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Desorption Isotherms and Drying Rates of
Shelled Corn in the Temperature Range of
40° to 140°F.

presented by

J. Rodriguez-Arias

has been accepted towards fulfillment
of the requirements for

Ph.D degree in Agricultural Engineering

Carl W. Hall

Major professor

Date July 26, 1956

DESORPTION ISOTHERMS AND DRYING RATES OF SHELLED CORN IN THE
TEMPERATURE RANGE OF 40° TO 140°F.

By
Jorge H. Rodriguez-Arias

AN ABSTRACT

Submitted to the School for Advanced Graduate Studies of
Michigan State University of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Agricultural Engineering

Year 1956

Approved by

Carl W. Hall, July 26, 1956

The investigation is primarily concerned with an experimental inquiry into the theoretical aspects of grain drying with the broad objective of gaining fundamental information pertaining both to the equilibrium and to the rate relationships of the drying process, with particular reference to shelled corn.

The experimental phase was directed toward obtaining hygroscopic equilibrium data over a wide enough range of constant drying conditions to permit the accurate construction of desorption isotherms for temperatures of 40° , 60° , 86° , 100° , 122° , and 140°F . A static method was used whereby thin layer samples of grain were equilibrated above saturated aqueous solutions of chemically pure salts maintained in thermostatically controlled constant-temperature cabinets. Data obtained throughout the equilibration period allowed accurate construction of drying curves corresponding to the testing conditions.

When examined with the B.E.T. two-constant equation the isotherms were found to yield very satisfactory linear plots in the prescribed region of validity as well as reasonable values for the equation constants. Further treatment with the B.E.T. three-constant equation and the Harkins-Jura equation led to the conclusion that multimolecular adsorption is the predominant water-binding mechanism in shelled corn. The analysis strongly suggests that in the region of relative pressures from zero to 0.75 the adsorbed water consists of a first unimolecular layer of firmly bound molecules plus four to five additional layers of decreasingly bound molecules; that beyond a relative pressure between 0.30 and 0.45 enough lateral interaction between adsorbed molecules develops

to cause the formation of a condensed film, with condensation in increasingly larger capillaries occurring beyond a relative pressure of about 0.75. The isotherms were found to obey Smith's equation in the range of relative pressures from 0.45 to 0.90. The average isosteric heats of desorption at various moisture levels from 8 to 22 percent, dry basis, over the temperature range from 60° to 122°F were calculated by three different methods, all based on the Clausius-Clapeyron equation.

Henderson's equation successfully describes the isotherms in the relative pressure range between 0.10 and 0.60, but it tends to considerably understate the sorption beyond that range and to slightly overstate it at the lower pressures. Furthermore, with single-valued constants the equation fails to account correctly for the temperature dependence of the isotherm.

The thin layer behavior of shelled corn was found to obey closely an exponential drying law analogous to Newton's law of cooling. However, the rate constant was found to decrease according to stepwise discrete changes in value at various intervals throughout the drying process, which seriously hinders the usefulness of the simple equation. The instantaneous vapor pressure potential appears not to be the most important single factor governing the instantaneous drying rate; widely divergent drying rates occurred under identical vapor pressure potentials. Over restricted ranges of moisture content the drying rate could be characterized by an equation analogous to Ohm's law with the vapor pressure potential as

the driving force and the reciprocal of a mass transfer coefficient as the resistance. Electromagnetic irradiation of shelled corn at a moisture level of 15 percent, dry basis, with doses of 10^6 and 10^7 reps applied on both sides of the corn kernels had no noticeable effect on the drying rate.

**DESORPTION ISOTHERMS AND DRYING RATES OF SHELLED CORN IN THE
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VITA

Jorge H. Rodriguez-Arias
candidate for the degree of
Doctor of Philosophy

Final examination, July 26, 1956, 10:00 A.M., Agricultural
Engineering Conference Room

Dissertation: Desorption Isotherms and Drying Rates of Shelled
Corn in the Temperature Range of 40° to 140°F.

Outline of Studies

Major subject: Agricultural Engineering

Minor subject: Food Technology (Horticulture)

Biographical Items

Born, April 24, 1915, Ponce, Puerto Rico

Undergraduate Studies

College of Agriculture and Mechanic Arts of the University of
Puerto Rico, 1932-36, B.S.A.

Texas Agricultural and Mechanical College, 1943-45, B.S.A.E.

Graduate Studies

Kansas State College, 1946-47, M.S.A.E.

Michigan State University, 1954-56

Experience

Instructor of Vocational Agriculture, 1936-37, Department of
Education, Government of Puerto Rico; At the College of Agri-
culture and Mechanic Arts of the University of Puerto Rico:
Instructor of Horticulture, 1937-43; On leave, 1943-47; Assis-
tant Professor of Agricultural Engineering, 1947-48; Associate
Professor of Agricultural Engineering, 1948-49; Associate Pro-
fessor and Head, Agricultural Engineering Department, 1949-53;
Professor and Head, Agricultural Engineering Department, 1953-
54; On leave, 1954-56; Graduate Research Assistant, Agricultural

Engineering Department, Michigan State University, 1955-56

Military Service: A.E.T.M. S 1/c (Radar Program) U.S. Navy,
1945-46; U. S. Naval Reserve, 1946-50

Professional and Scientific Societies

American Society of Agricultural Engineering, Member, 1939

American Society for Engineering Education, Member, 1948

Institute of Food Technologists, Professional Member, 1956

American Society of Agricultural Sciences, Member, 1940

Colegio de Agronomos de Puerto Rico, 1937

American Association for the Advancement of Science, 1938

Honorary Societies

Gamma Sigma Delta, Puerto Rico Chapter (Charter Member), 1938

Sigma Xi, Associate Member, 1956

Married to Carmen Teresa Quinones, May 9, 1948

Children: Jorge Humberto (1949); Jaime Osvaldo (1953);

Nelson Rafael (1955)

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LIST OF SYMBOLS

- A** Surface area of adsorbent; slope constant in Harkins-Jura linear equation.
- Å** Angstrom, 10^{-8} centimeter
- B** Intercept constant in Harkins-Jura linear equation
- B-E-T** Abbreviation for Brunauer, Emmett, and Teller (also B.E.T.).
- C** Constant of integration; concentration in differential equations for diffusion
- °C** Degrees Centigrade
- E_a** Energy of gas per gram in the adsorbed state
- E_g** Energy of gas per gram in the gas phase
- E_1** Heat of adsorption in the first unimolecular layer (B-E-T theory of multimolecular adsorption)
- E_L** Heat of liquefaction of adsorbate (B-E-T theory of multimolecular adsorption)
- F** Free energy of the system
- F** Change in free energy of the system
- °F** Degrees Fahrenheit
- H** Enthalpy, heat of adsorption
- H-J** Abbreviations for Harkins-Jura
- H** Change in enthalpy
- K** Constant in Harkins-Jura equation for area of adsorbent
- °K** Absolute temperature, degrees Kelvin
- K_g** Mass transfer coefficient, (lbs. H_2O) (100 lbs. dry grain) $^{-1}$ (hr) $^{-1}$ (psi) $^{-1}$
- K_L** Adsorption coefficient (Langmuir equation)
- L** Molar heat of adsorption (desorption) of adsorbate (Othmer equation)
- L'** Molar heat of vaporization of reference substance (water) in Othmer equation
- M** Molecular weight; moisture content, percent (either wet or dry basis as specified); amount of adsorbate per gram of adsorbent

LIST OF SYMBOLS (Cont.)

M_e	Equilibrium moisture content, percent dry basis
M_o	Initial moisture content, percent dry basis
N	Avogadro's number (6.023×10^{23} molecules per mole); experimental constant in Page's equation 55
N_a	Moles of gas adsorbed per gram of adsorbent (Equation 6)
Q_{int}	Integral heat of adsorption
Q_{isoth}	Isothermal heat of adsorption (= isosteric heat of adsorption)
Q_i	Isosteric heat of adsorption
R	Universal gas constant, $1.987 \text{ cal } (^{\circ}\text{K})^{-1}(\text{g-mole})^{-1}$
$^{\circ}\text{R}$	Absolute temperature, degrees Rankine
R.H.	Relative humidity, percent
S	Entropy
ΔS	Change in entropy
T	Temperature (either $^{\circ}\text{C}$, $^{\circ}\text{F}$, $^{\circ}\text{K}$, or $^{\circ}\text{R}$)
V	Molar volume of liquid
ΔV	Change in volume
X	Relative humidity
a	Moisture content, percent dry basis
a_1	Constant in B-E-T derivations
a_s	Bull's designation of moisture content at saturation pressure
b_1	Constant in B-E-T derivation
c	Energy constant in B-E-T equations; concentration (equation 52)
d.b.	Dry basis (referring to moisture content)
d_L	Density of liquid
e	Base of natural logarithms, 2.7128+
e_i	Adsorption potential, (Equation 13)
i	Number of layers in multimolecular adsorption
k	Constant in Henderson's equation (43); specific drying rate constant, hr^{-1} ; constant in Page's equation 55
n	Constant in Henderson's equation; number of molecules striking a unit area of surface per unit time (equation 45); size constant in B-E-T three-constant equation

LIST OF SYMBOLS (Cont.)

p_a	Partial aqueous vapor pressure
p_g	Equilibrium vapor pressure of grain
p_s	Saturation vapor pressure
p	Vapor pressure difference or potential, psi
psi	Pounds per square inch
psia	Pounds per square inch, absolute
q_d	Differential heat of adsorption (or desorption)
r	Radius of capillary (equation 14)
s_0	Bare surface area of adsorbent in B-E-T derivations
$s_1, s_2, \dots, s_i$	Surface area that is covered by 1, 2, ... i layers of adsorbed molecules
v	Volume of gas adsorbed
v_g	Molar volume of gas
v_m	Size constant of B-E-T two-constant equation
w	Water vapor adsorbed expressed in percent wet basis (Smith equation 42)
w'	Constant in Smith equation 42, slope of linear plot (percent wet basis)
w_b	Constant in Smith equation 42, intercept of linear plot, percent wet basis)
w.b.	Wet basis (referring to moisture content)
θ	Time, hours
ρ	Density of gas in bulk phase (equation 13)
ρ_i	Density of gas in adsorbed state (equation 13)
σ	Surface tension
Σ	Area of adsorbent (Harkins-Jura equation 41); summation sign

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INTRODUCTION

The problem of drying and storing cereal grains has long been of great importance to the American farmer and to the nation's interests as a whole. The same is undoubtedly true for any of the other grain-exporting or grain-importing areas of the world; in fact, the value of grain as a food for mankind makes the problem one of worldwide concern. The request made to the Food and Agricultural Organization — as a result of discussions at the International Meeting on Infestation of Foodstuffs held in London in August 1947 — to conduct a critical review of the methods of grain drying and storage in use in all parts of the world was only a reflection of the present and potential importance of the problem and sure evidence of its worldwide scope.

With the advent and subsequent development of mechanized harvesting methods, artificial drying of grain has attained unprecedented importance. In the United States alone it has been estimated that nearly ten percent of the grain produced on farms never gets to be utilized because of losses during harvesting and farm storage. (22) Both harvesting and storage losses can be greatly minimized by adoption and proper management of sound drying practices. Recent studies have revealed that for a picker sheller minimum field losses of corn will occur when the moisture content is as high as twenty-four to thirty percent wet basis (22). On the other hand, the

recommended maximum moisture content for safe storage as shelled corn is, under most conditions, around thirteen percent wet basis. Obviously, a method of removing the excess moisture is necessary in order to realize the benefits of mechanized harvesting and still assure safe storage after harvesting at high moisture levels. It was estimated in the above studies that approximately 55 percent of the normal harvest loss of corn could be saved by making proper use of artificial methods of drying. Similar results have been obtained elsewhere for wheat where harvesting by combine at about 18 percent moisture resulted in a reduction of one to two percent of the normal expected losses. Regarding losses in storage the possibilities of effecting savings by drying are even more impressive. Hall (22) has estimated that approximately 95 percent of the storage losses of both grain and hay could be prevented through proper storage and drying, and that possible savings of 75 percent of the total losses which occur during harvesting and storage could be realized by a combination of early harvest and subsequent drying. It is clear from the foregoing that the importance of artificial drying of grain can hardly be overemphasized.

Since the inception of artificial grain drying there has been a need for information concerning the drying characteristics of the various kinds of grains as a basis for design. While considerable research effort and funds have been increasingly spent in agricultural drying, most of the investigations to date have been concerned with finding immediate solution to practical problems without much

regard to theoretical analysis. As a result, present design practice concerning grain drying equipment and processes have remained largely dependent on experience and empirical knowledge rather than on precise scientific principles. Despite a few noteworthy contributions in recent years there still exists a pressing need for more extensive fundamental research which may yield additional engineering data and at the same time lead to the development of more exact relationships for grain drying. This need has been materially accentuated by the recent trend toward increased use of heated air in drying, and the consequent use of elevated temperatures in the drying process. Most of the present available data concerning hygroscopic equilibria of grains has been the result of pioneering work performed at a time when heated-air drying had not come into being. Consequently there is a great dearth of basic information pertaining both to the equilibrium and to the rate relationships of the drying process in the range of temperatures usually employed in drying with heated air.

It is a well-recognized fact that in any bulk drying process the decrease in moisture content of the grain is controlled by the drying characteristics of the individual kernels. For any given grain these characteristics are known to depend mainly on the moisture content, and on the temperature and humidity conditions of the drying air. A knowledge of the characteristic drying rates of fully exposed grain under a wide diversity of drying conditions is of unquestionable value in solving design problems and in the proper

management of drying equipment and processes. The energy relationships involved in any process are always of interest from the standpoint of economy and efficiency. It is well known that the heat required to remove one pound of water from grain is substantially larger than that required for the vaporization of one pound of free water. However, little is known as to the exact amounts of heat needed for drying the various kinds of grain at various moisture levels. In spite of recent contributions along that line, there is great need for additional data on the heats of drying of agricultural crops.

The far-reaching developments in the field of adsorption theory which have taken place over the past fifteen or twenty years have provided important tools with which to probe deeper into the mysteries of the water relations of cereal grains. It is felt that nothing can contribute more to pave the way toward the development of exact mathematical equations for grain drying than to elucidate the mechanisms by which water is bound in the grain. A most fruitful approach to the study of the fundamental water-grain relationships has been found in the theoretical analysis of desorption isotherms on the basis of existing adsorption theories. Obtaining accurate hygroscopic equilibrium data over a wide range of temperatures afforded a valuable opportunity for contributing to that end.

The investigation is primarily concerned with an experimental inquiry into the theoretical aspects of grain drying with the broad objective of gaining fundamental information pertaining both to the

equilibrium and to the rate relationships of the drying process, with particular reference to corn. There were several reasons for selecting shelled corn as the experimental material. In the first place it was considered that corn is by far the most important cereal grain in the United States where the annual crop of well over 3,000 million bushels is fed mostly to livestock and therefore must be safely stored until it is consumed. Secondly, while at present corn does not hold such an outstanding position in Puerto Rico as it does on the mainland, it is even now the only cereal crop grown to any considerable extent in the island. Furthermore, it occupies a high-ranking position among the potential crops which are being considered for expansion in the present efforts toward improving the balance in the existing agricultural pattern of the island. Mechanization of the corn crop is now being intently explored and most assuredly will soon be widely adopted; there is little doubt that artificial drying will have to go hand in hand with the mechanization effort. It was felt, therefore, that by working with corn the results of the investigation could make a more immediate contribution to Puerto Rican agriculture. In the third place it was considered that most of the recent work on grain drying theory has been done in Canada and the United Kingdom on wheat grain, there being perhaps more information available pertaining to wheat than to any other of the cereal grains. In view of the foregoing, it appeared logical that corn be selected as the material for this investigation.

OBJECTIVES

The investigation was undertaken with the following specific objectives in mind:

1. To obtain hygroscopic equilibrium data for shelled corn over a wide enough range of constant drying conditions to enable the construction of desorption isotherms at temperatures of 40° , 60° , 86° , 100° , 122° , and 140° F.
2. To obtain information on the characteristic drying rates of shelled corn under the various test conditions.
3. To test the validity of the vapor pressure theory of drying as applied to agricultural products, and in particular to grain.
4. To obtain information concerning the magnitudes of the heats of desorption for shelled corn at different moisture levels.
5. To investigate the applicability to the desorption isotherms of various isotherm equations and theories in an attempt to elucidate the exact nature of the water-binding mechanism in shelled corn.
6. To obtain experimental evidence of the validity of Henderson's equation in correctly accounting for the shape characteristics and temperature dependence of the desorption isotherms.
7. To explore in a preliminary way the possibilities of influencing the drying characteristics of shelled corn by means of electromagnetic irradiation.

RELATED LITERATURE

Hygroscopic Nature of Cereal Grains

Most problems related to cereal grains, whether they are concerned with harvesting operations, conditioning, storing, marketing, or even processing are dominated to a greater or lesser degree by considerations of water content. Depending on the vapor pressure that it is capable of exerting, the water associated with the grain has been conveniently divided into two general types: free water and bound water. According to this criterion, the water in the grain that exerts its full vapor pressure at any given temperature is called free water, while that which exerts less than its normal vapor pressure is classified as bound or hygroscopic water. The extent to which the latter type exhibits a lower than normal vapor pressure will depend on the particular type of binding involved. Each type of binding in turn is characterized by a particular energy of reaction, and for any given grain it has been found that both are related to the level of moisture content. In general, the lower the moisture content the greater is the binding energy involved and consequently the lower will be the vapor pressure exerted at any given temperature.

The water-binding property of solids is termed hygroscopicity, and it is perhaps the most important single characteristic of grains from the standpoint of conditioning and storing problems.

While conceivably cereal grains may at times contain appreciable amounts of free water, it is generally recognized that it is the hygroscopic type of water that plays by far the most important role in the practically important range of moisture contents. This practical range of water content has generally been defined between 10 and 35 percent wet basis. (25)

A deeper insight into the hygroscopic nature of cereal grains may be gained by a brief consideration of the structural characteristics of two of the predominant constituent substances occurring in grain, namely, starch and protein. Both of these are classified among the group of compounds generally known as high polymers, or macromolecules, so-called because their individual molecules are a result of the linking together by actual chemical bonds of a large number of ordinary chemical molecules to form a large molecule which then exhibits associative effects.

Starch, on the one hand, is a natural high polymer built up by repetition of the basic glucose unit into a long branched chain as represented by the formula shown in Figure 1. This natural high polymer is characterized by hydroxyl groups on the ring,

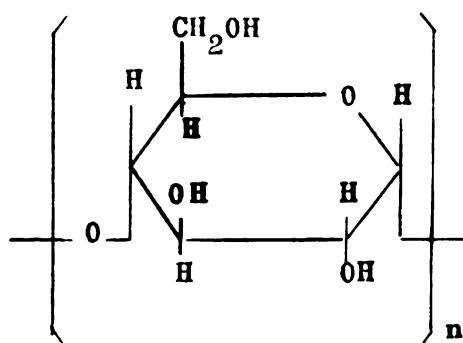
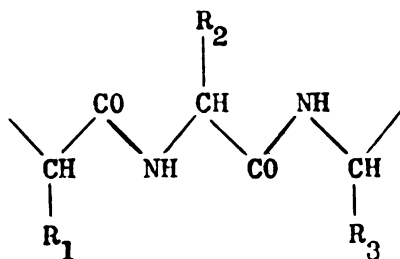


Figure 1. Diagram showing the structural arrangement of the starch molecule.

ring oxygen, and bridge oxygen, all of which are points of polarity in the molecule and therefore suitable foci for interaction with water molecules. Proteins, on the other hand, are derived essentially from the combination of amino acids and characterized by the presence of the polypeptide chain made up of repetitions of the peptide unit:



where each different R represents a side chain characteristic of particular amino acids to be found in various parts of the chain.

According to the results obtained independently by several investigators, summarized recently by Hlynka and Robinson (25), there are two hydrophilic groups in the structure of the proteins which are capable of binding water probably through the formation of hydrogen bonds. These are, in the first place, the amino acid side chains which usually carry a wide variety of polar and ionic groups; and secondly, the oxygen and nitrogen associated with the peptide bonds in the peptide chain. It has been suggested that the amount of water held by a protein is thus primarily determined by the number and availability of these two polar groups. The finding by Benson and his co-workers (5) that water adsorption

by proteins was independent of the surface area in the range below one-fourth the saturation vapor pressure led them to suggest that water adsorption takes place at specific sites on the protein molecules. In line with these views, Snow et al have also found a definite correlation between the relative amounts of protein and carbohydrate content and the general pattern of water sorption by various feedstuffs. There can be little doubt therefore as to the vital role that both proteins and starch play in the water relations of cereal grains.

Hygroscopic Equilibrium Relationships

The relationship between the vapor pressure of water over a hygroscopic solid and the moisture content of the solid can be determined by experiment, and is usually given in the form of a curve wherein the moisture content of the material is plotted against the relative humidity of the air in equilibrium with the material. The usual arrangement is for the moisture content values to be plotted as ordinates and the relative humidities as abscissae. Because the equilibrium relationship is usually obtained at a constant specified temperature, the curve is designated an isotherm. Furthermore, depending on whether water is taken up or given off by the solid in approaching equilibrium, the curve is referred to as a sorption or a desorption isotherm, respectively. More often the sorption isotherm is called an adsorption isotherm, since in most cases the sorption mechanism involved is specifically one of adsorption.

Since the isotherm represents an equilibrium relationship, the same curve should, theoretically, represent the end points of both water sorption and desorption processes applied to the material. In practice, however, when sorption and desorption isotherms have been obtained experimentally, the curves frequently do not coincide over their full length but the desorption curves give lower equilibrium relative pressures for a given moisture content than do the sorption curves. This phenomenon is generally known as hysteresis, and though it is not as yet fully understood, several hypotheses have been advanced to account for its occurrence. (25) The most satisfactory explanations are still based on the capillary theory of adsorption which will be briefly discussed in a later section. It may suffice to caution at this point that in the experimental determination of isotherm data it is important to adhere to the same direction of approach to equilibrium in order to avoid the adverse influence of hysteresis effects on the comparability of the data and on their suitability for constructing isotherm curves. It is likewise important to designate the data according to the particular process involved. It may be added that when problems concerning drying processes are under consideration it is preferable to refer to desorption isotherms, while adsorption data are more generally applicable to problems in storage.

