A STUDY OF THE SORPTION AND DESORPTION EQUILIBRIUM MOISTURE CONTENT ISOTHERMS OF BIOLOGICAL MATERIALS

By

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in partial fulfillment of the
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DOCTOR OF PHILOSOPHY
May, 1966

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ACKNOWLEDGMENTS

Funds from Oklahoma State Project 679 and from the National Science Foundation contributed to the financial support of this study.

I am especially grateful to my major adviser, Dr. G. L. Nelson, for his capable guidance during this study. His advice, criticism, and inspiration were a great aid to me throughout the study.

I wish to thank Professor E. W. Schroeder, Head of Agricultural Engineering Department, for serving on the advisory committee and for providing facilities and assistantships during the study.

Appreciation is also extended to Professor Jay G. Porterfield of the Agricultural Engineering Department; Dr. Jerald D. Parker of the Mechanical Engineering Department; and Dr. John B. West of the Chemical Engineering Department for serving on the advisory committee. Their assistance and suggestions were very helpful.

I am also grateful to Dr. G. Burns Welch for his assistance in the literature review and for the design of the chambers for humidity control.

Appreciation is extended to Dr. Alva M. Schlehuber and the Oklahoma State University Agronomy Department for the wheat which was provided for this study.

Special thanks go to my wife, Lou, for her sacrifices and assistance throughout this study and for her work in typing the rough drafts of this thesis.

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CHAPTER I

INTRODUCTION

The moisture content of biological materials is of major concern in their safe storage or proper handling. Moisture is exchanged between a biological material and its surroundings until the material reaches some equilibrium moisture content at which there is no net gain or loss of moisture. The equilibrium moisture content is known to be a function of temperature, relative humidity, and the type of material. Also, previous investigations indicate that the previous history of the material can affect the equilibrium moisture content of the material.

A plot of the equilibrium moisture content versus relative humidity at a constant temperature is called an equilibrium moisture content isotherm. A sorption isotherm indicates that the equilibrium was reached in a wetting environment and a desorption isotherm indicates that the equilibrium was reached in a drying environment.

Hysteresis

In most earlier investigations of equilibrium moisture content, it was not indicated whether the equilibrium moisture contents were obtained during a sorption or desorption process. This appears to have a definite effect upon the equilibrium moisture content of the material. The term "hysteresis effect" means that for the same atmospheric conditions the moisture content obtained by sorption is not the same as that obtained by desorption (Figure 1). This effect is discussed in more detail in Chapter III.

Equilibrium Moisture Curves or Isotherms

As indicated in Figure 1, a plot of the equilibrium moisture content versus relative humidity generally gives a sigmoidal or "S" shaped curve for biological materials in both sorption and desorption processes. Some previous theoretical work dealing with the shape of the isotherms is discussed in Chapter II and experimental results for biological materials are discussed in Chapter III.

Purpose of Study

The purpose of this study was the development of a theoretical equation by which the equilibrium moisture content of a biological material could be predicted. Accurate information pertaining to the equilibrium moisture content of biological materials is important in the processing and storage of these products. Most of the available data pertaining to equilibrium moisture

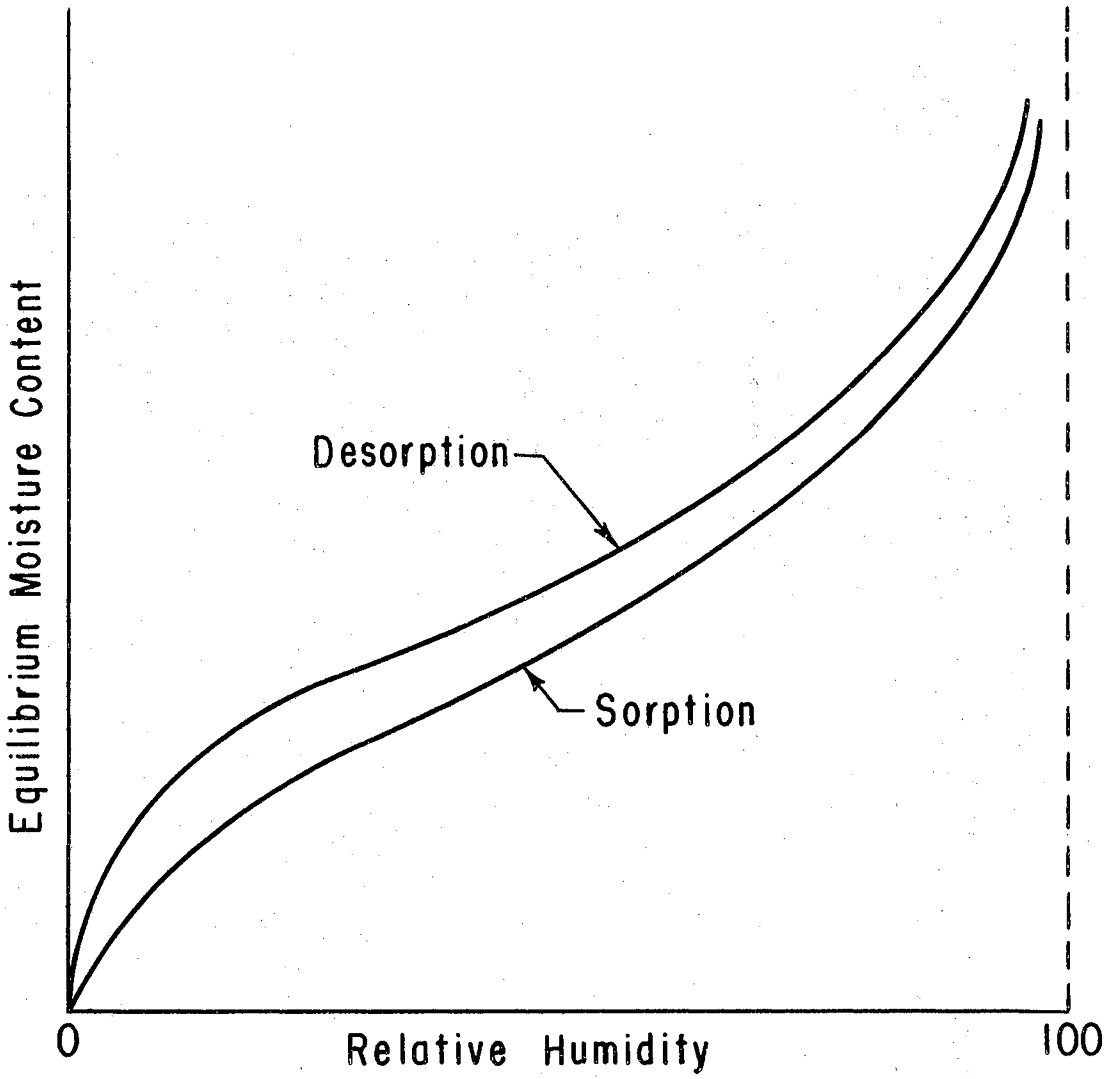

Figure 1. Equilibrium Moisture Content Versus Relative Humidity.

content is limited in use because the conditions in which it was obtained are not well defined. It is time consuming to determine the equilibrium moisture content of a material experimentally. Therefore, a mathematical equation that would permit rapid determination of the equilibrium moisture content of the material at any set of environmental conditions would be very useful.

CHAPTER II

REVIEW OF ADSORPTION THEORY

The atoms or molecules constituting a solid material are held together by different forces. These may be electrostatic or coulomb forces, exchange or homopolar valence forces, or van der Waals forces. In most cases, several different kinds of forces are active in binding the atoms or molecules together.

Whatever the nature of the forces, an atom located in the interior of the solid is subjected to equal forces in all directions, while an atom on the surface is subjected to unbalanced forces with the inward force being greater than the outward force. Therefore, work must be done on an atom in moving it from the interior of the solid to a position on the surface. This means that the surface atom, due to the work which has been done on it, possesses a higher state of energy than the interior atom. This results in a tendency to decrease the surface area. Thus, a solid has surface tension, just like a liquid.

When a molecule of a gas or liquid comes into contact with the surface of the solid, it may saturate some of the unbalanced forces of the surface. This results in a decrease in the surface tension. Thus adsorption phenomena may result in a reduction of the free energy at the surface.

The adsorbed particles may either be bound rigidly to the surface or they may be free to move over the surface in two dimensions. In either case there is a reduction of the energy of the particles. Thus, the adsorption process is an exothermic process. The heat given off in adsorption is of the same order of magnitude as the heats of condensation of gases. Since the adsorption process is always exothermic, the amount adsorbed at equilibrium decreases with increasing temperature according to the principle of LeChatelier.

The amount of gas or vapor adsorbed when equilibrium is established at a given temperature and pressure is a function of the solid material and of the gas being adsorbed. This includes the surface area, size, shape, and distribution of pores, and chemical constitution of the solid. On the other hand, it includes the physical and chemical characteristics of the adsorbed gas molecules.

Different combinations of adsorbents (the solid material) and adsorbates (the gas or vapor adsorbed) result in different forms of adsorption isotherms. Brunauer (1945) classifies them into five types as shown in Figure 2.

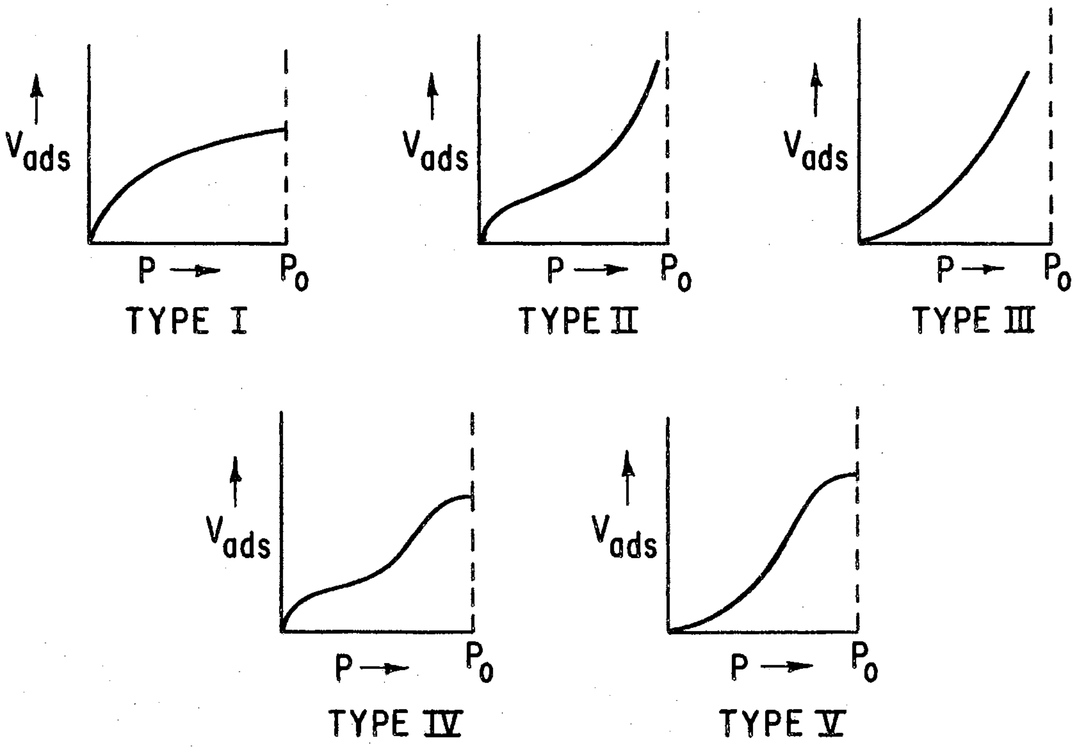

Figure 2. Adsorption Isotherms as Classified by Brunauer (1945).

The type I isotherm represents monomolecular adsorption. The other four types represent some kind of multimolecular adsorption. Bruanuer (1945) discusses several of these theories and a brief summary of some of them follows.

Monomolecular Adsorption

A. Empirical Equations

The type I curve is a simple type of van der Waals adsorption isotherm. In the low pressure region the volume adsorbed varies with the first power of the pressure,

$$v = k_1 p \qquad (1)$$

where

v = volume adsorbed, cm^3

k_1 = constant, $cm^5\ dyne^{-1}$

p = vapor pressure of adsorbate, $dynes\ cm^{-2}$

At higher pressures, many isotherms show a region in which the volume adsorbed is independent of the vapor pressure.

$$v = k_2 \qquad (2)$$

In the intermediate pressure range the volume adsorbed varies with a power of the pressure which is less than one but greater than zero,

$$v = k_3 p^{1/n} \qquad (3)$$

where

k_3 = constant, $\left(cm^{3n+2}\ dyne^{-1}\right)^{-n}$

n = number greater than one

Equation (3) is the Freundlich adsorption isotherm equation. The Freundlich equation is an empirical equation. Attempts have been made to find an analytical derivation for the equation, but they have been unsuccessful. The Freundlich equation is the oldest isotherm equation and is still used by some investigators despite the fact that it is an oversimplification.

B. The Langmuir Equation

Probably, the most widely known equation in the field of adsorption is the Langmuir equation. Langmuir (1918) made certain simplifying assumptions which enabled him to develop an analytical expression for the adsorption process. Langmuir began by assuming that at equilibrium the rate at which molecules were condensed on the surface was equal to the rate at which they were evaporated from the surface. The time lag between condensation and evaporation accounted for the volume of molecules adsorbed. Langmuir further assumed that the rate of condensation on the surface was proportional to the number of molecules striking the surface in unit time.

When the rate at which molecules strike the surface is μ and the rate at which they evaporate is ν, the net rate of adsorption is

$$\frac{ds}{dt} = \alpha_o \mu - \nu \tag{4}$$

where

s = surface concentration, molecules cm^{-2}

t = time, sec

α_o = proportion of molecules striking the surface which are adsorbed.

The value of the coefficient α_o is always close to unity because perfectly elastic collisions are infrequent. At equilibrium,

$$\frac{ds}{dt} = 0$$

and

$$\alpha_o \mu = \nu \tag{5}$$

The value of μ for a unit surface may be obtained from the kinetic theory of gases. A derivation of the relationship for μ is given by Moore (1955). The result is

$$\mu = \frac{p}{(2\pi mkT)^{\frac{1}{2}}} \tag{6}$$

where

p = vapor pressure, dynes cm^{-2}

m = mass of a molecule of the gas, gm $molecule^{-1}$

k = Boltzmann's constant, gm $cm^2 sec^{-2} molecule^{-1} {}^oK^{-1}$

T = absolute temperature, ^oK

The value of ν is dependent on the strength of binding between the solid and the adsorbed molecule. If q is the heat given off when a molecule is adsorbed, then only those molecules will be able to evaporate or desorb that acquire an energy quantity equal to or greater than q. Then, according to Boltzmann's Law, the rate of evaporation will be

$$\nu = k_o \exp(-q/kT) \tag{7}$$

where

k_o = coefficient of evaporation, molecules $\text{cm}^{-2}\text{sec}^{-1}$

Instead of the surface concentration, one may use the fraction of the surface covered,

$$\theta = \frac{s}{s_1} \tag{8}$$

where

s_1 = the surface concentration when a complete unimolecular layer has been formed.

Langmuir then introduced two important assumptions in the derivation of his equation. The first was that the probability of evaporation of a molecule is the same whether the neighboring positions on the surface are occupied by other molecules or not. This is equivalent to assuming that the forces of attraction between the adsorbed molecules are negligible. It is expressed by

$$\nu = \nu_1 \theta \tag{9}$$

where

ν_1 = rate of evaporation from a completely covered surface, molecules $\sec^{-1}\text{cm}^{-2}$

θ = fraction of surface covered by one layer of adsorbate molecules

It is also implied that the heat of adsorption is constant over the entire surface.

The second assumption is that every molecule coming from the gas phase that strikes a molecule already adsorbed on the surface is elastically reflected. Then,

$$\alpha_o \mu = \alpha_s (1 - \theta)\mu \qquad (10)$$

where

α_s = the condensation coefficient of the bare surface, dimensionless

$(1 - \theta)$ = the fraction of the surface that is bare

Then, by equation (5)

$$\nu_1 \theta = \alpha_s (1 - \theta)\mu \qquad (11)$$

Solving for θ gives,

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

where

$$b = \frac{\alpha_s \mu}{\nu_1 p} = \frac{\alpha_s}{k_o} \frac{\exp(q/kT)}{(2\pi mkT)^{\frac{1}{2}}} \qquad (13)$$

The ratio θ may also be expressed as

$$\theta = \frac{v}{v_m} \qquad (14)$$

where

v = volume adsorbed, cm^3

v_m = volume adsorbed when a complete unimolecular layer has been formed, cm^3

Substituting for θ, gives:

$$v = \frac{v_m bp}{1 + bp} \tag{15}$$

This equation gives a type I isotherm. When the adsorption is unimolecular, the data can often be fitted satisfactory by the Langmuir equation. This usually happens when one deals with a relatively homogeneous surface.

Multimolecular Adsorption

A. The Potential Theory

The formulation of the potential theory for explaining adsorption phenomena is credited to Polanyi (1914). He defined the adsorption potential at a point near the adsorbent as the work done by the adsorption forces in bringing a molecule from the gas phase to that point. This work is conceived as a work of compression and mathematically its value is given by a so-called hydrostatic equation:

$$\varepsilon_1 = \int_{p_x}^{p_i} V dp \tag{16}$$

where

ε_i = adsorption potential at a point where the pressure of the adsorbed substance is p_i, cal

p_x = pressure in the gas phase, dyne cm^{-2}

V = molar volume, cm^3 mole $^{-1}$

The equation of state of the adsorbed gas is unknown, but Polanyi assumed that the gas obeys the same equation of state in the adsorbed phase as in the gas phase. The assumption was based on the similarity between Van der Waals adsorption and condensation. The notable success of the theory indicates that the assumption is adequately fulfilled.

The potential theory assumes that the potential field in the adsorption space is the same for all temperatures. This may be expressed as:

$$\varepsilon = f(v) \tag{17}$$

where

v = volume of gas adsorbed, cm^3

The potential theory does not attempt to deduce the relationship between ε and v. It merely computes a characteristic curve from one experimental isotherm of the gas and then all other isotherms may be computed from this curve.

For a gas whose liquid in the adsorbed phase is incompressible,

$$\varepsilon_i = \int_{p_x}^{p_o} \frac{RT}{p}\, dp = RT \ln \frac{p_o}{p_x} \qquad (18)$$

where

p_x = pressure existing in gas phase, dyne cm^{-2}

p_o = saturation vapor pressure of the adsorbed liquid, dyne cm^{-2}

The work of creating a liquid surface is neglected. Then, for equal volumes of the gas adsorbed at two different temperatures:

$$RT_1 \ln \frac{p_{01}}{p_1} = RT_2 \ln \frac{p_{02}}{p_2}$$

or

$$\ln \frac{p_{01}}{p_1} = \frac{T_2}{T_1} \ln \frac{p_{02}}{p_2}$$

where

T_1 = absolute temperature of first isotherm, °K

T_2 = absolute temperature of second isotherm, °K

p_1 = vapor pressure of first isotherm, dyne cm^{-2}

p_2 = vapor pressure of second isotherm, dyne cm^{-2}

p_{01} = saturation vapor pressure at temperature T_1, dyne cm^{-2}

p_{02} = saturation vapor pressure at temperature T_2, dyne cm^{-2}

The potential theory has given very successful results when predicting the effect of temperature on the isotherm. The weakness of the theory is of course the inability to predict analytically the characteristic curve.

B. Capillary Condensation Theory

The capillary condensation theory is based on the Kelvin equation for vapor pressure in a capillary tube. This equation was first developed by Thomson (Lord Kelvin) (1871). The equation may be written as:

$$\ln \frac{p}{p_o} = -\frac{2\sigma V \cos\theta}{rRT} \qquad (20)$$

where

p_o = vapor pressure above plane surface, dyne cm^{-2}

p = vapor pressure in capillary, dyne cm^{-2}

σ = surface tension of liquid, dyne cm^{-1}

V = molar volume of gas, cm^3 $mole^{-1}$

r = radius of capillary, cm

R = universal gas constant, cal $^oK^{-1}$ $mole^{-1}$

T = absolute temperature, ^oK

θ = angle of wetting

The capillary condensation theory as developed by Zsigmondy (1911) and McGavack and Patrick (1920) considers the solid material to be filled with tiny capillaries of varying sizes. Since the vapor pressure reduction is greater for smaller capillaries, the condensation occurs first in the smallest capillaries and then proceeds to the larger capillaries as the vapor pressure is increased.

Taking equal volumes of the liquid adsorbed at two different temperatures, the Kelvin equation states that $r_1 = r_2$, and assuming complete wetting the equivalent pressure equation is:

$$\ln \frac{p_1}{p_{01}} = \frac{\sigma_1 V_1 T_1}{\sigma_2 V_2 T_2} \ln \frac{p_2}{p_{02}}$$

or

$$\ln \frac{p_{01}}{p_1} = \frac{\sigma_1 V_1 T_1}{\sigma_2 V_2 T_2} \ln \frac{p_{02}}{p_2} \qquad (21)$$

Equation (21) may be compared with equation (19) which was derived on the basis of the potential theory. Examination shows that if $\ln \frac{p_{01}}{p_1}$ is plotted versus $\ln \frac{p_{02}}{p_2}$ a straight line is obtained for both theories. However, the slope predicted by the potential theory is $\frac{T_2}{T_1}$ and the slope predicted by the capillary condensation theory is $\frac{\sigma_1 V_1 T_1}{\sigma_2 V_2 T_2}$. Experimental results have shown a much higher correlation with the potential theory than with the capillary condensation theory.

A striking characteristic of the capillary condensation theory is the appearance of hysteresis loops in the adsorption isotherms. Foster (1932) and Cohan (1938) attribute reversible hysteresis to a delay in the formation of the meniscus in the capillary.

It was suggested by Kraemer (1931) that the phenomenon of reversible hysteresis could be explained by the assumption that the pores are shaped like ink bottles, having narrow necks and wide bodies. Then during adsorption, condensation would take place in the body only when the vapor pressure was given by Kelvin's equation using the radius of the body of the pores. However, during desorption, the pore would empty only when the vapor pressure was reduced to the point where the liquid in the neck of the pore would evaporate.

C. The Multimolecular Adsorption Theory (BET Equation)

Brunauer (1945) outlines the derivation and discusses the advantages and disadvantages of each of the previously discussed theories. He then gives the theory first propounded by himself and his fellow workers in two papers in 1938 and 1940. The first was by Brunauer, Emmett and Teller (1938) and the second by Brunauer, Deming, Deming and Teller (1940). The theory is based on the assumption that the forces producing condensation are also chiefly responsible for the binding energy of multimolecular adsorption. The equation developed has become known as the BET equation.

