, 1948. (Original not available for examination; cited by Hukill, W. V., Drying of grain. In Anderson

J. A. and Alcock, A. W., eds. Storage of cereal grains and their products. pp. 402-435. St. Paul, Minnesota, American Association of Cereal Chemists. 1954.)

13. Hougen, O. A., Watson, K. M., and Rugatz, R. A. Chemical process principals. 2nd ed. New York, John Wiley and Sons. 1954.

14. Hukill, W. V. Drying of grain. In Anderson, J. A. and Alcock, A. W., eds. Storage of cereal grains and their products. pp. 402-435. St. Paul, Minnesota, American Association of Cereal Chemists. 1954.

15. Jones, C. R. Evaporation in low vacuum from warm granular material (wheat) during the falling-rate period. J. Sci. Food Agric. 2: 565-571. 1951.

16. Langmuir, I. The constitution and fundamental properties of solids and liquids. J. Am. Chem. Soc. 38: 2221-2295. 1916.

17. Lewis, W. K. Rates of drying of solid materials. Ind. Eng. Chem. 13: 427-432. 1921.

18. McLaren, A. D. and Rowen, J. W. Sorption of water vapor by proteins and polymers: A review. J. Polymer Sci. 7: 289-324. 1951.

19. Newman, A. B. The drying of porous solids: diffusion and surface emission equations. Trans. Am. Inst. Chem. Engrs. 27: 203-211. 1931.

20. ________. The drying of porous solids: diffusion calculation. Trans. Am. Inst. Chem. Engrs. 27: 310-333. 1931.

21. Page, G. Basis drying rates of different grains. Paper presented at Am. Soc. Ag. Eng. annual meeting, 1948. (Original not available for examination; cited by Hukill, W. V. Drying of grain. In Anderson, J. A. and Alcock, A. W., eds. Storage of cereal grains and their products. pp. 402-435. St. Paul, Minnesota, American Association of Cereal Chemists. 1954.)

22. Perry, J. H. Chemical engineer's handbook (2nd ed., pp. 398-399). New York, McGraw-Hill Book Company, 1941.

23. Pierce, C. and Smith, R. N. Adsorption-desorption hysteresis in relation to capillarity of adsorbents. J. Phys. and Colloid Chem. 54: 784-794. 1950.

24. Sherwood, T. K. Application of theoretical diffusion equations to the drying of solids. Trans. Am. Inst. Chem. Engrs. 27: 190-200. 1931.

25. ________. The drying of solids I. Ind. Eng. Chem. 21: 12. 1929.

26. ________. The drying of solids II. Ind. Eng. Chem. 21: 976-980. 1929.

27. ________. The drying of solids III. Ind. Eng. Chem. 22: 132-136. 1930.

28. ________. The drying of solids IV. Application of diffusion equations. Ind. Eng. Chem. 24: 307-310. 1932.

29. Simmonds, W. H. C., Ward, G. T. and McEwen, E. The drying of wheat grain. Part 1: The mechanism of drying. Trans. Inst. Chem. Engrs. London, 31: 265-278. 1953.

30. Smith, S. E. The sorption of water vapor by high polymers. J. Am. Chem. Soc. 69: 646-651. 1947.

31. Urquhart, A. R. The mechanism of the adsorption of water by cotton. J. Textile Inst. 20: T125-132. 1929

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