The moisture content of the material that corresponds to the relative humidity of the surrounding air after equilibrium

has been established is a point in the isotherm curve. This is usually called the equilibrium moisture content or quite frequently, the hygroscopic equilibrium of the material. Conversely, the corresponding relative humidity is referred to as the equilibrium relative humidity for the particular moisture content, or as the equilibrium relative pressure when it is expressed in decimal form. Actually, at equilibrium the vapor pressure of the water associated with the grain is equal to the partial aqueous vapor pressure of the surrounding atmosphere so that the ratio of either one to the saturation vapor pressure of water at the specified isotherm temperature gives the equilibrium relative pressure.

It follows from the above considerations and from the definitions of free and bound waters that the moisture content corresponding to a relative humidity of 100 percent is the moisture that divides the free and bound types of water in the material. Beyond this moisture content the material contains some free water and a maximum amount of bound water, while below it the material contains only bound water. It is well to caution at this time that the term "free water" as herein defined, must not be confused with the similar term "free moisture content" to be introduced later in connection with the discussion on drying relationships. The latter term refers to the difference between the moisture content at any instant and the equilibrium moisture content for the material in question, under a given set of drying conditions. This amount of moisture is actually the maximum that can possibly be removed from the

material under the specified drying conditions, and may obviously include both bound and free water depending on the particular moisture content under consideration.

While there are undoubtedly other ways in which water may be bound by cereal grains, such as in solution or in chemical combination, it is now generally agreed among investigators of the subject that the predominant binding mechanism involved is that of adsorption. Because of its tremendous importance in connection with the problem under investigation, it is deemed appropriate to review at this moment a few pertinent facts concerning the phenomenon of adsorption.

Nature of Adsorption

Whenever a gas or vapor is brought in contact with a solid, its molecules distribute themselves so that there will be a higher concentration of the gas at the surface of the solid than in the bulk of the gas. This is the phenomenon called adsorption; the solid that takes up the gas or vapor is called the adsorbent, while the adsorbed substance is called the adsorbate. The phenomenon of adsorption is not by any means confined to solid-gas interfaces; it may be expected to occur at any contact between a gas and a liquid, a liquid and a solid, between two liquids, and even, in certain circumstances, when two solids come into contact (9). In water-grain relationships, the dry grain may be considered as an adsorbent, and water—whether in the liquid or in the vapor phase—as the adsorbate.

There are two general types of adsorption depending on the relative strength of interaction between adsorbent and adsorbate. When there is a relatively weak interaction between adsorbent and adsorbate, involving only forces of the order of magnitude of those active in condensation phenomena, the adsorption is called physical or van der Waals adsorption. On the other hand, when strong interaction takes place, involving forces similar to those active in chemical reactions, the adsorption is called chemical adsorption or chemisorption. The fact that chemisorption can not take place without an energy of activation being supplied to the system led Taylor (9) to introduce the term "activated adsorption" by which name it is often cited in the literature. While the probability of chemisorption playing at least some minor role has been considered by several investigators, it is now generally agreed that it is the van der Waals type of adsorption that is almost wholly concerned in grain-water relationships.

Representing Adsorption Equilibrium Data

In any adsorption equilibrium the number of molecules falling on the surface and being adsorbed must be equal to the number of molecules which are set free from the surface to re-evaporate. For a given adsorbate and a unit weight of adsorbent, the amount of adsorbate adsorbed at equilibrium is a function of the final pressure and temperature only. This general relationship may be stated thus

$$M = f (p, T) \quad (1)$$

where M is the amount of adsorbate adsorbed per gram of adsorbent, p is the equilibrium pressure, and T is the absolute temperature. By keeping one of the three variables constant while the others are varying, the above relationship may be obtained in any one of three different ways.

When the pressure of the gas or vapor is varied while the temperature is held constant the plot of the amount adsorbed against the pressure is called the adsorption isotherm, and the general isotherm equation is

$$M = f(p) \quad T = \text{constant} \quad (2)$$

This is by far the most frequently determined and indeed the most important experimental relation in the field of adsorption. It can be readily identified with the equilibrium moisture content-relative humidity curve of cereal grains and similar hygroscopic materials which has been previously mentioned, since in describing sorption of vapors it is customary to plot relative pressures or relative humidities rather than absolute pressures. It may be pointed out at this point that except for the hysteresis effects commonly encountered, the general characteristics and energy relationships involved are the same for the equilibrium curve regardless of whether the isotherm is obtained by an adsorption or a desorption process.

The other two methods of representing adsorption equilibrium data are by means of the adsorption isobar and the adsorption isostere. The isobar is obtained by plotting the amount of

adsorbate adsorbed against the temperature at which the adsorption takes place while the pressure is kept constant. The relationship then becomes

$$M = f(T) \quad p = \text{constant} \quad (3)$$

The adsorption isostere is the curve obtained from a plot of the variation of the equilibrium pressure with temperature corresponding to a constant amount of adsorbate adsorbed. The equation of the isostere is thus

$$p = f(T) \quad M = \text{constant} \quad (4)$$

The isosteres resemble the vapor pressure curves of a psychrometric chart, increasing at first slowly then rapidly with temperature. Just as every point on the vapor pressure curve represents a pressure and a temperature at which water and its vapor are in equilibrium with each other, on the isostere every point represents a pressure and a temperature at which grain of a given moisture content is in equilibrium with the water vapor of the surrounding atmosphere.

Types of Isotherms

There are various types of isotherms which can be found in the literature. In 1940 Brunauer and his co-workers (9) proposed a classification of isotherm types which has since been widely adopted by other investigators and authorities in the field. Their classification includes five principal types, according to shape characteristics, which they designated by Roman numerals from I

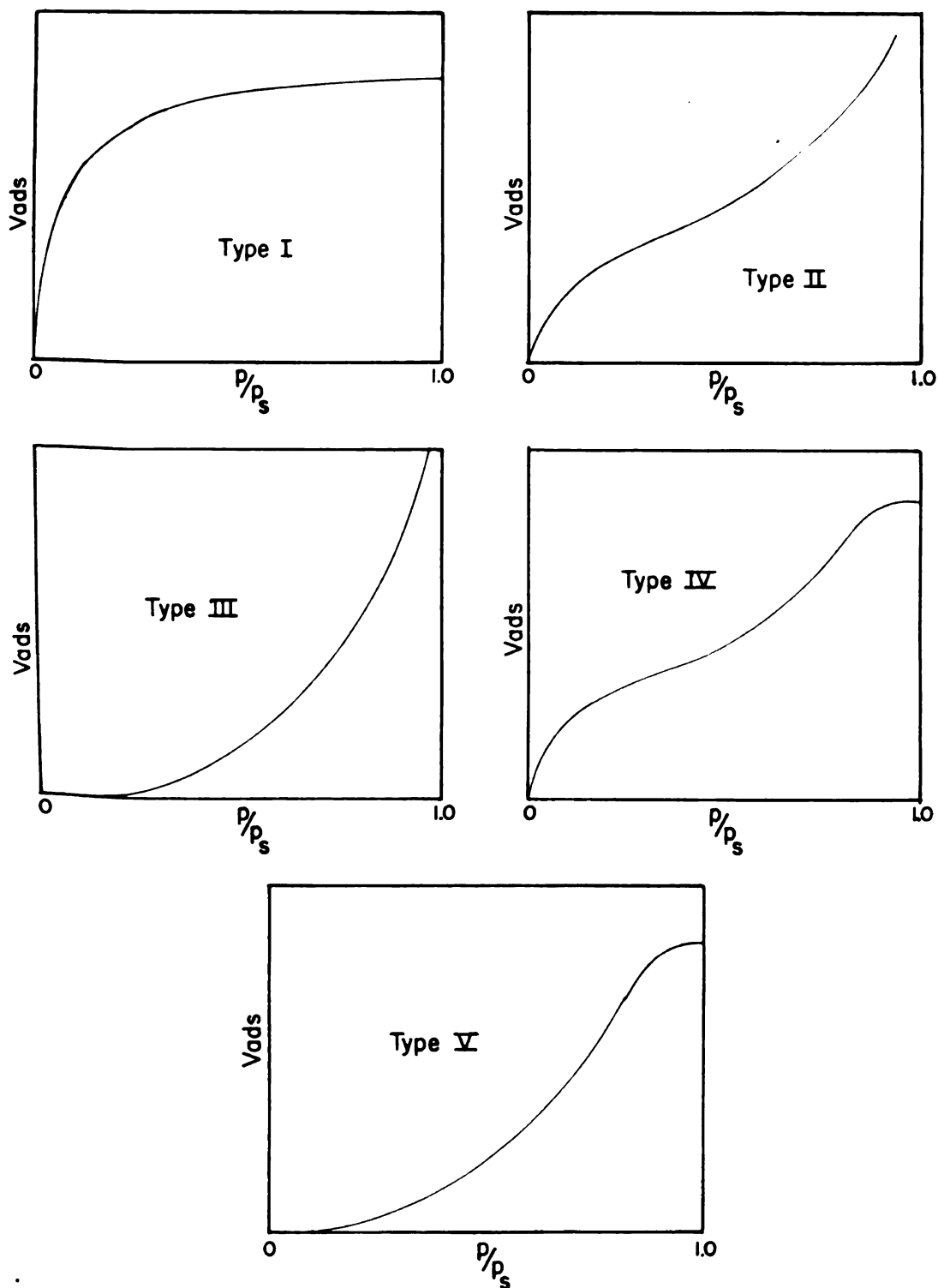


Figure 6 Brunauer's classification of the five isotherm types in physical adsorption.

to V as shown in Figure 6. The curves are imaginary isotherms which illustrate the general shape characteristics of each type. Brunauer et al also gave the names Langmuir isotherm and the S-shaped or sigmoid isotherm to Types I and II respectively, but none to the other three types. Type II isotherm has been generally attributed to multimolecular adsorption, and is of great importance in relation with cereal grains and related materials.

Thermodynamic Functions of Adsorption

When a gas or vapor is adsorbed by a solid, the adsorbed particles are either held rigidly to the surface, or they are free to move over the surface in two dimensions. Since prior to adsorption the gas molecules moved freely in three dimensions, it follows that the adsorption process must always be accompanied by a decrease in entropy.

The atoms or molecules constituting a given solid are held together by different forces. Whatever the nature of these forces an atom located inside the body of the solid is subjected to equal forces in all directions, whereas an atom in the plane of the surface is subjected to unbalanced forces, the inward pull being greater than the outward forces. This results in the solid exhibiting a surface tension, similar to that of liquids even though of much greater magnitudes (9). Upon adsorption of a substance by the solid, the atoms or molecules of the former tend to saturate some of the unbalanced forces of the surface, thereby decreasing

the surface tension and hence also the free surface energy, this being the product of the surface tension and the surface area. Since any process that tends to decrease the free surface energy occurs spontaneously, it is seen that all adsorption phenomena, whether physical or chemical, are spontaneous in character and always result in a decrease of the free surface energy of the system. Thermodynamically the state of adsorption equilibrium is attained when the change in the free surface energy of the system is zero.

The change in heat content of the adsorbent-adsorbate system is given by

$$\Delta H = \Delta F + T\Delta S \quad (5)$$

where ΔF is the change in the free energy of the system, T is the absolute temperature, and ΔS is the entropy change. Since, as was seen before, both ΔF and ΔS are always negative it follows that ΔH must also be negative. This means that the adsorption process results in the evolution of heat, and is therefore described as exothermic in character. The decrease in the heat content of the system is generally called the heat of adsorption. The general magnitude of the heat of adsorption serves as a measure of the nature of the forces involved in the process and may assist in distinguishing between physical and chemical adsorption. In van der Waals adsorption it is of the same order of magnitude as the heats of condensation of gases, whereas in chemisorption it compares with the heats of chemical reactions.

Various Heats of Adsorption

It is deemed necessary at this point to differentiate between the various heats of adsorption that can be found in the literature. Let it be assumed for the sake of illustration that a definite amount N_a moles of an ideal gas is adsorbed by the clean surface of 1 gram of adsorbent. The amount of heat liberated in this process is called the integral heat of adsorption. If the energy of the gas per gram in the gas phase is denoted by E_g and the energy of the gas per gram in the adsorbed state by E_a , and assuming that no external work is done in the process, this loss of heat from the system is given by

$$Q_{\text{int}} = N_a (E_g - E_a) \quad (6)$$

The integral heat of adsorption Q_{int} usually expressed in kilocalories per gram, is therefore proportional to the amount of gas which is adsorbed. Now if the amount of gas adsorbed is increased by an incremental amount dN_a , an additional amount of heat, dQ_{int} , will be liberated. Keeping the temperature constant, the differential coefficient

$$\left(\frac{dQ_{\text{int}}}{dN_a} \right)_T \quad (7)$$

is called the differential heat of adsorption, sometimes also referred to as the instantaneous heat of adsorption, which will be denoted by q_d .

If the expression for Q_{int} given above is now differentiated with respect to N_a , one obtains

$$q_d = \left(dE_{\text{int}} / dN_a \right)_T = E_g - E_a + N_a \left(\frac{d(E_g - E_a)}{dN_a} \right)_T \quad (8)$$

Since for an ideal gas E_g is a function of the temperature only, the above equation simplifies to

$$q_d = E_g - E_a - \left(\frac{dE_a}{dN_a} \right)_T \quad (9)$$

For the case in which the adsorption is performed under isothermal conditions and without change in the total number of molecules, then work is done in the process, since a volume dv of gas at a pressure p , corresponding to the number of molecules which are adsorbed, has disappeared. Applying the perfect gas law, this amount of work is

$$p dv = dN_a R T \quad (10)$$

where R is the universal gas constant. Therefore, the work done per mole of gas adsorbed is given by the product RT . Because of the isothermal conditions of the process, Huckel (9) has called the quantity

$$Q_{\text{isoth}} = q_d + RT \quad (11)$$

the isothermal heat of adsorption. Since, however, $q_d + RT$ always refers to a definite quantity of gas adsorbed at different temperatures and pressures, Brunauer preferred to call it the isosteric heat of adsorption, which term has been more widely adopted and which will therefore be adhered to throughout this dissertation. The fact that this amount of heat of adsorption



can also be derived by thermodynamic arguments from the explicit equation of the adsorption isostere (6) lends additional support to the adoption of the latter term.

The heat of adsorption may be measured directly by calorimetric determinations, in which case it is usually termed the calorimetric heat of adsorption. When it is thus determined, the value obtained usually lies somewhere between q_d and Q_{isoth} , depending on the conditions of the experiment. It is fortunate, however, that in most cases the fraction of heat RT is small as compared with both q_d and Q_{isoth} , usually not amounting to more than about 5-10 percent of the total heat of adsorption. (9)

From thermodynamic considerations it may be safely assumed that the same amount of energy involved in the process of adsorption will have to be supplied in order for desorption to take place. Exactly the same terms defined above and conveying essentially the same meaning may therefore be applied to the quantities of heat involved in desorption processes.

When the heats of adsorption are larger for a given adsorbent-adsorbate system than the corresponding heats of liquefaction of the adsorbate, as is usually the case for cereal grains and water, it is sometimes convenient to refer to the difference between the two by the general term of net heats of adsorption. Thus Becker and Sallans (4) have recently reported values on the differential net heats of desorption of water from wheat at 25°C as calculated from desorption isotherms. They also defined the heat of dehydration as the additional heat above the normal heat of vaporization

which is required to reduce the moisture content from saturation to a designated level, usually expressed in calories per gram of grain, dry basis. This actually corresponds to the net integral heat of desorption for the moisture level under consideration.

Besides the foregoing, the term latent heat of vaporization has also been frequently applied to the amount of heat necessary to evaporate water from agricultural crops. (17, 30) It should not be confused, however, with the same term as applied to free water. In the sense in which it is most frequently used with reference to grains, the term is intended to mean the differential heats of adsorption.

Adsorption Theories and Equations

It is beyond the scope of this dissertation to delve into adsorption theory in too much detail. Two very thorough discussions on the subject have been given by Brunauer and by de Boer in their well-known books on adsorption. However, it is considered necessary to review briefly some of the salient features of the most important theories of adsorption as a background to an understanding of later discussions pertaining to the analysis of the experimental data.

Langmuir's Equation

Although as early as 1814 T. de Saussure (9) had already outlined many of the points featured by the later adsorption theories, until 1914 no satisfactory treatment of these phenomena had

as yet been formulated. In 1915 Langmuir (33) proposed a theory based on his belief that adsorption was essentially a chemical process leading to a unimolecular layer of the adsorbate. In arriving at his isotherm equation Langmuir made two simplifying assumptions. He first assumed that the heat of adsorption was the same for every molecule striking the bare surface of the adsorbent and furthermore that this heat of adsorption was independent of the other molecules already adsorbed. Secondly, he assumed that every molecule striking another one already adsorbed was elastically reflected, and only those molecules condensed that made contact with the clean surface of the adsorbent. The Langmuir equation is

$$v = \frac{K_L p}{1 + K_L p} \quad (12)$$

where v is the volume of gas adsorbed, p is the pressure, and K_L is the adsorption coefficient which in turn is a function of the temperature only.

Despite the two simplifying assumptions involved in its derivation, which considerably limit its scope, the Langmuir isotherm equation is now regarded as perhaps the most important single equation in the field of adsorption, serving in many cases as the starting point in the derivation of other equations. Type I adsorption isotherms are best interpreted in terms of Langmuir's equation and accordingly, are sometimes referred to as Langmuir isotherms.



Potential Theory

About the same time that Langmuir postulated his theory, Polanyi (9) proposed another theory following an altogether different approach. He assumed that adsorption was a physical process due to long range attractive forces extending out from the surface of the adsorbent and leading to multimolecular adsorption. The Polanyi theory has also been known as the potential theory. Polanyi defined the adsorption potential at a point near the adsorbent surface 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 the so-called hydrostatic equation

$$e_i = \int_{\rho_x}^{\rho_i} V \, d\rho \quad (13)$$

where e_i is the adsorption potential at a point where the density of the adsorbed substance is ρ_i , ρ_x is the density in the gas phase, and $V = M/\rho$ where M is the molecular weight of the adsorbate. V is the molar volume of the adsorbate. It is fundamental to Polanyi's theory that the adsorption potential at any given point is characteristic of the adsorbent alone and is not affected by either the temperature or the presence of other molecules. Hence it is possible to map out the entire adsorption space into a number of equipotential surfaces, the disposition of which would be characteristic of the adsorbent. The potential theory applies to both unimolecular and multimolecular adsorption



and has been credited by Brunauer as being the only theory that can handle quantitatively adsorption on strongly heterogeneous surfaces. Another noteworthy feature of the theory is its success in predicting the temperature dependence of physical adsorption. However, since the theory does not attempt to formulate an isotherm equation, the scope of information obtainable is limited.

Capillary Condensation Theory

It has long been known that if a capillary is immersed in a liquid that wets its walls, the liquid rises in the capillary and forms a meniscus which is concave toward the vapor phase. The vapor pressure over the meniscus is lower than the normal vapor pressure of the liquid by an amount equal to the pressure exerted by the column of liquid in the capillary. The vapor pressure lowering over the cylindrical capillary is given by Kelvin equation

$$\ln p_s - \ln p = \frac{2 \sigma V}{r R T} \quad (14)$$

where p is the equilibrium vapor pressure over the meniscus in the capillary, p_s is the normal vapor pressure, σ is the surface tension and V is the molar volume of the liquid at temperature T , and r is the radius of the capillary. It will be seen that the smaller the radius, the greater will be the vapor pressure lowering according to equation (14).

It was Zsigmondy in 1911 who first correlated the adsorption of water with the capillary properties of the adsorbent (55). His conclusion that in capillaries of sufficiently small diameters

(such as those occurring in silica gel) liquid would condense at pressures far below the normal vapor pressure, may be regarded as the first formulation of the capillary condensation theory. In terms of the theory every value of relative pressure corresponds to a capillary radius that can be calculated from the Kelvin equation. As the vapor pressure is increased always larger capillaries fill until finally at the saturation pressure all the pores of the adsorbent fill with liquid.

Today most investigators agree that capillary condensation plays some role in physical adsorption. It is generally believed, however, that it becomes important only when adsorbents have capillaries at least several molecular diameters in width, and then only at the higher relative vapor pressures.

Polarization Theory

The polarization theory was first proposed by de Boer and Zwikker in 1929 (9) and again in a somewhat different form by Bradley in 1936 (7). It explains the adsorption of non-polar molecules on ionic adsorbents by assuming that the uppermost layer of the adsorbent induces dipoles in the first layer of adsorbed molecules, which in turn induce dipoles in the next layer, and so on until several layers are built up. Dipoles are molecules which though neutral, have both positive and negative charges. If the center of gravity of the negative charges does not coincide with the center of gravity of the positive charges

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the molecules are said to possess a permanent dipole moment. Their electrical nature enables them to induce an electric field in their neighboring molecules; they are also free to turn and align themselves in order to satisfy the charges. Water constitutes a good typical example of a dipole molecule.

The B-E-T Theory of Multimolecular Adsorption

This theory, first postulated by Brunauer, Emmett and Teller in 1938 (10) and two years later by Brunauer, Deming, Deming, and Teller (11) is based on the assumption that the same forces that produce condensation are also responsible for the binding energy of multimolecular adsorption. In contrast with the polarization theory which attributes adsorption to the action of induced dipoles, the B-E-T theory of multimolecular adsorption ascribes the cause for adsorption to the totality of the van der Waals forces. According to Brunauer, the B-E-T theory constitutes the first attempt to give a unified theory of physical adsorption. Its most general equation includes all five isotherm types as special cases and describes the shape of each isotherm type through the entire range of adsorption, from zero pressure to saturation pressure. This includes the region of unimolecular adsorption, multimolecular adsorption and capillary condensation, in contrast to the separate treatments accorded to these regions by the previously mentioned theories.