Let S_0, S_1, S_2...... S_i ...... represent the net surface area that is covered by 0, 1, 2 ..... i ..... layers of adsorbed molecules as shown in Figure 3. Since

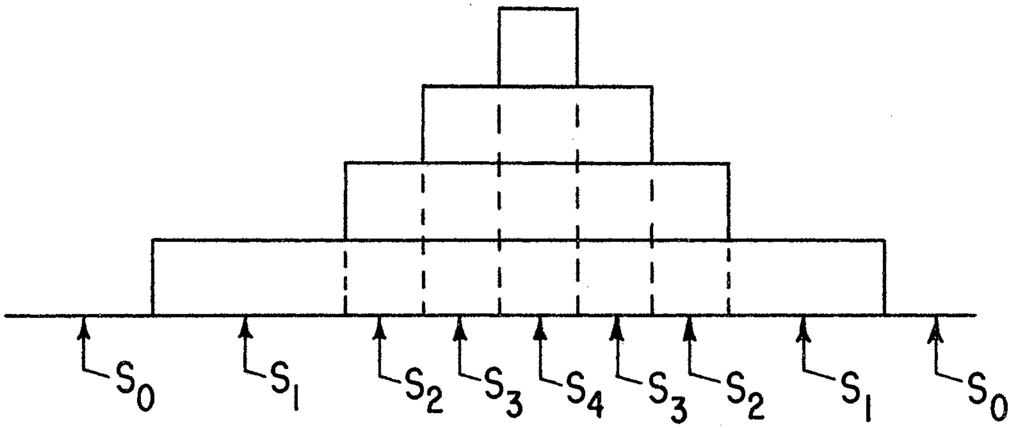

Figure 3. Layers of Adsorbed Molecules Assumed in the Derivation of the BET Equation

at equilibrium S_0 must remain constant, it was assumed that the rate of condensation on the bare surface must be equal to the rate of evaporation from the first layer or

$$a_1 p S_0 = b_1 S_1 \exp(-E_1/RT) \tag{22}$$

where

p = the vapor pressure, dyne cm^{-2}

E_1 = heat of adsorption in the first layer, cal $mole^{-1}$

T = absolute temperature, ^oK

R = universal gas constant, cal $^oK^{-1}$ $mole^{-1}$

$a_1 = \alpha_{01}(2mkT)^{-\frac{1}{2}}$, sec gm^{-1} cm^{-1}

b_1 = evaporation coefficient of first layer, molecules cm^{-2} sec^{-1}

α_{01} = condensation coefficient for the first layer, dimensionless

Also, for the other layers

$$a_2\ p\ S_1 = b_2\ S_2 \exp(-E_2/RT)$$

$$a_3\ p\ S_2 = b_3\ S_3 \exp(-E_3/RT)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$a_i\ p\ S_{i-1} = b_i\ S_i \exp(-E_i/RT)$$

These equations neglect any transfer of adsorbed liquid from one layer to another. The total surface area, A, of the adsorbent is the sum of all the partial surfaces.

$$A = \sum_{i=o}^{\infty} S_i$$

The total volume of the gas adsorbed is

$$v = v_o \sum_{i=o}^{\infty} i S_i$$

where

v = the volume adsorbed

v_o = volume adsorbed on a unit area when it is covered by a unimolecular layer of gas

Dividing by the area of the surface gives,

$$\frac{v}{Av_o} = \frac{\sum_{i=o}^{\infty} iS_i}{\sum_{i=o}^{\infty} S_i}$$

or

$$\frac{v}{v_m} = \frac{\sum_{i=o}^{\infty} iS_i}{\sum_{i=o}^{\infty} S_i} \tag{23}$$

where

v_m = volume of gas adsorbed when the entire adsorbent is covered with a complete unimolecular layer

Two important assumptions were made in order to simplify equation (23). First, it was assumed that the heats of adsorption of all layers other than the first were equal to the heat of liquefaction of the gas. Then,

$$E_2 = E_3 = \ldots\ldots\ldots = E_i = E_L$$

The second assumption was that the ratio b/a was a constant for the second and higher layers.

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \ldots\ldots = \frac{b_i}{a_i} = g$$

where

g = a constant

With these assumptions, S_1, S_2, S_3 ...... S_i ...... can be expressed in terms of S_o.

$$S_1 = \frac{a_1}{b_1} p \exp(-E_1/RT)\ S_o = yS_o$$

where

$$y = \frac{a_1}{b_1} p \exp(-E_1/RT)$$

$$S_2 = \frac{a_2}{b_2} p \exp(-E_2/RT)\ S_1 = xS_1 = xyS_o$$

where

$$x = \frac{a_2}{b_2} p \exp(-E_2/RT) = \frac{p}{g} \exp(-E_2/RT)$$

Also

$$S_3 = x\ S_2 = x^2\ S_1 = y\ x^2\ S_o = c\ x^3\ S_o$$

....

$$S_i = x\ S_{i-1} = x^{i-1}\ S_1 = yx^{i-1}\ S_o = c\ x^i\ S_o$$

where

$$c = \frac{y}{x} = \frac{a_1 g}{b_1} \exp\left[(E_1 - E_L)/RT\right]$$

Substituting into equation (23) gives,

$$\frac{v}{v_m} = \frac{\sum\limits_{i=o}^{\infty} icx^i \; S_o}{S_o + \sum\limits_{i=1}^{\infty} cx^i \; S_o}$$

or

$$\frac{v}{v_m} = \frac{c\sum\limits_{i=o}^{\infty} ix^i}{1 + c\sum\limits_{i=1}^{\infty} x^i} \tag{24}$$

Assuming the absolute value of x to be less than one allows the evaluation of the two series.

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1 - x}$$

and

$$\sum_{i=o}^{\infty} ix^i = x\frac{d}{dx}\sum_{i=o}^{\infty} x^i = \frac{x}{(1-x)^2}$$

Then equation (24) becomes,

$$\frac{v}{v_m} = \frac{cx}{(1-x)(1-x+cx)} \tag{25}$$

To make $v = \infty$ when $p = p_o$, x must approach 1 as p approaches p_o. Therefore:

$$\frac{p_o}{g}\exp(E_L/RT) = 1$$

and

$$x = \frac{p}{p_o} \tag{26}$$

Substituting equation (26) into equation (25) gives,

$$v = \frac{c\,v_m\,p}{(p_o-p)\left[1 + (c-1)\frac{p}{p_o}\right]}$$

or

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_o} \tag{27}$$

If $\frac{p}{v(p-p_o)}$ is plotted versus $\frac{p}{p_o}$, a straight line should result. The intercept of the line is $\frac{1}{v_m c}$ and the slope is $\frac{c-1}{v_m c}$. Thus the values of c and v_m can be determined from the experimental data if the equation is satisfied.

Equation (27) can give either a Type II or Type III isotherm depending on whether E_1 is less than or greater than E_L. If the adsorption does not take place on a free surface but in a limited space, then at saturation not an infinite but only a finite number of layers can build up on the surface of the adsorbent. If the maximum number of layers that can be adsorbed on each wall of the capillary is n, then the summation of the two series in equation (24) is to be carried to n terms only, and not to infinity. The result is

$$v = \frac{v_m c \ x}{1 - x} \quad \frac{1-(n+1)\ x^n + n\ x^{n+1}}{1+(c-1)\ x \ - c\ x^{n+1}} \tag{28}$$

If n is equal to one, equation (28) reduces to

$$v = \frac{v_m \frac{c}{p_o} p}{1 + \frac{c}{p_o} p} \tag{29}$$

This is equivalent to Langmuir's equation with the constant b having the value c/p_o.

The shapes of Type IV and V isotherms suggest that a complete or almost complete filling of the pores and capillaries of the adsorbent occurs at a pressure lower than the vapor pressure of the gas. This suggests that as the pressure of the gas is increased some additional forces appear that make the heat of adsorption, or the energy of binding, in some higher layer to be greater than E_L, the heat of liquefaction of the gas. Brunauer (1945) believes this to be the result of the last adsorbed layer in a capillary being attracted on both sides. Therefore, its heat of adsorption must be greater than that of the other layers. This additional energy of evaporation may be denoted by Q. Then the rate of adsorption from the last layer will not be proportional to $\exp(-E_L/RT)$ but to $\exp\left[(E_L+Q)/RT\right]$.

Assuming that the adsorption takes place in a capillary consisting of two plane walls into which a maximum of 2n-1 layers can fit, a summation may be carried out in a manner similar to that in the derivation of equation (27). The result is:

$$v = \frac{v_m cx}{1-x}\,\frac{1+(\frac{1}{2}ng-\frac{1}{2}n)x^{n-1} - (ng+1)x^n + (\frac{1}{2}ng+\frac{1}{2}n)x^{n+1}}{1+(c-1)x + (\frac{1}{2}cg-\frac{1}{2}c)x^n - (\frac{1}{2}cg+\frac{1}{2}c)x^{n+1}} \qquad (31)$$

Thus, the multimolecular equation proposed by Brunauer and his associates may give any of the five types of adsorption isotherms. If Q is zero it gives Type II or III isotherms. If Q is not negligible Type IV or V isotherms are obtained and if $n = 1$ the Type I isotherm is obtained.

At this point it should be pointed out that the summation carried out by Brunauer et al in the development of the multimolecular adsorption theory is only valid if x is less than one. The value of x is given by:

$$x = \frac{p}{g} \exp(-E_1/RT) \tag{32}$$

Brunauer does not give a reason for being able to assume that this quantity would be less than one.

Experimental results have shown the BET equation to give discrepancies at very low vapor pressures and also to give high values for the volume adsorbed for ratios of p/p_o greater than 0.35. This latter observation has prompted several attempts at altering the equation by introducing another constant with no real physical meaning. Since these can only be called empirical equations, they will not be discussed here.

D. The Smith Equation

Smith (1947) considers the sorbed water to be of two principal classes: (1) that which is in some way bound on the inner or outer surface of the solid adsorbent by forces in excess of the normal forces responsible for condensation of water to the liquid state and; (2) that which is normally condensed within the adsorbent.

Smith defines the regain to be the weight ratio of sorbate to dry sorbent or the moisture content on the dry basis. He then writes:

$$\alpha_t = \alpha_b + \alpha \tag{33}$$

where

α_t = the total regain

α_b = the part of the regain which is bound by excessive forces

α = the part of the regain which is condensed with a normal heat of condensation

While α_b may be expected to reach a virtual maximum at a vapor pressure well short of saturation, α must increase progressively toward the saturation vapor pressure. The isotherm for α_b will be concave, and that for α convex, toward the axis of relative vapor pressures. The summation of the isotherms for the two fractions results in the sigmoidal isotherm typical of high polymer sorption.

Smith first considers the case of sorption by a non-swelling gel. The dependence of α_b on the relative vapor pressure may be expected to follow approximately the formulation of the Langmuir adsorption isotherm. The value of α_b should reach a maximum at a vapor pressure, p_b, well short of saturation.

The normally condensed fraction, α, theoretically begins to form at the outset of the sorption process, though obviously it can only form in those regions where the bound water molecules are already in place. Let α' be defined as the weight of normally condensed vapor (per gram of sorbent) required to saturate the first layer of the fraction. Additional water molecules condense in multiple layers on those of the α' -fraction. When a molecule condenses on top of the α' layer it prevents a molecule in the α' -fraction from evaporating by placing upon it an overburden. Hence, additional layers superimposed upon the first do not materially augment the evaporating surface and α' may be considered a meausre of the total potential evaporating surface. Smith assumed that the α' -fraction is complete only at the saturation vapor pressure. He further considers the completed fraction of α' at any stage of the sorption to be p/p_o, while the uncompleted fraction is $(1 - p/p_o)$.

If it may be assumed that positions in the α' and succeeding layers are equally accessible to condensing water molecules, an increment of condensing vapor $d\alpha$, will be distributed uniformly over the completed and uncompleted areas of the α' -layer. The effective increment for the α' -layer will be $(1 - p/p_o)d\alpha$.

Providing all increments in α' are equally effective in augmenting the vapor pressure, it follows that:

$$(1 - p/p_o)\frac{d\alpha}{\alpha'} = \frac{dp}{p_o} \tag{34}$$

That is, the increment in α' bears the same ratio to the total capacity of α' as the corresponding increment in vapor pressure bears to the total vapor pressure at saturation. Integration of equation (34) gives:

$$\alpha = -\alpha' \ln(1 - p/p_o) \tag{35}$$

The total regain is the sum of the bound and the normally condensed fractions. Thus:

$$\alpha_t = \alpha_b + \alpha = \alpha_b - \alpha' \ln(1 - p/p_o). \tag{36}$$

For all values of $p/p_o > p_b/p_o$, at which the bound fraction is complete, α_b should be constant and independent of p/p_o. In the case of a non-swelling gel a plot of α_t versus the dimensionless pressure function $-\ln(1 - p/p_o)$ should therefore be linear beyond $p/p_o = p_b/p_o$.

Equation (36) fails to take into account the progressive enlargement of the effective sorbing surface of the gel which accompanies swelling. In order to express the effect of swelling it is convenient to replace the weight ratio of sorbate to sorbent, α_t, by the ratio $\alpha_t/\left[1 + f(\alpha_t)\right]$, where $f(\alpha_t)$ represents the effective increase in the sorptive capacity of the swollen gel in terms of an undetermined general function of the regain.

Smith discusses one special case where the effective sorbing surface, at all stages of sorption, is approximately proportional to the volume of the sorbing gel. Under these circumstances, the number of sorptive points exposed within the swollen structure will be proportional to its total mass, and $1 + f(\alpha_t)$ may be replaced by $(1 + \alpha_t)$. In all cases which permit this simplification, the formulation $\alpha_t/[1 + f(\alpha_t)]$ reduces to $\alpha_t/(1 + \alpha_t)$ which is identical with the weight fraction, $\bar{w}_t$, of sorbate in the swollen gel or simply the moisture content on the wet basis when the sorbate is water vapor. Equation (36) may then be written:

$$\bar{w}_t = \bar{w}_b + \bar{w} = \bar{w}_b - \bar{w}' \ln(1 - \frac{p}{p_o}) \qquad (37)$$

where the definitions of the various weight fractions parallel those of the regains of equation (36).

A mechanism for the development of hysteresis is suggested by Smith from his treatment of the sorption phenomena. Additional points of attachment for water molecules of the bound fraction are developed, as a result of swelling, throughout all of the adsorption process. Above the critical relative vapor pressure p_b/p_o these points are saturated as rapidly as they appear. On desorption the regression of these centers of attraction is delayed by the persistence of a portion of the bound water which intervenes to block the collapse of the structure.

Discussion

Each of the theories presented in this section have had some degree of success in representing experimental data. However, none of them have been able to give consistently accurate results throughout the whole range of relative vapor pressures and for varying adsorbents and adsorbates.

Each of the theories is based on a somewhat different hypothesis concerning the manner in which the molecules of the adsorbate are attracted and held by the adsorbent. In most cases only one of several possible forces was considered to be responsible for the adsorption phenomena.

The Langmuir and BET equations assume that the adsorption is due only to a time delay between the condensation and evaporation of a molecule of the adsorbate after a collision with the adsorbent.

The potential theory considers the work which must be done on the adsorbate to compress it to its saturation vapor pressure so that it condenses. The capillary condensation theory considers the adsorption to be due to condensation in the capillaries of the adsorbent according to the Kelvin equation.

Although none of these theories give completely satisfactory results when considered alone, it seems probable that some combination of these theories might give a relationship which would adequately describe the adsorption process. At least, a study of these theories is a help in understanding what actually takes place in adsorption.

CHAPTER III

REVIEW OF MOISTURE CHARACTERISTICS OF WHEAT AND OTHER BIOLOGICAL MATERIALS

Equilibrium Moisture Relations

The best known and most widely used relationship for the equilibrium moisture content of biological materials was developed by Henderson (1952). Using data collected for a number of different materials, Henderson found the following mathematical characteristic to hold for the equilibrium moisture content curve:

$$1 - rh = \exp(-k'M^n) \qquad (38)$$

where

rh = equilibrium relative humidity, expressed as a decimal

M = equilibrium moisture content, dry basis, per cent

k' = factor varying with material, dimensionless

n = exponent varying with material, dimensionless

Henderson further attempted to develop an analytical basis for equation (38). He began with Gibb's thermodynamic adsorption isotherm and developed an equation similar to equation (38) which also included an effect due to temperature. This equation is:

$$1 - rh = \exp(-kTM^n) \tag{39}$$

where

T = absolute temperature, $^{\circ}R$

k = constant varying with material, $^{\circ}R^{-1}$

Unfortunately, there are some mathematical errors in the derivation of equation (39) and there appears to be no mathematically correct derivation. Also, some relationships assumed in the derivation apparently have no analytical or experimental verification. However, the formula satisfies the following recognized characteristics of equilibrium moisture curves:

(a) The equilibrium relative humidity is zero at zero moisture content.

(b) The equilibrium relative humidity approaches 100 per cent as the moisture content becomes infinite.

(c) The curve slope approaches infinity as the moisture content approaches infinity.

Pichler (1956) applied Henderson's equation to observed curves for grain and rape and found several deviations which were considerable in parts. By limiting the equation to a certain range (15 to 50%

rh for rape) much better agreement was obtained. Pichler found that Henderson's equation did not permit the mathematical determination of the shift of the equilibrium moisture content due to temperature, because n and k are not constants independent of temperature. Consequently the equation should not be used as a strictly physical expression unless k and n are known as a function of temperature which would merely give a better interpolation formula.

Pichler briefly states the results of his investigations by saying that the uptake of water vapor by porous materials is not a homogeneous process. It is effected in two ways: (a) by adsorption, and (b) by capillary condensation. However, the two processes do not take place simultaneously. At low relative humidity values, moisture is taken up primarily by adsorption, and at higher values by capillary condensation which is physically a completely different process. He suggests that this is the reason that no single mathematical relationship successfully represents the equilibrium moisture curve throughout the entire range of humidities.

Day and Nelson (1963) developed an equilibrium moisture content relationship for wheat from the basic form of Henderson's equation by expressing k and n in terms of the temperature. The developed relationship adequately accounted for the temperature effect for relative humidities of 70 per cent or lower. The relationships above 70 per cent were not defined mathematically but were estimated by using a relationship developed for obtaining the maximum grain moisture content for an isotherm, a smooth curve was drawn from 70 per cent to 100 per cent relative humidity. The form of the equilibrium moisture relationship was:

$$1 - rh = \exp\left[-(P_1 t^{P_2}) M^{(P_3 t^{P_4})}\right] \qquad (40)$$

where

t = temperature, °F(not absolute)

P_i = coefficients and exponents for a given kind of grain

The form of the equation developed for maximum grain moisture was:

$$M_{max.} = P_1 T^{P_2} \qquad (41)$$

where

$M_{max.}$ = equilibrium grain moisture content at 100% relative humidity, dry basis, as a decimal

T = absolute temperature, °R.

P_i = coefficients and exponents for a given kind of grain

Becker and Sallans (1956), in a study of the desorption isotherms of wheat, used three different curves to give a fit of their experimental data. The BET equation was used in the initial curved portions of the sigmoidal type curve. The Smith equation for a swelling gel was used in the final curved portions of the isotherm. The intermediate region of the desorption isotherm was approximated by a straight line drawn tangential to the Smith curve to intersect the BET curve at its point of inflection. The use of the three different curves allowed them to get a good fit of the data throughout the whole range of humidities.

Becker (1958) developed an equation for the moisture desorption isotherm on the basis of Cassie's (1947) statistical-thermodynamic analysis of the BET and Langmuir equations and on Gibb's equation. The developed equation was:

$$\frac{N}{S} = (1 + K'f^n)\left(\frac{Kf}{1 + Kf}\right) \qquad (42)$$

where

N = number of adsorbed molecules

S = number of localized sites

f = relative vapor pressure

K',n,K = Constants

He found K' and n to be independent of temperature and found that K was dependent on temperature. $Kf/(1 + Kf)$ is a Langmuir-type factor for adsorption of the low energy fraction of molecules, and $K'f^n$ is a factor for adsorption of the normally condensed fraction of molecules.

Gay (1946) experimentally determined the moisture content of wheat when in equilibrium with relative humidities between 20 and 80 per cent at temperatures of 50 to 100°F. Triplicate samples of wheat were placed in vacuum desiccators over sulfuric acid solutions selected to provide the desired relative humidities.

Initially, the samples were exposed at a temperature of 50°F to relative humidities of 20, 30, 40, 50, 60, 70, and 80 per cent, and each sample was dried to constant weight. This process was repeated by increments of 10°F up to 100°F.

At any level of relative humidity throughout the range studied, the effect of increasing the temperature was found to be a decrease in the equilibrium moisture content. This reduction became smaller as the humidity was increased, ranging from approximately 0.25 per cent for each 10°F rise at 20 per cent relative humidity down to 0.15 per cent for each 10°F rise at 80 per cent relative humidity.

Hysteresis

All the previously mentioned equations and the experimental work were concerned only with a sorption or a desorption isotherm. They made no comparison between the two curves. However, Babbitt (1945) measured the equilibrium moisture content for some No. 1 Garnet wheat at various relative humidities. He found a very definite hysteresis between the sorption and desorption curves with the equilibrium moisture contents for the desorption curve being larger than those for the sorption curve at the same relative humidity.

This hysteresis was further established by Hubbard et al. (1957). Hysteresis loops were established for wheat and corn at 25, 30 and 35°C. over the range 0 to 97 per cent relative humidity. Both the sorption and the desorption isotherms for corn and wheat were found to be sigmoidal. The maximum hysteresis was found between 12 and 14% relative humidity amounting to 1.6% and diminishing to less than 0.2% at 92% humidity. No consistent differences were found in the extent of hysteresis with temperature changes over the range of temperatures studied.

Breese (1955) established a hysteresis in the hygroscopic equilibria of rough rice. A difference greater than 1% between the adsorption and desorption equilibrium moisture contents was maintained over the range of relative humidities from 20 to 80%, but exceeded 1.5% only at relative humidities from 50 to 70%. He found that rough rice with a moisture content anywhere between 12.6 and 14.1% might be in equilibrium with a relative humidity of 75%.

Weight and Volume Changes

Although it is evident that there is swelling of the grain as the moisture content increases, the volume versus moisture content curve is not well defined. Bushuk and Hlynka (1960) used the toulene-displacement pycnometric method to measure the change in volume of whole wheat with gain or loss of moisture after equilibration at various relative pressures of water vapor. The corresponding weight changes were also determined. A plot of the volume changes against the equilibrium relative pressure gave a volume isotherm with hysteresis between the sorption and desorption branches similar to that in the weight isotherm.

A definite hysteresis was also found to exist between the sorption and desorption branches of the plots of change in volume against change in weight.

The dry grain showed a net increase in volume after a complete sorption-desorption cycle in the relative pressure range 0 to 0.94.

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

Internal Moisture Movement

Since it has been shown that there is a hysteresis between the adsorption and desorption isotherms, it appears that there must be some difference in the forces causing movement of the moisture within the grain. Therefore, some of the theories of internal moisture movement were reviewed. However, none of the theories studied give any hint as to the cause of hysteresis.

Most of the theories which have been advanced concerning internal moisture movement are dependent on Fick's Law with a diffusion coefficient defined as follows:

$$D \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} = \frac{\partial C}{\partial \theta} \quad (43)$$

where

D = diffusivity, length squared per unit time

C = concentration, mass per unit volume

θ = time

x,y,z = spatial dimensions

This equation is discussed by Becker (1959) and by Fan, Chung, and Shellenber (1951) and an approximate solution is given for a particle of arbitrary shape under the assumption that the surface-to-volume ratio remains constant.

Becker and Sallans (1957) made a more thorough study of the mechanism of moisture diffusion in wheat and found evidence that the diffusive flow of moisture could be described by a three-dimensional mechanism at moistures above a critical level 10 to 12%, dry basis, and by a two-dimensional mechanism below this critical level.

The three-dimensional flow was described by the following equation which was developed from the data of many investigators and is applicable to the flow of liquids through randomly packed fixed beds and suspensions of spheres:

$$J = \frac{- D_s^2 \ \rho \ \varepsilon^{4.75}}{18\mu \ (1 - \varepsilon)} \cdot \frac{dp}{dx} \qquad (44)$$

where

D_s = diameter of spherical particle, cm

ρ = liquid density, gm cm^{-3}

μ = liquid viscosity, gm cm^{-1} sec^{-1}

ε = fractional pore space

dp/dx = pressure gradient, dynes cm^{-3}

J = mass liquid flow rate, gm cm^{-1} sec^{-1}

The two-dimensional flow is described by the equation:

$$J = -\eta C \frac{\delta \pi}{\delta x} \qquad (45)$$

where

η = a resistance coefficient

C = adsorbate concentration, gm cm^{-3}

$\frac{\delta \pi}{\delta x}$ = film pressure gradient, dynes cm^{-2}

These two types of flow mechanisms improve the degree to which the moisture movement may be described mathematically but they still do not account for any hysteresis between wetting and drying operations.

Effect of Physical Structure of Wheat on Moisture Movement

The wheat kernel is composed of four principal layers in addition to the wheat germ. The outer layer is the pericarp, followed by the testa, the hyaline layer and the endosperm. Some experimental work has been done to determine the effect of these different layers on the moisture movement within the kernel. It is generally believed that the pericarp absorbs moisture very readily thus offering little resistance to moisture movement into the kernel.