Because of the great importance which the theory of Brunauer, Emmett and Teller have obtained during the last years, and also

because of its bearing on the analysis of the experimental data of this investigation, the arguments followed by its originators in the derivation of their most useful equations will be now presented in some detail.

Let $s_0, s_1, s_2, \dots, s_i, \dots$ represent the surface area that is covered by 0, 1, 2, $\dots, i, \dots$ layers of adsorbed molecules. Since at equilibrium s_0 must remain constant, the rate of condensation on the bare surface must be equal to the rate of evaporation from the first layer, or

$$a_1 p s_0 = b_1 s_1 e^{-E_1/RT} \quad (15)$$

where p is the pressure, E_1 is the heat of adsorption in the first layer; and a_1 and b_1 are constants.

At equilibrium s_1 also must remain constant. From the principle of microscopic reversibility it follows therefore that

$$a_2 p s_1 = b_2 s_2 e^{-E_2/RT} \quad (16)$$

or the rate of condensation on top of the first layer is equal to the rate of evaporation from the second layer. In equation (16) E_2 is the heat of adsorption in the second layer, and a_2 and b_2 are constants. Extending the same argument to $s_2, s_3, \dots$

$$\begin{array}{rcl} a_3 p s_2 & = & b_3 s_3 e^{-E_3/RT} \\ \vdots & & \vdots \\ a_i p s_{i-1} & = & b_i s_i e^{-E_i/RT} \end{array} \quad (17)$$

The total surface of the adsorbent is given by

$$A = \sum_{i=0}^{i=\infty} s_i \quad (18)$$

and the total volume adsorbed is

$$v = v_0 \sum_{i=0}^{i=\infty} i s_i \quad (19)$$

where v_0 is the volume adsorbed on one square centimeter of the adsorbent surface when it is covered with a complete unimolecular layer. It follows that

$$\frac{v}{A v_0} = \frac{v}{v_m} = \frac{\sum_{i=0}^{i=\infty} i s_i}{\sum_{i=0}^{i=\infty} s_i} \quad (20)$$

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

The summation indicated in equation (20) can be carried out, if the simplifying assumptions are made that

$$E_2 = E_3 = \dots E_i = E_L \quad (21)$$

where E_L is the heat of liquefaction, and

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \frac{b_i}{a_i} = g \quad (22)$$

where g is an appropriate constant.

This is equivalent to assuming that the evaporation-condensation properties of the molecules in the second and higher layers are the same as those of the liquid state. The assumption is deemed reasonable on the grounds that the effect of the adsorbent is probably quite small already in the second layer, since the van der Waals forces have a very short range of action. Now $s_1, s_2, s_3, \dots, s_i \dots$ can be expressed in terms of s_0 thus

$$s_1 = y s_0, \text{ where } y = (a_1/b_1) p e^{E_L/RT} \quad (23)$$

$$s_2 = x s_1, \text{ where } x = (p/g) e^{E_L/RT} \quad (24)$$

$$s_3 = x s_2 = x^2 s_1 \quad (25)$$

$$s_i = x s_{i-1} = x^{i-1} s_1 = y x^{i-1} s_0 = c x^i s_0, \quad (26)$$

where

$$c = y/x = (a_1 g/b_1) e^{(E_1 - E_L)/RT} \quad (27)$$

Substituting into equation (12)

$$v/v_m = \frac{c s_0 \sum_{i=1}^{\infty} i x^i}{s_0 [1 + c \sum_{i=1}^{\infty} x^i]} \quad (28)$$

The summation represented in the denominator is merely the sum of an infinite geometric progression

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x} \quad (29)$$

About the summation in the numerator it is noted that

$$\sum_{i=1}^{\infty} i x^i = x \frac{d}{dx} \sum_{i=1}^{\infty} x^i = \frac{x}{(1-x)^2} \quad (30)$$

Substituting (29) and (30) into (20)

$$v/v_m = \frac{c x}{(1-x)(1-x+cx)} \quad (31)$$

If the adsorption takes place on a free surface, then at p_s , the saturation pressure of the gas, an infinite number of layers can build up on the adsorbent. To make $v = \infty$ when $p = p_s$, x must be equal to unity in equation (31). From equation (24) it follows that

$$(p_s/g) e^{E_L/RT} = 1 \quad (32)$$

$$\text{and} \quad x = p/p_s \quad (33)$$

Substituting into equation (31) the B-E-T isotherm equation is obtained:

$$v = \frac{v_m c p}{(p_s - p)(1 + (c-1)(p/p_s))} \quad (34)$$

For the purpose of testing, equation (34) may be put in the form

$$\frac{p}{v(p_s - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} (p/p_s) \quad (35)$$

Equation (35) is the isotherm equation of the multimolecular adsorption theory for adsorption taking place on a free surface.

It is a linear equation so that the plot of function $p/v(p_s - p)$ against p/p_s gives a straight line, if the theory is obeyed.

The intercept of the straight line is $1/v_m c$, and the slope is $(c-1)/v_m c$. The constants v_m and c can be obtained from the experimental data.



The constant c is given by equations (19) and (14).

$$c = (a_1 b_2 / b_1 a_2) e^{(E_1 - E_L)/RT} \quad (36)$$

From the nature of the constants a_1 , b_1 , a_2 , and b_2 it follows that $a_1 b_2 / b_1 a_2$ will not differ much from unity. As a first approximation it may therefore be written that

$$c = e^{(E_1 - E_L)/RT} \quad (37)$$

Thus from constant c the value of E_1 , the average heat of adsorption in the first layer, can be calculated.

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. For instance, if the maximum number of layers that can be adsorbed on each wall of a capillary is denoted by n , then the summation of the two series in equation (20) is to be carried to n terms only and instead of equation (35) the following is obtained.

$$v = \left[\frac{v_m c x}{1 - x} \right] \left[\frac{1 - (n+1) x^n + n x^{n+1}}{1 + (c-1) x - c x^{n+1}} \right] \quad (38)$$

It will be seen that this is identical to Langmuir's isotherm equation with the constant b having the value c/p_s .

The other limit is when $n = \infty$, which is equivalent to the adsorption taking place on a free surface. In this case equation (38) reduces to equation (35). It should also be noted that when x is small and n at least as large as 4 or 5, equation (35) becomes a very good approximation to (38). To use equation (38) the

experimental data should therefore be plotted in the low pressure region according to the linear equation (35), in order to evaluate the constants v_m and c from the slope and intercept of the straight line. These values of v_m and c should then be used in equation (38) in order to solve for the value of n that gives the best agreement with the experimental data. Equation (30) includes as special cases the isotherm types designated as I, II, and III, in Figure 6. If $n=1$, it reduces to (31) and the Type I isotherm is obtained. If n is larger than 1, either Type II or Type III isotherms are obtained depending on the value of the constant c . If the attractive forces between adsorbent and adsorbate are greater than the attractive forces between the molecules of the adsorbate in the liquid state, Type II isotherms are obtained. If, on the other hand, the forces between adsorbent and adsorbate are small so that E_1 is smaller than E_L , then Type III isotherms are obtained.

While equation (30) includes the first three isotherm types as special cases it does not account for Types IV and V. The shapes of these isotherms suggest that capillary condensation sets in at the higher relative pressures. To take care of this situation, Brunauer, Deming, Deming, and Teller (11) have derived other equations involving two additional constants. These need not be gone into here since aside from their theoretical significance in successfully accounting for the shape of Types IV and V isotherms they are of little practical usefulness.

In general, the two-constant B-E-T equation has been found to be obeyed very closely for many adsorbents over the range of relative pressures between 0.05 or 0.10 to at least 0.35, and sometimes 0.50. Outside of this range the equation usually breaks down. In recent years several investigators have applied the equation successfully to hygroscopic equilibrium data on grains and other biological materials. For instance, Bull (12) measured the adsorption of water vapor by a large number of proteins and found that the B-E-T simple equation fitted the isotherms over the full range of validity specified for the equation, namely, from a relative pressure of 0.05 up to 0.50. Quite recently, Becker and Sallans (4) obtained perfectly linear plots of desorption equilibrium data for wheat at 25°C up to a relative vapor pressure of about 0.35, which is the usual upper limit of applicability of the equation. Hogan and Karon (26) also applied the equation to their data on hygroscopic equilibria of rough rice and obtained fairly good linear plots over a range of relative pressures between 0.10 and 0.40. All of these results tend to favor the view that the water-binding mechanism predominating in cereal grains involves multimolecular adsorption as postulated by the B-E-T theory.

Harkins-Jura Equation

The accurate determination of the surface area of adsorbents has long posed a difficult problem of great practical as well as theoretical importance. One of the most useful applications of the B-E-T two-constant equation relates to this particular problem.

It will be recalled that the constant v_m of the B-E-T equation represents the amount of adsorbate needed for the completion of a unimolecular layer over the surface of the adsorbent. It follows that having determined a value for v_m according to the procedure previously outlined, a knowledge of the area occupied by one molecule of the adsorbate would readily allow the calculation of the effective surface area of the adsorbent. The method, though simple, still involves the assumption of a molecular area for the adsorbate, a requirement that is sometimes difficult to fulfill.

In 1914, Harkins and Jura of the University of Chicago (23) proposed a simple method of determining the surface area from the adsorption isotherm without the need of assuming a molecular area for the adsorbate. Their method consists first, in plotting the logarithm of the relative vapor pressure against the reciprocal of the square of the volume adsorbed. According to their theory, straight lines are thereby obtained over the range of relative pressures where a condensed film of the adsorbate is involved. Their equation for the above-mentioned linear plot is

$$\text{Log } (p/p_s) = B - A/V^2 \quad (40)$$

where V represents the amount of adsorbate corresponding to a given equilibrium relative pressure. The area of the adsorbent is then given by the equation

$$\sum = K A^2 \quad (41)$$

where $\sum$ is the surface area of the adsorbent, A is the slope of the linear plot referred to above, and K is a constant which

has to be determined for a given adsorbed vapor at a given temperature. By means of an absolute method Harkins and Jura have standardized values of K for a few gases and vapors at various temperatures. The areas obtained by application of their method have been found to be in very good agreement with those calculated by means of the B-E-T procedure. However, the usefulness of the H-J method has been greatly limited by a lack of knowledge concerning the behavior of the constant K in the above equation. Liang (34) has correlated the results of both the Harkins-Jura and the B-E-T equations and found that the square root of the slope A of the H-J equation corresponds closely with the value of the constant v_m of the B-E-T equation.

Dunford and Morrison (15) have applied the Harkins-Jura equation to Bull's water-protein adsorption isotherms and obtained good linear plots in most cases over the relative vapor pressure range from 0.5 or 0.6 to 0.95. They also used Liang's method for correlating the H-J and the B-E-T equations and found good agreement between the calculated values of v_m and $A^{\frac{1}{2}}$. It should be noted that whereas the value of v_m relates to the lowermost portion of the isotherm, that of $A^{\frac{1}{2}}$ corresponds to the higher pressure region. The general observation that the same value is obtained for these two opposite regions of the isotherm led Dunford and Morrison to suggest that the same number of adsorption sites and hence the same surface area are probably involved in the formation of both the first monolayer at the lower pressures and the condensed film at the higher relative pressures.

Smith's Equation

Searching for an explanation of the mechanism involved in the sorption of water by high polymers, Smith (44) derived the linear equation

$$w = w_b - w' \ln(1 - p/p_s) \quad (42)$$

where w is the amount of water vapor adsorbed expressed in percent wet basis. It will be seen that in the plot of values of w as ordinates against those of the function $\ln(1 - p/p_s)$ as abscissae, w' and w_b correspond respectively to the slope and intercept of the straight lines obtained. In general, Smith found the equation to yield good straight lines between relative pressure values of 0.5 and 0.95. According to Smith's treatment, w' represents at each stage of the sorption the weight fraction of water required to complete the first layer of normally condensed water molecules and in that sense is roughly comparable to the constant v_m of the B-E-T equation. The intercept, w_b , on the other hand is to be regarded as the measure of a tightly bound substratum of water molecules which paves the sorbing surface of the polymer and effectively reduces the intensities of the surface forces of attraction to the level of the forces in a liquid water surface. Smith found a striking agreement between the values of the B-E-T constant v_m and those obtained by averaging the values of w' and w_b , which led him to suggest that the surface area given by the B-E-T procedure really corresponds to an average between that covered by the tightly bound water molecules and that covered by the first normally condensed layer.

Becker and Sallans (4) also applied Smith's equation to their desorption isotherms of wheat and obtained curves which were essentially linear in the range of relative pressures from 0.50 to 0.95, which is the prescribed range of validity for the equation. Beyond a relative pressure of 0.95 the function $-\ln (1 - p/p_s)$ becomes highly sensitive to small absolute errors in the measurement of pressure.

Noting that the B-E-T and the Smith isotherm equations tend to complement each other as to their respective regions of validity, Becker and Sallans suggested an interesting method of defining the intermediate linear region characteristic of Type II isotherm by plotting the data according to both equations on the same graph and drawing a line tangential to the Smith curve and intersecting the B-E-T curve at its point of inflection. They found that this procedure resulted in an excellent fit of the experimental data and gave a smooth unbroken transition into the curved regions described by both equations.

Henderson's Equilibrium Equation

In an attempt to formulate an isotherm equation which could account for the temperature dependence of the experimental curve Henderson (24) derived by thermodynamic reasoning the following equation:

$$1 - p/p_s = e^{-k T M_e^n} \quad (43)$$

where T is the absolute temperature, and k and n are experimental constants characteristic of any given hygroscopic material.

The starting point for Henderson's derivation was Gibbs' adsorption equation which relates the surface tension of the adsorbed liquid, σ , the wetted surface of the adsorbent, s , the volume of the liquid adsorbed, v , and the osmotic pressure, P , as follows:

$$\frac{d\sigma}{dv} = - (dP/ds)_T \quad (44)$$

His complete derivation need not be included here; it may suffice to say that his derived equation turned out to be identical to an empirical relationship previously established, except for the addition of the temperature factor in the course of his derivation. He found remarkable agreement between observed and calculated values when the equation was applied to limited data available in the literature. Accordingly, he calculated and published the values of constants k and n for a large number of agricultural materials. While the equation appeared generally acceptable in describing the shape of the isotherm and fitting limited experimental data, Henderson himself cautioned against its general use pending further experimental confirmation of its validity.

Adsorption Rates and Equilibria

Theoretically, adsorption phenomena on a free surface take place with enormous rapidity, almost instantaneously. A brief look at the kinetic picture of the process will assist in realizing the order of magnitude of adsorption rates. Consider as an illustration that the clean surface of a hygroscopic substance such as

starch, or protein is suddenly exposed to an atmosphere with a relative humidity of 10 percent at a temperature of 20°C. This is a relatively dry atmosphere in which the pressure of the water vapor is 1.75 mm of mercury. From the kinetic theory of gases the number, n , of molecules of water striking each square centimeter of the surface per second is given by

$$n = N p / (2 \sqrt{M R T})^{\frac{1}{2}} \quad (45)$$

$$n = 3.52 \times 10^{22} \times p / (M T)^{\frac{1}{2}} \quad (45a)$$

where p is the vapor pressure in millimeters of mercury, T is the absolute temperature in degrees Kelvin, and M is the molecular weight of water. Equation (45a) then states that 8.5×10^{29} water molecules will strike each square centimeter of the surface each second. Such enormously large number of molecules striking the surface every second should cause adsorption phenomena to take place nearly instantaneously. It must be emphasized, however, that such great speeds of adsorption as suggested by the number n can only occur immediately after the surface is exposed to the atmosphere, at which moment there are sufficient water molecules in the direct proximity of the surface. As the immediate neighborhood of the surface is exhausted, a further supply of water molecules has to come from more remote parts. The speed with which this takes place is determined by the rate of diffusion of water molecules in the intervening air. After the adsorption equilibrium is established, n water molecules will strike each square centimeter of surface



per second and the same number n will evaporate, this being the condition of the dynamic equilibrium.

It will be clear from the above considerations that when an adsorption equilibrium requires considerable time to establish itself, the cause of the delay is to be found in diffusion problems. These may involve principally the transport of the gas molecules from the bulk phase to the surface of the adsorbent, as in the case of the above example, or may also involve diffusion of the adsorbed gas from the outer surface of the adsorbent to the more interior parts of the porous structure. The latter would undoubtedly be the case with such materials as cereal grains, which often require equilibration periods in the order of weeks and even months.

Drying of Hygroscopic Solids

The drying of hygroscopic materials such as cereal grains involves the removal or desorption of water, which may include both free and bound waters depending on the initial moisture content of the material and on the extent of the drying process. In any drying process, the equilibrium moisture content of the material as determined by the temperature and humidity conditions of the drying air, represents the limit to which the material can be dried. It is the free moisture content that is susceptible of being removed by drying rather than the total moisture content.

Periods of Drying

Among the most fundamental investigations on drying theory are those of Sherwood (43) and Lewis (33). Sherwood has developed a theory, now generally accepted, that postulates three possible distinct periods in the drying process. These drying stages, classified according to the rate of drying under constant drying conditions, are: (1) a constant-drying rate period, during which the surface remains completely wet, the rate of evaporation being the same as that from a free liquid surface of constant area; (2) a first falling-rate period, during which there is a falling off of wetted surface, the drying rate being directly proportional to the fraction of the surface that is wet; and (3) a second falling-rate period during which the rate of transfer of water from the interior of the material to the surface becomes the controlling factor.

The moisture content of the material which marks the end of the constant-rate period and the beginning of the first falling-rate period is designated as the critical moisture content. If the critical moisture content is less than the required moisture content, the constant-rate period will constitute the whole drying process. On the other hand, if the initial moisture content is less than the critical moisture content, the whole drying process will take place in the falling-rate period. It has now been pretty well established that practically all agricultural drying processes take place in the falling rate period. In recent studies on the

drying of wheat grain, Simmonds and his co-workers (44) found that the critical moisture for wheat varied between 69 and 85 percent dry basis. They also found the critical moisture contents to show the same tendency to increase at lower air temperatures as was observed with the equilibrium moisture contents. It may safely be assumed that in the practically important range of moisture content for cereal grains in general, the drying process takes place entirely in the second falling-rate period, which henceforth will be referred to simply as the falling-rate period.

Equations for the Falling-rate Period

It has been pointed out that during the falling-rate period of drying the rate of internal moisture transfer controls the drying rate. While several controlling mechanisms have been postulated to account for the internal flow of moisture—including capillary flow, shrinkage and pressure gradients, and diffusion—it is now generally agreed that in the practically important range of moisture content the most likely mechanism is one of diffusion (1, 3, 43).

Differential Equations for Diffusion

Numerous investigators have attempted to correlate drying rates with standard diffusion equations. (43,33) The limitations of the diffusion equations in drying have been summarized, and their restrictions to various materials and certain times of the drying cycle noted (27). The classical hypothesis of Sherwood and Newman (37,43) is worth mentioning. According to this theory,

the potential producing movement of moisture within the solid is identified with a concentration difference. The differential equation expressing the change in concentration C at any point with respect to time is as follows for one-dimensional diffusion (infinite slab)

$$\partial C / \partial \theta = D (\partial^2 C / \partial x^2) \quad (46)$$

where D is the diffusivity of moisture in the material. Equation (46) is analogous to the temperature-time-distance equation for heat flow. In the case of diffusion in three dimensions the equation is

$$\partial C / \partial \theta = k (\partial^2 C / \partial x^2 + \partial^2 C / \partial y^2 + \partial^2 C / \partial z^2) \quad (47)$$

where the diffusivity coefficient is now denoted by k . The equation involves no implication that the flow at time θ at a point (X, Y, Z) is not in some definite direction. It merely resolves the direction of flow into components along the previously selected rectangular coordinates X , Y , and Z .

The above differential equations merely express the general law for diffusional flow and are of no practical use as they stand. Following the approach of finding an equation which could be proved consistent with the differential equation and with the specific conditions of the problem, Newman (37) proposed solutions for solids of various shapes. Recently, Becker and Sallans (3) applied the standard solution of the non-stationary state diffusion equation out of spheres to the drying of wheat. On the basis of their

findings they postulated that the diffusion coefficient was independent of moisture content in the range from 12 to 30 percent dry basis, and reported values for the coefficient as lying between 0.069×10^{-6} and 2.77×10^{-6} square centimeters per second in the temperature range 20° to 80°C .

Lewis Exponential Equation

Based on the diffusion differential equation and assuming certain approximations, Lewis (33) derived the following expression for drying under constant drying conditions,

$$\ln \frac{(M - M_e)}{(M_0 - M_e)} = -k\phi \quad (48)$$

where M is the moisture content at any time, M_0 is the initial moisture content, M_e is the equilibrium moisture content (all moisture contents expressed on a dry basis), ϕ is the time in hours, and k a proportionality constant which he called the drying coefficient. Equation (48) is analogous to Newton's law of cooling and has come to be regarded as a fairly good approximation for fully exposed drying rates. Hukill (28) employed this relationship in his analysis of bulk drying of grains. In their recent investigation on the drying of wheat grain, Simmonds et al found good agreement between their experimental data and equation (48). They used a dynamic method with air velocities in the range of 30 to 160 feet per minute, and employed drying temperatures in the range 70° to 170°F .

Law of Exponential Growth

Because of its importance in the analysis of drying phenomena, equation (48) merits closer examination. As stated earlier, it is analogous to Newton's law of cooling; or more generally, it is an application of the compound interest law, often referred to as the law of exponential growth (or decay). Both of these names emphasize the fact that the increase (or decrease) is proportional to the size of the thing that is increasing (or decreasing). In other words, if c is the concentration at time ϕ then the rate of decrease in concentration is given by

$$-\frac{dc}{d\phi} = k c \quad (49)$$

where k is a proportionality constant. The minus sign indicates that the concentration is decreasing with an increase in time.

Equation (49) can be transposed giving

$$-\frac{dc}{c} = k d\phi \quad (50)$$

Integrating between the limits c_2 at the time ϕ_2 and c_1 at ϕ_1 , where ϕ_2 is greater than ϕ_1 ,

$$\int_{c_1}^{c_2} -\frac{dc}{c} = \int_{\phi_1}^{\phi_2}$$

one obtains

$$\ln (c_1/c_2) = k(\phi_2 - \phi_1) \quad (51)$$

If c_0 is taken as the concentration at zero time and c the concentration at any time ϕ , equation (51) simplifies to

$$\ln (c_0/c) = k \phi \quad (52)$$

or
$$\ln (c/c_0) = -k \phi \quad (53)$$

It is evident that equation (53) is analogous to equation (48), the moisture ratio $(M - M_e)/(M_0 - M_e)$ of the latter taking the place of the concentration ratio c/c_0 of the former. The same relationship expressed by the foregoing logarithmic equations can be expressed in exponential form as follows

$$c = c_0 e^{-k \phi} \quad (54)$$

Equation (54) can be readily converted to the logarithmic form by taking logarithms of both sides.

The law of exponential growth finds wide application in describing natural phenomena. It is applicable whenever it is found that the value of a quantity or property is changing with respect to some variable at a rate which is proportional to the magnitude of the property. It can be deduced from the above equations that the fraction of the property or quantity which is undergoing change—say, molecules in a unimolecular reaction; atoms in radio-active disintegration; temperature decrease in a cooling process (Newton's law of cooling); or molecules desorbed in a drying process under constant-drying conditions—in a given period of time is independent of the amount that is present. The constant k is known

as the specific reaction rate and may be expressed in any unit of time, such as reciprocal minutes, hours, or seconds. It should be noted that equation (48) is a linear equation so that if the function $\ln ((M - M_e)/(M_o - M_e))$ is plotted against the drying time a straight line will be obtained if the experimental data obeys the law of exponential growth. The slope of the straight line will give the value of the rate constant k directly. These features coupled with the fact that it has been found to fit experimental data surprisingly well in many cases have enhanced the usefulness of this equation in grain drying studies.

In applying the law of exponential growth to any specific problem it is customary to refer to the time period corresponding to one half of unaccomplished change as the term period of half-response. In the case under consideration it is obvious that the change involved is moisture desorption or removal, that the total amount amenable to change is the initial free moisture content, $M_o - M_e$, and that the amount of change yet to be accomplished is the free moisture content at any given time, $M - M_e$. Sometimes the free moisture ratio $(M - M_e)/(M_o - M_e)$ is called the unaccomplished moisture change. In drying processes, as in other similar phenomena, the half-response period has attained some importance as a parameter in the formulation of approximation equations with which to characterize the drying process. When used in this connection, it is usually employed as a unit with which to measure the drying time. Hukill (28) employed it thus in developing a method for predicting approximately bulk drying rates. It

is also of general value in drawing drying curves of different samples on a more comparable basis, and in permitting constructing the curves over a longer span of drying time.

It is clear from the foregoing that a knowledge of the magnitude of the half-response period for different drying conditions would constitute a fund of valuable engineering data for use in practical drying problems. The value of the half-response period for any given drying process under constant drying conditions may be determined experimentally from the drying curve obtained by plotting the moisture ratio as ordinates against the drying time as abscissae. Or, provided the rate constant k is known for the drying conditions under consideration, it may be calculated by equating the right-hand side of equation (48) to 0.50, and solving for the corresponding value of time θ .

Page's Modified Equation

In an investigation of basic drying rates of shelled corn, Page (40) analyzed his results by using a modification of equation (48) as follows

$$(M - M_e)/(M_o - M_e) = e^{-k \theta^N} \quad (55)$$

where the value of constant k was determined on the basis of time expressed in half-response units, and N is an experimental constant. He found that constant N was a function of relative humidity and obtained values of 0.60, 0.65, and 0.83 for relative

humidities of 35, 50, and 70 percent respectively; for the constant k he obtained a value of 0.68.

EXPERIMENTAL

Materials

The corn used in all tests for determination of hygroscopic equilibria and drying data was obtained from a lot purchased at a local elevator during the fall of 1954 and subsequently stored at 40°F. The corn was of the yellow dent type and of hybrid origin. About ten pounds of this lot were set aside for use in the investigation and sealed in two glass jars which were kept in the same 40°F storage box. A representative sample of this corn taken at this time was tested for moisture content and found to be of 25.43 percent, dry basis.

The samples used for the irradiation tests were obtained from a stock of five pounds of air-dried seed corn, variety Mayorbela, which was flown directly from Puerto Rico. Immediately upon arrival in August 1955, the seed was placed in tightly closed jars and stored at 40°F. Its moisture content was found to be 15.35 percent, dry basis.

The salts for preparing the saturated salt solutions used as controllers of relative humidity were all of chemically pure grade, and were obtained from the stock rooms of the Chemistry Department of the University.

The material used for making the sample containers consisted of a screen mesh sixteen-to-the-inch made of saran plastic. This material proved to be particularly suitable for this purpose owing

in part to the ease with which it could be worked, but mainly because of its resistance to corrosion.

Apparatus and Procedure

Since it was considered essential for the purposes of the investigation to obtain the drying data in the greatest possible detail, particularly over the initial stages of the desorption process, it was decided to employ a static method for obtaining the experimental data. The most serious objection which is generally alleged against static methods lies on the long periods of time necessary for attainment of equilibrium. Yet, this very circumstance made it feasible to obtain drying data to a degree of detail and precision not ordinarily attainable with dynamic methods. The method consisted essentially of exposing the samples of grain to atmospheres of constant temperature and relative humidity maintained in moisture-tight glass chambers by saturated aqueous solutions of selected chemically pure salts. The glass chambers were kept in thermostatically-controlled storage cabinets maintained at constant temperature within plus or minus one degree Fahrenheit. Periodic weighing of the samples at appropriate intervals provided the necessary data for determining the drying rates. When essentially constant weight was maintained over a period of at least two weeks, it was generally decided that equilibrium had been virtually attained. Longer times were allowed for the samples held at the lower temperatures. As soon as possible thereafter the samples were

tested for moisture content by the air-oven method. A more detailed description of the apparatus and procedure employed shall presently be given.

Controlling Relative Humidity

The fact that a saturated aqueous solution of a salt at a given temperature will maintain a constant humidity within any enclosed space has long been recognized as a valuable instrumentation technique for controlling relative humidity in small chambers, particularly under static conditions. Numerous investigators (13, 50, 51, 52) have undertaken to determine the equilibrium relative humidities maintained by various salts at various temperatures, and published values are now available from various sources. The salts used in the present investigation were selected after a thorough search of the literature and are given in Table I together with their corresponding values of relative humidity at the various temperatures.

In the preparation of the various saturated salt solutions two different procedures were followed. The first method consisted of weighing a predetermined amount of the salt on an ordinary platform balance and thoroughly mixing it in a beaker with approximately 250 milliliters of distilled water. The mixture was then heated to a temperature of 212°F and held at this temperature long enough to make sure that the salt necessary to saturate the solution at the lower temperature had entirely dissolved. The solution was then transferred to the glass chambers

TABLE I

EQUILIBRIUM RELATIVE HUMIDITIES ABOVE SATURATED SALT SOLUTIONS
AT VARIOUS TEMPERATURES

Salt	Formula	R.H.	Authority
40° F			
Lithium chloride	$\text{LiCl} \cdot \text{H}_2\text{O}$	14.0	Wexler and Hasegawa
Magnesium chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	34.6	" "
Sodium dichromate	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	59.3	" "
Sodium chloride	NaCl	75.1	" "
Potassium nitrate	KNO_3	96.6	" "
Potassium sulphate	K_2SO_4	98.4	" "
60° F			
Lithium chloride	$\text{LiCl} \cdot \text{H}_2\text{O}$	12.8	Carr and Harris
Magnesium chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	33.9	Wexler and Hasegawa
Chromic oxide	CrO_3	37.5	Wink and Sears
" "	"	45.4	Carr and Harris
Sodium dichromate	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	56.6	Wexler and Hasegawa
Sodium chloride	NaCl	75.9	Carr and Harris
Potassium nitrate	KNO_3	94.3	Wexler and Hasegawa
Potassium sulphate	K_2SO_4	97.5	" "
86° F			
Lithium chloride	$\text{LiCl} \cdot \text{H}_2\text{O}$	11.2	Wink and Sears
Potassium fluoride	$\text{KF} \cdot 2\text{H}_2\text{O}$	27.4	Carr and Harris
Magnesium chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	32.4	Wink and Sears
Chromic oxide	CrO_3	40.0	" "
Potassium carbonate	K_2CO_3	43.5	" "
Sodium dichromate	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	54.2	Carr and Harris
" "		52.0	Wink and Sears
Sodium bromide	$\text{NaBr} \cdot 2\text{H}_2\text{O}$	56.3	" "
Sodium nitrite	NaNO_2	63.3	" "
" "	"	64.8	" "
Cupric chloride	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	68.3	
Sodium nitrate	NaNO_3	72.8	Carr and Harris
Sodium chloride	NaCl	75.2	Wink and Sears
Ammonium monophosphate	$\text{NH}_4\text{H}_2\text{PO}_4$	92.0	" "

TABLE I (Cont.)

Salt	Formula	R.H.	Authority
100°F			
Lithium chloride	$\text{LiCl} \cdot \text{H}_2\text{O}$	11.1	Wink and Sears
Magnesium chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	32.4	" "
Chromic oxide	CrO_3	40.2	" "
Potassium carbonate	K_2CO_3	43.4	" "
Sodium dichromate	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	50.0	" "
Sodium bromide	$\text{NaBr} \cdot 2\text{H}_2\text{O}$	53.7	" "
Sodium nitrite	NaNO_2	61.8	" "
Sodium chloride	NaCl	75.1	" "
Ammonium sulphate	$(\text{NH}_4)_2\text{SO}_4$	79.1	" "
Potassium chromate	K_2CrO_4	86.3	" "
Ammonium monophosphate	$\text{NH}_4\text{H}_2\text{PO}_4$	92.0	" "
Potassium nitrate	KNO_3	96.2	Wexler and Hasegawa
122°F			
Lithium chloride	$\text{LiCl} \cdot \text{H}_2\text{O}$	11.4	Wexler and Hasegawa
Potassium fluoride	$\text{KF} \cdot 2\text{H}_2\text{O}$	20.4	Carr and Harris
Sodium iodide	$\text{NaI} \cdot 2\text{H}_2\text{O}$	28.4	" "
Magnesium chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	31.4	Wexler and Hasegawa
Chromic oxide	CrO_3	45.4	Carr and Harris
Sodium dichromate	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	47.1	Wexler and Hasegawa
Sodium nitrite	NaNO_2	59.8	" "
Sodium nitrate	NaNO_3	68.7	Carr and Harris
Sodium chloride	NaCl	74.7	Wexler and Hasegawa
Potassium chloride	KCl	81.2	Carr and Harris
Potassium nitrate	KNO_3	85.0	Wexler and Hasegawa
Potassium sulphate	K_2SO_4	95.8	" "

TABLE I (Cont.)

Salt	Formula	R.H.	Authority	
140°F				
Potassium fluoride	KF	21.0	Carr and Harris	
Sodium iodide	NaI.2H ₂ O	25.3	"	"
Chromic oxide	CrO ₃	45.8	"	"
Sodium bromide	NaBr.2H ₂ O	49.9	"	"
Sodium dichromate	Na ₂ Cr ₂ O ₇ .2H ₂ O	55.2	"	"
Sodium nitrite	NaNO ₂	59.2	"	"
Sodium nitrate	NaNO ₃	67.5	"	"
Sodium chloride	NaCl	74.9	"	"
Potassium chloride	KCl	80.7	"	"

and allowed to cool at room temperature whereupon a suitable excess of salt was added to guard against the possibilities of supersaturation. Where the cost and the amount of salt available permitted, it was desirable to use a considerable excess of salt so that mounds of crystals protruded above the liquid surface. It should be cautioned, however, that too much of an excess may result in drying up the solution. For relative humidities above 85 percent the extreme excess of salt is not necessary, though it is still important to have some crystals present in the solution. Enough of the prepared solution was then placed in the jar to fill it to a depth of approximately one and a half inches. The jar was then sealed, properly labeled, and placed in the corresponding constant-temperature cabinet where it was allowed to stand for at least 24 hours prior to use. As a guide in predetermining the approximate amount of salt necessary for obtaining a given amount of saturated solution Seidell's encyclopedia on Solubilities of Inorganic and Metal Organic Compounds (42) is probably the best source of information.

The second method consisted essentially of placing the predetermined amount of the salt in the empty glass jar or chamber and adding the appropriate amount of distilled water to produce the required saturated solution. The mixture was thoroughly stirred, whereupon the jar was sealed, labeled properly, and placed in the corresponding constant-temperature cabinet. The solutions prepared according to this method were allowed to stand for at least one

week prior to use in order to insure complete saturation. The same precaution of providing for an excess of salt crystals in the solution was followed as explained for the first method.

Wink and Sears (52) compared both of the above methods and obtained relative humidities which agreed within 0.3 percent.

Constant-Humidity Chambers and Sample Containers

Two principal types of containers were employed as constant-humidity chambers, namely, one-gallon wide-mouthed glass jars of the type generally used for pickles or mayonnaise in the food industries, and one-half gallon mason fruit jars. The metallic screw-on type of lids of the former were furnished with a suitable gasket in order to insure a moisture-tight seal and also as a means of holding the hanger for the sample container. This hanger was made of a piece of brass wire formed in a loop with a straight section bent at right angles to the plane of the loop and threaded through the center of the circular lid gasket to provide a terminal pig-tail hook for suspending the sample container above the solution. The mason fruit jars were provided with special lids made of polystyrene plastic and similarly equipped with a gasket and hanger. Both types of jars allowed for an adequate ratio between the free surface area of the salt solution and the estimated external surface area of the kernels making up the sample. Likewise, the ratio of free surface area of the solution and the estimated external surface area of the kernels making up the sample. Likewise, the ratio of free surface area of the solution

to the volume of the chamber above the solution was adequate in both cases. Both of these factors are of importance in determining the time required for humidity equilibrium to be reached, and for restoration of the original conditions after disturbances incidental to the weighing operations. The length of the sample hangers was so adjusted as to bring the sample as close to the surface as was considered safe from the standpoint of minimizing the chances of accidentally splashing the solution over the samples. This height usually varied from one to three inches. Extreme care was always exercised in handling the jars, and only in very few instances were samples ruined by accidental splashing. Figure 2 illustrates both types of containers described above with the samples suspended in the regular manner. One of the plastic lids used with the mason jars lies on the table to show the gasket and sample hanger; also one of the mason jars is shown with a type of zinc cap used with a few of the jars.

The sample holders were made of the plastic material previously described in the form of cylindrical baskets about two to four and a half inches in diameter and two to four inches high. They were provided with a handle in the form of a loop made of strands of the same material. While adhesive cements may be helpful in making the baskets, their use was found objectionable owing to their hygroscopicity which may cause the tare weight of the basket to change appreciably throughout the test period. Accordingly the seams of the baskets were stitched together with strands of the same plastic



Figure 2. The two main types of containers used as constant-humidity chambers. Samples are seen suspended in their regular position above the saturated salt solutions.

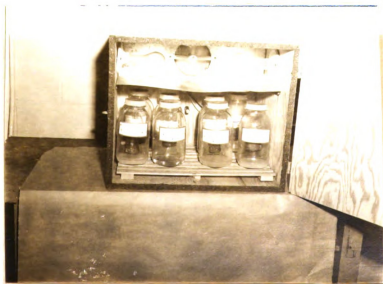


Figure 3. Constant-temperature cabinet with regular load of constant-humidity chambers.

material. Small labels made of aluminum foil on which the code number was typed were attached to the baskets as a means of identification.

Temperature Control

Six different temperatures were employed for the tests on hygroscopic equilibria and drying rates, namely, 40° , 60° , 86° , 100° , 122° , and 140° F. The selection of these temperatures was partly governed by the availability of suitable data pertaining to the relative humidities obtainable with various salts.

The 40° F temperature was maintained by thermostatic on-off control in a walk-in type refrigerated cabinet with forced draft air circulation. The 60° F temperature was similarly maintained in a smaller cabinet of the same general dimensions as those showed in Figures 3 and 4. The 86° F temperature was maintained in walk-in type storage cabinet similar to the one used for the 40° F temperature but equipped with a thermostatically-controlled lamp bank as a source of heat and with suitable shielding to protect the constant-humidity chambers against direct radiation from the lamps. The higher temperatures were maintained in wooden storage cabinets provided with lamp bulbs as a heat source, with forced draft air circulation, with suitable on-off thermostatic control, with a mercury-in-glass thermometer for checking the temperature, with a sheet metal shelf to serve as a radiation shield and as an aid to air circulation, and with a slatted false floor which insured adequate air circulation underneath the jars. Figures 3 and 4

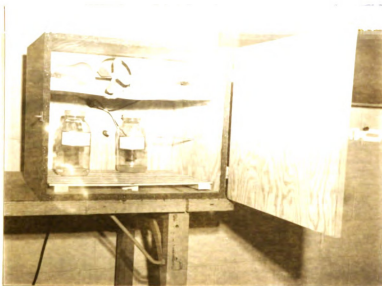


Figure 4. Constant temperature cabinet with most jars removed to show construction features.

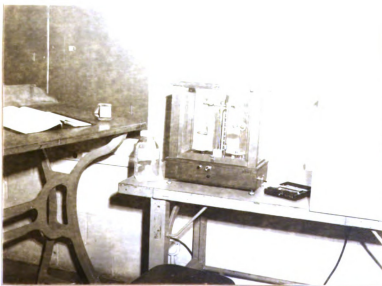


Figure 5. Weighing equipment and general set-up for the weighing operation.

shows one of these cabinets in wide-opened position in order to illustrate all of the above features. In all cases, constancy of temperature was maintained within plus or minus one degree Fahrenheit.

Preparation of the Samples

The corn samples were either taken directly from the regular stock previously described with no further preparation other than allowing the corn to warm up to room temperature, or from portions of this same stock previously conditioned to higher moisture contents as it was deemed necessary. No specific values of initial moisture content were particularly aimed at, as long as high enough levels were obtained to allow for a wide enough range of desorption vapor pressure differences and still have the drying process take place in the falling-rate period. This conditioning treatment was particularly necessary in the case of the samples intended for equilibration at high relative humidities.

The conditioning procedure followed consisted generally of soaking the required amount of seed in distilled water for a period of four to six hours. Throughout the soaking period the grain was kept inside the 40°F cabinet. The excess water was then drained off and the kernels spread singly over a sheet of towel paper and allowed to stand at room temperature until all the surface water had dried out. The seed was then placed in a clean dry jar, sealed tightly, properly labeled, and returned to the 40° box until ready to use. Enough time was allowed to insure moisture equilibrium within the individual kernels. The evening before the test was to

be started the jar was removed from cold storage and allowed to remain overnight at room temperature. The resulting moisture content of the seed conditioned according to the foregoing treatment varied from 37.25 to 45.52 percent, dry basis. No harmful effects whatsoever were detected as a result of this conditioning procedure.

In any case, the samples were made up of anywhere from twenty to thirty singly selected kernels of normal shape and size characteristic of the variety. The kernels were spread in a thin layer one grain deep on the bottom of the basket. The basket and sample were then accurately weighed to the closest tenth of a milligram and immediately placed in the corresponding constant-humidity chamber. This was immediately placed, in turn, inside the corresponding constant-temperature cabinet. All necessary information was subsequently recorded on a data sheet especially prepared for the purpose. One separate sheet was used for each sample and all subsequent data pertaining to that sample was recorded therein. One example of these data sheets is shown in Table II, with typical information pertaining to one of the samples. The time of weighing was recorded to the nearest minute.

Drying Rate Data

Measured from the time they were first weighed and placed in the drying chambers at the beginning of the run, the samples were weighed at periodic intervals. The sequence of steps involved in each drying operation was as follows:

(1) The analytical balance was prepared with the approximate anticipated gross weight of the sample on the corresponding pan.

(2) The constant-temperature cabinet was opened, the desired jar was removed promptly and carefully with a steady motion aimed at producing the least possible disturbance of the contents, and the cabinet was reclosed.

(3) The lid of the jar was unscrewed and lifted with care, the sample was removed and placed in position on the balance as shown in Figure 5.

(4) The weighing pans were released and the actual weighing of the sample performed.

(5) The sample was returned to the jar, the jar was sealed tightly, and returned to the constant temperature cabinet.

(6) The gross weight and the time of weighing were then recorded on the corresponding data sheet.

The whole operation generally required not more than 75 to 90 seconds, while the time that the sample remained out of the drying chamber and the chamber out of the constant-temperature cabinet seldom exceeded thirty and forty-five seconds respectively. Promptness and accuracy were the objectives to strive for in each weighing operation.

The weighing intervals adopted for the first series of runs were in the order of twenty-four hours during the initial stages of the drying process, and were gradually increased after the first two weeks, as the rates of drying slowed down. It was soon

realized, however, that an observation interval of twenty-four hours was far too long to permit a detailed enough study of the drying rates during the all-important initial stages of drying. In all subsequent runs, therefore, the observations were made at intervals which were in the order of one-half hour for the first eight to twelve hours, twice or four times every day for the next seven to eight days, once a day for the next fourteen or sixteen days, and at longer intervals thereafter as it was deemed appropriate on the basis of the observed drying rates.