Hinton (1955) found that the effective barrier to ready entry of water is the testa rather than the hyaline layer which had previously been considered to be most important. Becker (1960) believed that the resistance due to the testa was not due to a decrease of the diffusional coefficient but that it eliminated capillary flow into the kernel. He found that there was a very rapid initial absorption in which the pericarp was saturated by capillary imbibition. Then the lack of an appropriate capillary structure in the testa sealed the capillary channels by which liquid water might be conducted into the interior of the kernel. The only part of the kernel not so sheathed is the germ end, and the rate of absorption was abnormally high in this region; but because the germ area is small, the effect of this on the total rate of absorption cannot be large. Becker found no reason for assuming that the testa importantly limits a process of pure diffusion.

Both Hinton and Becker believed that the slow movement of water in the endosperm is responsible for the long period required for the complete distribution of water throughout the kernel.

Discussion

This review of literature revealed that the equilibrium moisture relationships available today are largely empirical and that those which have some analytical basis have been only partially successful at representing the experimental data. Also, it is apparent that an explanation of the hysteresis effect is lacking. Actually this hysteresis has been neglected in many experiments so that much of the available data makes no reference to whether equilibrium was obtained in a drying or a wetting environment.

CHAPTER IV

OBJECTIVES

With the results of the review of literature in mind, the following objectives were established for this research:

1. To develop a theory of the mechanisms involved in moisture sorption and desorption which would explain the equilibrium moisture curves which are obtained for biological materials.
2. To mathematically express the equilibrium moisture content as a function of relative humidity, temperature, and previous moisture condition of the material.
3. To determine whether the theoretical equation would fit the experimental data for a particular biological material. Wheat was chosen as the biological material used in experimental evaluation.

Some requirements of this hypothesis and the relationships to be developed are:

1. The effect of temperature should be accounted for by the theory.
2. Hysteresis should be explained.

and

3. The sorption and desorption isotherms should agree with experimental observations throughout the entire range of relative humidities.

CHAPTER V

ANALYSIS OF THE PROBLEM

Since a biological material is a combination of many biological cells, three mechanisms are hypothesized by which water is held by the grain. First, there can be a unimolecular layer of water molecules bound to the surface of the cells. Secondly, there can be multimolecular layers of molecules stacked on top of the first layer. Thirdly, there can be moisture within the cells.

Moisture held in the first two ways may correctly be called adsorbed moisture, if adsorption is considered to be the moisture held on the surface of the cells rather than the exterior surface of the material. However, the moisture within the cells cannot be called adsorbed moisture, because it has actually entered into the cell rather than adhering to the surface. It will be called absorbed moisture in the future. Figure 4 illustrates the three types of moisture within a biological material.

It is known from past experimentation that the heat of adsorption of the water decreases as the

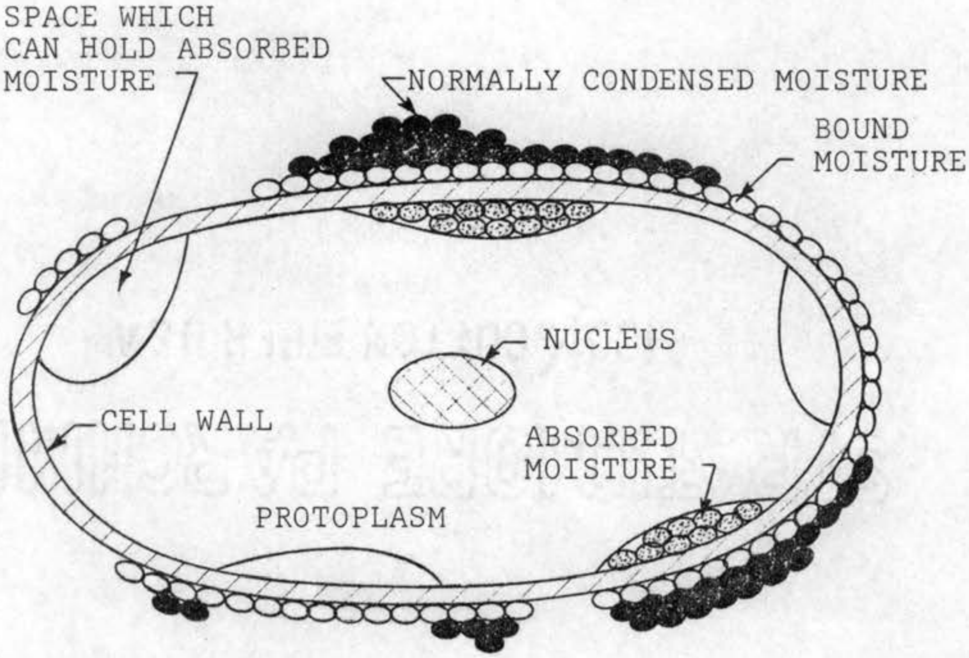

Figure 4. Schematic Drawing of a Cell of a Biological Material Illustrating the Three Types of Moisture

moisture content increases. This may be explained by the following hypothesis. Assume that the first layer of water molecules is bound to the surface of the cells by forces in excess of those which would bind the water molecules to each other in normal condensation. Then assume that the second and higher layers of moisture are condensed with a normal heat of condensation. When the moisture content of the grain is very low, practically all of the adsorbed moisture will be in the first layer, and will thus have a high heat of adsorption. As the moisture content increases, more and more of the moisture adsorbed will be in the second or higher layers where the condensation is normal, and thus the average heat of adsorption will decrease. With this hypothesis in mind, the first two types of moisture held by the grain may be called unimolecular bound moisture and normally condensed moisture respectively.

It may be predicted from the BET and Smith equations that the adsorption process is completely reversible so that the amount of adsorbed moisture in the grain at equilibrium conditions would be the same, regardless of whether the equilibrium was reached in a drying or wetting environment. Then the hysteresis effect must be due to the absorbed moisture. If a dry biological material is subjected to a wetting environment, moisture first adheres to the surface of the cells, primarily in a unimolecular layer. When a layer of molecules builds upon the surface, increasing diffusional forces tend to cause transfer of moisture into the cell. However, the surface molecules of the cell exert binding forces on the water molecules which prevent them from moving inward. As more and more molecules adhere to the surface, the diffusional forces exceed the binding forces and allow some moisture to move inside the cell. Then, upon a reduction of the vapor pressure of the environment, outward diffusional forces are not developed until all the moisture has been removed from the surface. At this time, diffusional forces caused by the concentration gradients cause the absorbed moisture to move out of the cell. Thus, a hysteresis effect occurs between the sorption and desorption curves.

This absorption process may be further explained by considering the mechanical analogy of a block sliding on an inclined plane. Consider such a block as follows. When the plane is horizontal, there are no horizontal forces on the block. However, if the right side of the plane is elevated, there is a tendency for the block to slide to the left. This force may be overcome, though, by a frictional force which prevents the block from moving. If the right side of the plane is raised high enough, the gravity component down the plane to the left overcomes the friction force, and the block slides to the bottom of the plane at the left. Now, if the right end of the plane is lowered, the block still remains at rest until the plane slopes to the right at an angle sufficient to allow the block to slide toward the right.

In this mechanical analogy, the block is analogous to a moisture molecule on the surface of the cell, the component of the force of gravity along the plane is analogous to the diffusional force tending to move the moisture into the cell, and the frictional force is analogous to the binding forces at the surface of the cell which tend to prevent movement of moisture into the cell.

One difference between the mechanical analogy and the absorption process is that the frictional force prevents the block from moving in either direction unless the slope is sufficiently steep, while the binding forces at the surface of the cell only prevent movement into the cell. The transfer of absorbed moisture out of the cell is a function of diffusional forces which are proportional to the concentration gradient. As soon as a slight gradient is established, this moisture begins moving outward with its rate being determined by the magnitude of the gradient.

With these general ideas in mind, it is possible to consider each of the three types of moisture individually and, by making some simplifying assumptions, to derive equations to describe the processes which take place.

Unimolecular Bound Moisture

At equilibrium, the rate at which moisture is condensed on the surface must be equal to the rate of evaporation from the surface. Consider only the bound layer of water molecules at this point. Then the rate at which the unimolecular layer of bound moisture condenses per unit area of adsorbent surface is:

$$\mu = \frac{p}{(2\pi mkT)^{\frac{1}{2}}} (1 - \theta) \qquad (46)$$

where

μ = number of molecules condensed per unit surface area of the adsorbent per unit of time, molecules cm^{-2} sec^{-1}

p = vapor pressure of water, dynes cm^{-2}

m = mass of a water molecule, gm $molecule^{-1}$

k = Boltzmann's constant, g cm^{2} sec^{-2} $molecule^{-1}$ $^{o}K^{-1}$

T = absolute temperature, ^{o}K

θ = fraction of surface already covered by a layer of bound moisture

This assumes that all the vapor molecules which hit the uncovered portion of the surface are condensed and held by forces greater than those exerted on normally condensed (condensed with the normal heat of condensation of water vapor) molecules. Assume that the vapor molecules which collide with the portion of the surface which is already covered by a monomolecular layer form a second layer of molecules on top of the first, and that this layer has no effect on the first except to prevent the molecules of the lower layer from evaporating. Then the rate of evaporation of the molecules from the bound moisture layer is:

$$\nu = k_o e^{-q_1/kT} (\theta - \phi) \qquad (47)$$

where

ν = number of molecules evaporated per unit surface area of adsorbent per unit time, molecules cm^{-2} sec^{-1}

k_o = evaporation coefficient, molecules cm^{-2} sec^{-1}

q_1 = heat of adsorption of the molecules bound to the surface, cal $molecule^{-1}$

k = Boltzmann's constant, cal $molecule^{-1}$ $^{o}K^{-1}$

T = absolute temperature, ^{o}K

θ = fraction of surface already covered by a layer of bound moisture

ϕ = fraction of surface covered by two or more layers of molecules

Equating equations (46) and (47) gives:

$$\theta = \frac{p(2\pi mkT)^{-\frac{1}{2}} + k_o\phi\exp(-q_1/kT)}{k_o\exp(-q_1/kT) + p(2\pi mkT)^{-\frac{1}{2}}} \tag{48}$$

Assuming that in the second and higher layers of molecules the condensation occurs with a normal heat of condensation q_L, then

$$p(2\pi mkT)^{-\frac{1}{2}}(\theta) = k_o\phi\exp(-q_L/kT) \tag{49}$$

or

$$\phi = \frac{p\theta}{k_o\exp(-q_L/kT)\,(2\pi mkT)^{\frac{1}{2}}} \tag{50}$$

At a vapor pressure of p_o, the saturation vapor pressure, the evaporation and condensation from a water surface must occur at equal rates. Therefore:

$$p_o(2\pi mkT)^{-\frac{1}{2}} = k_o\exp(-q_L/kT)$$

or

$$p_o = k_o(2\pi mkT)^{\frac{1}{2}}\exp(-q_L/kT) \tag{51}$$

Substituting equation (50) into equation (48) and dividing the numerator of the right-hand side by p_o and the denominator by the equivalent of p_o given by equation (51) yields:

$$\theta = \frac{rh}{rh + (1 - rh)\exp\left[-(q_1 - q_L)/kT\right]} \qquad (52)$$

where

rh = relative humidity = $\frac{p}{p_o}$

Equation (52) relates the fraction of the surface covered by a unimolecular bound layer of moisture to the relative humidity of the environment. There are no arbitrary constants, and the only quantity on the right-hand side of the equation which is difficult to measure is the heat of adsorption of the bound layer, q_1.

Several assumptions had to be made in the derivation of equation (52) and it seems fitting that they be listed here even though some of them have been previously discussed. It will be noted that some of these assumptions have not been discussed but that they were used in an indirect manner. The assumptions are:

1. Multimolecular adsorption
2. Normal condensation occurs in second and higher layers of adsorbed molecules
3. Rate of condensation equals rate of evaporation at equilibrium
4. Vapor obeys ideal gas laws
5. The probability of evaporation from a site in the first layer is the same whether the

neighboring positions on the surface are occupied or not

6. Uniform heat of adsorption
7. All molecules colliding with the surface are condensed there
8. Surface area remains constant

A comparison of this derivation with the derivation of Langmuir's equation shows many similarities. The main difference is that Langmuir did not allow for multimolecular adsorption and thus did not account for the effect the second and higher layers would have on the evaporation rate from the first layer.

Normally Condensed Moisture

By combining equations (50) and (51), the following relationship may be obtained:

$$\phi = rh\,\theta \tag{53}$$

Then by differentiation:

$$d\phi = rh d\theta + \theta d(rh) \tag{54}$$

Let α be the total amount of normally condensed moisture on the surface, measured in molecular layers. Then consider the addition of a differential element of normally condensed moisture $d\alpha$ to the surface. This differential element will be divided into two parts. Some of it will condense on the portion of the surface which is covered only by the layer of bound molecules, and some of it will condense on the portion which is already covered by one or more layers of normally condensed moisture. The moisture which condenses on the bare surface of the cell is not normally condensed, and has already been considered in the derivation of the equation for the unimolecular bound moisture. The division of the normally condensed moisture is proportional to the fraction of the bound layer which is covered by a normally condensed layer. According to equation (53) this fraction is rh. Thus, if a differential element of normally condensed molecules $d\alpha$ is added to the surface, rh $d\alpha$ of this will form higher layers of normally condensed molecules and (1 - rh) $d\alpha$ of this will increase the area which is covered by one layer of normally condensed molecules. Thus,

$$d\phi = (1 - rh)\, d\alpha \qquad (55)$$

or

$$(1 - rh)\, d\alpha = rh\, d\theta + \theta d(rh) \qquad (56)$$

Substituting equation (52) into equation (56) and integrating the resulting differential equation yields:

$$\alpha = -\frac{E\ rh}{E-(E-1)rh} + \frac{E^2}{E-1}\ln\left[\frac{E-(E-1)rh}{E}\right] - (E+1)\ln(1-rh) \qquad (57)$$

where

$$E = \exp\left[-(q_1 - q_L)/kT\right]$$

The substitution and integration resulting in equation (57) is given in Appendix A.

The total amount of adsorbed moisture can be obtained by adding equations (52) and (57). This gives an equation which is very close to the BET equation at low humidities and to the Smith equation at high humidities. In the intermediate range of humidities, the addition of the two equations gives a very nearly straight line. This curve then is very similar to the one used by Becker and Sallans (1956) to describe the equilibrium moisture curve of wheat.

Absorbed Moisture

In the dry state, the surface molecules of a biological cell, due to the work which has been done on them in moving them to the surface, possess a higher state of energy than the interior molecules. This results in surface tension forces which tend to increase the density of the molecules at the surface. It is hypothesized that this increased density of molecules at the surface acts as a barrier to moisture movement through the cell wall into the interior of the cell.

The first layer of water molecules which is adsorbed on the surface saturates some of the unbalanced forces at the surface. This results in an increase in the volume of the biological material. However, these bound molecules are not able to move inside the cell due to the binding forces. When a normally condensed layer of molecules is adsorbed on the surface of the cell, the diffusional forces acting inward would be sufficient to allow some moisture to move through the cell wall into the interior of the cell.

Assume that a volume of water, V, may enter into the cells of the biological material so that it cannot be considered as adsorbed moisture. Assume that this volume is uniformly distributed throughout the material. Then, for an initially dry material, the amount of absorbed water held by the material would be proportional to the area covered by at least one layer of normally condensed water molecules. Then:

$$\gamma_s = V\phi \tag{58}$$

where

γ_s = volume of absorbed moisture during a sorption process

V = volume of absorbed moisture at saturation

ϕ = fraction of surface covered by one or more layers of normally condensed moisture

If the biological material is completely saturated and then subjected to a drying environment, the absorbed moisture is not drawn out of the grain until the layer of bound molecules is removed. Thus:

$$\gamma_d = V\theta \qquad (59)$$

where

γ_d = volume of absorbed moisture during a desorption process

θ = per cent of surface covered by a layer of bound molecules

If a material is initially dry and is allowed to reach equilibrium with some maximum relative humidity rh, the amount of absorbed moisture held during a desorption process is then proportional to the area covered by a bound layer of molecules multiplied by the maximum relative humidity which was reached. Then,

$$\gamma_d = V\theta rh_{max}$$

Total Moisture Content

The total amount of moisture held by a biological material may be obtained by adding the amounts of the three different types held. Then,

$$W_s = \rho v_m(\theta+\alpha) + \rho V\phi \qquad (61)$$

and

$$W_d = \rho v_m(\theta+\alpha) + \rho V\theta rh_{max} \qquad (62)$$

where

W_s = total mass of moisture held by the biological material during a sorption process

W_d = total mass of moisture held by the biological material during a desorption process

ρ = density of water in mass per unit volume

v_m = volume of moisture in unimolecular layers of water molecules

V = volume of absorbed moisture at saturation

rh_{max} = maximum relative humidity to which the material has been subjected, decimal.

θ, α, and ϕ are given by equations (52), (57), and (53) respectively.

The moisture content is then obtained by dividing by the dry weight of the biological material. Then

$$M_s = \frac{\rho v_m}{W}(\theta+\alpha) + \frac{\rho V}{W}\phi \qquad (63)$$

and

$$M_d = \frac{\rho v_m}{W}(\theta+\alpha) + \frac{\rho V}{W}\theta rh_{max} \qquad (64)$$

where

M_s = moisture content in sorption process, dry basis

M_d = moisture content in desorption process, dry basis

W = mass of dry material

Discussion

There are three unknown quantities which are needed in order to use equations (63) and (64). They are: (1) the heat of adsorption of the first layer of moisture, (2) the volume of moisture in a complete unimolecular layer on the surface, and (3) the volume of moisture which may be absorbed by the cells. The latter two quantities should be essentially independent of temperature. However, the heat of adsorption would probably vary and its variation with temperature is needed.

There is no accurate means for determining the heat of adsorption of the first layer of molecules since any measurements, direct or indirect, would be an average of all the moisture absorbed during the time the measurement was made.

A method for determining the heat of adsorption which has been commonly used is the Othmer method (Othmer, 1940). Thompson and Shedd (1954) used this method to determine the heat of vaporization of shelled corn and wheat at various moisture contents. The heat of adsorption which is needed in this case is equal to the heat of vaporization of the biological material at zero moisture content. This cannot be determined from the Othmer method. Also, the assumptions, upon which the use of the Othmer method for biological materials is based, are not compatible with the assumptions made in this analysis. Therefore, the heat of adsorption must be evaluated from the experimental data by statistically fitting the data to the derived equations.

The other two unknown quantities are physical properties of the biological material. However, it is not possible to measure them by known techniques. Therefore, they also must be determined from the fit of the experimental data to the derived equations.

In order to determine the overall effect of a change in temperature, it is necessary to know how three other quantities vary with the temperature. They are:

1. ρ - density of water in mass per unit volume
2. q_1 - heat of adsorption of the bound layer of moisture, cal molecule^{-1}
3. q_L - normal heat of condensation of water vapor, cal molecule^{-1}

The variation of ρ and q_L may be found in the literature. Although q_1 is unknown, it would be expected to decrease with an increase in temperature. Also, the difference $(q_1 - q_L)$ would be expected to decrease with an increase in temperature. An increase in temperature then would result in a smaller value of the exponential term, E.

Therefore some indication of the effect of a change in temperature may be obtained by plotting $(\theta+\alpha)$, which is directly proportional to the amount of adsorbed moisture, versus relative humidity for several values of E. Figure 5 shows such a plot for E values of 0.0, 0.1, and 1.0. These values were chosen to show the two extremes and an intermediate curve. E values of 0.0 correspond to either an infinitely large value of the heat of adsorption of the bound layer or an infinitely small value of temperature. In this case, the limiting values of equations (52) and (57) are:

$$\theta = \frac{rh}{rh} = 1.0 \tag{65}$$

and

$$\alpha = -\ln(1 - rh) \tag{66}$$

An E value of 1.0 corresponds to equal values of q_1 and q_L or an infinitely large value of temperature. In this case, the limiting values of equations (52) and (57) are:

$$\theta = rh \tag{67}$$

and

$$\alpha = -2\left[rh + \ln(1 - rh)\right] \tag{68}$$

Thus, Figure 5 indicates that an increase in temperature at low relative humidities results in a decrease in moisture adsorbed while at high relative humidities it results

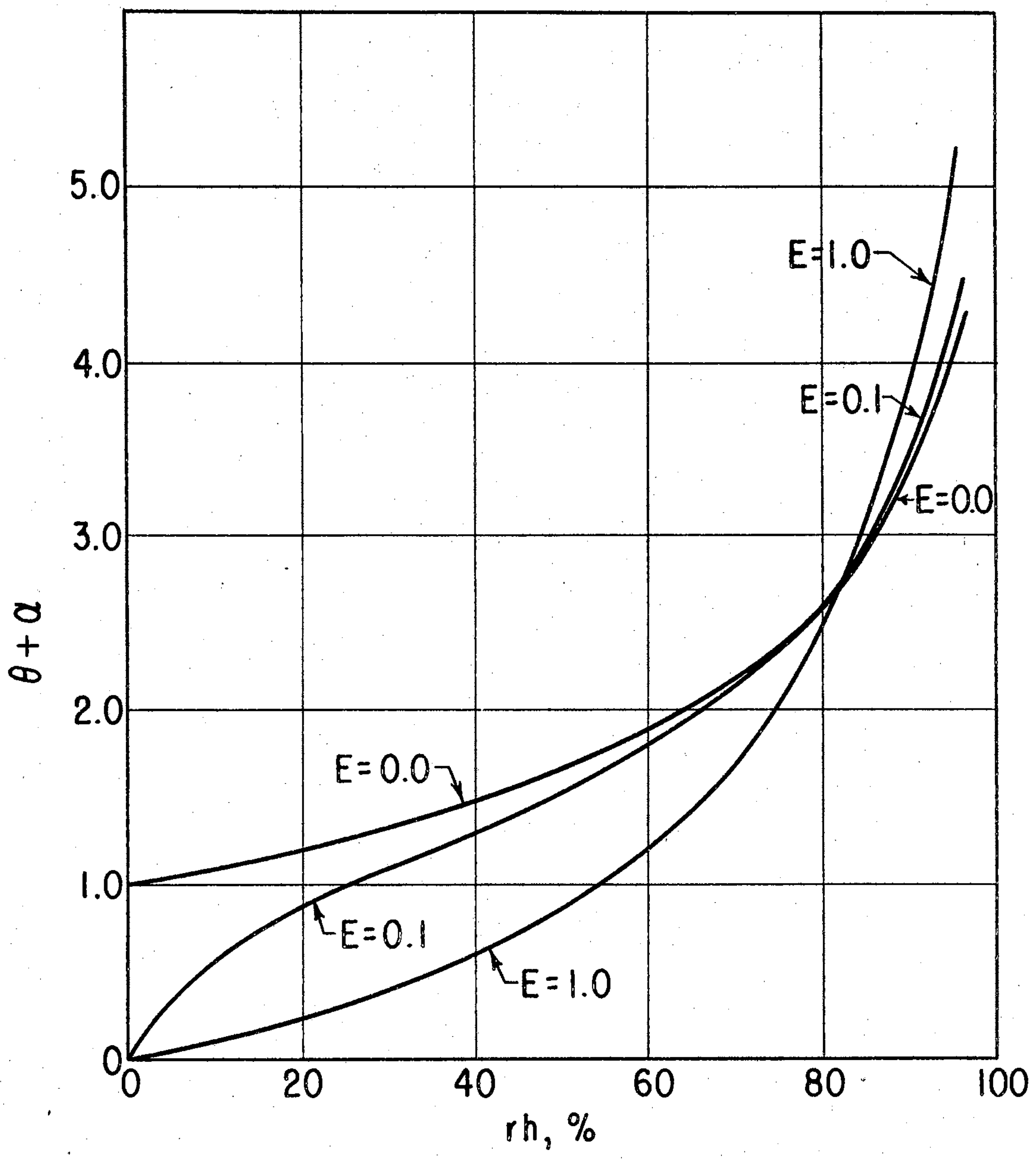

Figure 5. Plot of ($\theta + \alpha$) Versus Relative Humidity for E Values of 0.0, 0.1, and 1.0

in an increase in moisture adsorbed. This is an unprecedented prediction and experimental data will be carefully observed to see if this phenomena actually takes place.