Determination of Moisture Contents

The general procedure followed upon termination of a run for any given sample was as follows:

The final gross weight of the sample was obtained as explained above and the kernels promptly transferred to a weighing can. The terminal tare weight of the sample container was then determined and recorded after which the basket was returned to its corresponding drying chamber. The weighing can was then closed and placed in a desiccator for transferring to the oven. The corresponding data was entered in the appropriate data sheet. The same procedure was followed with all samples due for termination. The weighing cans were then taken to an electric air-oven, where they were placed with the lids removed and placed underneath the corresponding cans. The samples were thus held at a temperature of 212°F for a period of seventy-two to eighty hours, which had been previously decided as adequate to achieve constancy of

weight. After this period the cans were closed while still in the oven, removed, and placed in an aluminum desiccator charged with activated alumina where they were allowed to cool to room temperature. The cans with their contents were then weighed immediately, each at a time, and their weight recorded on the corresponding data sheets. The cans were then emptied, weighed again, and their tare weight recorded. All samples were handled in quick succession, one at a time. Processing of these data yielded the net terminal weights of the samples and their dry matter content. From the recorded initial weight of the samples the instantaneous moisture contents at the various times of observation were calculated. Both the initial and the equilibrium moisture contents were accurately calculated to the closest hundredth of one percent. Slide-rule accuracy was judged sufficient for all intermediate moisture content values, even though readings were still read to two decimal places whenever possible. The results of all these calculations were entered in the type of data sheet shown in Table II.

Irradiation Tests

It is a well recognized fact that the drying rate of any given material under a given set of drying conditions is a function of the particular characteristics of the material. Many experimenters have concerned themselves with the nature and distribution of the resistance to the movement of moisture within the

grain in response to a drying potential. Several noteworthy explanations have been advanced concerning the mechanism whereby moisture escapes from the grain. It has been speculated whether the resistance to moisture transfer is uniform throughout the kernel or rather concentrated at some particular site within the grain or at the surface. Oxley (38) has suggested that this resistance might be concentrated somewhere below the surface of the grain, basing his judgment on Edholm's findings in experiments on intermittent drying. On the other hand, the suggestion has also been made that the open tissue at the tip of the corn kernel is probably the exit space for moisture during the drying process. It was therefore considered of interest in connection with the investigation to explore the possibilities of improving the moisture transfer characteristics of the grain with electromagnetic irradiation. Accordingly a short series of experiments was planned for this purpose.

As was pointed out before, the stock of Mayorbela corn from Puerto Rico was used in this series of experiments. Typical samples were prepared from a small batch of seed previously irradiated with a dose of 10^6 reps applied on each side of the kernels and placed in drying chambers corresponding to the following drying conditions: 11.1 percent relative humidity and 100°F ; 75.1 percent relative humidity at 100°F ; 49.9 percent relative humidity at 140°F . Control samples were run simultaneously under the same conditions. The test was repeated following exactly the same

procedure, except that the irradiation dose was increased tenfold to 10^7 reps. Again exactly the same procedure as previously described was followed in obtaining the drying data of these samples.

Results

The hygroscopic equilibrium data for shelled corn obtained as a result of the foregoing experiments and the initial processing of the observational data are tabulated in Table II. The table includes information on the salt solution employed as constant-humidity controller, the corresponding temperatures and relative humidities, the initial moisture contents of the samples, the calculated values of hygroscopic equilibria, and the duration in hours of the corresponding tests. It should be pointed out that in many cases the runs were extended well beyond the virtual attainment of equilibrium and therefore, the duration of the run is not necessarily to be interpreted as the time required for equilibration. It is felt that the equilibrium moisture content values obtained are as close to true equilibrium as it is possible to obtain in such tests. Subsequent processing and analysis of these data will be dealt with in the next chapter.

The drying data consists principally of the instantaneous values of moisture content and their respective times of occurrence as obtained from the preliminary processing of the observational data as previously explained. The extensiveness of the data definitely precludes their inclusion here, and only Table III—

TABLE II
EXPERIMENTAL EQUILIBRIUM MOISTURE CONTENTS OF SHELLED CORN AT VARIOUS
RELATIVE HUMIDITIES AND TEMPERATURES

Salt Solution	Relative Humidity percent	Initial Moisture Content M_e , % d.b.	Equilibrium Moisture Content M_e , % d.b.	Duration of run ϕ hours
40°F				
Lithium chloride	14.0	18.20	8.09	1587
Magnesium chloride	34.6	18.40	11.71	1587
Chromic oxide	37.0	18.36	12.27	1943
Sodium chloride	75.9	24.30	20.51	2217
		25.90	21.14	69.12
Sodium dichromate	59.3	27.12	16.35	1520
Manganese chloride	53.4	27.22	15.00	1454
60°F				
Magnesium chloride	33.9	18.42	10.52	1496
Chromic oxide	37.5	18.20	11.40	1496
		28.10	11.20	390
		20.93	11.38	586
		23.12	11.08	450
Sodium dichromate	56.6	17.86	13.77	1534
Potassium fluoride	32.35	18.04	10.51	540
Sodium chloride	75.9	18.75	18.23	1496
Potassium nitrate	94.4	43.7	28.7	205
86°F				
Lithium chloride	11.2	20.77	4.86	925
Potassium fluoride	27.4	24.59	8.10	560
		17.95	7.96	1580
		21.75	9.02	900
		18.15	8.90	1686
Magnesium chloride	32.4	24.25	8.74	1885
		23.70	8.97	1613
		22.44	10.32	2311
		21.66	9.60	689
Chromic oxide	40.0	18.02	9.87	1492

TABLE II (Cont.)

Salt Solution	Relative Humidity percent	Initial Moisture Content M_o , % d.b.	Equilibrium Moisture Content M_e , % d.b.	Duration of run hours
86°F				
Potassium carbonate	43.5	21.14	10.50	941
Sodium dichromate	53.1	18.36	11.90	1687
		23.03	11.48	1893
		23.98	11.93	1800
		23.48	11.88	1914
		18.15	11.90	1586
Sodium nitrite	63.3	18.08	13.64	1466
		17.86	13.57	814
Cupric chloride	68.3	23.00	14.89	1638
		18.03	14.52	1689
Sodium chloride	75.2	24.85	15.83	1107
		20.92	15.83	867
Sodium bromide	56.3	20.08	12.38	880
Potassium chromate	86.3	21.20	19.28	97

100°F				
Lithium chloride	11.1	18.60	4.78	1618
Magnesium chloride	31.9	18.44	8.46	1062
Potassium carbonate	43.4	18.35	9.95	1062
Sodium dichromate	50.0	27.79	10.86	1365
Sodium nitrite	61.8	18.49	12.78	1062
Sodium chloride	75.1	18.55	15.28	1061
		32.82	15.35	839
Ammonium sulphate	79.1	28.85	16.88	856
Potassium sulphate	96.3	17.61	24.81	242

122°F				
Lithium chloride	11.4	37.48	3.93	870
		44.00	3.83	1188
		17.98	4.12	1047
Sodium iodide	28.4	36.79	7.48	507

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Salt Solution	Relative Humidity percent	Initial Moisture Content M_o , % d.b.	Equilibrium Moisture Content M_e , % d.b.	Duration of run hours
122°F				
Potassium fluoride	20.4	38.10	5.97	1038
Sodium dichromate	47.1	32.28	9.88	1153
Sodium nitrite	59.8	38.35	11.65	1042
Sodium nitrate	68.7	32.11	13.31	506
Sodium chloride	74.7	37.66	14.78	1040
Potassium nitrate	85.0	37.77	17.74	1047
		41.79	17.79	213
		17.70	17.33	975

140°F				
Lithium chloride	11.2	42.70	3.39	981
Potassium fluoride	21.0	43.80	5.21	1304
Sodium iodide	25.3	17.48	6.12	981
Sodium bromide	49.9	43.70	8.59	1006
Sodium dichromate	55.2	43.58	8.92	170
		19.71	9.65	1086
Sodium nitrite	59.3	43.12	9.75	994
Sodium chloride	74.9	18.33	12.43	941
Potassium chloride	80.7	27.40	13.71	168
		44.58	14.03	218
Sodium nitrate	67.5	28.50	10.78	205

which partially shows the results obtained for one of the samples—is offered as an example. Table III-A on the other hand illustrates a form employed for recording the results of further processing of the data of each sample for the purpose of obtaining basic values necessary for subsequent treatments. These basic values include, the moisture contents converted to a wet basis, the free moisture content on a dry basis, the moisture content ratio on a dry basis, the equilibrium relative humidities as given by the constructed experimental isotherms, the equilibrium vapor pressures, p_g , obtained by multiplying the equilibrium relative pressures by the saturation vapor pressure, p_s , of water corresponding to the drying temperature as given by thermodynamic steam tables, and the values of vapor pressure potentials ($p_g - p_a$) as obtained from the difference between the equilibrium vapor pressure and the partial aqueous vapor pressure, p_a , of the drying air. All of the vapor pressures given in Tables III and III-A are expressed in pounds per square inch absolute.

As in the case of the hygroscopic equilibrium data, further treatment and analysis as well as the results obtained will be discussed in the next chapter.

The results of the irradiation tests are illustrated in Figure 35 which shows the drying curves for one of the samples irradiated with a dose of 10^6 reps and its corresponding control sample. Since the point values for both curves were nearly coincident the curve for the control sample was displaced as shown in order to be

Side	
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TABLE III
EXPERIMENTAL DATA SHEET

Code No. I-3 Salt Solution K₂CO₃ Temp. 100°F Rel. Hum. 43.4%
 Sat. vapor pressure, p_s 0.9492 psi Vapor pressure, p_a 0.129 psi
 Date run started 9/18/55 Date run ended 11/1/55 Duration 1062 hrs.
 Basket no. 10 Tare weight 3.4201 gm Gross weight 13.8353 gm
 Net weight sample 10.4152 gm Initial water content 1.6155 gm
 Initial moisture content, M_o 15.52 % w.b. 18.35 % d.b.

Final Moisture Determination

Moisture can no. 8 Date and hour to oven 11/1/55 at 3:00 P.M.
 Tare weight can 23.9854 gm Date and hour out of oven 11/4 at 5:00 P.M.
 Weight can + sample = 33.6707 gm Terminal net wt. 9.6853 gm
 Gross wt out of oven 32.7899 gm Weight dry matter 8.8045 gm
 Equilibrium moisture content, M_e 9.08 % w.b. M_e 10.00 % d.b.

Date	Time	± hrs.	Gross wt. grams	Wt. H ₂ O lost-cum.	Wt. H ₂ O remaining	Calculated M % d.b.
9/18 A	8:45	0.00	13.8353	0.0000	1.6155	18.35
	9:15	0.50	13.7860	0.0493	1.5662	17.78
	9:45	1.00	13.7451	0.0902	1.5253	17.31
	10:18	1.55	13.7117	0.1236	1.4919	16.94
	10:58	2.21	13.6755	0.1598	1.4557	16.52
	11:15	2.50	13.6620	0.1733	1.4422	16.36
	11:45	3.00	13.6377	0.1976	1.4179	16.08
	P 12:15	3.50	13.6179	0.2174	1.3981	15.85
	12:45	4.00	13.5988	0.2365	1.3790	15.65
	2:15	5.50	13.5507	0.2846	1.3309	15.10
	2:45	6.00	13.5375	0.2978	1.3177	14.94
	3:15	6.50	13.5238	0.3115	1.3040	14.80
	3:45	7.00	13.5109	0.3244	1.2911	14.68
	:	:	:	:	:	:
	:	:	:	:	:	:
11/1 P	2:45	1062.00	13.1022	0.7395	0.8760	10.00

TABLE IIIA
ANALYSIS OF DATA SHEET

Summary from Data Sheet

Code no. I-3 Salt solution K₂CO₃ Temp. 100°F Rel. Hum. 43.4%
 P_g 0.9492 psia P_a 0.4129 psia M_o 15.52% w.b. M_o 18.35% d.b.
 Duration of run 1062 hrs. Half-response period, $\phi_{1/2}$ 9 hrs.
 M_e 9.08% w.b. M_e 10.00% d.b. $M_o - M_e$ 8.35% d.b.

ϕ , hrs.	M, percent		$M - M_e$	$\frac{M - M_e}{M - M_o}$	(R.H.) _e	p_g	$p_g - p_a$
	% w.b.	% d.b.	% d.b.		percent	psi	psi
0.00	15.52	18.35	8.35	1.000	86.60	0.822	0.409
0.50	15.10	17.78	7.78	0.931	84.40	0.801	0.388
1.00	14.75	17.31	7.31	0.875	83.40	0.792	0.379
1.55	14.50	16.94	6.94	0.831	82.10	0.779	0.366
2.21	14.30	16.52	6.52	0.780	80.50	0.764	0.351
2.50	14.18	16.36	6.36	0.761	79.90	0.758	0.345
3.00	13.83	16.08	6.08	0.728	78.60	0.746	0.333
3.50	13.70	15.85	5.85	0.700	77.70	0.737	0.324
4.00	13.54	15.65	5.65	0.676	76.80	0.729	0.316
5.50	13.10	15.10	5.10	0.610	74.30	0.705	0.292
6.00	13.01	14.94	4.94	0.591	73.50	0.698	0.285
6.50	12.90	14.80	4.80	0.575	73.00	0.693	0.280
7.00	12.78	14.68	4.68	0.562	72.30	0.686	0.273
7.50	12.66	14.50	4.50	0.539	71.50	0.679	0.266
8.00	12.55	14.38	4.38	0.525	70.80	0.672	0.259
8.50	12.45	14.26	4.26	0.510	70.40	0.668	0.255
13.84	11.78	13.35	3.35	0.400	65.50	0.622	0.209
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
1062.00	9.08	10.00	0.00	0.000	43.40	0.413	0.000

able to plot both curves distinctly. It is evident from the character of the curves that there was no noticeable effect of the irradiation on the drying behavior of the corn. Similar results were obtained under the other drying conditions used in these tests, and the curves presented are typical.

ANALYSIS AND DISCUSSION

It has undoubtedly become evident that the scope of the investigation has touched on two distinct aspects of the water relations of shelled corn: the equilibrium or thermodynamic relationships on the one hand, and the time-dependent rate processes on the other. However closely related these two phases of the problem are—both from the theoretical and the practical viewpoints—it has been deemed convenient for the purposes of the analysis and discussion that will follow to keep them under separate headings. The results pertaining to desorption equilibrium data shall be dealt with in the first place; the drying rate data shall be considered next.

Desorption Equilibrium Data

The experimentally determined values of equilibrium moisture content for the various test conditions investigated have been presented in Table II. The next step in the analysis of the data was concerned with the construction of desorption isotherms for the temperatures of the investigation.

Construction of Desorption Isotherms

The isotherms were constructed by plotting for each temperature separately the equilibrium moisture content values (dry basis) as ordinates against the corresponding values of equilibrium relative

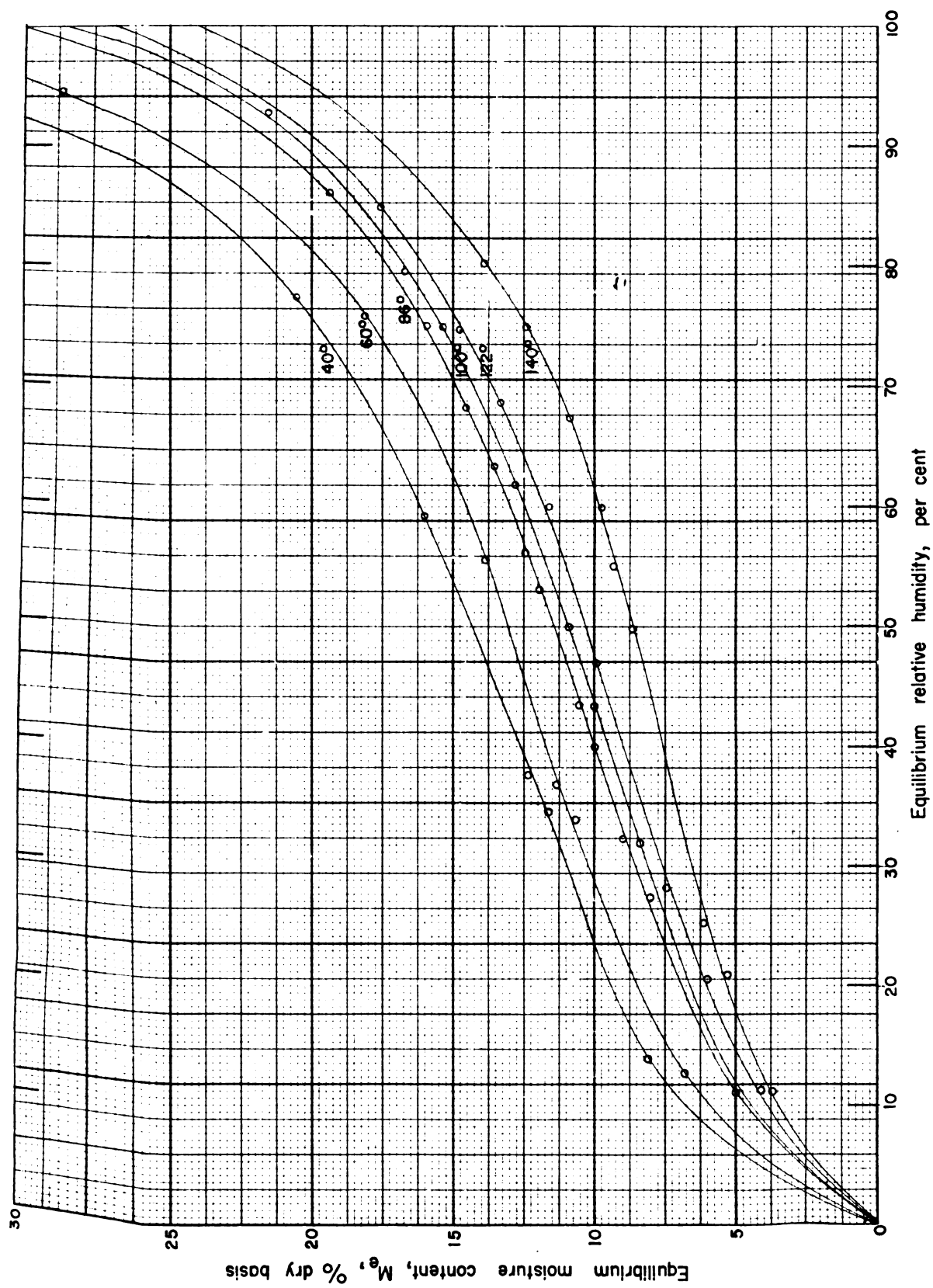


Figure 7 Desorption isotherms for shelled corn

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humidity as abscissae. The curves were then drawn as smoothly as possible through the point values corresponding to each temperature. In the absence of experimental data for relative pressures below 0.10, the lowermost portions of the isotherms could be constructed by extrapolating the curves to converge at the origin, since it is well-established characteristic of all isotherms that at zero pressure the amount of adsorbate adsorbed is also zero. While a certain degree of uncertainty may still be recognized concerning the exact course of the isotherms in that region, whatever inaccuracy may exist must necessarily be very slight. There is therefore little doubt as to the reliability of the isotherms even in that lowermost region, for all practical purposes.

The uppermost region of the isotherms beyond a relative pressure of about 0.85 presented a similar problem as described above for the lowermost region in that not enough data was at hand to complete each isotherm up to saturation pressure. It will be remembered that herein lies one of the shortcomings of the static method in securing hygroscopic equilibrium data at the higher relative humidity, owing to the susceptibility of the samples to molding over protracted periods of equilibration. To circumvent this difficulty an interesting method suggested by Bull (12) for extrapolating the curves up to saturation pressure was resorted to, with very satisfactory results. This method required the plotting of the function a/X as ordinates against corresponding values of X as abscissae for each one of the isotherms; where a represents the

TABLE IV
COMPUTATION OF DATA FOR a/X VERSUS X PLOTS
FROM DESORPTION ISOTHERMS

Isotherm Temperature - 100°F

X Equilibrium Relative Humidity, (R.H.) _e percent	a Moisture Content, M percent dry basis	a/X M/(R.H.) _e
2.50	1.90	0.7600
5.00	2.90	0.5800
10.00	4.30	0.4300
15.00	5.50	0.3660
20.00	6.40	0.3200
30.00	8.10	0.2700
35.00	8.80	0.2510
40.00	9.50	0.2370
45.00	10.25	0.2280
50.00	10.90	0.2180
55.00	11.65	0.2120
60.00	12.49	0.2080
65.00	13.25	0.2040
70.00	14.25	0.2038
75.00	15.30	0.2040
80.00	16.75	0.2093
85.00	18.40	0.2163
90.00	20.50	0.2280
95.00	23.75	0.2500
96.40	24.75	0.2560
97.50	26.00	0.2665