CHAPTER VI

EXPERIMENTAL DESIGN AND PROCEDURE

Experimental Design

In order to determine whether the derived equations describe the equilibrium moisture content curves of wheat, four series of tests were planned.

Series 1

Objectives: To obtain data which could be used for evaluating the unknown parameters in the theoretically obtained equations for a constant temperature environment.

Procedure: Equilibrium moisture content data were obtained for samples initially at three different moisture conditions when subjected to a range of relative humidities at 10°C.

Environmental Conditions: The following table gives the initial and final environmental relative humidities desired in the tests.

TABLE I

ENVIRONMENTAL CONDITIONS DESIRED FOR SERIES I

Initial Condition \ Final Condition	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%
Oven Dry	X	X	X	X	X	X	X	X	X	X
80% Rh*	X	X	X	X	X	X	X			
Saturated	X	X	X	X	X	X	X	X	X	X

X - Indicates this combination of initial and final condition was to be tested.

* - Indicates grain samples were initially in equilibrium with an 80 per cent relative humidity environment.

Series 2

Objectives: To determine the effect of initial equilibrium relative humidity on the equilibrium moisture content obtained when the samples were subjected to a constant drying environment.

Procedure: Initially oven dry samples were subjected to various humidities between 50 and 90 per cent relative humidity and after reaching an equilibrium with that environment were placed in a drying environment at 10 per cent relative humidity. A temperature of 20°C was maintained during these tests.

Environmental Conditions: The relative humidities desired for the sorption portion of the tests were 50, 60, 70, 80, and 90 per cent while the relative humidity desired for the desorption portion of the tests was 10 per cent.

Series 3

Objective: To obtain data for use in conjunction with the data of Series 1, 2, and 4 to determine the effect of a shift in temperature on the equilibrium moisture content curve.

Procedure: Initially dry samples were subjected to environments ranging from 50 to 90 per cent relative humidity at 30°C.

Environmental Conditions: The relative humidities desired were 50, 60, 70, 80, and 90 per cent.

Series 4

Objective: To provide further data for determining the effect of temperature on the equilibrium moisture content curve.

Procedure: Initially dry samples were subjected to environments ranging from 50 to 90 per cent relative humidity at 40°C.

Environmental Conditions: The relative humidities desired were 50, 60, 70, 80, and 90 per cent.

It may be noted that in the outline of each of the four series of tests the "desired" relative humidities were listed. The word "desired" is included because these were not actually maintained in the tests but humidities were maintained as close to these as possible with the procedure which was chosen for humidity control. This procedure will be discussed further in the section of this chapter dealing with control of relative humidity.

Equipment Used

Temperature control

The temperature was controlled within an insulated cubic chamber (Figure 6) with inside dimensions of 6 feet by 6 feet by 6 feet. An air conditioner (Figure 7) and electrical resistance heating coils were used in conjunction with a dual action thermostat to control the temperature with a differential of approximately plus or minus one degree Centigrade. A five-minute time delay circuit was used to protect the compressor of the air conditioner against starting under a load. This circuit (Figure 8) made it impossible for the compressor to restart during the first five minutes after it had been turned off.

Relative humidity control

The relative humidity was controlled by saturated salt solutions within small plexiglass chambers (Figure

Figure 6. Temperature Control Chamber

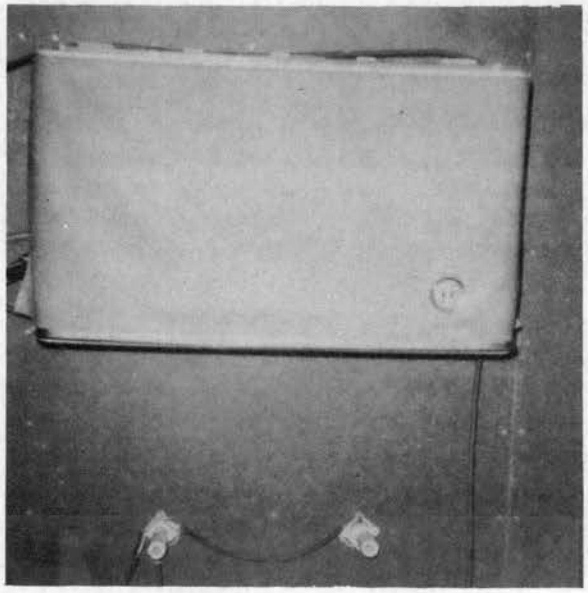

Figure 7. Air Conditioner and Heating Coils

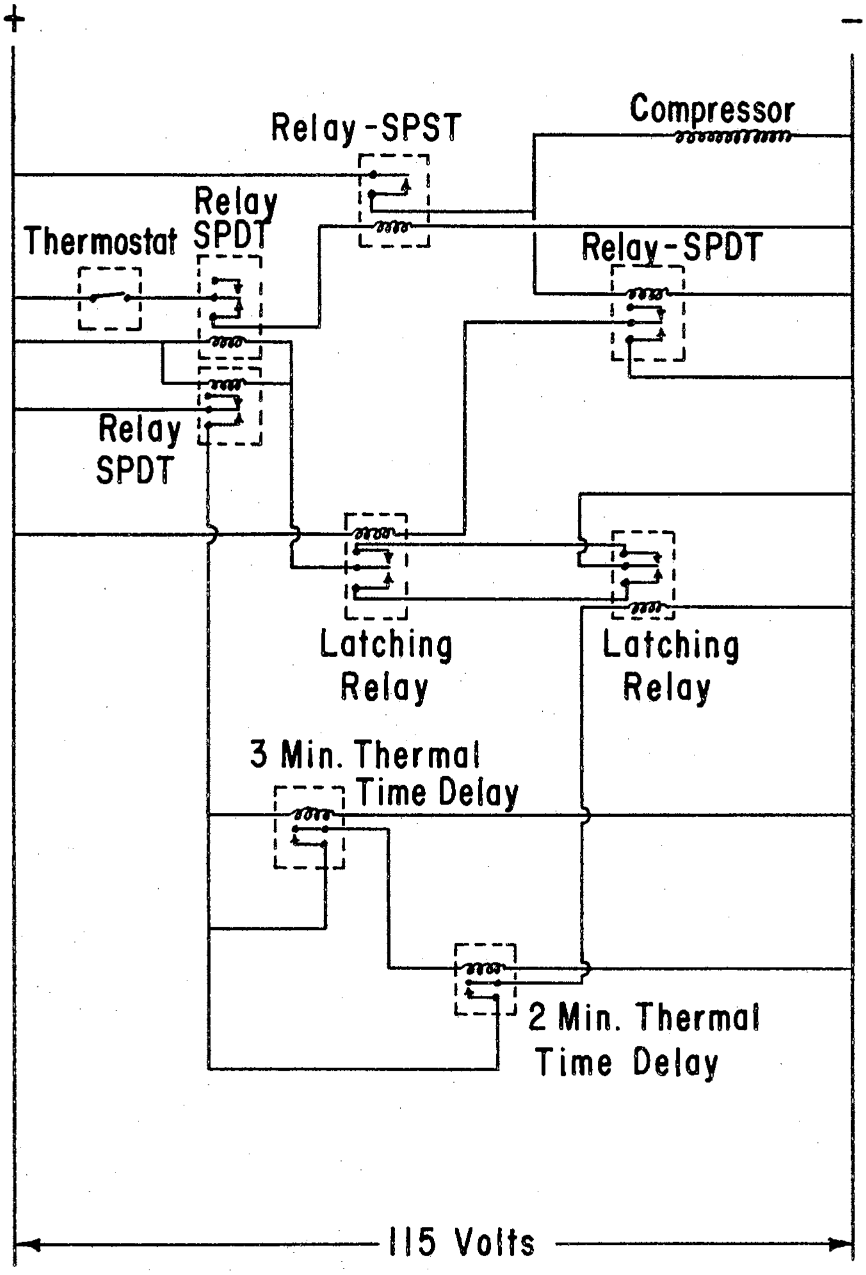

Figure 8. Time Delay Circuit Used for Protection of Compressor of Air Conditioner

9) located within the larger chamber. Five of these chambers were used so that five different relative humidities were available at the same time. The salts used for controlling the humidity were chosen to give humidities corresponding as closely as possible to those given in the test outlines. The data given by Hall (1957) (pages 33-34) was used in the selection of the salts. In some cases it was necessary to interpolate the given data to obtain the relative humidity maintained by a given salt at the temperature desired. Each of the small chambers was equipped with a small electric fan to keep the air from becoming stratified. The samples were placed in the chambers in small wire containers which were suspended from rubber stoppers in the top of the chambers.

The humidity within the chambers was measured by obtaining wet bulb and dry bulb temperatures with a sling psychrometer. The air flow from the fans within the chambers was utilized for obtaining the wet bulb depression. This eliminated the need for "slinging" the psychrometer within the chambers. However, the relative humidity readings obtained in this manner were higher than those expected. This was believed due to insufficient air flow over the wet bulb

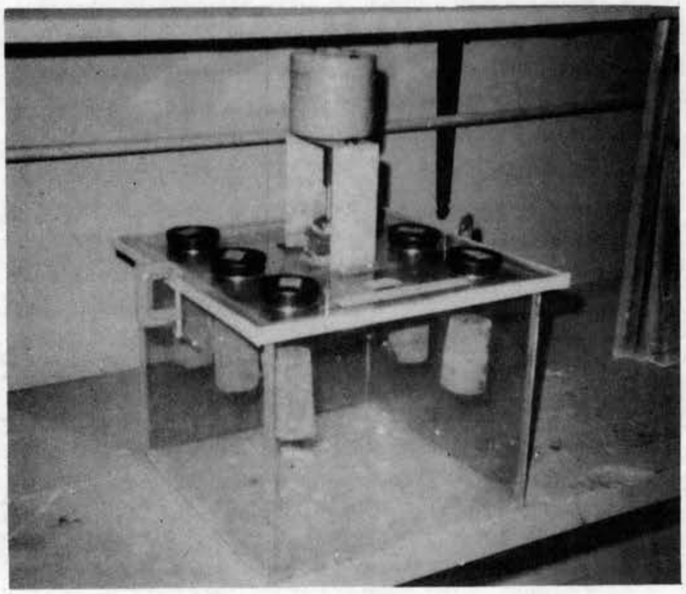

Figure 9. Relative Humidity Control Chamber.

thermometer. Therefore, a calibration of the psychrometer readings versus the expected readings was made. This assumed that the values obtained from the literature for the relative humidities maintained were, on the average, correct. However, in some cases, these values were definitely in error and in others slight variations were suspected. These variations could be due either to impurities in the salt solutions or to inaccuracies in previous determinations of the relative humidities maintained by various salt solutions.

Figure 10 is a plot of the expected relative humidities versus the measured relative humidities and shows that an approximately linear relationship was found between them. The slope and intercept of the line was found by minimizing the sum of the squares of the deviations between the expected relative humidities and the calibrated relative humidities. The result was:

$$Y = -9.751 + 1.059\ X \qquad (69)$$

where

Y = calibrated relative humidity, per cent

X = measured relative humidity, per cent

The coefficient of correlation between the expected

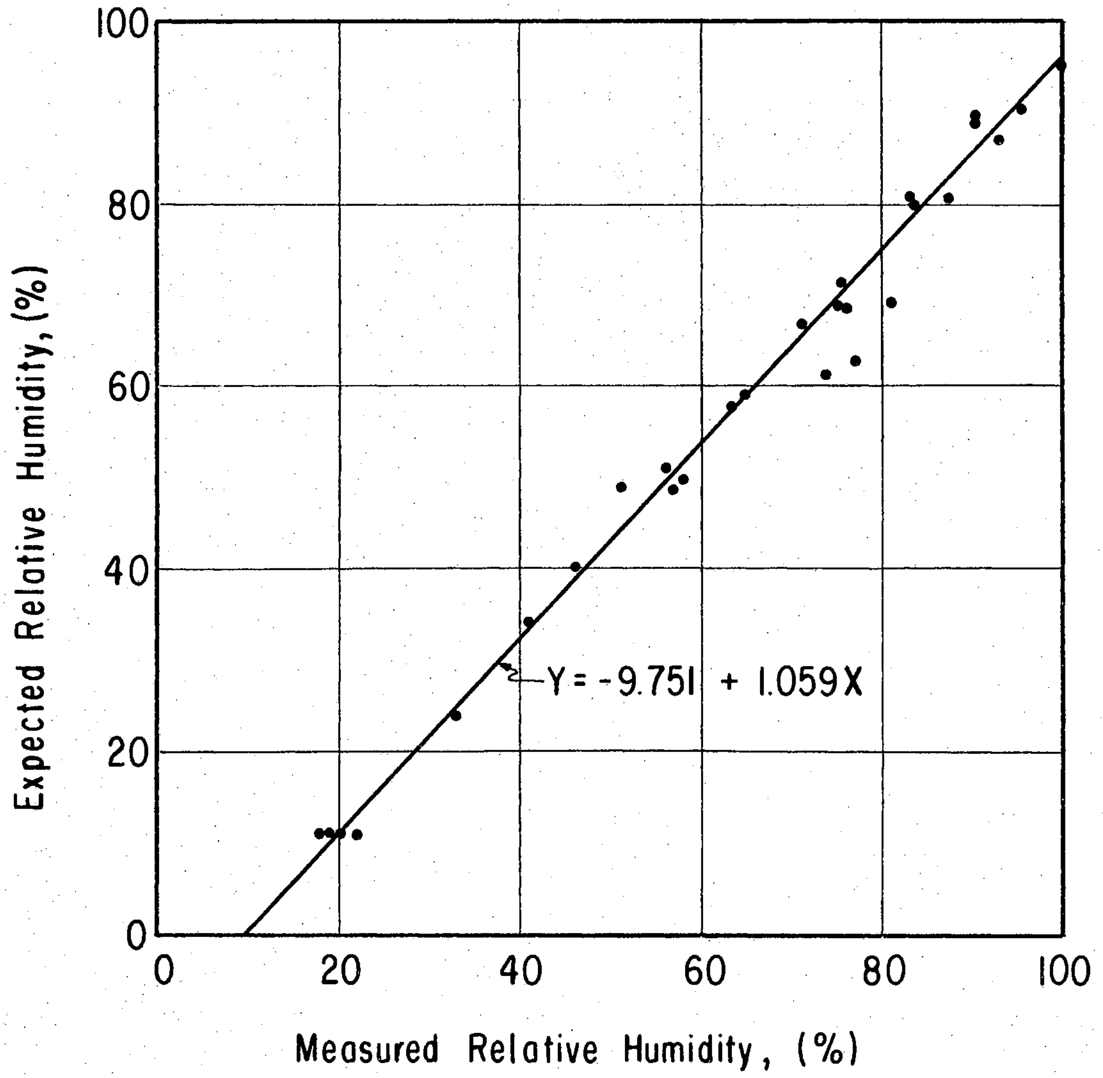

Figure 10. Plot of Expected Versus Measured Relative Humidities

values and the calibrated values computed by equation (69) was 0.99. Figure 11 is a plot of the calibrated relative humidity values versus the expected values.

The original plan was to use the relative humidity values expected from the data given for the various salt solutions in all calculations. However, due to the apparent variation between expected and actual values in some cases, the decision was made to use the calibrated values. This procedure gave values which were of the same order of magnitude as the expected relative humidities but which were shifted slightly up or down by using the calibration curve to put all humidity values on a common basis. It was believed that the magnitude of the values measured with the psychrometer were too high, but that they were proportional to the actual values maintained. Thus using these values and equation (69) gave a common reference by which the humidities maintained by the different solutions could be compared. Table 2 gives the salt solutions used in the tests, the expected relative humidities, and the calibrated relative humidities.

It is acknowledged that there is still some uncertainty as to the actual values of the relative humidities maintained. However, the use of the

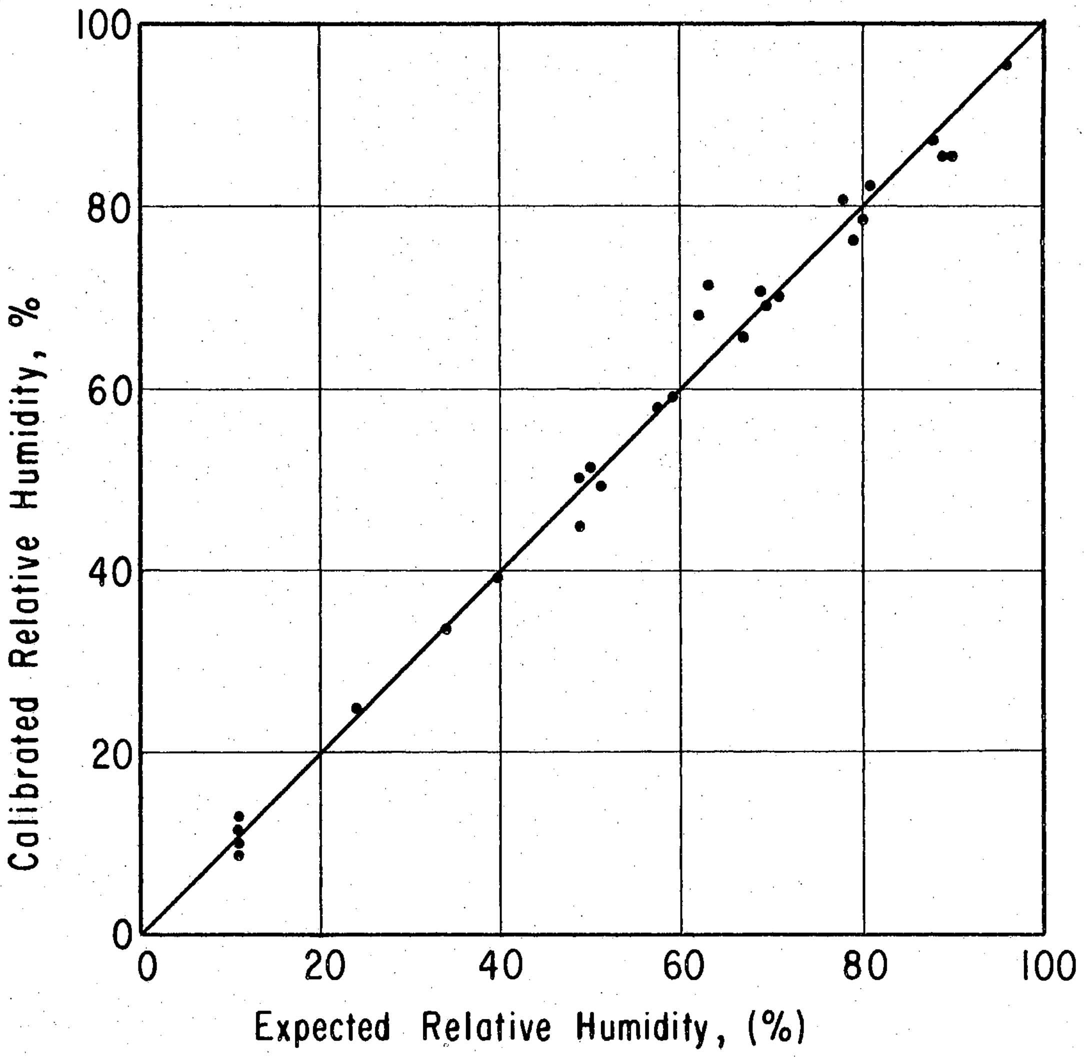

Figure 11. Plot of Calibrated Versus Expected Relative Humidities

TABLE II

SALT SOLUTIONS USED AND RELATIVE HUMIDITIES MAINTAINED

Salt	Expected RH(%)*	Calibrated RH(%)**
	10°C	
LiCl(Lithium Chloride)	11.2	11.4
$KC_2H_3O_2$(Potassium Acetate)	24.0	25.2
$MgCl_2$ $6H_2$)(Magnesium Chloride)	34.2	33.7
$CaCl_2$(Calcium Chloride)	40.0	39.0
KNO_2(Potassium Nitrite)	50.0	51.7
$NaCr_2O_7$ $2H_2O$(Sodium Dichromate)	57.9	57.5
$CuCl_2$ $2H_2O$(Cupric Chloride)	69.0	69.7
NH_4Cl(Ammonium Chloride)	81.0	78.2
K_2CrO_4(Potassium Chromate)	87.0	88.2
KNO_3(Potassium Nitrate)	95.5	96.2
	20°C	
LiCl(Lithium Chloride)	11.2	11.4
KNO_2(Potassium Nitrite)	49.0	50.6
NaBr(Sodium Bromide)	59.2	59.1
$CuCl_2$ $2H_2O$(Cupric Chloride)	68.7	70.8
$(NH_4)_2SO_4$(Ammonium Sulfate)	80.6	82.4
KCl(Potassium Chloride)	89.2	85.6

TABLE II (Continued)

Salt	Expected RH(%)*	Calibrated RH(%)**
30°C		
$Mg(NO_3)_2$(Magnesium Nitrate)	51.4	49.6
$NaNO_3$(Sodium Nitrate)***	63.3	71.8
$Na\ C_2\ H_3O_2\ 3H_2O$(Sodium Acetate)	71.3	70.2
$(NH_4)_2SO_4$(Ammonium Sulfate)	80.0	78.7
KNO_3(Potassium Nitrate)	90.7	90.9
40°C		
$Mg(NO_3)_2$(Magnesium Nitrate)	49.0	44.8
$NaNO_3$(Sodium Nitrate)***	61.8	68.1
$CuCl_2\ 2H_2O$(Cupric Chloride)	67.4	66.0
$(NH_4)_2SO_4$(Ammonium Sulfate)	79.6	76.1
$BaCl_2\ 2H_2O$(Barium Chloride)	89.7	85.6

---

*Expected RH values are those obtained from the table given by Hall(1957).

**Calibrated RH values are those computed from the psychrometer readings using equation (69).

***Salt solution which definitely did not maintain the expected relative humidity. Upon checking the paper by Wink and Sears (1950), it was found that sodium nitrite should have been used rather than sodium nitrate as is mistakenly given by Hall.

calibrated relative humidities resulted in reasonably smooth equilibrium moisture curves and values comparable with those found by other investigators. Also, it may be noted that the use of the calibrated relative humidities gave values for the parameters in the theoretical equations which were very similar to those obtained by using the expected relative humidities. However, there was a better correlation between the theoretical and experimental curves when the calibrated relative humidities were used.

Weighing of samples

An analytical balance (Figure 12) was used for weighing the samples. This balance had an accuracy of 0.0005 grams and a capacity of 160.0 grams. The balance was electrically operated and readings could be obtained in approximately 45 seconds. This was important since the sample had to be removed from its environmental chamber for only short periods of time.

Drying of samples

Samples were dried in a forced convection oven (Figure 13) in which a temperature of 100 ± 0.25°C was maintained. The samples were dried in the oven for a period of fourteen days. This extended drying period was chosen after some preliminary drying tests

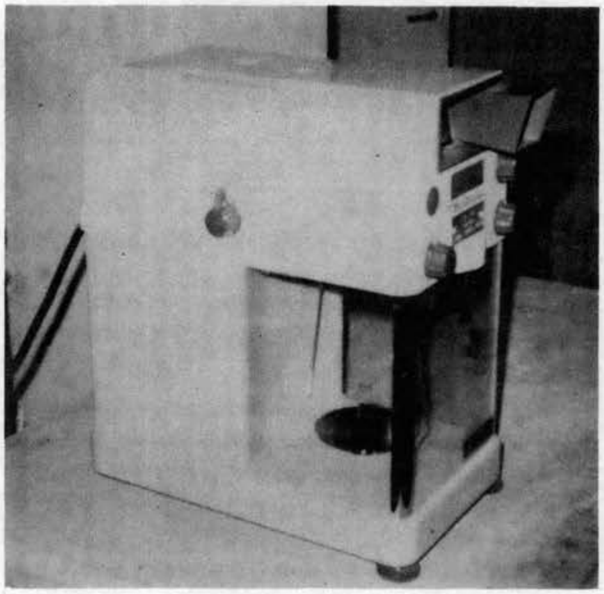

Figure 12. Analytical Balance

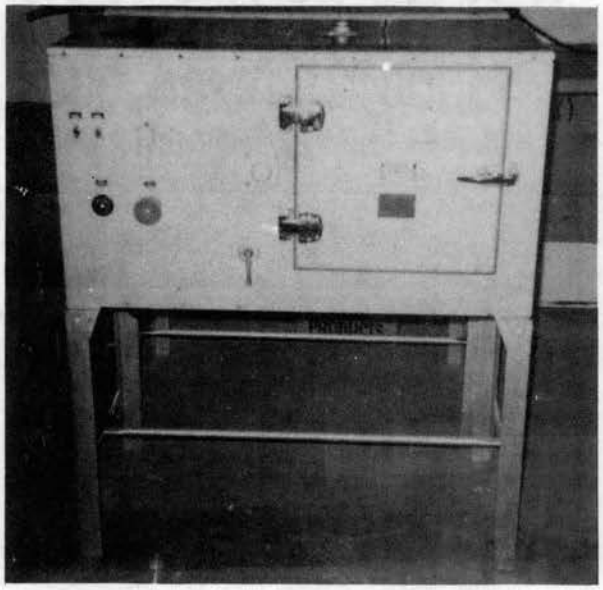

Figure 13. Forced Convection Oven

indicated that this length of time was required for the samples to reach a steady weight. Since air was drawn in from the surrounding environment, there were still some weight variations from day to day due to changes in humidity of the outside environment. These changes were small, however, compared with the total weight of the material. The lowest weight obtained during the fourteen-day drying period was used as the dry weight of the sample.

It is acknowledged that this extended drying period darkened the grain somewhat and may have changed its hygroscopic properties. However, the resulting material was still a biological material and thus was quite suitable for testing the applicability of the theoretical equations. The equilibrium moisture contents may have been somewhat different, though, from grain which had not been subjected to this extended drying period.

Experimental Procedure

Preparation of Samples

"Concho" wheat from the 1964 crop supplied by the Oklahoma State University Agronomy Department was used as the sample material. It was treated with a fungicide, "Arasan 75," to reduce molding at higher relative humidities. Each sample consisted of five subsamples of approximately 50 grams initial weight. These subsamples were tested along with one empty wire basket. This was to obtain an indication of how much moisture was picked up or lost by the baskets themselves. In most cases this was found to be insignificant and therefore no corrections for changes in basket weight were used in the analysis of the data.

After treatment with the fungicide, all samples were dried in the oven for a period of fourteen days to obtain their oven dry weight. This gave a common starting point for all samples.

Saturation of samples

The samples which were to be initially saturated for desorption tests were saturated by immersion in distilled water for a period of 24 hours. This method was chosen over subjection to a 100% relative humidity environment because of the time required by the latter technique. Also, molding occurred before equilibrium was reached when the latter method was tried.

The immersion technique created one problem for which a correction had to be made. The samples were found to actually lose some of their dry matter to the water during the immersion period. This was probably due to a washing effect. However, it is possible that there could have been some leaching of the kernel constituents. Therefore, additional experiments were conducted to determine how much weight was lost in the process. Samples were dried in the oven, then immersed and then dried again to determine the decrease in dry weight. Any additional losses due to the second drying period were neglected since drying periods of 28 days or longer showed no appreciable decrease in weight over the weight obtained after a fourteen-day drying period. The average loss of weight was found to be approximately one per cent of the initial dry weight. Thus this correction was used in determining the equilibrium moisture contents for the samples subjected to a drying environment after being saturated.

Equilibrium moisture content determination

In order to determine the equilibrium moisture content at various relative humidities, the samples were placed in the small environmental chambers where the desired relative humidities were maintained. They were then weighed each day until their change in weight during the past day was less than 0.01 grams. The weight at this time was used for calculating the equilibrium moisture content. Since the dry weight of the grain in each basket was in the range of forty to fifty grams, the 0.01 gram change per day represented a maximum change in moisture content of 0.025 per cent.

CHAPTER VII

ANALYSIS OF DATA

Series 1

The data of Series 1 were fitted to the theoretically derived equations by a combination of an iteration and a multiple regression technique. Values of the exponential term,

$$E = \exp\left[-(q_1 - q_L)/kT\right]$$

were assumed and values of θ, ϕ, and α were calculated by equations (52), (53), and (57) respectively. Then equations (63) and (64) were written as,

$$M_S = A(\theta + \alpha) + B\phi \qquad (70)$$

and

$$M_d = A(\theta + \alpha) + B\theta r h_{max} \qquad (71)$$

where

$$A = \frac{\rho V_m}{W} \qquad (72)$$

$$B = \frac{\rho V}{W} \qquad (73)$$

Then using a multiple regression technique, the values of A and B were found which minimized the sum of the squares of the deviations between the computed and experimentally observed values of the equilibrium moisture content for each assumed value of E. Thus by assuming various values of E in an iteration process, unique values of A, B, and E which minimized the error sum of squares were obtained for the experimental data. The values obtained were:

$A = 0.05251$

$B = 0.06688$

$E = 0.1117$

In making these calculations, the sorption data were entered twice so that the sorption and desorption curves would be equally important in evaluating the three unknown parameters.

Figure 14 shows a plot of equations (70) and (71) with the calculated values of A, B, and E. The experimental values of the equilibrium moisture content are also shown. As indicated in Chapter 6, the calibrated relative humidities were used in all calculations and are given as the abscissa in Figure 14.

For comparison, the values of A, B, and E were also computed using the expected values of the relative humidities. The results of these computations

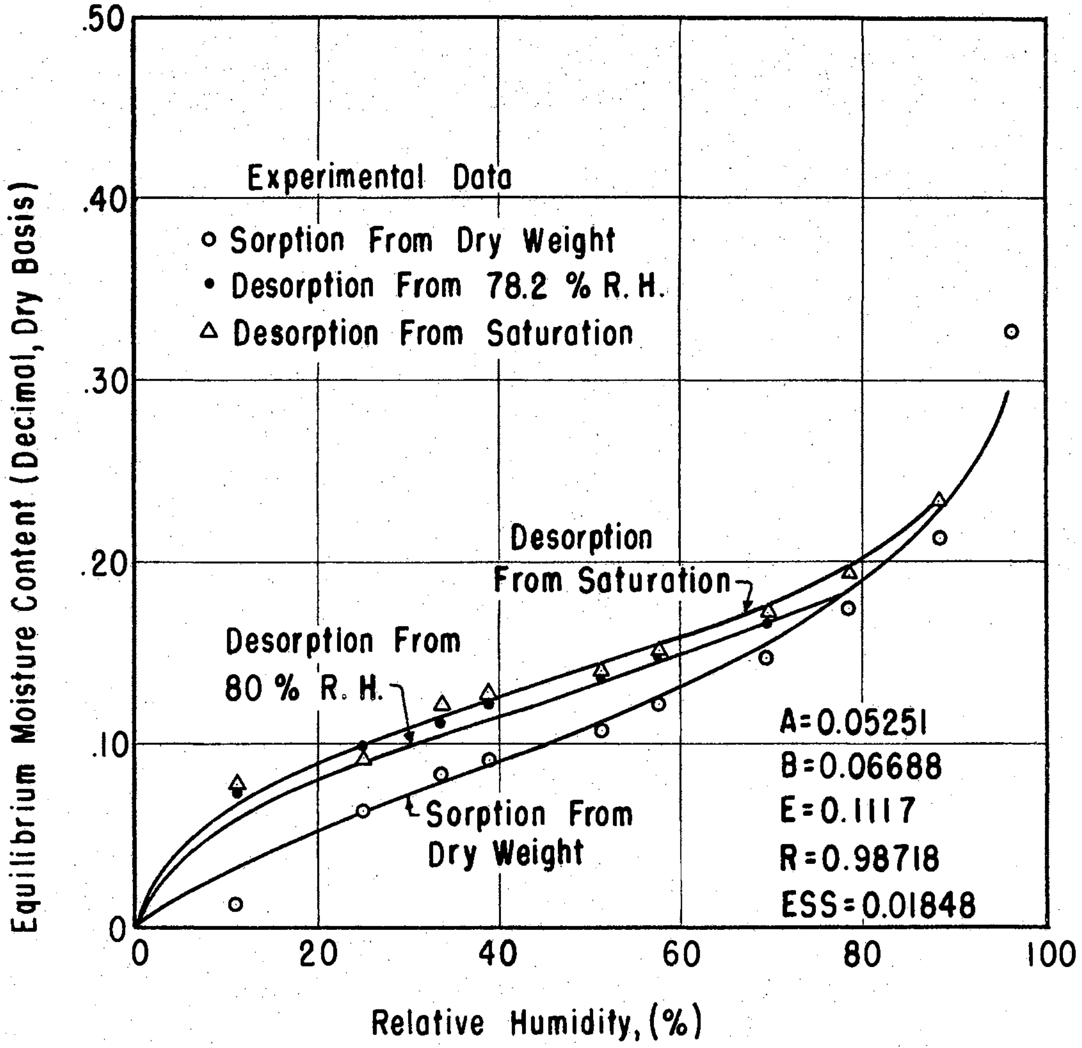

Figure 14. Equilibrium Moisture Content Versus Relative Humidity for Series 1 at 10°C. (Sorption curve computed by equation 70 and desorption curves computed by equation 71 with the given values of A, B, and E)

were:

$A = 0.05387$

$B = 0.06419$

$E = 0.1119$

Thus, the values of the three parameters were not greatly changed but the curves obtained by using the calibrated relative humidities gave a better fit of the experimental data.

The correlation coefficient R was calculated for the computed versus observed values of equilibrium moisture content using the best values of A, B, and E. This correlation coefficient was computed by the approximate formula:

$$R = (1 - ESS/EMS)^{\frac{1}{2}} \qquad (74)$$

where

ESS = The sum of the squares of the deviations of the theoretical values from the observed values.

EMS = The sum of the squares of the deviations of the observed values from their mean.

The value of ESS was found to be 0.01848 and R was found to be 0.98718.

As shown by Figure 14, the equilibrium moisture content obtained during sorption at 11.4% was quite low and did not fit the sigmoidal curve. However, this was believed to be a consequence of the low rate at which moisture was adsorbed at this humidity and temperature. The rate of sorption was so low that the daily weight gain was less than .01 grams long before the equilibrium moisture content was reached. The sorption rate will be further discussed in Appendix B.

Figure 15 is a plot of the bound moisture and the normally condensed moisture versus the relative humidity and Figure 16 shows the absorbed moisture as a function of relative humidity. These were calculated using the best values of A, B, and E from the experimental data.

The sorption data of Series 1 were plotted according to equation (27) in order to determine how well the BET Equation fit the data and to solve for the two unknown parameters. With moisture content of the material substituted for volume of moisture adsorbed, equation (27) becomes,

$$\frac{rh}{M(1-rh)} = \frac{1}{M_m c} + \frac{c-1}{M_m c} rh \qquad (75)$$

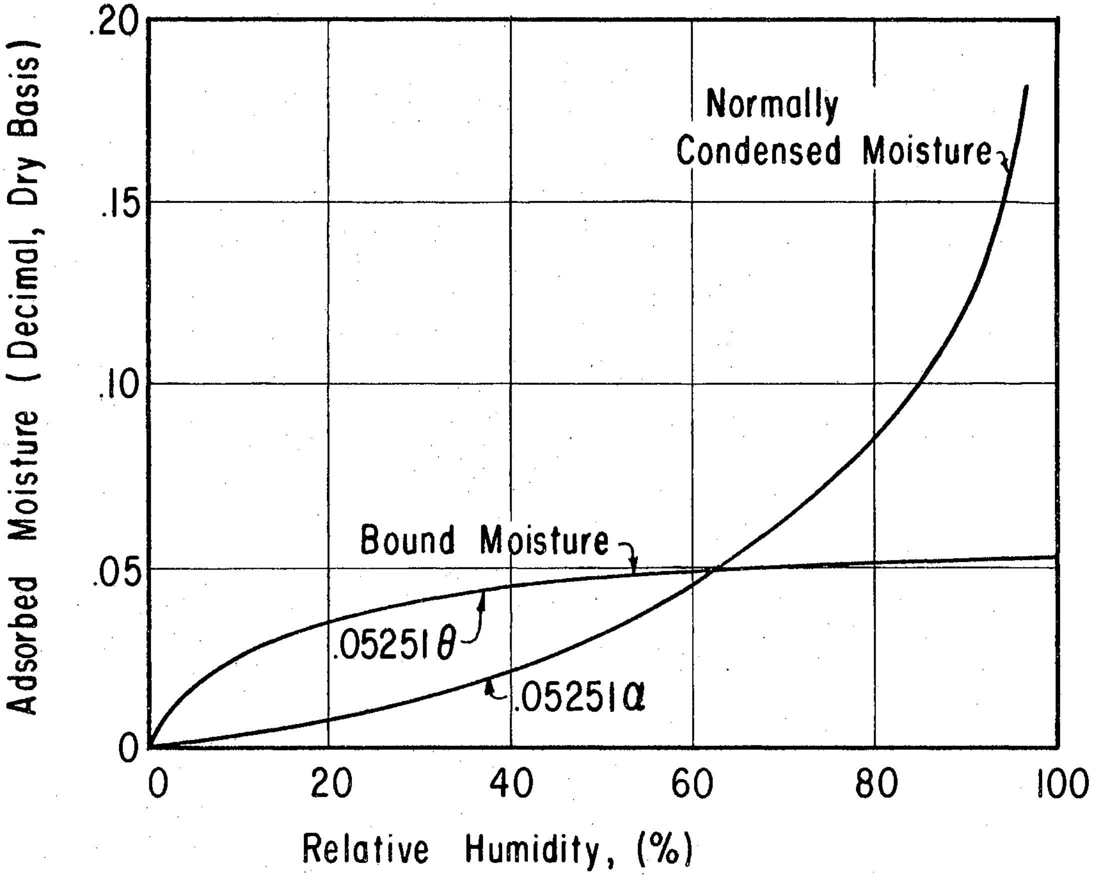

Figure 15. Bound and Normally Condensed Moisture Versus Relative Humidity (Expressed as per cent of dry weight)

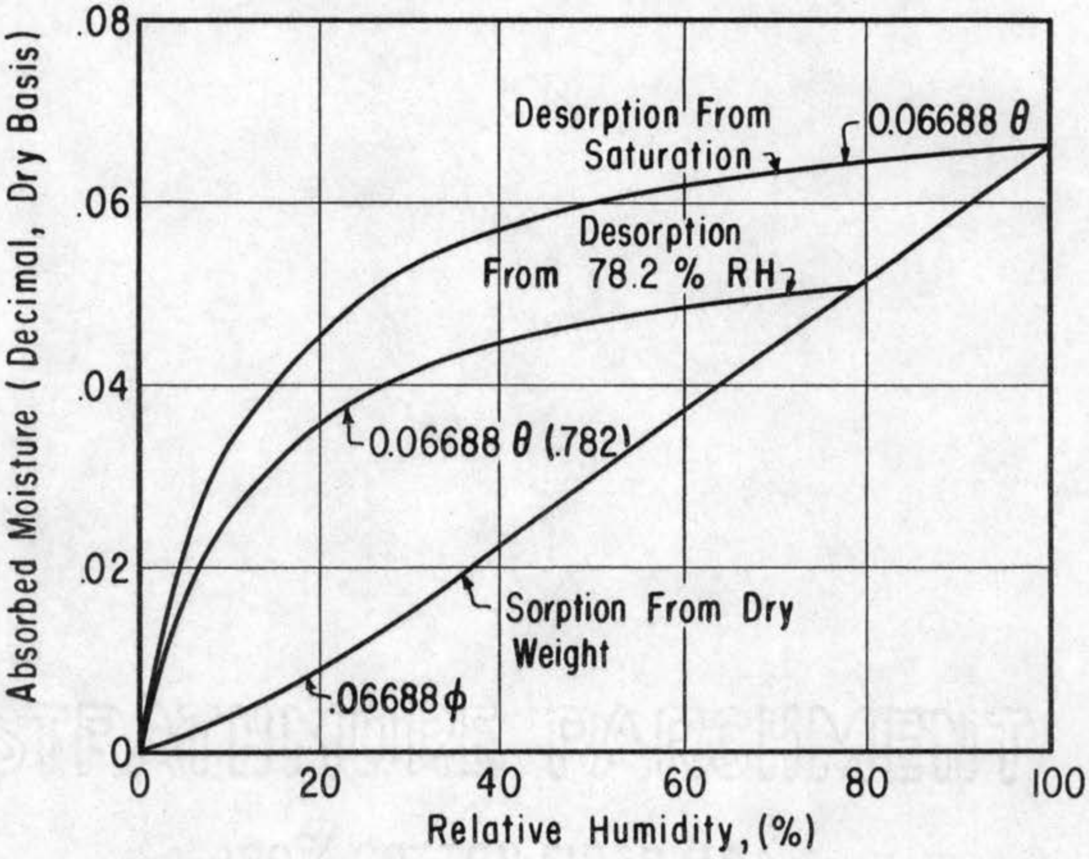

Figure 16. Absorbed Moisture Versus Relative Humidity (Expressed as per cent of dry weight)

where

M = moisture content expressed as a decimal

M_m = moisture content corresponding to one complete layer of moisture

rh = relative humidity, $\frac{p}{p_o}$, expressed as a decimal

Figure 17 shows the plot used to evaluate the two parameters of the equation. As can be observed from the figure, the BET Equation is applicable only at low relative humidities. The constants M_m and c were calculated from the straight line section at low humidities. These values were then used to plot the BET Equation over a range of humidities. Figure 18 shows this plot along with the experimental values of the moisture content. It can be seen that the BET Equation approaches infinity much too rapidly at relative humidities of 50 per cent or greater.

The sorption data were also fitted to the dry basis Smith equation (equation 36). This was done by plotting the moisture content versus -ln(1-rh) and solving for the two unknown parameters from the resulting straight line. This plot is shown in Figure 19 and the resulting equation was,

$$M = 0.04633 - 0.08438 \ln(1-rh) \qquad (76)$$

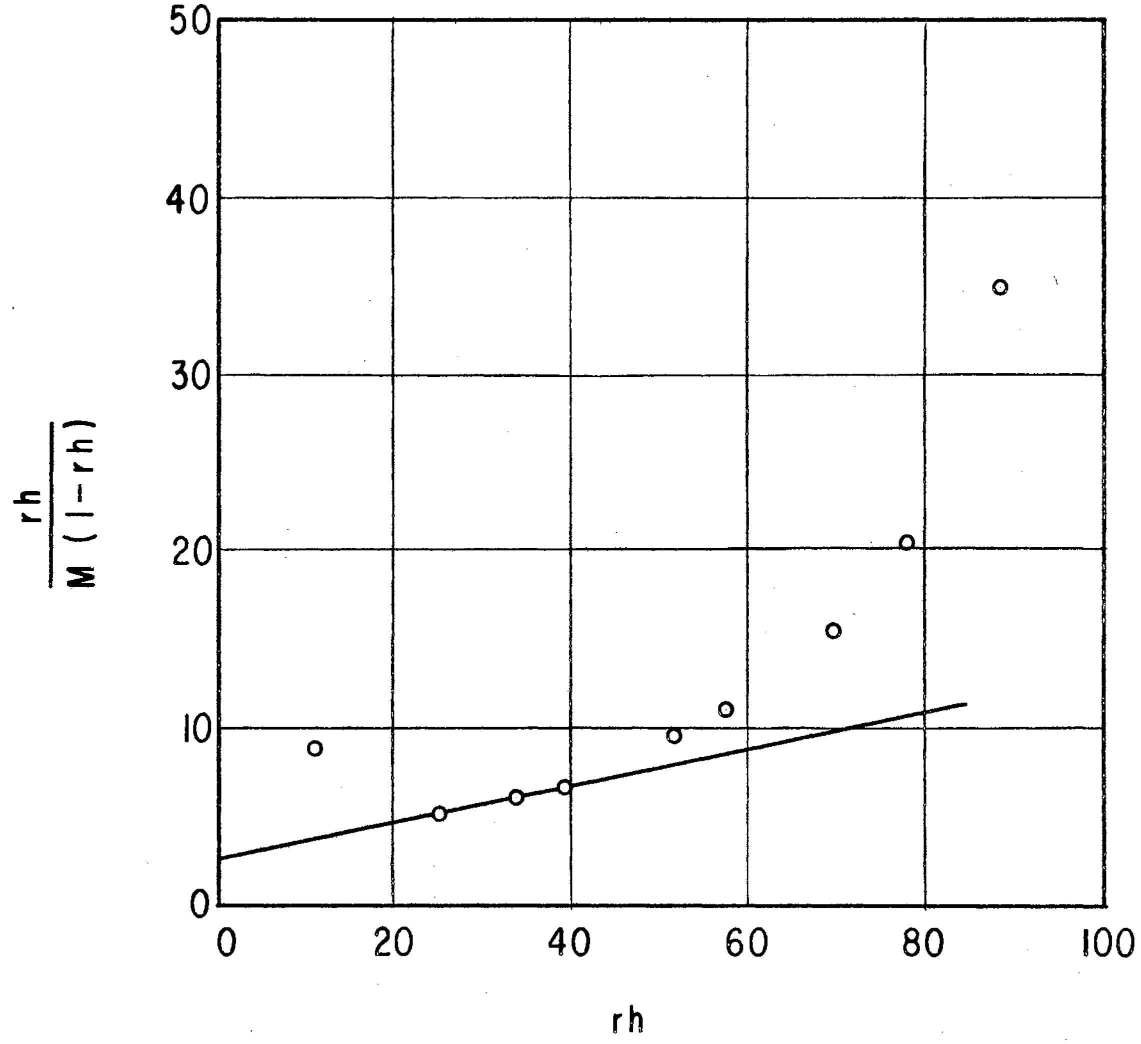

Figure 17. Plot of rh/M(1-rh) Versus rh for Determining Unknown Parameters in the BET Equation

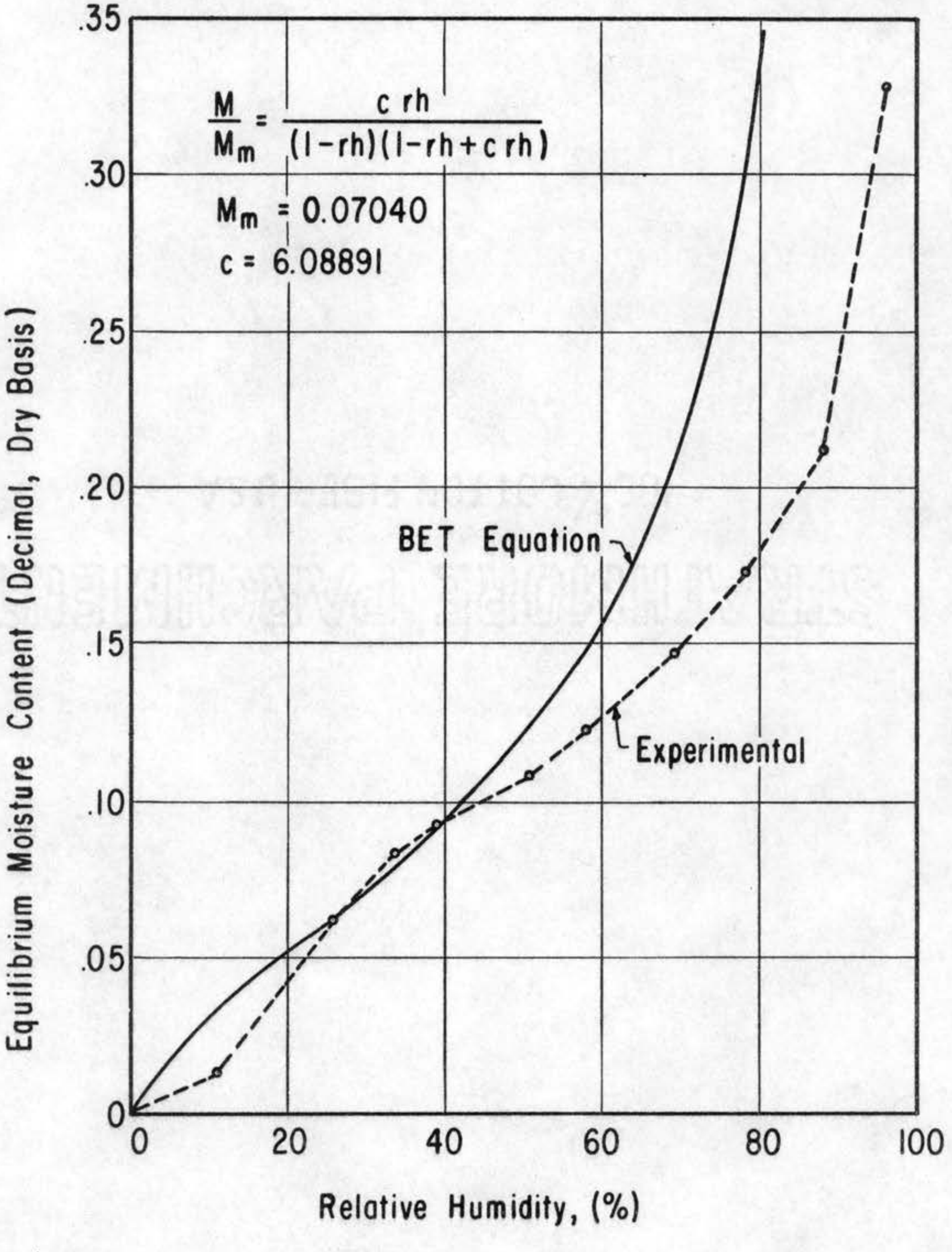

Figure 18. Plot of BET Equation for Sorption Equilibrium Moisture Content (Note: BET Equation does not predict a hysteresis effect)