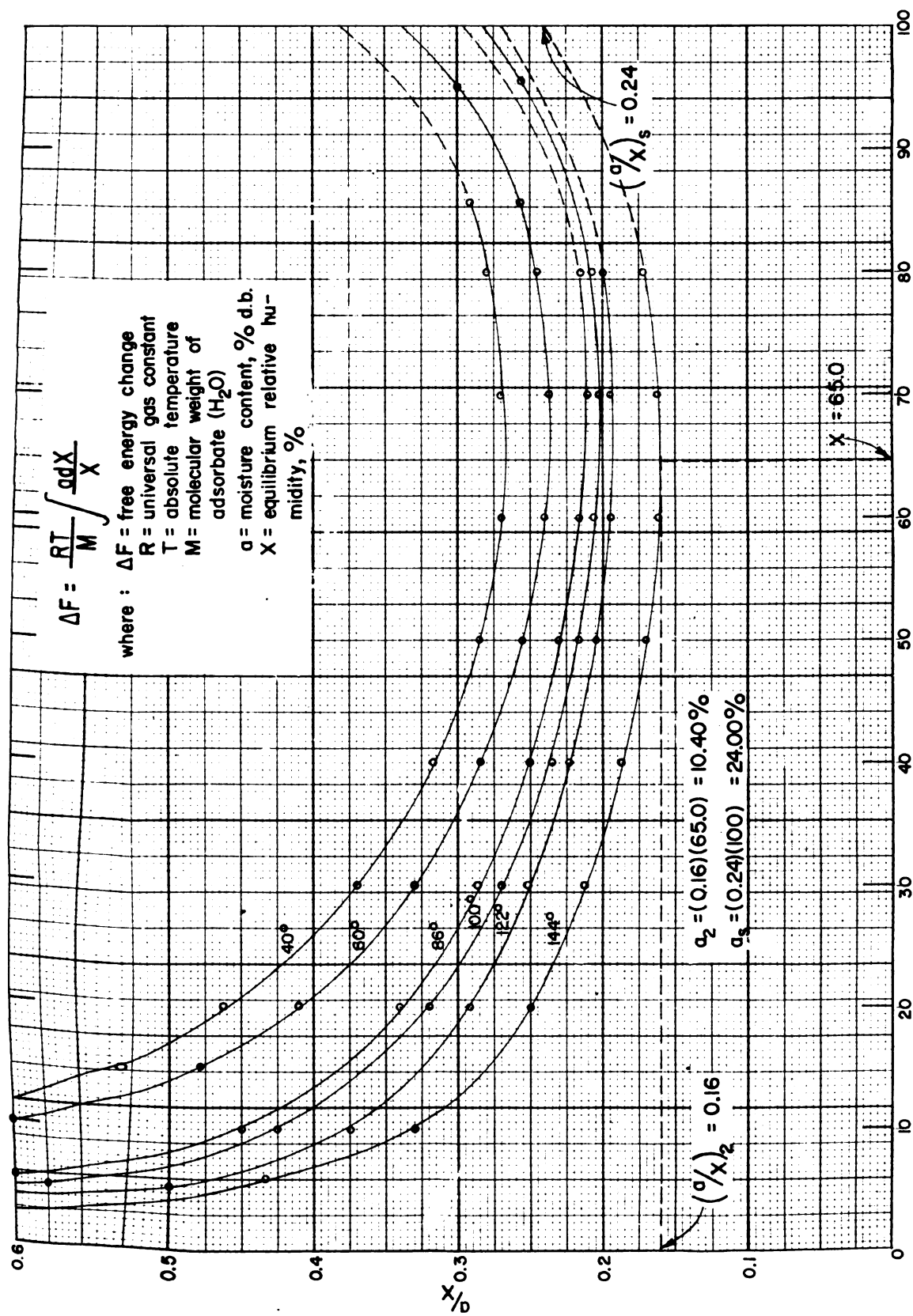


Figure 8 Plots of a/X vs. X from desorption data, showing method of evaluating a_2 and a_3 .

moisture content on a dry basis and X stands for the equilibrium relative humidity. In order to compute point values for constructing the plots, values of relative humidity were selected at intervals of 5 percent up to 85 percent. Table IV shows the results of the computations involved in calculating the plot for the 100°F isotherm. The same procedure was followed for each of the isotherms. The completed plots are shown in Figure 8. It will be seen that smooth curves were obtained which, though swinging upwards rather abruptly in the low pressure region, do show only moderate changes in slope at the higher relative pressures. It was thus possible to extrapolate the curves beyond the last plotted point up to saturation pressure without much chance for ambiguity. The values of a/X , given by the intersection of the curves with the vertical at saturation pressure, yielded the desired values of equilibrium moisture content corresponding to 100 percent relative humidity. The extrapolated sections of the plots are shown in dashed lines in Figure 8, while the circles indicate the point values calculated as explained above. The three points which appear beyond the plotted curves represent actual experimental values which could be obtained in this region, and which served as a valuable check of the reliability of this procedure. In Table V columns 5 and 6, the values of a/X at saturation and of the corresponding equilibrium moisture contents, respectively, are shown for all isotherms. As a further test of the correctness of this method the values of equilibrium moisture content thus determined were checked against comparable data from the literature, with gratifying results. While information available

TABLE V
EVALUATION OF a_2 AND a_s FROM PLOTS OF FIGURE 8

Isotherm	$(a/X)_2$	X_2	a_2	$(a/X)_s$	a_s	a_2/v_m
40°F	0.2693	65.0	17.50	0.380	38.0	2.012
60°F	0.2355	67.5	15.90	0.340	34.0	2.008
86°F	0.2100	72.5	15.25	0.297	29.7	2.140
100°F	0.2038	70.0	14.25	0.285	28.5	2.125
122°F	0.1940	65.0	12.6	0.270	27.0	1.905
140°F	0.1615	67.5	10.4	0.240	24.0	1.790

on hygroscopic equilibria at high relative pressures is extremely meager, two instances could be found which provided the required evidence. On the one hand, Coleman and Fellows (14) reported a value of 23.8 percent on a wet basis as the equilibrium moisture content of shelled corn (yellow dent) at a 100 percent relative humidity and a temperature of 77°F . This is equivalent to 31.20 percent on a dry basis, which, as will be seen from both Figure 7 and Figure 8, represents a remarkably good agreement with the extrapolated values. The other instance was furnished by a complete adsorption isotherm for maize at 10°C (50°F) taken from an investigation of R. Gave (19) and given by de Boer in his book on adsorption. This particular curve was cited by de Boer specifically as an example of an isotherm which exhibits a definite intersection with the vertical axis at 100 percent relative pressure. The value of moisture content, given by this intersection was found to be 33.5 percent dry basis, which again agrees closely with values established by the method suggested by Bull. Perhaps the greater significance of the foregoing evidence lies in showing that the isotherms of shelled corn, and probably of cereal grains in general, do intersect the vertical at saturation pressure contrary to the general assumption that the isotherm only approaches it asymptotically. The significance of the plots of Figure 8 goes beyond serving the purpose discussed, and will be referred to again later.

Construction of Isosteres

Because of the practical usefulness which they may serve it was considered appropriate to represent the experimental data in the form of isosteres. Isosteres represent the relationship between the equilibrium vapor pressure and temperature for a given constant amount of adsorbate adsorbed, as given by equation (4). Having obtained isotherms at six different temperatures, the experimental data may be used conveniently for representation as isosteres. The procedure involves the calculation of the equilibrium aqueous vapor pressure of the grain at each of the various temperatures for selected values of moisture content. These were obtained by multiplying the values of equilibrium relative pressure, as given by the isotherm curves, by the saturation vapor pressure of water at the temperature under consideration. The values thus determined for each of the moisture content levels selected were then plotted as ordinates against the corresponding temperatures as abscissae. A smooth curve was drawn through the points, which then constitutes the desorption isostere for the particular value of equilibrium moisture content. Figure 9 shows a family of desorption isosteres for shelled corn obtained according to the foregoing procedure. The resemblance between the family of isosteres and a psychrometric chart is immediately evident. With the aid of Figure 9 the equilibrium vapor pressure of shelled corn may be readily determined with fair accuracy for any conditions of temperature and moisture content within the range of the chart. In

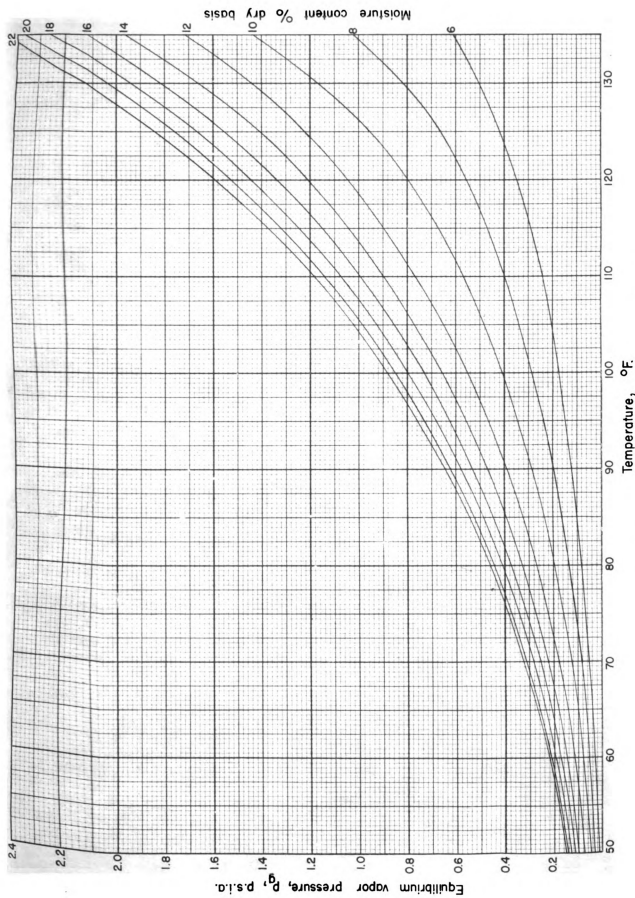


Figure 9 Desorption isotherms for shelled corn

the next section it will be seen how a modified form of the isostere may be useful in the indirect determination of the heats of desorption (or adsorption).

Calculation of Isosteric Heats of Desorption

For equilibrium systems the well-known Clausius-Clapeyron equation, which was first deduced from the Carnot cycle by Clapeyron and later derived from thermodynamics by Clausius (9), permits the evaluation of the heat change involved in the transition from one phase to the other. It may similarly be used to evaluate the heat changes involved in adsorption or desorption processes. The equation relates the rate of change of pressure with respect to temperature, with the changes in heat content and in volume of the system as follows

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad (45)$$

Equation (45) may be used directly without integration for processes where dP/dT is approximately constant over the range considered.

From a consideration of the isosteres of Figure 9 it is evident that the vapor pressure changes rapidly with temperature and not at all linearly. Therefore, for the grain-water vapor system, dP/dT does not remain constant over wide temperature ranges so that equation (45) must be integrated. However, it can not be integrated unless

ΔH and ΔV can be expressed as functions of temperature or pressure. This can be achieved with the aid of two simple approximations. In the first place, because the molar volume, v_g , of

the vapor is large compared with the volume of the adsorbed state, the change in volume ΔV is approximately that of the vapor itself so that

$$\Delta V \doteq v_g \quad (46)$$

Secondly, if ideal gas behavior is assumed for the vapor the molar volume, v_g , is given approximately by

$$\Delta V \doteq \frac{R T}{P} \quad (47)$$

When this value of ΔV is substituted in equation (45), H being the molar heat of adsorption (or desorption), it becomes

$$\frac{dP/P}{dT} = \frac{d \ln P}{dT} = \frac{\Delta H}{R T^2} \quad (48)$$

Equation (48) can be integrated whenever ΔH is known as a function of T . For the case where ΔH does not vary with temperature equation may be transformed to

$$d \ln P = \frac{\Delta H dT}{R T^2} \quad (49)$$

which, becomes, on integration

$$\ln P = - \frac{\Delta H}{R} \frac{1}{T} + C \quad (50)$$

It will be recognized that this is a linear equation of the type $y = ax + b$. Therefore if $\ln P$ is plotted as ordinate against the reciprocal of the absolute temperature, $1/T$, as abscissa, the resulting curve is a straight line with a negative slope equal to $\Delta H/R$ and an intercept on the $1/T$ - axis equal to C , the integration constant. These straight lines are also referred to as

isosteres since they correspond to a constant amount of adsorbate adsorbed, or in the case of grain, to a constant equilibrium moisture content. The isosteric plots described above may serve to identify inaccurate vapor pressure data by their refusal to fall on or near a straight line. By constructing such plots and evaluating the slopes of the straight lines the isosteric heats of desorption can be evaluated.

Table VI shows the results of the computation involved in the evaluation of the isosteric heats of desorption by the foregoing graphical method. For the purposes of constructing the plots, the isotherm temperatures were first expressed in degrees Kelvin and their reciprocals calculated. In order to use consistent units, the vapor pressures were converted from lb per square inch, as are mostly expressed throughout this work, to millimeters of mercury as shown. The equilibrium vapor pressures were then obtained for selected values of moisture content by multiplying the corresponding equilibrium relative pressure by the saturation vapor pressure of water at the temperature under consideration, just as it was done in the construction of the isosteres of Figure 9.

For the sake of simplicity a semi-logarithmic graph paper was employed and suitable scales laid off on the linear axis for the reciprocals of the absolute temperature and on the logarithmic axis for the equilibrium vapor pressures. Figure 10 shows the completed plots for various moisture content levels. It will be seen that quite satisfactory straight lines were obtained over a

TABLE VI
POINT VALUES FOR THE GRAPHICAL EVALUATION OF ISOSTERIC HEATS OF DESORPTION

Temperature, °F	Reciprocals of Absolute Temperature 1/K°	Saturation Vapor Pres- sure, P _s mm. Hg.	Equilibrium Vapor Pressure of Grain, p _g , mm. Hg					
			M = 8	M = 10	M = 12	M = 14	M = 16	M = 18 M = 22
40	3.61	6.2941	0.8812	1.4791	2.2470	3.0526	3.7135	4.2170 4.9723
60	3.47	13.2537	2.4917	4.2379	5.8979	7.6871	8.9860	9.9403 11.3187
86	3.30	31.8186	8.4319	12.7274	17.1820	21.0003	23.8640	26.2503 29.1140
100	3.22	49.0855	14.4802	21.1100	28.2260	33.7233	38.0416	41.3823 45.6022
122	3.10	87.5233	30.0671	44.3094	57.0778	66.4227	73.6422	79.4693 86.9588
140	3.00	149.3825	65.7298	91.8716	109.7961	121.0028	129.2150	135.9380 145.6501

Note: M = percent moisture content dry basis

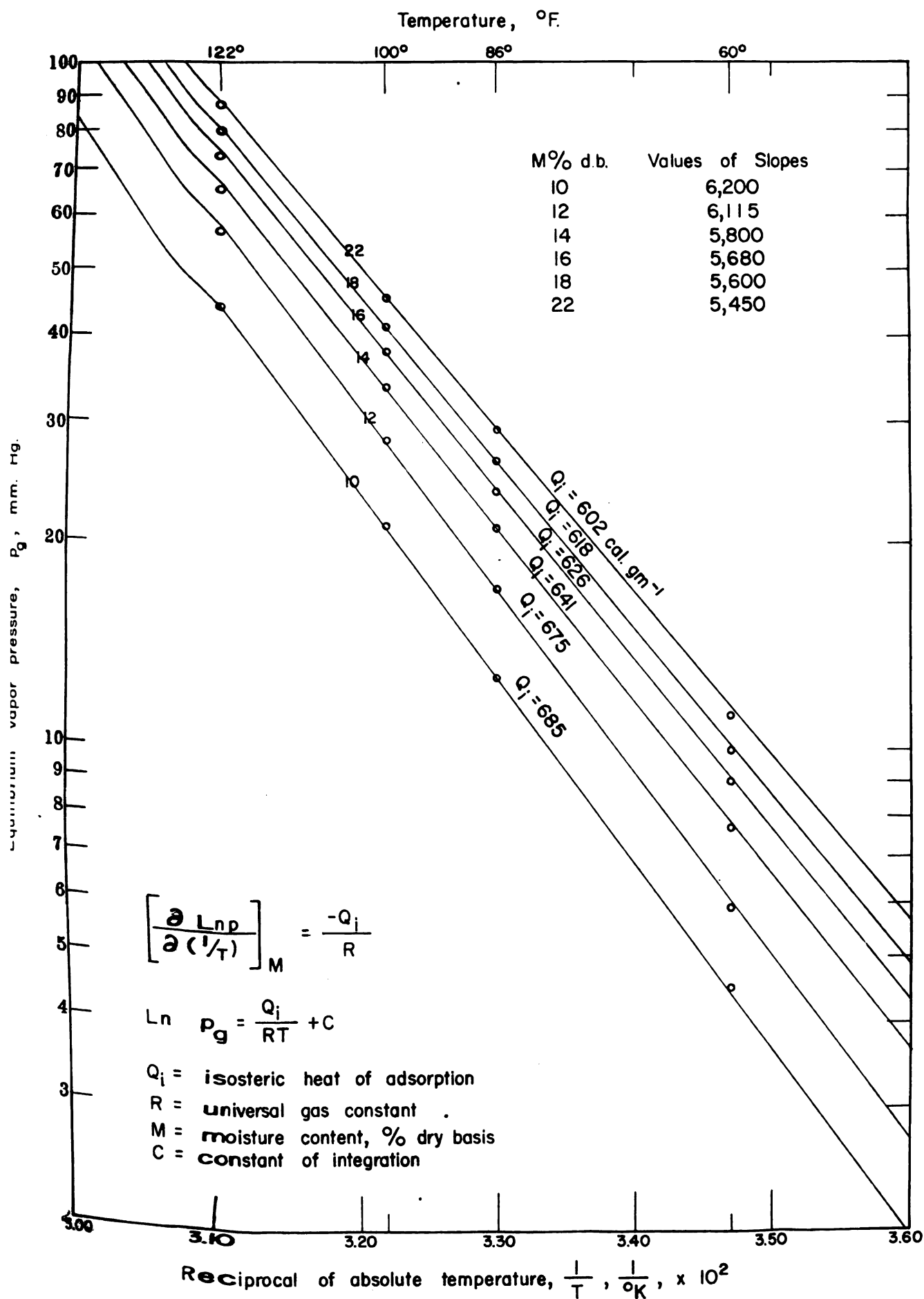


Figure 10. Estimation of isosteric heat of adsorption from plotted curve of

temperature range from 60° to 122°F. Over a wider range appreciable deviations from linearity resulted, as could have been expected in view of the simplifying assumptions involved in the derivation of equation (50). The slopes of the straight lines were then determined and the values of the isosteric heats of desorption evaluated from these by multiplying by 1.9871 calories per degree Kelvin per gram-mole, the consistent value for the universal gas constant, R . The isosteric heats thus obtained are expressed in terms of calories per gram-mole. In order to convert these values to calories per gram they were multiplied by 18, the molecular weight of water, which is the equivalent of one gram-mole of water. To obtain these values in English units, the conversion factor is

$$10 \frac{\text{I T. cal.}}{\text{gm.}} = 18 \frac{\text{BTU}}{\text{lb.}}$$

The Clausius-Clapeyron equation is frequently met in the form of the definite integral. If equation (49) is integrated between the temperatures T_1 and T_2 where the equilibrium vapor pressures are p_1 and p_2 , assuming that ΔH remains constant, one obtains

$$\ln (p_2/p_1) = - \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (51)$$

Equation (51) may be written thus

$$\Delta H = Q_{\text{isosteric}} = \frac{R T_1 T_2}{T_1 - T_2} \ln (p_1/p_2) \quad (52)$$

This equation rests on all the approximations that were used in transforming equation (45) to (50).

TABLE VII
CALCULATION OF ISOSTERIC HEATS OF DESORPTION FOR SHELLLED CORN
OVER THE TEMPERATURE RANGE 86° TO 122° F

Saturation vapor pressures: At 86°F = 0.6152 psia 122°F = 1.7888 psia								
Moisture Content percent d.b.	Equilibrium Rel. Pressure		Equilibrium Vapor Pressure, psia		Isosteric Heats of Desorption			
	303°K	323°K	303°K	323°K	Total Values			Net
					cal/mole	cal/gm	BTU/lb	BTU/lb
	T ₁	T ₂	P ₁	P ₂				
6	0.160	0.205	0.0985	0.3667	12,780	710	1,279	244
8	0.265	0.325	0.1630	0.5815	12,385	687	1,238	203
10	0.400	0.480	0.2460	0.8575	12,110	673	1,210	175
12	0.537	0.617	0.3302	1.1030	11,700	650	1,170	135
14	0.660	0.720	0.4065	1.2879	11,500	638	1,148	113
16	0.751	0.798	0.4624	1.4280	11,285	626	1,128	93
18	0.825	0.860	0.5075	1.5390	11,080	614	1,105	70
22	0.915	0.940	0.5630	1.6800	10,950	608	1,095	60
26	0.967	0.990	0.5950	1.7700	10,900	605	1,090	55

Equation

$$Q_i = \frac{R (T_1 \times T_2)}{T_2 - T_1} \times \ln (p_2/p_1)$$

where

Q_i = isosteric heat of desorption, cal. per mole

T = absolute temperature, °K

p = equilibrium vapor pressure, psia

R = universal gas constant, 1.9871 cal. °K⁻¹ mole⁻¹

The isosteric heats of desorption were also calculated according to this equation both as a check on the degree of accuracy obtainable by the graphical method described above, and also to secure more accurate values since the lack of precision which is usually inherent to graphical methods is thus avoided. Table VII shows the results of the computations obtained by this method. The isosteric heats of desorption are given in three different units as shown, and also in terms of net values. The latter values were obtained by subtracting from the total isosteric heats the mean of the latent heats of vaporization of water at 86° and 122°F.

Othmer Graphical Method

Another method employed in evaluating the heats of desorption from the experimental data was Othmer's graphical method of vapor pressure correlation. This method has been recently employed by several investigators (17, 30) in determining the latent heats of vaporization of various grains.

Based on the Clausius-Clapeyron equation, Othmer derived the following relationship

$$\ln p = \frac{L}{L'} \ln p' + C \quad (53)$$

where L is the total heat required to desorb one mole of adsorbed material at a given temperature, L' is the molal latent heat of vaporization of the reference substance at the same temperature, p is the equilibrium vapor pressure of the material, p' the saturation vapor pressure of free water, and C is a constant of integration.

1

It is evident from the foregoing relationship that a logarithmic plot of the equilibrium vapor pressure values pertaining to the grain against the saturation vapor pressure of free water at the same temperature will yield a straight line the slope of which represents the ratio of the molal latent heat of the grain to the molal latent heat of free water over the temperature range under consideration. Figure 11 shows such a plot for shelled corn of various moisture contents constructed from the desorption isotherm curves over the temperature range from 40° to 100°F. The method of constructing the plots was similar to that used for the isosteric plots of Figure 10. Using logarithmic graph paper, a suitable scale was laid off on the x-axis to cover the range of water saturation pressures involved. The isotherm temperatures were also indicated on the x-axis (top margin) at the appropriate values corresponding to the saturation vapor pressures of free water. A scale was laid off on the y-axis for the equilibrium vapor pressures corresponding to the grain. The equilibrium vapor pressures corresponding to selected moisture content levels were then plotted on the respective temperature ordinates, and appropriate points connected by the isosteric lines. It will be seen that a very satisfactory fit was obtained over the temperature range selected. As in the case of the plots of Figure 10, deviation from the straight line was already noticeable for points outside of that range. This again was to be expected in view of the limitations inherent to the Clausius-Clapeyron equation, on which the method is based.