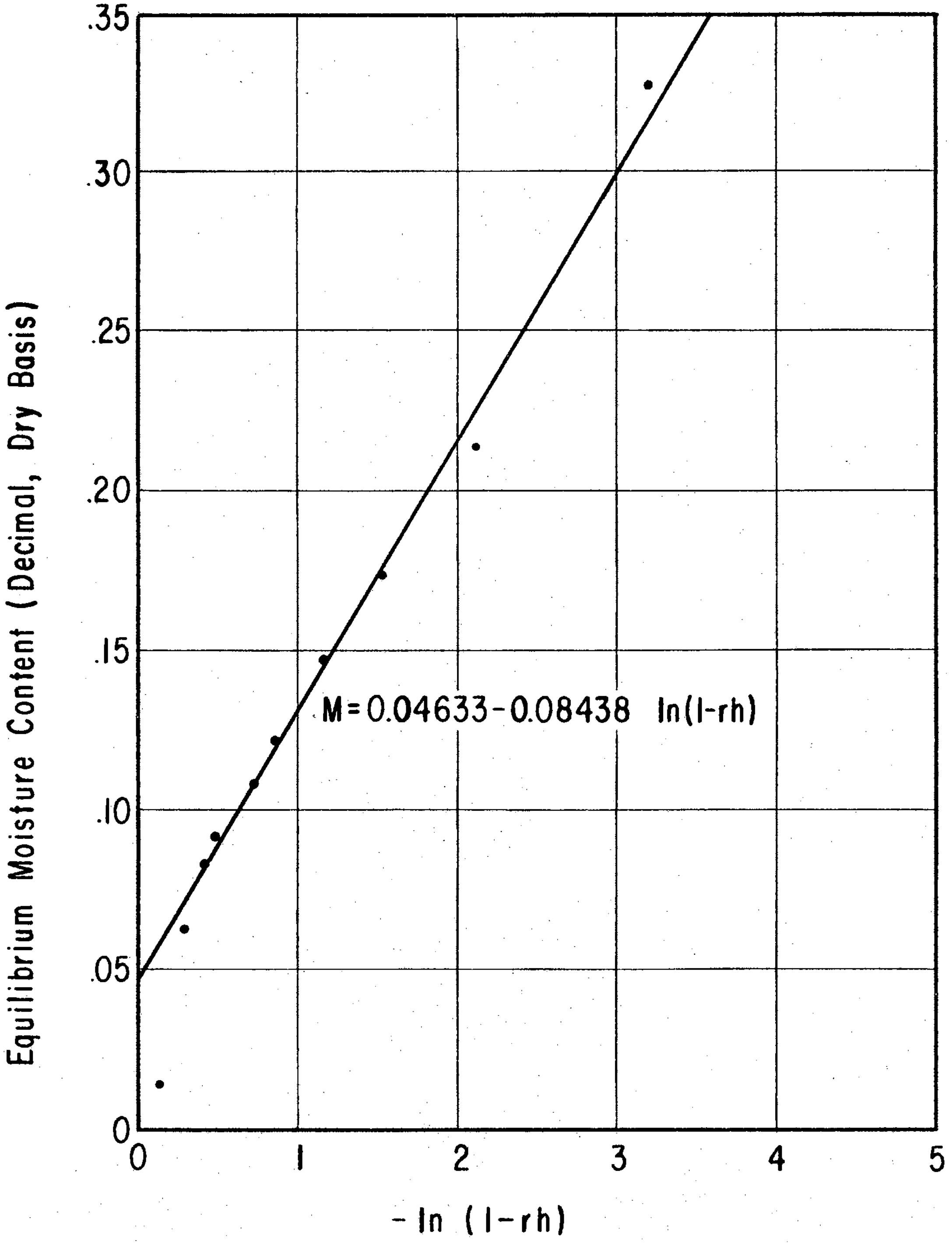

Figure 19. Plot of Equilibrium Moisture Content Versus -ln (1-rh) for Determination of the Unknown Parameters in the Dry Basis Smith Equation

Figure 20 shows the resulting equilibrium moisture content isotherm along with the experimental data. The constants for the wet basis Smith equation (equation 37) were also calculated but the fit of the experimental data was not as good as the dry basis equation.

Figure 21 is a plot of the equilibrium moisture content for sorption using the BET Equation for low humidities, the dry basis Smith equation at high humidities, and a linear segment connecting the two. This was the procedure used by Becker and Sallans (1956) for representing the equilibrium moisture content isotherms.

Finally, the parameters of the Henderson equation (equation 39) were evaluted by plotting $\ln\left[-\ln(1-rh)\right]$ versus log M (Figure 22) and calculating log k and n from the resulting straight line. The equation for the sorption isotherm at 10°C was then found to be,

$$1-rh = \exp(-0.013168\ M^{1.67442}) \qquad (77)$$

This equation is plotted in Figure 23.

Series 2

Series 2 was conducted at a temperature of 20°C. Thus the values of A, B, and E were changed due to

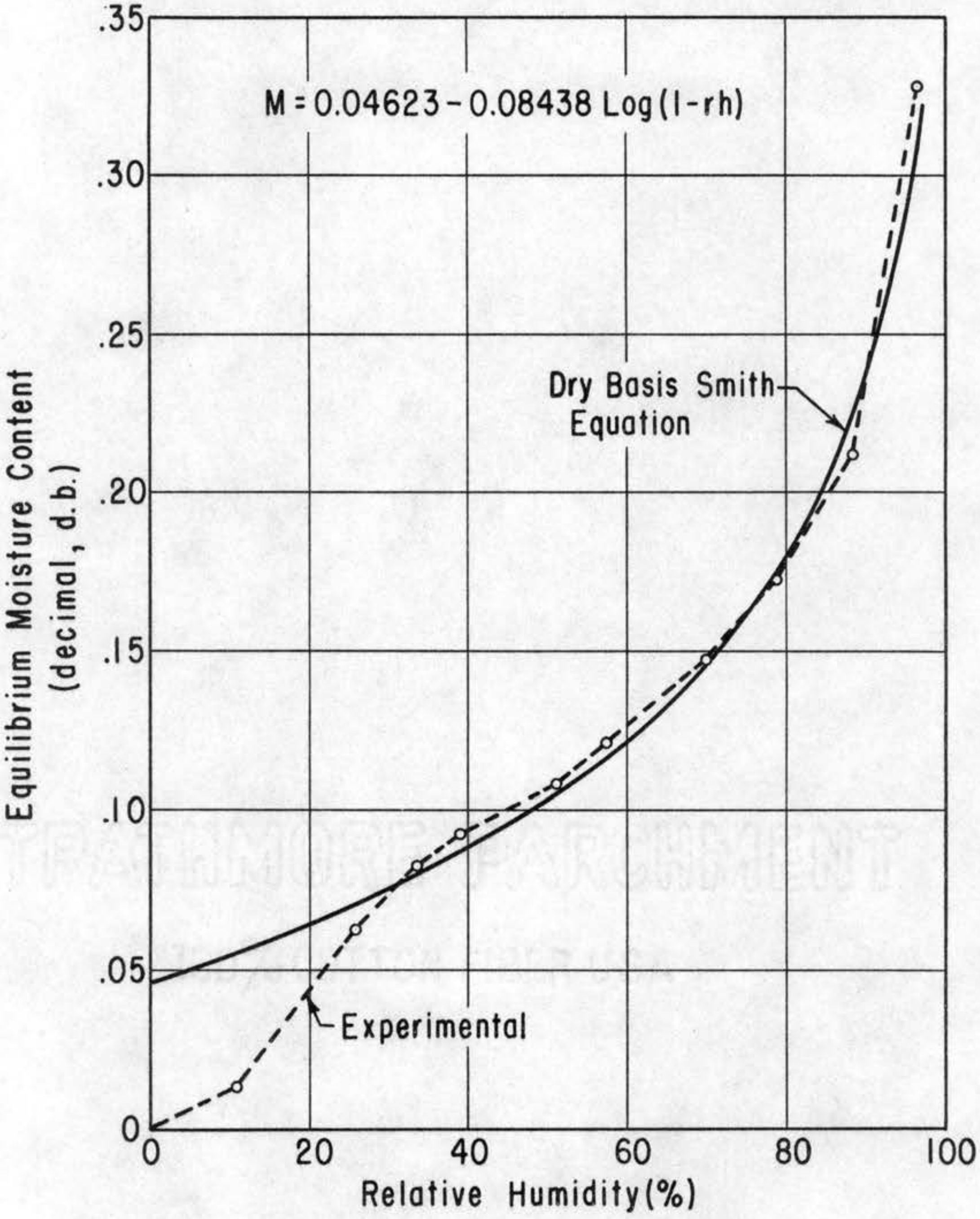

Figure 20. Dry Basis Smith Equation for Equilibrium Moisture Content

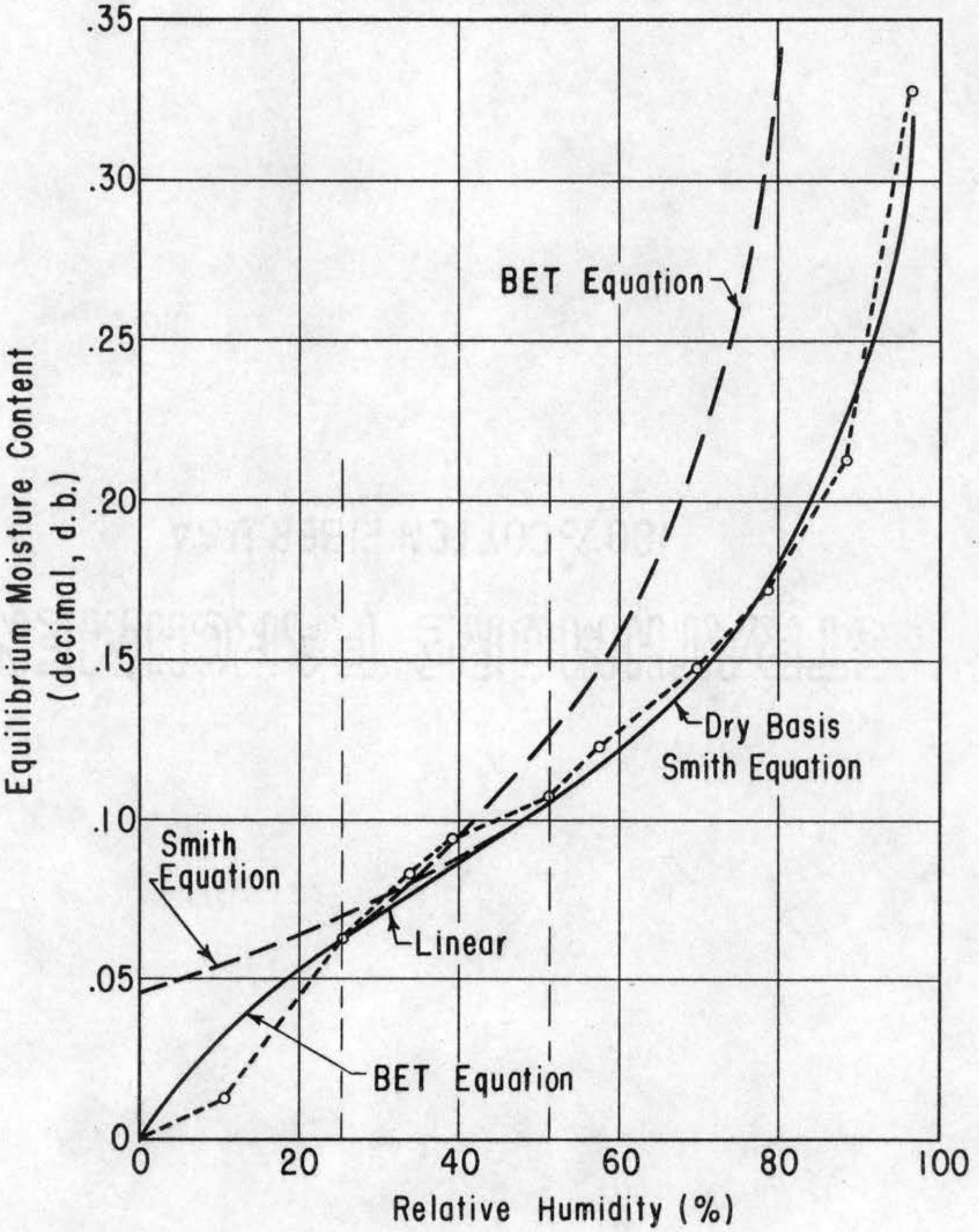

Figure 21. Equilibrium Moisture Content of Sorption Data of Series 1 at 10°C Fitted to the BET and Smith Equations with Straight Line Connecting Section.

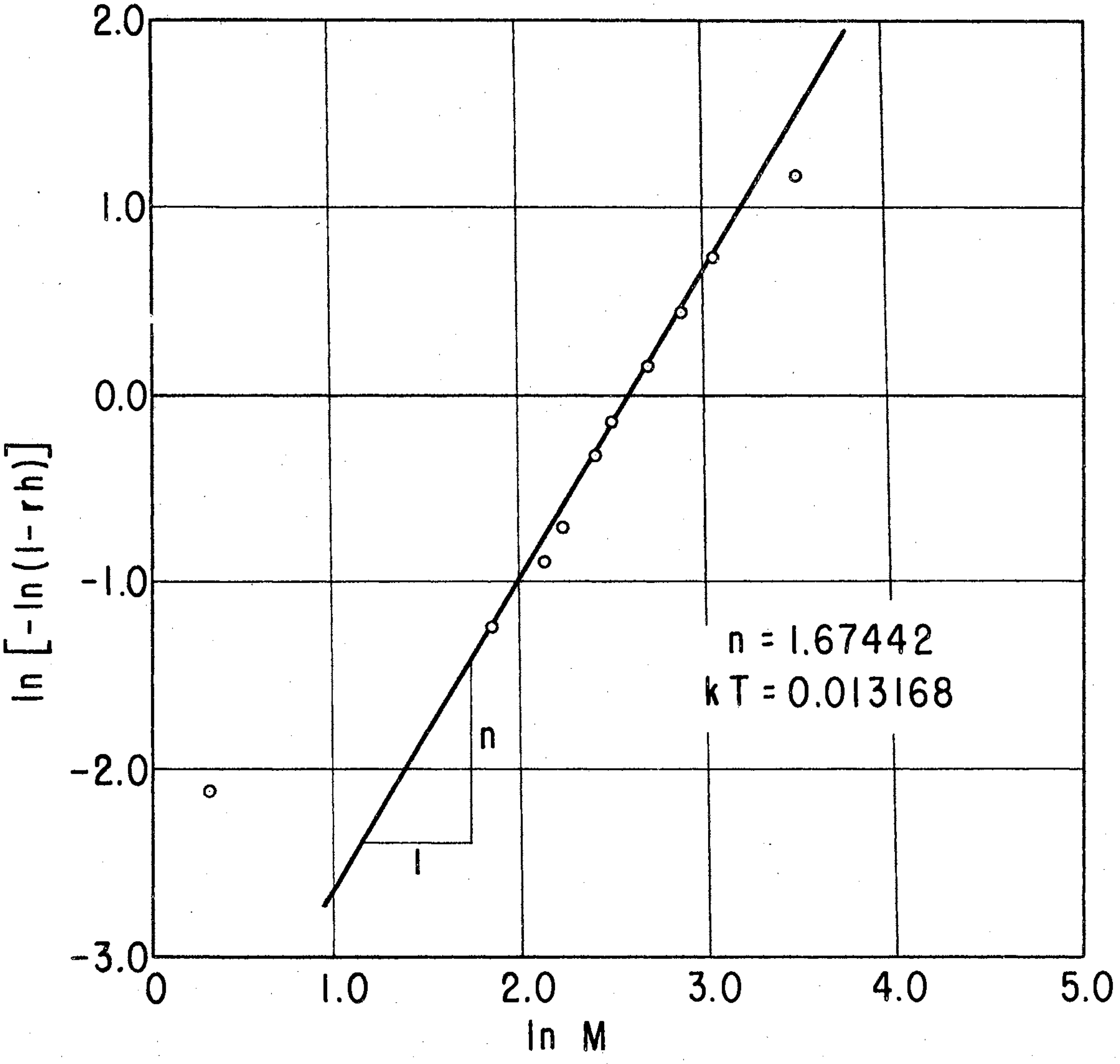

Figure 22. Plot of ln[-ln(1-rh)] Versus lnM for Determining Unknown Parameters in Henderson's Equation

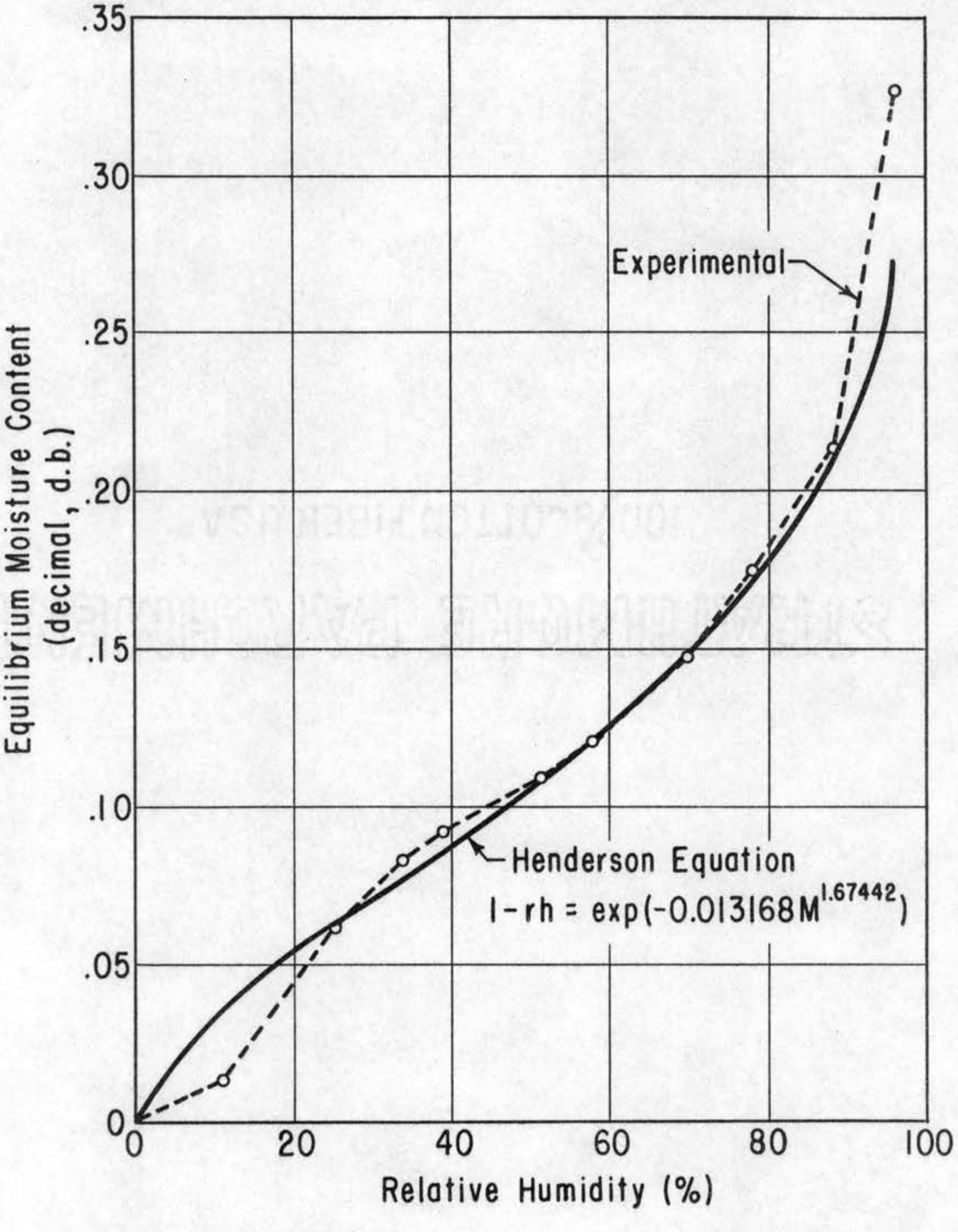

Figure 23. Henderson Equation for Equilibrium Moisture Content

the change in temperature. However, since v_m and V are essentially independent of temperature, the change in A and B was directly proportional to the change in the density of the adsorbed moisture. Since the major portion of the moisture is normally condensed, the density of the adsorbed moisture was assumed to be the same as that of normally condensed moisture. The density values were obtained from the literature as:

$\rho = 62.410 \text{ lb/ft}^3$ at 10°C

$\rho = 62.316 \text{ lb/ft}^3$ at 20°C

The new values of A and B were computed and found to be:

$A = 0.05243$

$B = 0.06678$

A new value of E was computed by assuming that $(q_1 - q_L)$ was constant over the range of temperatures studied. This assumption was made because q_L drops by less than 3 per cent in the range of temperatures from 10°C to 40°C and a similar drop in q_1 would be expected. Then the following relationships hold:

$$E_1 = \exp\left[-(q_1 - q_L)/kT_1\right]$$

$$E_2 = \exp\left[-(q_1 - q_L)/kT_2\right]$$

$$\ln E_1 = -(q_1-q_L)/kT_1$$

$$\ln E_2 = -(q_1-q_L)/kT_2 = \left[-(q_1-q_L)/kT_1\right]\left(\frac{T_1}{T_2}\right)$$

$$\ln E_2 = \ln E_1 \left(\frac{T_1}{T_2}\right)$$

$$E_2 = E_1^{\,(T_1/T_2)} \qquad (78)$$

Using equation (78), the value of E at 20°C was computed from the value found for 10°C from Series 1. This value was found to be 0.1204.

Figure 24 shows a plot of the computed values of the equilibrium moisture content using these calculated values of A, B, and E. Also shown is the experimental data for the sorption processes conducted in Series 2. It is seen that the computed values are somewhat higher than the experimental values. However, it should be remembered that this particular range of humidities also gave the poorest agreement between the observed and experimental values at 10°C as shown in Figure 14.

The desorption data of Series 2 are plotted in Figure 25. In these tests the samples were first subjected to some humidity between 50 and 90 per cent and then dried to equilibrium with an 11.4 per cent relative humidity. The figure shows the final moisture content obtained versus

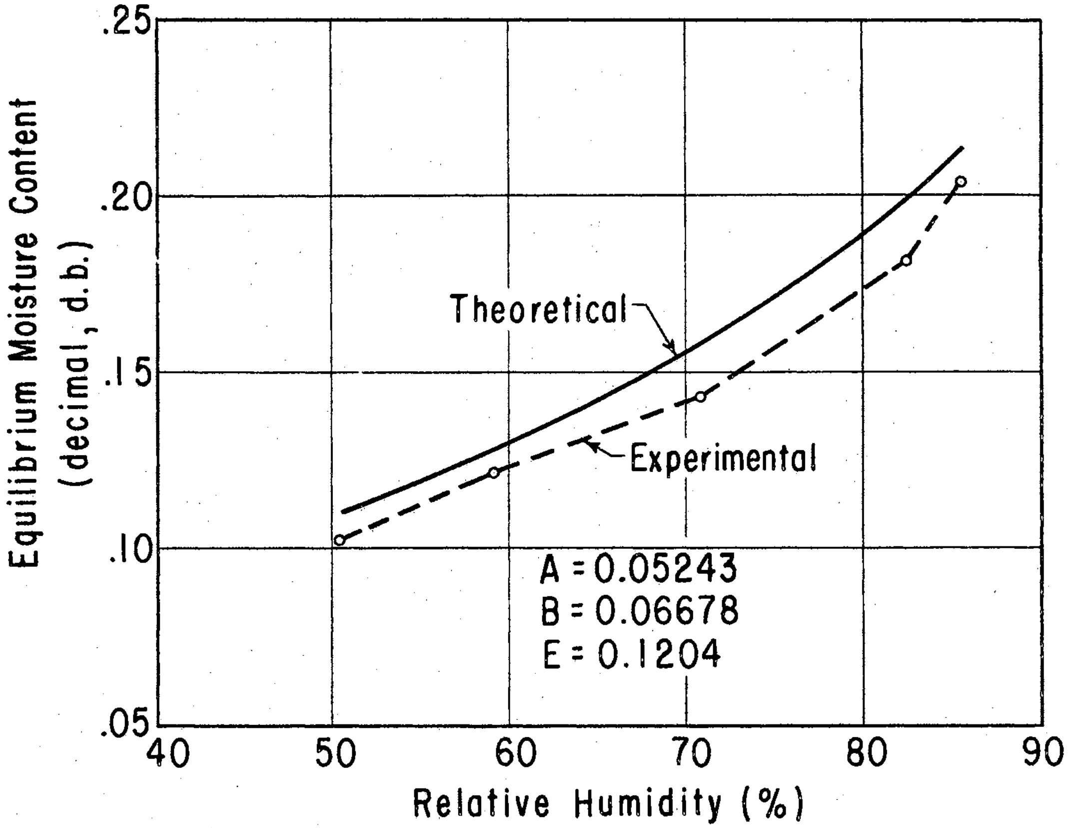

Figure 24. Equilibrium Moisture Content Versus Relative Humidity for the Sorption Data of Series 2 at 20°C

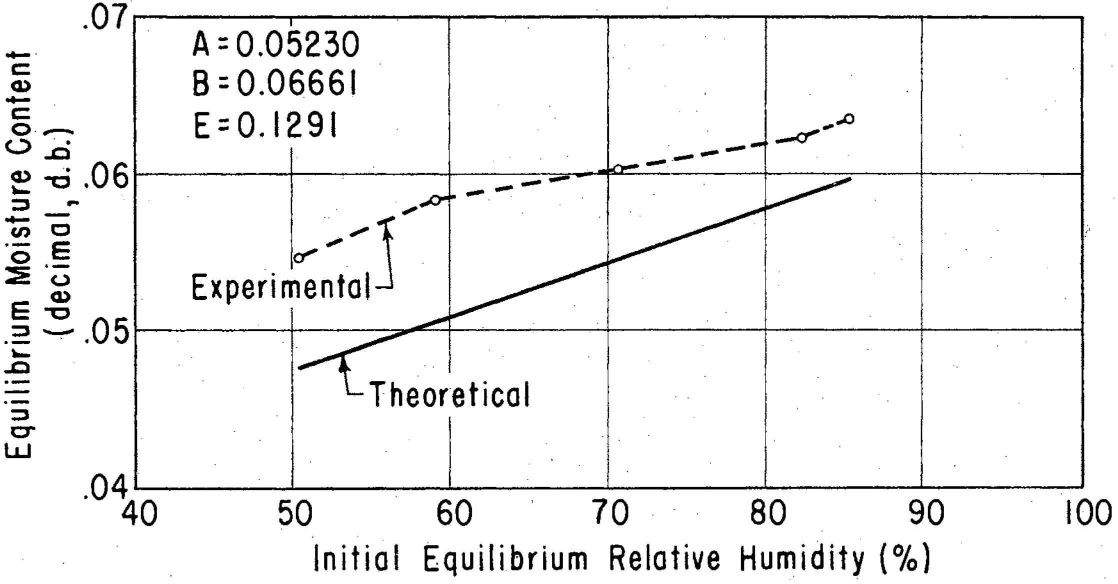

Figure 25. Plot of Equilibrium Moisture Content Obtained at 11.4% Relative Humidity After Initial Subjection to Humidities Between 50 and 90% at 20°C (Note: The ordinate scale has been expanded in this figure to show the deviation between the experimental and theoretical results.)

the initial relative humidity to which the grain had been subjected. Equation (71) was used to obtain theoretical values of the moisture content obtained. In this case, the experimental values were higher than the calculated values. However, the difference was between only 0.4% and 0.8% in moisture content.

Series 3

Using the value $\rho = 62.157$ lb/ft^3 at 30°C, the values of A and B were calculated and found to be 0.05230 and 0.06661 respectively. A new value of E was calculated using equation (78) and was found to be 0.1291. These values were used in equation (70) to give the theoretical curve shown in Figure 26. A correlation coefficient of 0.98555 was found between the theoretical and experimental values.

Series 4

Using the value $\rho = 61.941$ lb/ft^3 at 40°C, the values of A and B were found to be 0.05212 and 0.06638 respectively. The new E value was found from equation (78) to be 0.1378. The resulting theoretical moisture contents are found in Figure

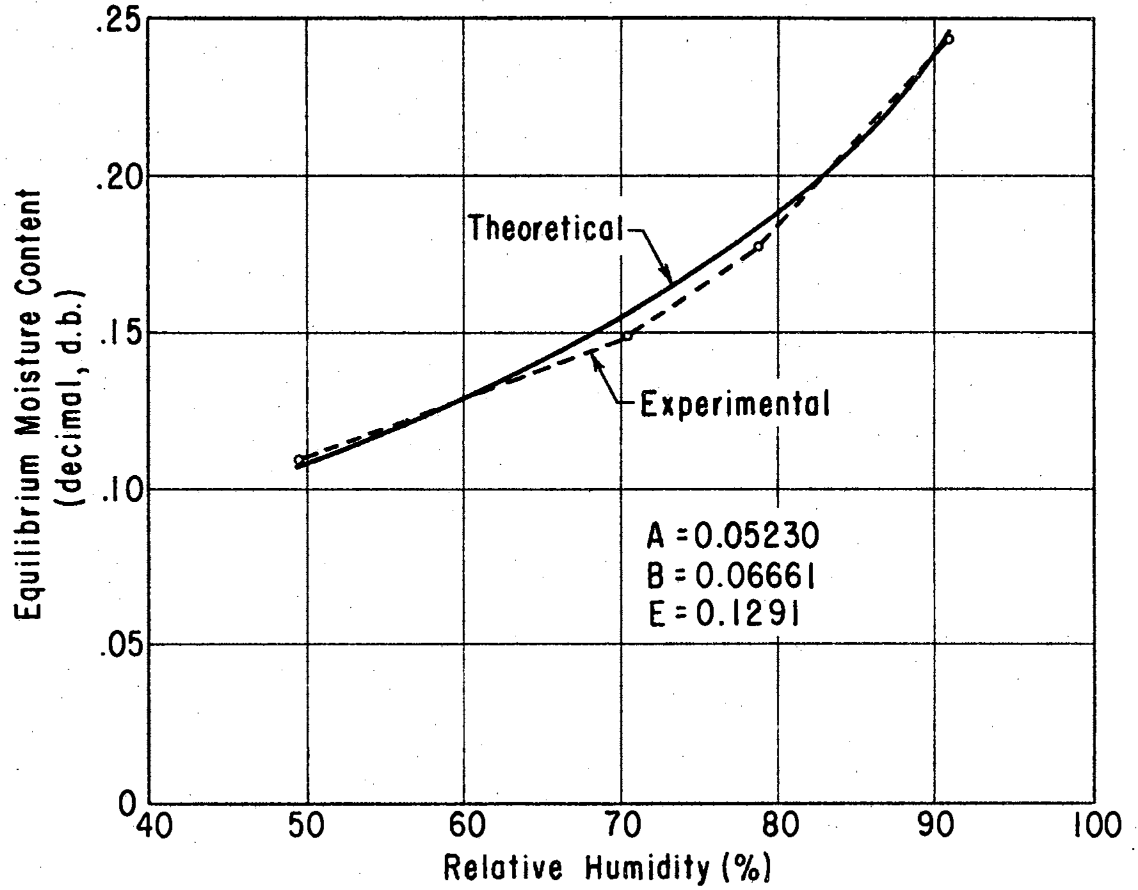

Figure 26. Equilibrium Moisture Content Versus Relative Humidity for the Sorption Tests of Series 3 at 30°C

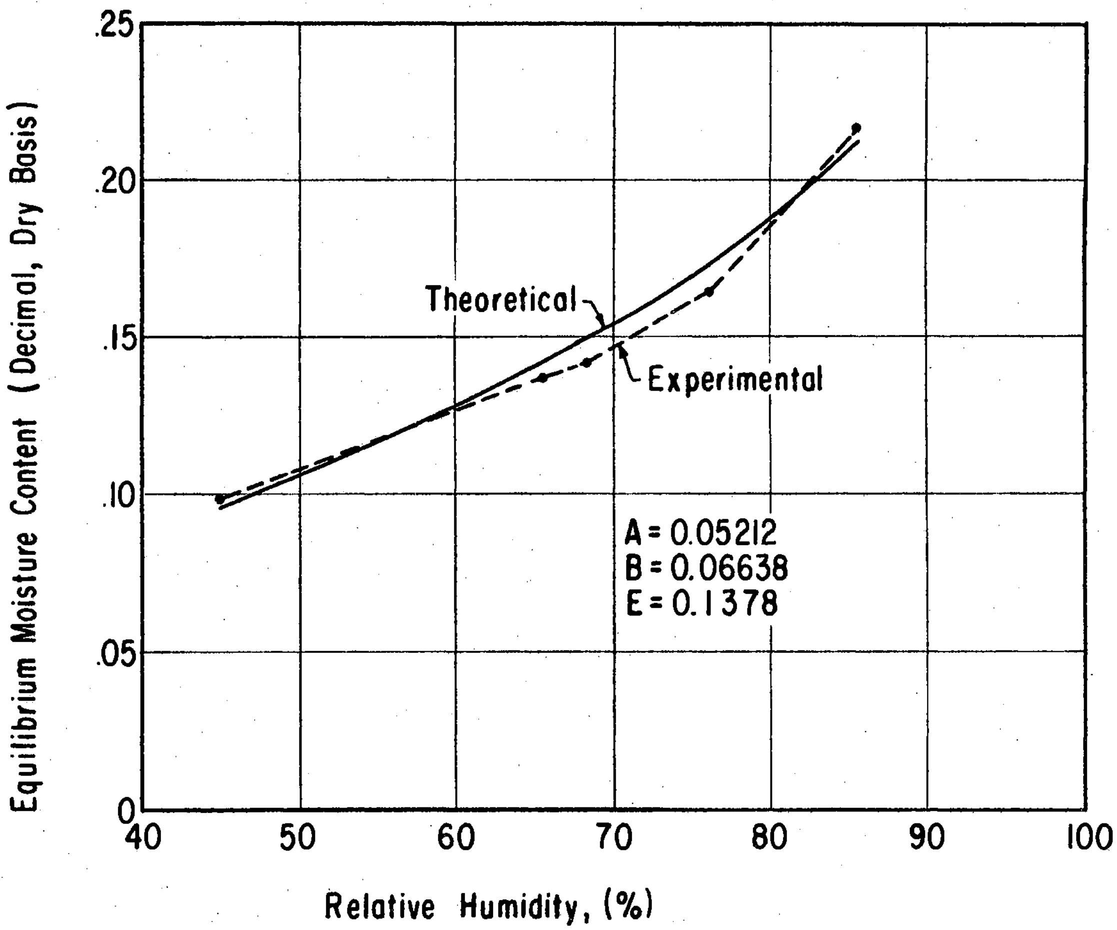

Figure 27. Equilibrium Moisture Content Versus Relative Humidity for the Sorption Tests of Series 4 at 40°C

27. The correlation coefficient between the theoretical and experimental values was found to be 0.98640 in this case.

CHAPTER VIII

DISCUSSION OF RESULTS

Agreement Between Theoretical and Experimental Sorption Isotherms

It was found in these tests that the theoretically derived equations agreed quite well with the experimental data for a given temperature if the three unknown parameters were properly evaluated. The theoretical equations give sigmoidal shaped curves as have been observed from experiments. The fit of the theoretical sorption curve to the sorption data of Series 1 (the lower curve of Figure 14) indicated that the theoretical values were somewhat higher than the experimental values of equilibrium moisture content in the range of humidities between 50 and 90 per cent. The maximum difference between the experimental and theoretical values was found at 88.2 per cent relative humidity where the difference in equilibrium moisture content was found to be 1.4 per cent. However, this agreement between the sorption data and the theoretical equations was felt to be quite good since the parameters of the equation were evaluated to give the best fit of the sorption and the desorption data simultaneously. The fact that it was possible to find values of the parameters which gave a good fit of both the sorption and the desorption data supports the theory upon which the equations were based. The difference between the functions θ and ϕ seems to adequately account for the hysteresis between sorption and desorption isotherms.

The sorption data at 10°C were also found to fit Henderson's equation and the BET and Smith equation combination (method used by Becker and Sallans) quite well. However, there are three major advantages of the equations developed in this thesis over those previously developed equations. First and most important, the equations developed here allow for hysteresis between the sorption and desorption isotherms. Secondly, the equations predict an effect of temperature which at least seems to be in the right direction. Thirdly, the derived equations are based on a theoretical analysis of the physical phenomena taking place in sorption and desorption and are applicable throughout the range of humidities.

Hysteresis

In these experiments, a greater hysteresis was found between the sorption and desorption isotherms than had previously been reported. The maximum hysteresis was found to be approximately 4 per cent in equilibrium moisture content. This greater hysteresis was believed to be due to the procedure used for preparing the grain samples for the sorption or desorption tests. This procedure was quite different from that used by Hubbard et al., (1957) when a maximum hysteresis of 1.6 per cent was found. In these experiments the sorption tests were conducted with grain which had been dried in a 100°C oven for 14 days. This is compared with the grain dried at 72 to 76°C for 3 days which was used in Hubbard's experiments. Thus, it is believed that the initial moisture content of the samples was much lower in the tests reported here. Then, since more of the absorbed moisture was removed prior to the sorption tests reported here, the sorption curves would be expected to be lower than those found by Hubbard. There was also a difference in the preparation of the samples for the desorption tests. In these experiments the samples were immersed in water for 24 hours whereas in Hubbard's experiments they were subjected to a 97% relative humidity overnight. Thus, the initial moisture content in these tests was considerably higher than in Hubbard's tests. This means that more absorbed moisture was present at the beginning of the desorption tests reported here and that higher desorption equilibrium moisture contents would be expected. As expected, the sorption curves found by Hubbard were higher than those found in this study and his desorption curves were lower than those found.

The experimental data for desorption from some relative humidity less than 100 per cent was generally higher than the theoretical values predicted by equation (64). This was not surprising since equation (64) really assumes that during the desorption process the bound moisture which is covered by a layer of normally condensed moisture has just as high a probability of evaporating as that which is not covered. This is definitely not true but as shown by Figure 25 the magnitude of the error introduced is not too large. A more accurate representation of this data would most likely involve a very complex probability study.

Effect of Temperature

As discussed in Chapter V, the theory predicts a decrease in equilibrium moisture content with an increase in temperature at lower humidities and an increase in equilibrium moisture content with an increase in temperature at relative humidities greater than approximately 84 per cent. Figure 28 shows theoretical sorption isotherms for temperatures of 10°C and 40°C. These isotherms are seen to cross at approximately 85 per cent relative humidity. Figure 29 shows the experimental sorption isotherms for the same two temperatures. In this case, they cross at approximately 78 per cent relative humidity.

Plots of experimental sorption isotherms at the other temperatures tested showed similar behavior. One exception was the 20°C isotherm which indicated a lower moisture content than either the 30°C or the 40°C isotherms at lower humidities. However, at higher humidities the magnitudes of the equilibrium moisture contents fell in the same order as the magnitudes of the temperatures. Thus, the highest moisture content was obtained at 40°C, the next highest at 30°C, third highest at 20°C, and the lowest at 10°C.

It can be seen from Figures 28 and 29 that the magnitude of the shift in equilibrium moisture content

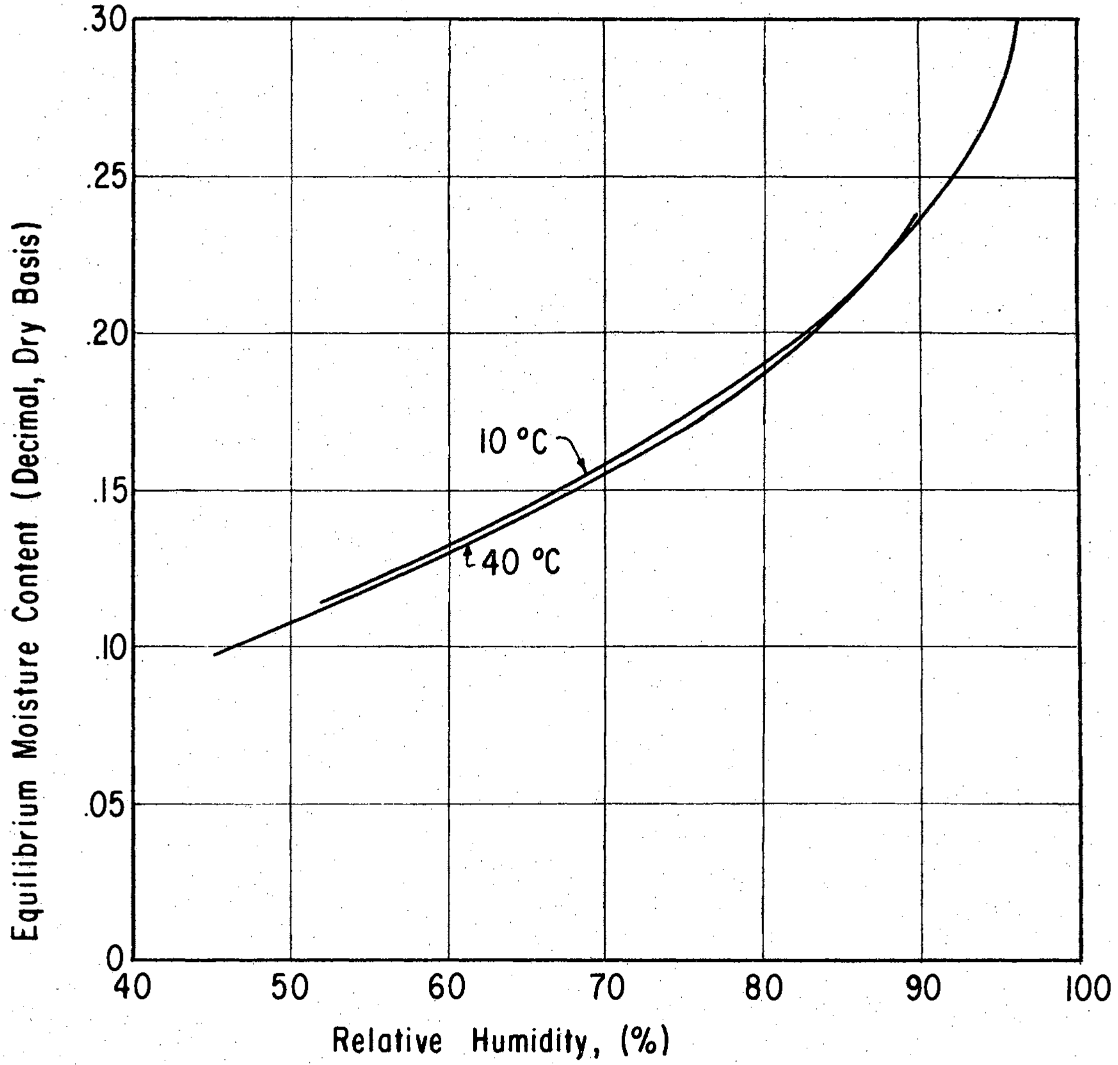

Figure 28. Theoretical Sorption Isotherms for $10^{\circ}C$ and $40^{\circ}C$

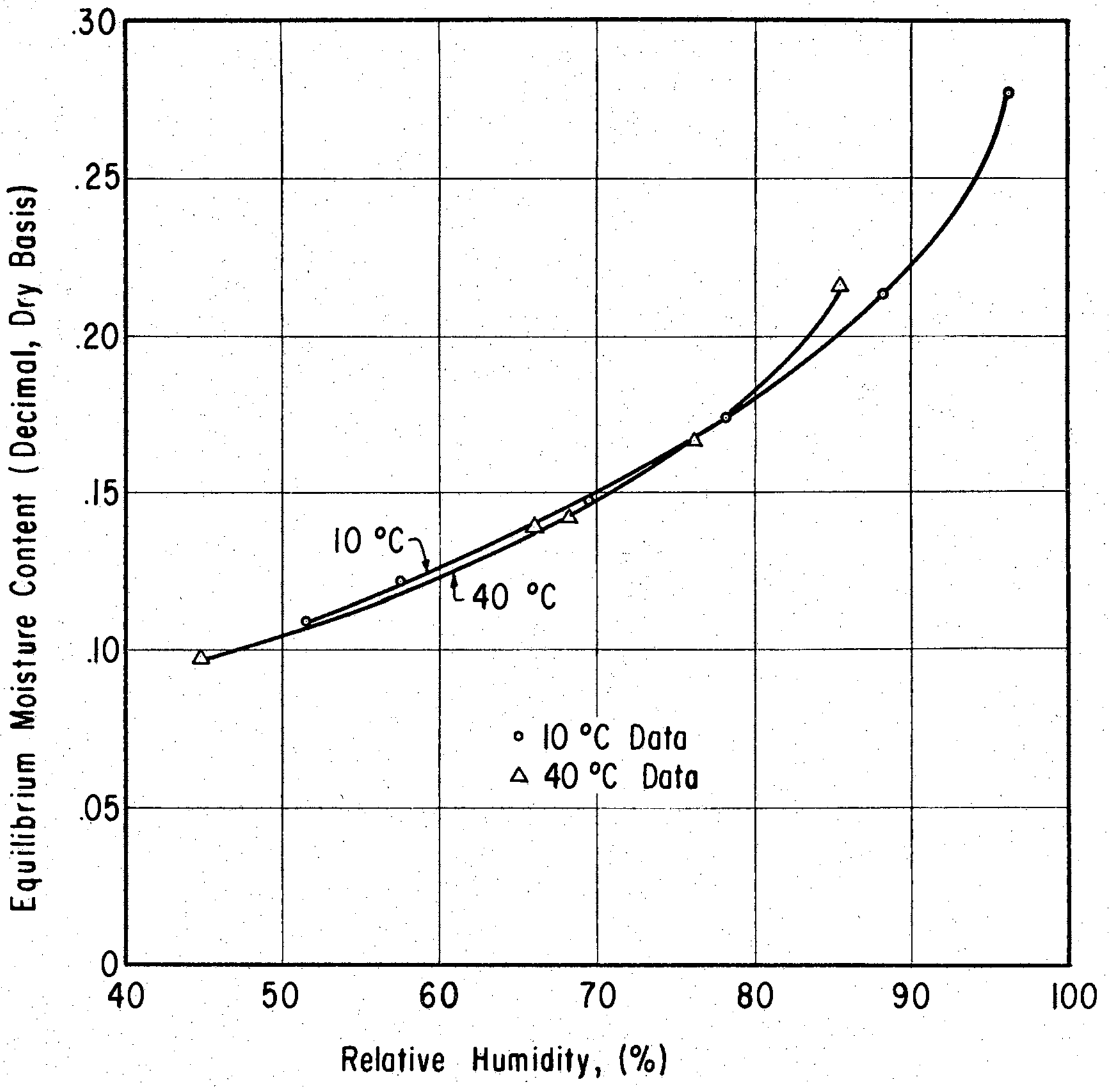

Figure 29. Experimental Sorption Isotherms for 10°C and 40°C

due to a change in temperature is small throughout the range of humidities studied. Therefore, a small amount of experimental error would cause the experimental sorption isotherms to exhibit unusual behavior. For this reason, it was felt that the experimental data obtained was insufficient to draw any definite conclusions concerning the applicability of the derived equations for predicting the magnitude of the shift in the isotherms due to a change in temperature. However, the shifts predicted by the theory seemed in general to be similar to those found experimentally.