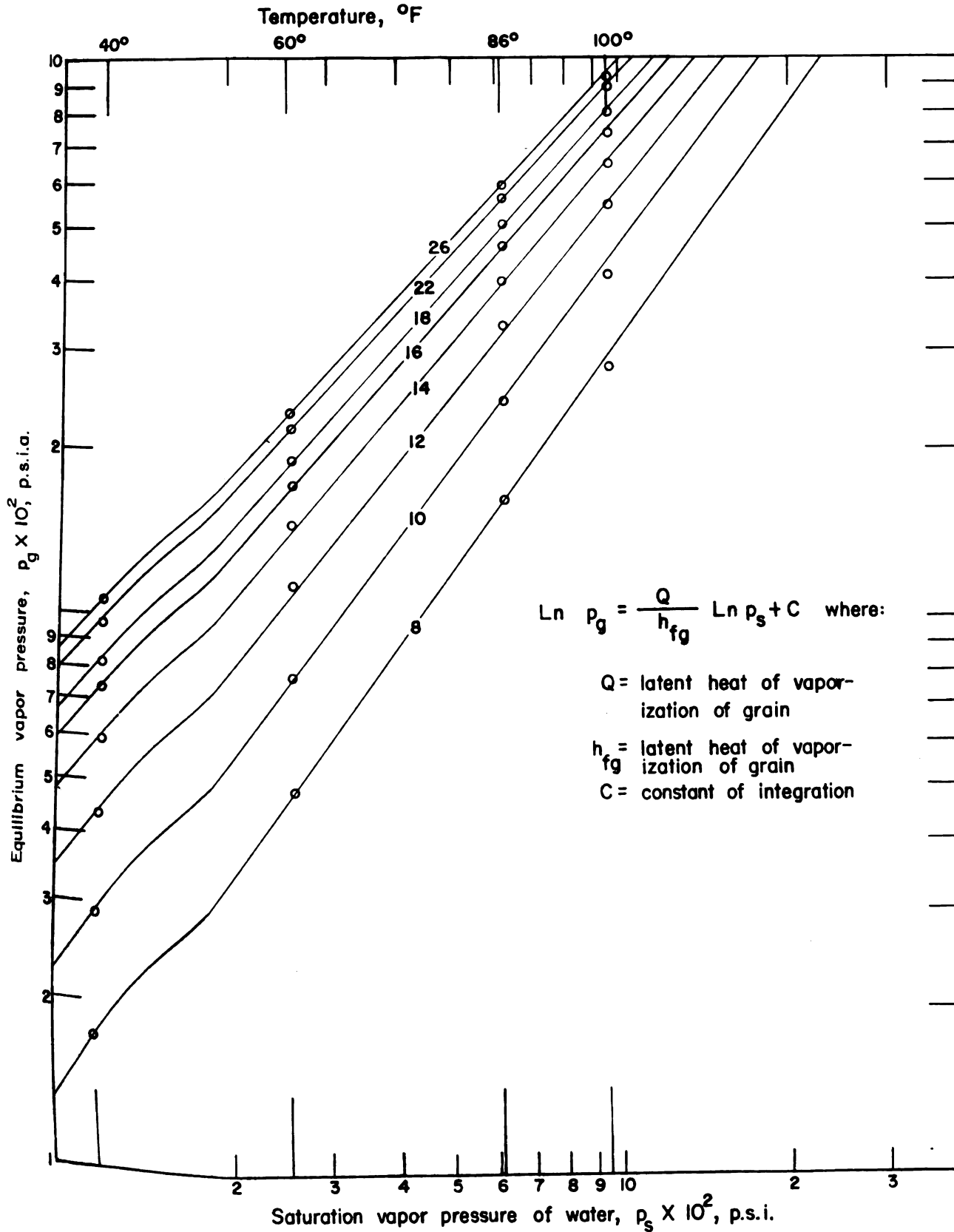


Figure 11 Othmer plots of desorption data for shelled corn of various moisture levels.

In order to determine the differential heats of desorption from the Othmer plots the slopes of the isosteric lines were measured and their values tabulated as latent heat ratios as shown in Table VIII. As the method is usually applied, these ratios are multiplied by the latent heat of vaporization of water at the temperature desired in order to obtain the differential (isosteric) heats of desorption, and so it was done for the purposes of constructing Table VIII which gives the values in terms of BTU per lb corresponding to eight different moisture levels and to each of the six isotherm temperatures. Strictly speaking, however, a more correct procedure should be to apply such ratios only over the temperature range for which straight Othmer plots were obtained, and to multiply the ratios by the mean value of the latent heat of water over that range. After obtaining the latent heat ratios from the Othmer plots these values were plotted against moisture content and a curve drawn through the points. The curve thus obtained is shown in Figure 12. It will be seen that the ratio is quite high for the lowest moisture level and decreases rather rapidly and uniformly with increasing moisture content, leveling off at about 16 percent (dry basis). This behavior will be examined later in the discussion. Figure 12 should be valuable for predicting heats of desorption corresponding to other moisture levels within the range of the curve.

TABLE VIII
DIFFERENTIAL HEATS OF DESORPTION FOR SHELLLED CORN FROM
OTHER PLOTS OF ISOTHERM DATA

Temperature, °F		40	60	80	100	122
h_{fg} , BTU/lb.		1071.3	1059.9	1048.6	1037.2	1025.8
Moisture Content, % d.b.	Latent Heat Ratio q_d/h_{fg}	Differential Heats of Desorption, BTU/lb.				
8	1.385	1484	1467	1451	1437	1421
10	1.310	1403	1390	1372	1360	1344
12	1.230	1319	1304	1290	1278	1249
14	1.165	1249	1235	1221	1210	1195
16	1.125	1206	1191	1180	1168	1154
18	1.102	1180	1169	1157	1143	1131
22	1.078	1152	1141	1129	1118	1105
26	1.072	1148	1138	1123	1112	1100

Note:

h_{fg} = latent heat of vaporization of free water

q_d = differential heat of desorption

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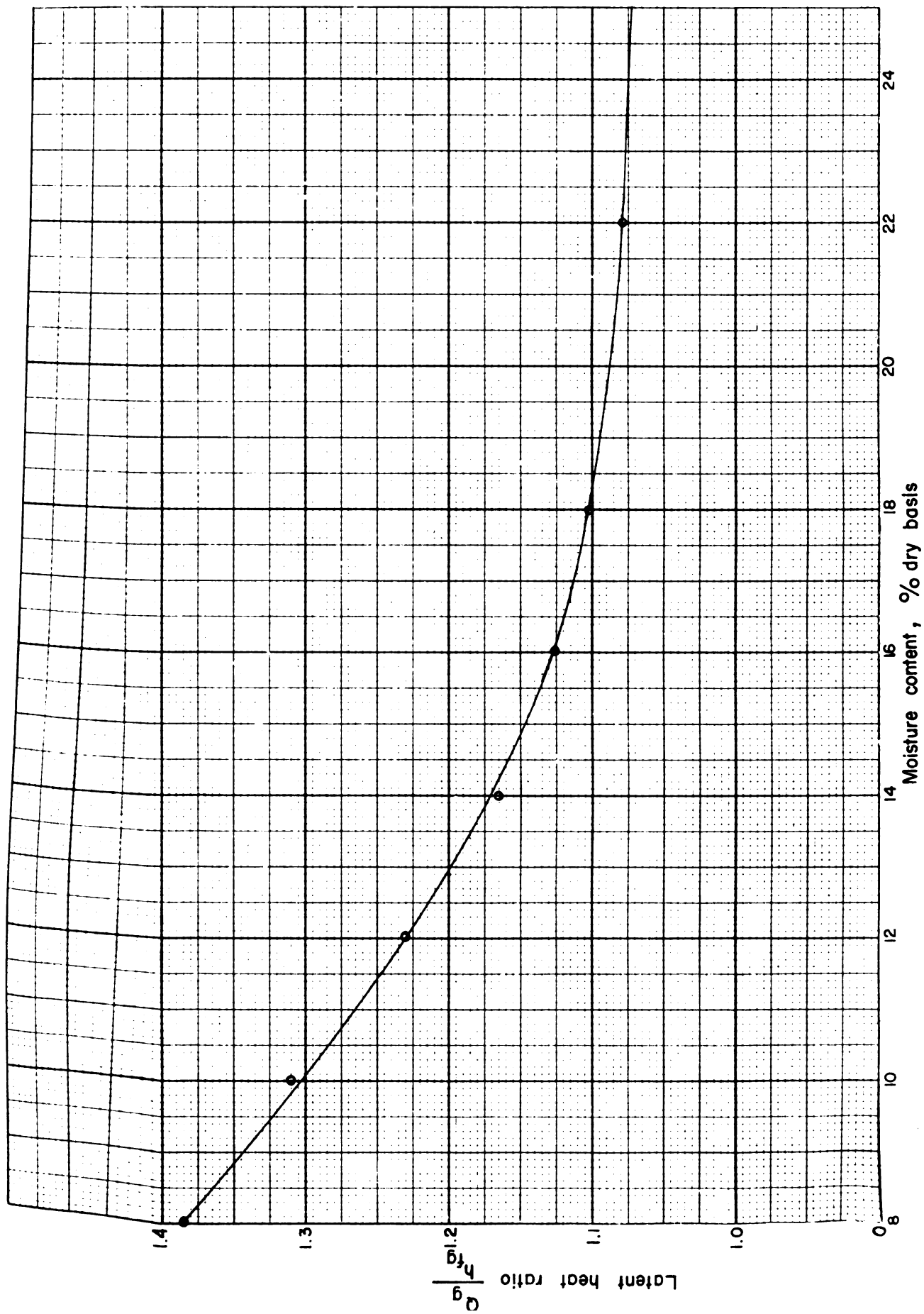


Figure 12 Variation of the Othmer ratio of latent heats with moisture content of shelled corn.

The Brunauer, Emmett, and Teller Equations

Probably the most fruitful approach to the end of elucidating the mechanism responsible for the hygroscopic properties of grain was afforded by an analysis of the experimental isotherms according to the Brunauer, Emmett and Teller theory of multimolecular adsorption. The salient features of this theory, which is more often referred to as the B-E-T theory, have been discussed briefly in a previous section. The present discussion will deal in some detail with the application of the theory to the experimental data.

It will be recalled that the B-E-T isotherm equation for adsorption on a free surface may be written in the form of a two-constant linear equation suitable for testing experimental data. The equation is restated here for convenience.

$$\frac{p}{v(p_s - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_s} \quad (35)$$

The constant v_m is a size constant which depends on the number of molecules required to cover the entire surface with a unimolecular adsorbed layer so that the surface area of the adsorbent can be measured in terms of the cross-sectional area of the adsorbed molecule. The constant c on the other hand is an energy constant the value of which is determined by the heat of adsorption in the first unimolecular layer.

Because of the simplifying assumptions involved in the derivation of equation (35) it is only valid in the region of relative pressure values between 0.05 and 0.35 and occasionally up to 0.50.

If the theory of multimolecular adsorption is obeyed by any system under consideration the plot of the function $p/v (p_s - p)$ as ordinates against the relative pressure values as abscissae should give a straight line in the above prescribed region of relative pressures. Furthermore, it is also necessary that the evaluated constants should have reasonable values. An examination of equation (35) will reveal that the values for the constants will be given by the slope and intercept of the linear plot.

In the equation, p corresponds to the equilibrium vapor pressure p_g of the grain which in turn is given by the product of the equilibrium relative pressure and the aqueous saturation vapor pressure, p_s , at the isotherm temperature under consideration; v represents the equilibrium moisture content, M , at any time and is expressed in percent dry basis in the present treatment. As a first step in applying the equation to the experimental data, the values of the function $p_g/M(p_s - p_g)$ were evaluated for values of equilibrium moisture content from 1.5 to 26 percent dry basis. Table X shows the results of such calculations for the 100°F isotherm, by way of illustration. It is well to clarify that such a detailed computation of the isotherm is actually not necessary, as may well be realized from the fact that the region of validity of the equation is restricted to relative pressures between 0.05 and 0.50. However, it was desired to follow the course of the B-E-T isotherm over as long a range of relative pressures as possible, and to determine the full extent of the region of

TABLE X
COMPUTATION OF DATA FOR B-E-T PLOT OF THE 100°F ISOTHERM

$M, \% \text{ d.b.}$	$(p_g/p_s)_e$	p_g	$p_s - p_g$	$p_g/M(p_s - p_g)$
1.50	0.015	0.01424	0.9350	0.01015
2.50	0.040	0.03797	0.9113	0.01662
3.00	0.052	0.04936	0.8999	0.01830
4.00	0.087	0.08258	0.8661	0.02380
5.00	0.127	0.12055	0.8287	0.02910
6.00	0.175	0.16611	0.7831	0.03540
7.00	0.235	0.22305	0.7262	0.04380
8.00	0.295	0.28000	0.6692	0.05230
9.00	0.360	0.34170	0.6075	0.06150
10.00	0.430	0.40820	0.5410	0.07550
11.00	0.505	0.47930	0.4701	0.0930
12.00	0.575	0.54580	0.4034	0.1150
14.00	0.688	0.65300	0.2962	0.1570
16.00	0.775	0.7356	0.2136	0.2160
18.00	0.842	0.7992	0.1500	0.2960
20.00	0.892	0.8467	0.1025	0.4130
22.00	0.930	0.8828	0.0664	0.6030
24.00	0.955	0.9065	0.0427	0.8450
26.00	0.977	0.9274	0.0218	1.6350

Note:

M = moisture content

p_g = equilibrium vapor pressure, psia

p_s = water saturation vapor pressure = 0.9492 psia

$(p_g/p_s)_e$ = equilibrium relative pressure

validity of the equation as applied to shelled corn. The next step involved constructing the plots according to equation (35).

Figure 13 shows the B-E-T plots, calculated as explained above, for each of the six experimental isotherms. It will be seen that very satisfactory straight lines were obtained in all cases over the range of relative pressures between 0.05 and 0.35. At relative pressures greater than 0.30 to 0.40 the plots deviate with increasing pressure more and more strongly from the straight line. The constants v_m and c were next evaluated for each isotherm from the slopes and intercepts of the respective plots. These values are shown in Table IX, columns 4 and 5. From the value of constant c the magnitude of $(E_1 - E_L)$, the net heat of desorption for the first monomolecular layer was also calculated for each isotherm. These values along with those of E_1 , the gross heat of desorption (adsorption) are also shown in columns 6 and 7 of the same table. As an example, the computations involved in evaluating the constants for the 100°F isotherm will be shown here in detail.

From the corresponding plot of Figure 12 the value of the intercept was found to be

$$1/v_m c = 0.0118$$

from which

$$v_m c = 1/0.0118 = 84.8 \quad (c)$$

The value of the slope was found as follows

$$\begin{aligned} (c - 1)/v_m c &= (0.0667 - 0.0118)/0.40 \\ &= 0.1375 \end{aligned}$$

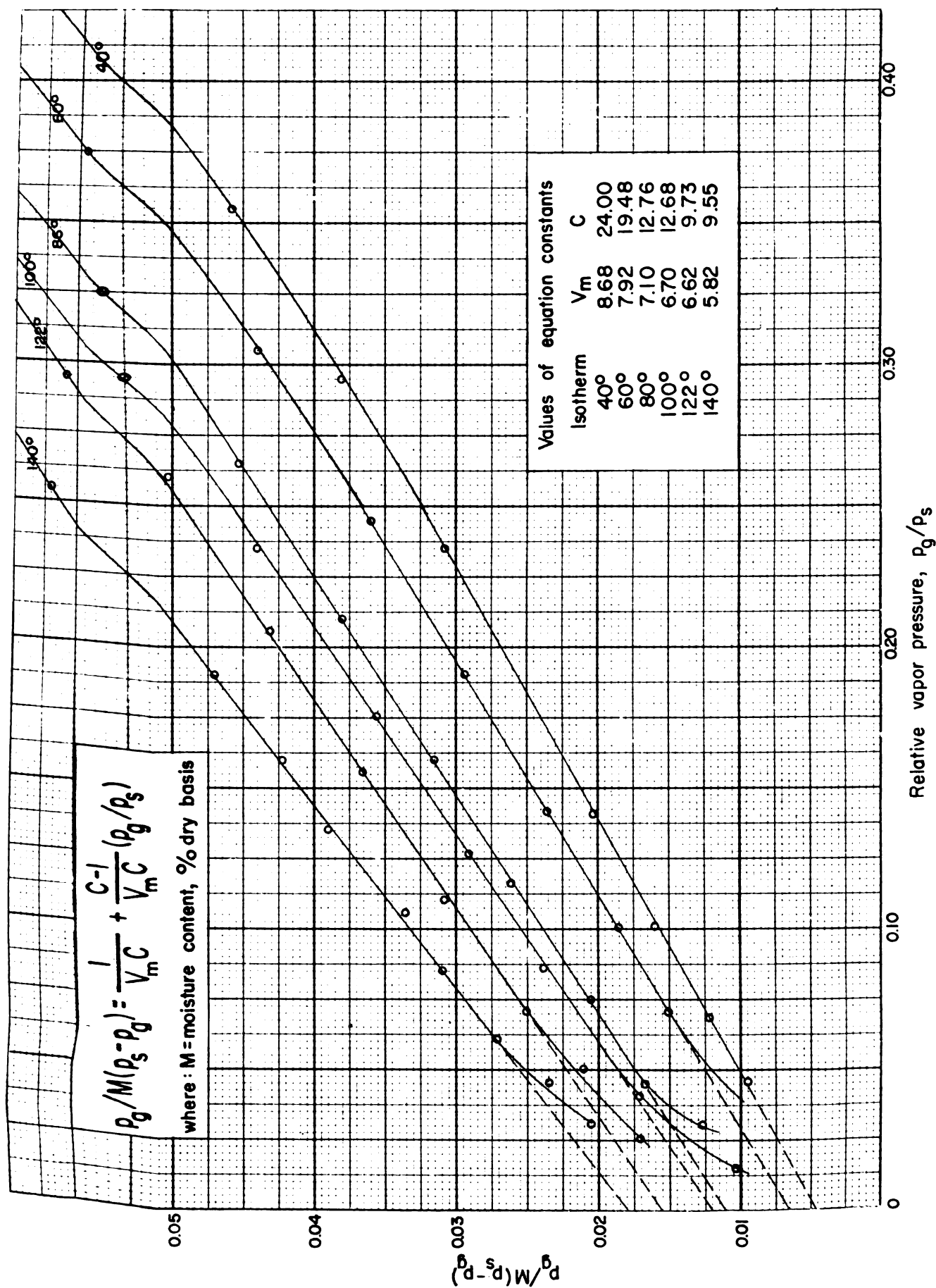


Figure 13 B.E.T. plots of desorption isotherms for shelled corn

TABLE IX
DESORPTION ISOTHERM CONSTANTS FOR SHELLD CORN¹

Isotherm Temperature °F	Henderson's Equation			B-E-T Theory			Smith's Equation		Harkins-Jura Equation	
	k	n	c	v_m	E_1	Point B	w_b	w'	A	$A^{\frac{1}{2}}$
40	1.90×10^{-6}	2.47	24.00	8.68	693	8.50	0.084	0.0614	0.0161	0.1268
60	2.82×10^{-6}	2.40	19.48	7.92	683	8.00	0.078	0.0656	0.0134	0.1159
86	5.17×10^{-6}	2.25	12.76	7.10	666	7.00	0.072	0.0468	0.0110	0.1050
100	7.13×10^{-6}	2.15	12.68	6.70	663	6.75	0.070	0.0458	0.0098	0.0991
122	8.93×10^{-6}	2.08	9.73	6.62	651	6.50	0.064	0.0457	0.0086	0.0925
140	9.68×10^{-6}	2.20	9.55	5.82	646	5.75	0.048	0.0450	0.0058	0.0765
Averages	6.59×10^{-6}	2.81	14.70	7.14	667	7.08	0.069	0.0496	0.0108	0.1034

$1/v_m$ is expressed in percent moisture content, dry basis

E_1 is expressed in terms of calories per gram

Point B values are expressed in percent moisture content, dry basis

w_b and w' are both expressed in grams of water per gram of grain, wet basis

$A^{\frac{1}{2}}$ is given in grams per gram of dry grain

from which, substituting the value of $v_m c$

$$c - 1 = (0.1375) (84.8) = 11.68$$

and $c = 12.68$

Substituting now in (c) and solving for v_m ,

$$\begin{aligned} v_m &= 84.8/12.68 \\ &= 6.70 \text{ percent dry basis} \end{aligned}$$

In order to evaluate E_1 from constant c , equation (37)

is used thus

$$c = e^{(E_1 - E_L)/RT} \quad (37)$$

Substituting values

$$12.68 = e^{(E_1 - E_L)/(1.987)(311)}$$

Taking logarithms

$$\ln 12.68 = (E_1 - E_L)/(1.987)(311)$$

$$\begin{aligned} E_1 - E_L &= (\ln 12.68)(1.987)(311) \\ &= 1,570 \text{ cal. mole}^{-1} \end{aligned}$$

In the above, the universal gas constant is expressed in terms of calories per $^{\circ}\text{K}$ per gram-mole, and the temperature in degrees Kelvin.