Limitations of Derived Equations

In the derivation of equations (63) and (64), it was assumed that at equilibrium the rate of condensation was equal to the rate of evaporation. However, there are situations in which this would not be true. At very high moisture contents moisture might drip or flow out of the material due to gravitational forces. Thus, the derived equations would not be expected to represent the equilibrium moisture content at relative humidities approaching 100 per cent. The moisture content at very high relative humidities would be expected to actually reach some maximum rather than approach infinity as predicted by the equations. However, within the range of humidities of interest in the processing of biological materials the gravitational effects would be insignificant.

A second assumption involved in the equation is that the surface area remains constant and that the area which may be covered by two or more layers of moisture is equal to that which may be covered by only one layer of moisture. However, in an actual material one layer of moisture might fill the available space around a cell. In this case there could be no normally condensed moisture on the cell. For this reason, there might be some merit in changing equations (63) and (64) from three parameter equations to four parameter equations. They could then become:

$$M_s = \frac{\rho v_m}{W}\theta + \frac{\rho v_n}{W}\alpha + \frac{\rho V}{W}\phi \qquad (79)$$

and

$$M_d = \frac{\rho v_m}{W}\theta + \frac{\rho v_n}{W}\alpha + \frac{\rho V}{W}\theta \; rh_{max} \qquad (80)$$

where

v_m = volume of moisture in a unimolecular layer of bound water molecules

v_n = average volume of moisture in a unimolecular layer of normally condensed water molecules

This was not done in this study because it was felt that the three parameter equations adequately described the experimental sorption isotherms.

CHAPTER IX

SUMMARY AND CONCLUSIONS

Summary

Accurate information pertaining to the equilibrium moisture content of biological materials is important in the processing and storage of these products. Due to the time required for obtaining equilibrium moisture content data experimentally under all environmental conditions, a theoretical equation was desirable for predicting the equilibrium moisture content for either sorption or desorption processes. The purpose of this study was the development of such an equation.

A theory of the mechanisms involved in sorption and desorption processes was developed which led to the development of theoretical relationships from which the moisture content could be predicted. This theory involves three different classes of moisture based on the mechanisms by which the moisture is held within the material. They are: (1) bound moisture held on the surface of the cells by forces in excess of those acting on normally condensed water molecules,

(2) normally condensed moisture held by forces equal to those acting on water condensed on a normal water surface, and (3) absorbed moisture which has actually entered into the protoplasm of the cells. The absorbed moisture accounts for the hysteresis between the sorption and desorption data. Based on this theory, equations (63) and (64) were developed for predicting the equilibrium moisture content. These equations contained three unknown parameters which had to be experimentally evaluated.

Experiments were conducted on wheat samples to determine their equilibrium moisture contents for various initial relative humidities, final relative humidities, and temperatures. From these data the parameters of the derived equations were evaluated and the agreement between the theoretical and experimental values was observed.

Conclusions

As a result of the experimental study the following conclusions were made:

1. Equations (63) and (64) adequately describe the experimental data for both sorption and desorption

processes throughout the range of humidities when the three unknown parameters are properly evaluated for the material of interest.

2. The theoretical equations predict a shift in equilibrium moisture content due to temperature which is in the direction observed from the experimental data.
3. An increase in temperature results in an increase in equilibrium moisture content at high relative humidities.
4. An increase in temperature results in a decrease in equilibrium moisture content at lower relative humidities.
5. The equilibrium moisture content for a desorption process is higher than for a sorption process.
6. An increase in the maximum relative humidity to which a material has been subjected results in an increase in the equilibrium moisture content obtained when the material is subjected to a drying environment.

Suggestions for Further Study

In this study, values of the parameters A, B, and E of the theoretically derived equations were evaluated from the data for wheat samples. These values were based on only one series of tests. Therefore, a further study of the variations of the parameters for a particular material would be useful as well as evaluation of the parameters for a wide variety of biological materials. Also, a further study of the effect of temperature on the equilibrium moisture content would be helpful in determining whether the value of $(q_1 - q_L)$ remains constant and whether the equations predict the correct magnitude of the shift in equilibrium moisture content due to a change in temperature.

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APPENDIX A

INTEGRATION OF EQUATION (56) TO OBTAIN EQUATION FOR NORMALLY CONDENSED MOISTURE

INTEGRATION OF EQUATION (56) TO OBTAIN EQUATION FOR NORMALLY CONDENSED MOISTURE

The differential equation relating α, θ, and rh is:

$$(1-rh)\ d\alpha = rh\ d\theta + \theta d(rh) \qquad (56)$$

However, θ is a function of rh as given by equation (52):

$$\theta = \frac{rh}{rh + (1-rh)E} \qquad (52)$$

where

$$E = \exp\left[-(q_1-q_L)/kT\right]$$

Then

$$d\theta = \frac{\left[rh + (1-rh)E\right] - rh(1-E)}{\left[rh + (1-rh)E\right]^2}\ d(rh)$$

$$d\theta = \frac{E\ d(rh)}{\left[rh + (1-rh)E\right]^2}$$

Then by substitution into equation (56):

$$(1-rh)\ d\alpha = \frac{E\ rh\ d(rh)}{\left[rh + (1-rh)E\right]^2} + \frac{rh\ d(rh)}{\left[rh + (1-rh)E\right]^2}$$

or

$$d\alpha = \frac{E\ rh\ d(rh)}{(1-rh)\ [rh + (1-rh)E]^2} + \frac{rh\ d(rh)}{(1-rh)\ [rh + (1-rh)E]}$$

Then

$$\alpha = \int_0^{rh} \frac{E\ rh\ d(rh)}{(1-rh)\quad rh + (1-rh)E^{\ 2}} + \int_0^{rh} \frac{rh\ d(rh)}{(1-rh)[rh + (1-rh)E]}$$

If

$$x = 1-rh$$

$$dx = -d(rh)$$

Then

$$\alpha = \int_1^{1-rh} \frac{-E(1-x)\ dx}{x\ [(1-x) + Ex]^2} + \int_1^{1-rh} \frac{-(1-x)dx}{x\ [(1-x) + Ex]}$$

$$\alpha = \int_1^{1-rh} \frac{Edx}{[(1-x) + Ex]^2} - \int_1^{1-rh} \frac{Edx}{x\ [(1-x) + Ex]^2}$$

$$+ \int_1^{1-rh} \frac{dx}{[(1-x) + Ex]} - \int_1^{1-rh} \frac{dx}{x\ [(1-x) + Ex]}$$

or

$$\alpha = \int_1^{1-rh} \frac{Edx}{[1 + x(E-1)]^2} - \int_1^{1-rh} \frac{Edx}{x[1 + x(E-1)]^2}$$

$$+ \int_1^{1-rh} \frac{dx}{[1-x(E-1)]} - \int_1^{1-rh} \frac{dx}{x[1+x(E-1)]^2}$$

But

$$\int_{1}^{1-rh} \frac{E\,dx}{[1+x(E-1)]^{2}} = \left[-\frac{E}{(E-1)\,[1+x(E-1)]}\right]_{1}^{1-rh}$$

$$= -\frac{E}{(E-1)\,[1+(E-1)(1-rh)]} + \frac{E}{(E-1)E}$$

$$= \frac{-E + [1+(E-1)(1-rh)]}{(E-1)[1+(E-1)(1-rh)]}$$

$$= \frac{-E + 1 + E - E\,rh - 1 + rh}{(E-1)\,[1+(E-1)(1-rh)]}$$

$$= \frac{-rh(E-1)}{(E-1)\,[1+(E-1)(1-rh)]}$$

$$= \frac{-rh}{1 + E - Erh - 1 + rh}$$

$$= \frac{-rh}{rh + E(1-rh)}$$

$$\int_{1}^{1-rh} \frac{E\,dx}{x\,[1+x(E-1)]^{2}} = \left[\frac{E}{[1+(E-1)x]} - E\log\frac{[1+(E-1)x]}{x}\right]_{1}^{1-rh}$$

$$= \frac{E}{1+(E-1)(1-rh)} - \frac{E}{E} - E\log\left[\frac{[1+(E-1)(1-rh)]}{(1-rh)\,E}\right]$$

$$= \frac{E}{rh + E(1-rh)} - 1 - E\log\left[\frac{rh+E(1-rh)}{E(1-rh)}\right]$$

$$= \frac{E-rh-E(1-rh)}{rh + E(1-rh)} - E\log\left[\frac{rh + E(1-rh)}{E(1-rh)}\right]$$

$$= \frac{rh(E-1)}{rh + E(1-rh)} - E\log\left[\frac{rh+E(1-rh)}{E(1-rh)}\right]$$

$$\int_{1}^{1-rh} \frac{dx}{1 + (E-1)x} = \frac{1}{E - 1} \log \left[1 + (E-1)x\right] \Bigg|_{1}^{1-rh}$$

$$= \frac{1}{E - 1} \log \left[\frac{1+(E-1)(1-rh)}{E}\right]$$

$$= \frac{1}{E - 1} \log \left[\frac{rh + E(1-rh)}{E}\right]$$

and

$$\int_{1}^{1-rh} \frac{dx}{x\left[1+(E-1)x\right]} = - \log \left[\frac{1+(E-1)x}{x}\right] \Bigg|_{1}^{1-rh}$$

$$= -\log \left[\frac{1+(E-1)(1-rh)}{(1-rh)E}\right]$$

$$= -\log \left[\frac{rh+E(1-rh)}{E(1-rh)}\right]$$

Then

$$\alpha = - \frac{rh}{rh+E(1-rh)} - \frac{rh(E-1)}{rh+E(1-rh)} + E \log \left[\frac{rh+E(1-rh)}{E(1-rh)}\right]$$

$$+ \frac{1}{E-1} \log \left[\frac{rh + E(1-rh)}{E}\right] + \log \left[\frac{rh + E(1-rh)}{E(1-rh)}\right]$$

$$\alpha = \frac{-rh\ -rhE + rh}{E + rh - Erh} + (E+1)\ \log\left[\frac{rh + E(1-rh)}{E}\right]$$

$$- (E+1)\ \log(1-rh) + \frac{1}{E-1}\ \log\left[\frac{rh + E(1-rh)}{E}\right]$$

$$= - \frac{rh\ E}{E\ -(E-1)rh} + (E + 1 + \frac{1}{E-1})\log\left[\frac{E\ -(E-1)rh}{E}\right]$$

$$- (E+1)\ \log(1-rh)$$

$$\alpha = - \frac{rh\ E}{E\ -(E-1)rh} + (\frac{E^2-1 + 1}{E-1})\ \log\left[\frac{E\ -(E-1)\ rh}{E}\right]$$

$$- (E+1)\ \log(1-rh)$$

$$\alpha = - \frac{rh\ E}{E\ -(E-1)rh} + \frac{E^2}{E-1}\ \log\left[\frac{E-(E-1)rh}{E}\right] - (E+1)\ \log(1-rh) \tag{57}$$

APPENDIX B

RATE OF MOISTURE ABSORPTION BY INITIALLY DRY SAMPLES

RATE OF MOISTURE ABSORPTION BY INITIALLY DRY SAMPLES

An interesting and unexpected aspect of the equilibrium moisture content tests was the time required for the samples to reach equilibrium with the various relative humidities. A plot of the time required to reach equilibrium versus the relative humidity of the environment (Figure B-1) shows that a greater length of time was required for grain to reach equilibrium at lower humidities than at higher humidities up to approximately 70 per cent relative humidity. There was a minimum in the curve at about 70 per cent and the time required increased with humidity beyond this point. These results indicate that the diffusivity for moisture movement into the material is a function of the moisture content of the material.

Henderson and Perry (1955) state that the drying rate of agricultural products is proportional to the difference in moisture content between the material being dried and the equilibrium moisture

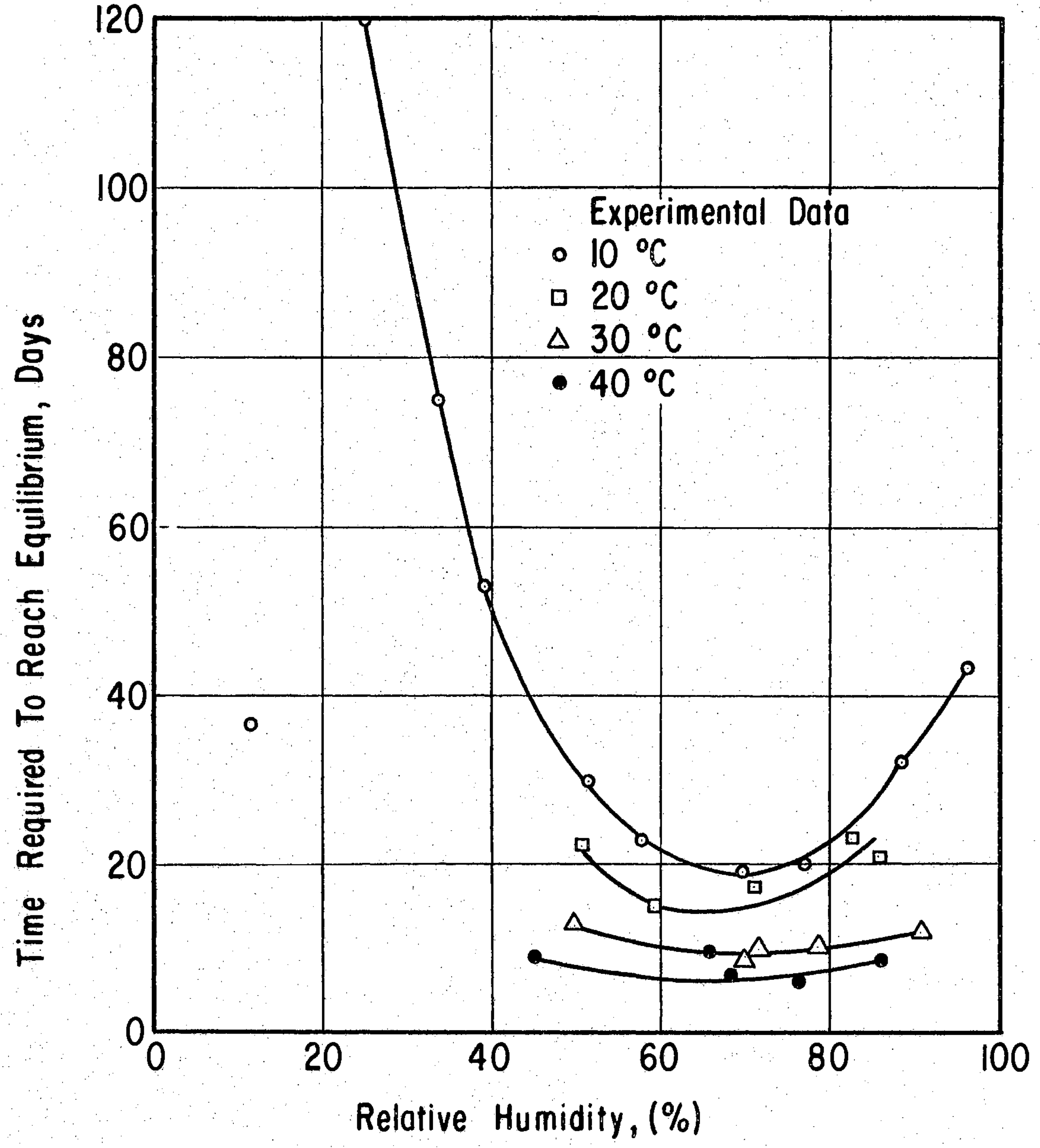

Figure B-1. Time Required for Initially Dry Samples to Reach Equilibrium with Various Relative Humidities at 10, 20, 30, and 40°C content at the drying air state or:

$$\frac{dM}{dt} = - c \ (M-M_e) \qquad \text{(B-1)}$$

where

M = moisture content of material

M_e = equilibrium moisture content of material at the given environmental conditions

c = constant depending on environmental conditions and the properties of the material, hr^{-1}.

The results shown in Figure B-1 indicate that this equation does not hold for wetting processes since the equation would always require an increase in the time required for equilibrium with an increase in the relative humidity of the environment. Thus, if an equation of the form of (B-1) were used for the wetting process, the value of c would have to be treated as a variable and its dependence on the moisture content would have to be known.

As is shown in Figure B-1, the time required for the initially dry grain to reach equilibrium with an 11.4% relative humidity was much less than would be expected from extending the curve drawn through the higher humidities. This was believed to be a consequence of the criteria used for defining equilibrium. The rate of absorption in this case was so low that the daily gain fell below the figure chosen to describe an equilibrium position long before equilibrium was actually reached. This could also be a source of some error at the higher humidities but it was felt that this error was insignificant at other points tested.

APPENDIX C

EXPERIMENTAL EQUILIBRIUM MOISTURE CONTENTS

APPENDIX C-1

EQUILIBRIUM MOISTURE CONTENTS FOR SERIES 1

Sample	Equilibrium Moisture Content	Sample	Equilibrium Moisture Content
11012	.01331	11072	.14653
11013	.01451	11073	.14747
11015	.01418	11074	.14763
11016	.01428	11075	.14771
11021	.06279	11082	.17395
11022	.06422	11083	.17799
11023	.06266	11084	.17416
11024	.06356	11085	.17406
11025	.06313	11086	.17294
11031	.08486	11091	.21297
11033	.08322	11092	.21130
11034	.08343	11093	.21266
11035	.08334	11094	.21403
11036	.08464	11096	.21516
11041	.09352	11101	.32419
11042	.09073	11103	.32162
11043	.09090	11105	.32997
11044	.09083	11106	.33397
11046	.09312	12012	.07501
11051	.10955	12013	.07504
11052	.10879	12014	.07432
11055	.10940	12015	.07546
11056	.11043	12016	.07418
11061	.12132	12021	.09959
11062	.12126	12022	.09943
11063	.12040	12024	.09939
11065	.12130	12025	.09846
11066	.12154	12026	.09850
11071	.14747	12031	.11309

APPENDIX C-1

(Continued)

Sample	Equilibrium Moisture Content	Sample	Equilibrium Moisture Content
12032	.11337	13031	.12223
12033	.11352	13032	.12278
12034	.11335	13034	.12151
12036	.11342	13035	.12198
12041	.12131	13036	.12366
12043	.12313	13041	.12604
12045	.12427	13042	.12592
12046	.12140	13043	.12708
12051	.13598	13044	.12633
12052	.13676	13045	.12646
12054	.13874	13051	.14046
12055	.13675	13052	.14057
12056	.13722	13054	.14154
12061	.14680	13055	.13905
12062	.14723	13061	.14814
12063	.14973	13062	.14984
12064	.14782	13063	.14933
12065	.14751	13064	.15064
12071	.16413	13065	.14719
12072	.16337	13071	.17001
12073	.16397	13072	.17122
12074	.16389	13073	.17029
12075	.16411	13074	.17139
13011	.07968	13081	.19223
13012	.07944	13082	.19324
13014	.07759	13083	.19466
13015	.07891	13084	.19301
13016	.07734	13085	.19385
13021	.09143	13091	.23042
13022	.09161	13092	.23345
13023	.09466	13093	.23360
13024	.09381	13095	.23621
13025	.09355	13096	.23364

APPENDIX C-1

(Concluded)

Key to Sample Identification:

First digit - 1 - Series 1 at 10°C

Second digit - 1 - Initially oven dry

2 - Initially at 80% RH

3 - Initially Saturated

Third and Fourth digits - Final Relative Humidities

1 - 11.4%, 2 - 25.2%, 3 - 33.7%, 4 - 39.0%, 5 - 51.7%
6 - 57.5%, 7 - 69.7%, 8 - 78.2%, 9 - 88.2%, 10 - 96.2%

Fifth digit - Sample number

APPENDIX C-2

EQUILIBRIUM MOISTURE CONTENTS FOR SERIES 2

Sample	Sorption Equilibrium Moisture Content	Desorption Equilibrium Moisture Content
21051	.10211	.05484
21052	.10179	.05463
21053	.10215	.05496
21054	.10232	.05484
21055	.10220	.05478
21061	.12127	.05822
21063	.12134	.05827
21064	.12167	.05842
21065	.12157	.05846
21066	.12122	.05822
21071	.14264	.05997
21073	.14469	.06072
21074	.14335	.06050
21075	.14342	.05988
21076	.14261	.06004
21081	.18141	.06256
21083	.18016	.06158
21084	.18188	.06250
21085	.18182	.06245
21086	.18177	.06230
21091	.20348	.06360
21094	.20411	.06363
21095	.20448	.06374
21096	.20457	.06375

APPENDIX C-2

(Concluded)

Key to Identification of Samples:

First digit: 2 - Series 2 at 20°C

Second digit: 1 - Initially Oven Dry

Third and Fourth digits: Relative Humidities for
for Sorption Portion of Tests
5 - 50.6%, 6 - 59.1%, 7 - 70.8%, 8 - 82.4%,
9 - 85.6%

Fifth digit: Sample Number

APPENDIX C-3

EQUILIBRIUM MOISTURE CONTENTS FOR SERIES 3

Sample	Equilibrium Moisture Content	Sample	Equilibrium Moisture Content
31051	.10876	31074	.14985
31052	.10931	31075	.14896
31053	.10929	31081	.17713
31056	.10910	31083	.18024
31062	.15437	31084	.17657
31063	.15546	31085	.17772
31064	.15372	31086	.17724
31065	.15467	31091	.25117
31066	.15340	31093	.22912
31071	.14631	31094	.24589
31072	.14993	31096	.24807
31073	.14935		

Key to Identification of Samples:

First digit: 3 - Series 3 at 30°C

Second digit: 1 - Initially Oven Dry

Third and fourth digits: Final Relative Humidities

5 - 49.6%, 6 - 71.8%, 7 - 70.2%, 8 - 78.7%, 9 - 90.9%

Fifth digit - Sample Number

APPENDIX C-4

EQUILIBRIUM MOISTURE CONTENTS FOR SERIES 4

Sample	Equilibrium Moisture Content	Sample	Equilibrium Moisture Content
41051	.09848	41074	.14113
41053	.09882	41075	.14143
41054	.09857	41081	.16565
41055	.09960	41082	.16625
41056	.09874	41083	.16646
41061	.14022	41084	.16654
41062	.14150	41085	.16657
41063	.14165	41091	.21761
41065	.14184	41092	.21416
41066	.14120	41093	.21829
41072	.13952	41095	.22053
41073	.13938	41096	.21799

Key to Identification of Samples:

First digit: 4 - Series 4 at 40°C.

Second digit: 1 - Initially Oven Dry

Third and Fourth digits: Final Relative Humidities

5 - 44.8%, 6 - 68.1%, 7 - 66.0%, 8 - 76.1%, 9 - 85.6%
Fifth digit: Sample Number

VITA

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