To convert the above result to calories per gram, it is divided by 18, the molecular weight of water, thus

$$1,570 \text{ cal. g-mole}^{-1}/18 \text{ gm g-mole}^{-1} = 87 \text{ cal. gm}^{-1}$$

Since E_L , the heat of liquefaction of water at 100°F is 576 cal gm^{-1} , then

$$E_1 = 87 + 576 = 663 \text{ cal. gm}^{-1}$$

Expressed in English units

$$663 \text{ cal. gm}^{-1} \times 1.8 \frac{\text{BTU lb.}^{-1}}{\text{cal. gm.}^{-1}} = 1195 \text{ BTU lb.}^{-1}$$

A comparison of the heats of adsorption thus obtained, and shown in Table VIII, with the values of the isosteric heats of adsorption obtained according to the various methods based on the Clausius-Clapeyron equation will show that they agree remarkably well both in magnitude and in their general behaviour of decreasing with increasing temperature. This is particularly gratifying in view of the fact that the E_1 values were obtained from individual isotherms, while the isosteric heats were calculated from more than two isotherms, and by entirely different methods. In all cases the net heats of adsorption as calculated from the values of c were positive in value, which is interpreted to mean that the attractive forces between the surface of the adsorbent and the adsorbed moisture are greater than the attractive forces between the molecules of water in the liquid state. This is in accord with the observation that the differential heat of desorption is a decreasing function of the level of moisture content in the grain. It was seen before that the B-E-T equation breaks down for relative pressure values smaller than about 0.06. According to the theory this is ascribed to the fact that at those low pressures the adsorption takes place on the strongly heterogeneous fraction of the surface which can not be characterized by a constant heat of adsorption. It is reasonable to visualize the picture of adsorption taking place during that initial stage of the process on the most active centers of the proteins in the grain.

It may be concluded from the foregoing that the values of constants c obtained from the linear B-E-T plots are reasonable and therefore give considerable support to the theory.

A closer examination of constant v_m seems now in order. It has been pointed out that v_m represents the amount of moisture that is necessary to complete the first unimolecular layer on the internal surface of the grain. According to the theory, its value corresponds to that of the beginning of the intermediate linear region of the sigmoid or Type II isotherm, which can usually be chosen by visual inspection from the experimental isotherm. This particular point on the isotherm has been designated by Brunauer as Point B, and is usually referred to as such in the literature. In fact, the determination of Point B constitutes an alternative method of obtaining the amount of adsorbate in the first monomolecular layer and accordingly, has been called the empirical method while the determination of v_m values is known as the theoretical method. When both methods can be applied to a given set of data, that is, when complete experimental isotherms are available for the analysis, the degree of agreement between both sets of values can be a valuable tool in testing the validity of the theory. With this purpose in mind, Point B values were ascertained for each of the isotherms and compared with the corresponding v_m values obtained from the B-E-T plots. Point B values are also given in Table IX, column 7. It will be seen that there is an excellent agreement between the Point B values and the theoretical v_m values.

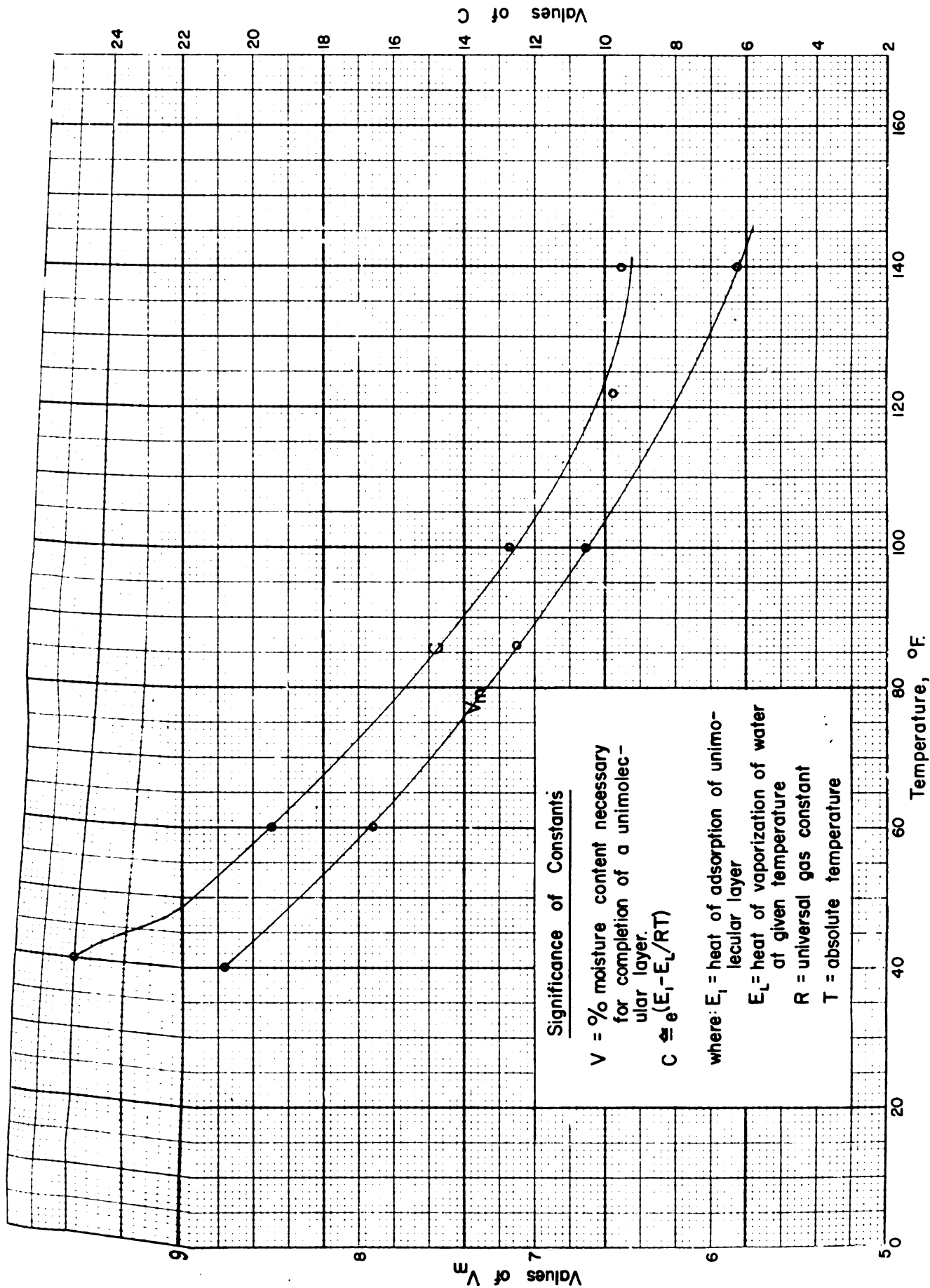


Figure 14 Variation of constants ' C ' and ' V_m ' of the B.E.T. equation, with temperature

This can be regarded as a mutual confirmation of the empirical method of selecting the point on the isotherm corresponding to a monolayer and the fundamental assumptions underlying the theory of multimolecular adsorption.

The use of constant v_m in determining the effective surface area of adsorbents has been mentioned. Industrial adsorbents are known to possess enormously large internal surface areas and negligible external surfaces. For instance, the surface area of gas mask charcoal as determined from actual crystal dimensions has been found to be 1940 square meters per gram (9). In view of the hygroscopic properties of cereal grains it is reasonable to assume that they also possess large internal areas available for adsorption of moisture. In connection with his studies on the adsorption of water vapor by proteins, Bull (12) determined the areas of a large number of proteins according to the B-E-T method. He reported values of surface area for B-zein and C-zein, two of the proteins in corn, of 0.145 and 0.138 square meters per milligram, respectively. It was considered a matter of great interest to investigate the order of magnitude of the internal surface area of shelled corn, on the basis of the knowledge of v_m values gained from the B-E-T plots. The crucial problem in the application of the B-E-T method for this purpose lies in the assumption of a molecular area for the adsorbed molecules. In his book on adsorption, Brunauer gives the following equation for the calculation of molecular areas

$$\text{Area (L)} = (4) (0.866) (M/5.65 N d_L)^{2/3} \quad (56)$$

where M is the molecular weight of the gas or vapor, N is the Avogadro's number or 6.023 molecules per gram-mole, and d_L is the density of the liquid. This equation assumes that the packing of the molecules on the surface approximates that of the liquefied gas. Calculation of the molecular area of water from the density of liquid water at 30°C according to equation (56) gives a value of 10.5 Å². Based on the finding by Hendricks that a unit cell of the layer crystal montmorillonite adsorbs four molecules of water, Brunauer (9) gives a value of 11.5 Å². De Boer (6) states that approximately 10¹⁵ molecules of water are needed to cover one square centimeter of surface at a temperature of 20°C. For the purposes of this discussion it was assumed that a water molecule occupies an area of 11.0 Å² (11.0 x 10⁻¹⁶ sq cm). Taking the value of v_m as 7.10 grams per 100 grams of dry grain as obtained for the 86°F (30°C) isotherm, there will be

$$\begin{aligned} n &= \frac{7.10 \text{ gm}}{\text{gm per molecule}} = \frac{7.10}{M/N} \\ &= \frac{7.10}{18/6.023 \times 10^{23}} = 2.375 \times 10^{23} \text{ molecules} \end{aligned}$$

comprising a monolayer. The surface area will then be

$$\begin{aligned} S &= 2.375 \times 10^{23} \times 11.0 \times 10^{-16} \\ &= 26.2 \times 10^7 \text{ sq cm per 100 grams of dry grain} \end{aligned}$$

This is equivalent to 262 square meters per gram or 0.262 square meters per milligram, which is about twice the area that Bull reported for C-zein. Expressed in terms of acres per 100 grams of

1

dry grain, the area is approximately 6.5 acres. In view of the foregoing considerations this value for the surface area of shelled corn **does** not appear unreasonable. The decrease of the v_m value with **increasing** temperature can readily be accounted for in terms of the thermal expansion of the monolayer. It has thus been seen that **not** only have the experimental data yielded very satisfactory linear plots over the range of validity prescribed for the B-E-T theory, but also quite reasonable values of the equation constants have been obtained from the linear plots. It can therefore be concluded that the water-binding mechanism involved in shelled corn, and probably in all other cereal grains, is one of multimolecular adsorption.

It has been pointed out that beyond a relative pressure of about 0.50 the simple two-constant equation fails to describe the course of the isotherm. Beyond that relative pressure the amount of water adsorbed increases more and more slowly than it would if governed by equation (35). It should be remembered that equation (35) was derived for adsorption on a free surface; certainly the internal surface of grain is by no means a free surface. Within the range of relative pressures for which the equation holds satisfactorily the influences that restrict the number of layers have generally not yet become strong enough to make themselves noticeable. Beyond that range, however, it becomes necessary to use the three constant equation (38).

The B-E-T three-constant equation was derived to take care of the situation where only a finite number of layers can be

adsorbed at saturated pressure. While there may be other causes for such a restriction, the effect of the pores and capillaries which characterize the surface is probably the most conspicuous. The equation introduces one more constant in addition to the constants v_m and c of the simple equation. This constant, denoted by n , represents the maximum number of layers that can be adsorbed on each wall of a capillary. The equation, however, does not take into account the forces of capillary condensation which usually sets in at the higher pressures. It is therefore to be regarded only as a more or less approximation in the higher pressure region. Notwithstanding its limitations the equation can be very helpful in ascertaining the general character of the surface, particularly concerning the size and relative distribution of the micropores. It is the size distribution of the micropores (pores with radii less than $100 \text{ \AA}$) that largely determines the shape of the isotherm beyond the region of unimolecular adsorption. With the purpose in mind of gaining information in this respect the experimental data was analyzed according to the B-E-T three-constant equation.

The application of the three-constant equation called first for the evaluation of constants v_m and c according to the simple two-constant equation as explained in a previous section. One obtains then, by the method of trial and error, the value of constant n that best fits the experimental points. Figure 15 shows the results obtained with a value of $n = 5$, and $n = 6$ for the 100°F

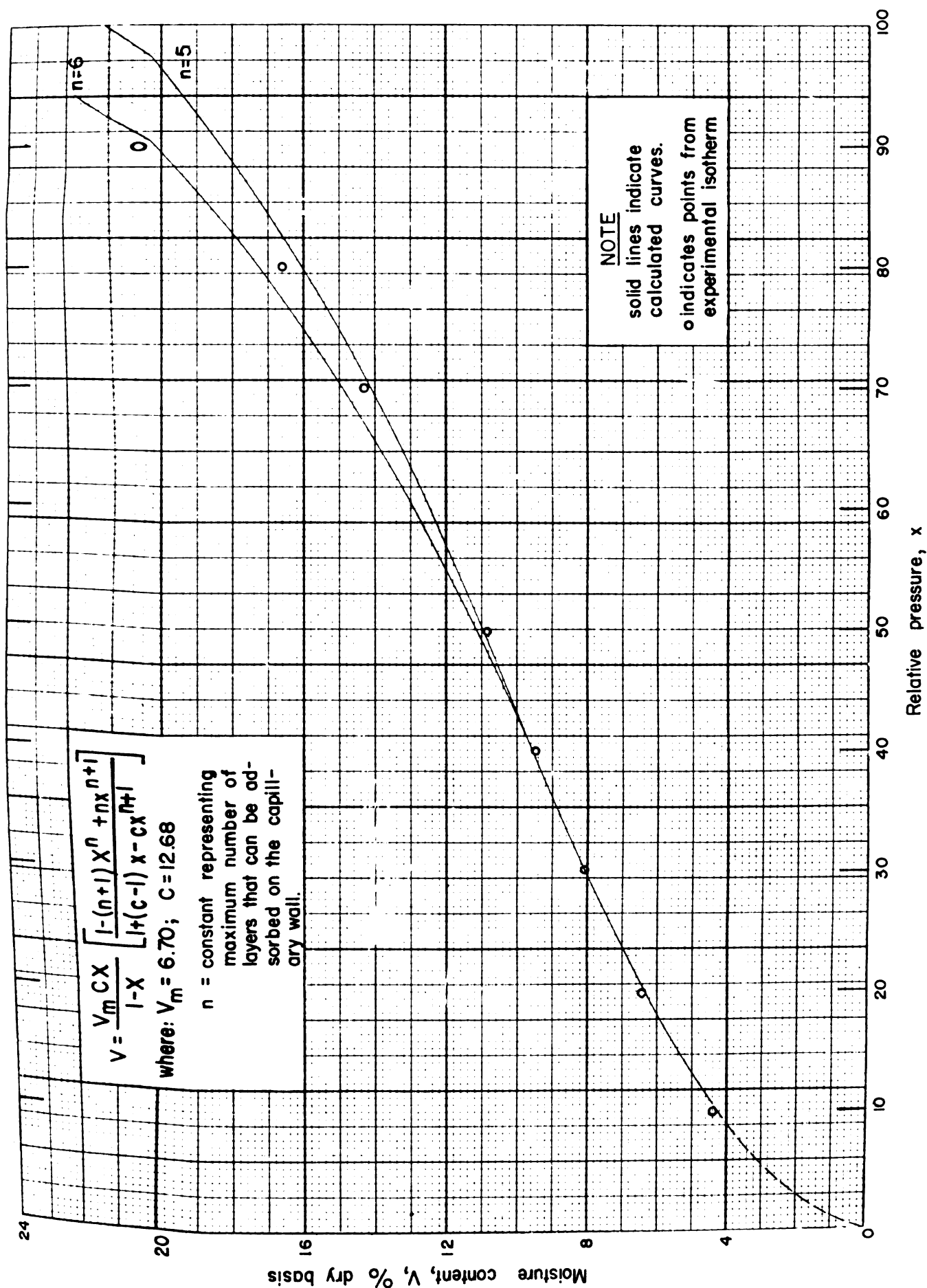


Figure 15 Desorption isotherm for 100° F. plotted according to the 3-constant equation of the B.E.T. theory, as compared with experimental points.

isotherm. The solid lines represent the calculated curves while the circles and dashed lines indicate the experimental isotherm. It should be noted that up to a relative humidity of 70 percent the value of $n = 5$ gives almost a perfect fit with the experimental isotherm. Beyond that value of relative humidity, however, the experimental isotherm deviates more and more strongly from the calculated curve. At a relative humidity of 90 percent already a value of $n = 6$ gives a fairly good fit. At a relative humidity of 80 percent an intermediate value of n would be required in order to bring about agreement between the experimental and the calculated isotherm. Thus with only two values of n equation (38) succeeded in reproducing the isotherm correctly up to as high a relative humidity as 90 percent. This can be interpreted to mean that the micropores characterizing the internal surface of shelled corn are comparatively uniform in size. Both the capillary condensation theory and the B-E-T theory of multimolecular adsorption agree that the narrower pores fill up at the lower relative pressures, while the wider pores fill up at the higher pressures. Thus as the relative pressure increases the average width of the pores that still participate in the adsorption process gets larger.

In the light of the foregoing results some idea may also be inferred as to the order of magnitude of the average width of the micropores which make up the major part of the effective internal surface of shelled corn, at least to a first approximation. Thus it has been seen from the application of the three-constant equation

that the maximum number of molecular layers which could be accommodated on each wall of the average-sized capillary was 5 up to a relative pressure of 0.70, and 6 up to a relative pressure of 0.90. For the purposes of estimation a number of 5.5 may be assumed. It will be remembered from the derivation of equation (38) that it was assumed that adsorption occurs in a capillary of two plane parallel walls. With this in mind, and assuming a molecular diameter for the water molecule of $2.9 \text{ \AA}$ it may justly be inferred that the average width of the micropores participating in adsorption up to a relative pressure of 0.90 is of an order of magnitude of $32 \text{ \AA}$.

The Harkins - Jura Equation

The Harkins-Jura equation afforded another interesting theoretical treatment by which the experimental data could be examined. It will be recalled that when adsorption (or desorption) equilibrium data is plotted according to equation

$$\ln (p_g/p_s) = B - A/M^2 \quad (40)$$

straight lines are obtained over the range of relative pressures where the adsorbed gas or vapor is in the form of a condensed film. Having established from the results of applying the B-E-T equations that the water-binding mechanism involves multimolecular adsorption, the Harkins-Jura equation offered a convenient tool with which to explore further the exact nature of the process. Accordingly, the experimental data was processed as shown in Table XI, namely, by computing the reciprocals of the squares of the values of equilibrium moisture content, dry basis. The plots were

TABLE XI
COMPUTATION OF DATA FOR HARKINS-JURA AND SMITH PLOT
Isotherm Temperature - 100°F

M, % d.b.	M, % w.b.	p_g/p_s	$1 - (p_g/p_s)$	$\ln(1 - p_g/p_s)$	$M^{-2} \times 10^4$ (dry basis)
3.00	2.91	0.05	0.95	0.050	---
5.50	5.22	0.15	0.85	0.162	330
6.50	6.10	0.20	0.80	0.223	236
7.75	7.20	0.25	0.75	0.288	167
8.10	7.50	0.30	0.70	0.356	153
8.80	8.10	0.35	0.65	0.430	129
9.50	8.66	0.40	0.60	0.505	111
10.25	9.30	0.45	0.55	0.600	95
11.00	9.90	0.50	0.50	0.694	83
11.65	10.45	0.55	0.45	0.800	74
12.45	11.07	0.60	0.40	0.918	64
13.25	11.68	0.65	0.35	1.050	57
14.35	12.45	0.70	0.30	1.205	49
15.35	13.30	0.75	0.25	1.385	42
16.70	14.32	0.80	0.20	1.610	36
18.25	15.42	0.85	0.15	1.900	30
19.25	16.13	0.875	0.125	2.080	27
20.50	17.00	0.90	0.10	2.300	24
23.50	19.00	0.95	0.05	3.000	18

Notes:

M = moisture content

p_g/p_s = relative vapor pressure

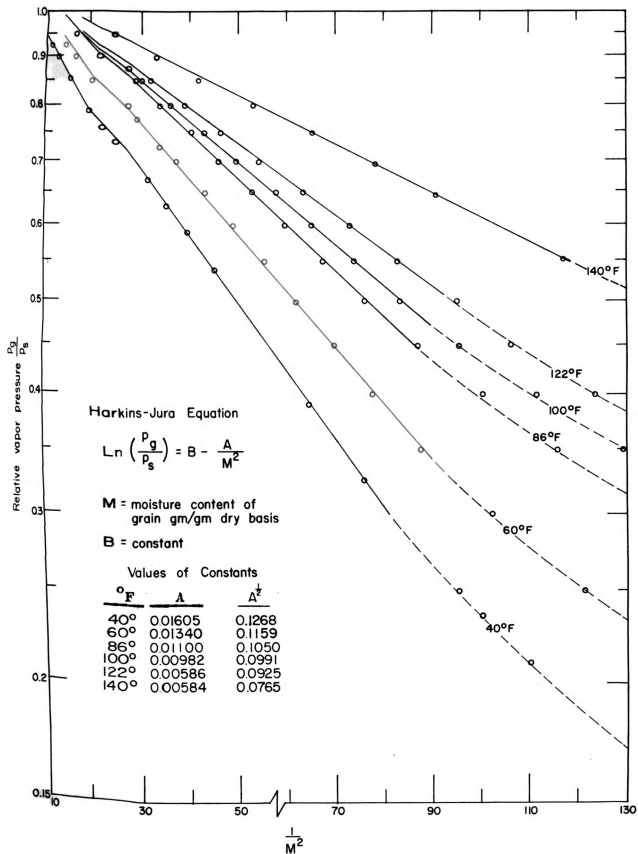


Figure 16 H-J plots of desorption isotherms for shelled corn.

then constructed on semilogarithmic graph paper as shown in Figure 16. It should be noted that the plots yielded very satisfactory straight lines in the case of all isotherms, over the range of values of the function $1/M^2$ between approximately 10 or 15 up to about 90. Translated in terms of moisture levels in the grain and of relative pressures, these values represent approximately ranges between moisture contents and relative pressures near saturation down to about 10 percent dry basis and about 0.40 to 0.45 relative pressure. According to the theory, these results indicate that in these ranges the adsorbed water occurs as a condensed film. It should be remembered that the amount of water necessary to complete the first unimolecular layer over the surface was given by the constant v_m of the B-E-T equation as 7.1 percent dry basis (average of all isotherms). It would seem then that shortly after this first layer is completed, i.e., upon adsorption of enough additional molecules to account for the difference between 10 percent dry basis obtained above and the value of v_m , two-dimensional condensation sets in to form a more or less continuous film which then constitutes the new surface for further adsorption.

Interestingly, further analysis of the Harkins-Jura plots produced additional evidence that lent support to the above theory. It has been pointed out that Liang (34) correlated the Harkins-Jura and the B-E-T equations and found that the square root of the slope, A , of the H-J plot actually corresponded to the value of v_m of the B-E-T equation. Some confirmatory evidence to that

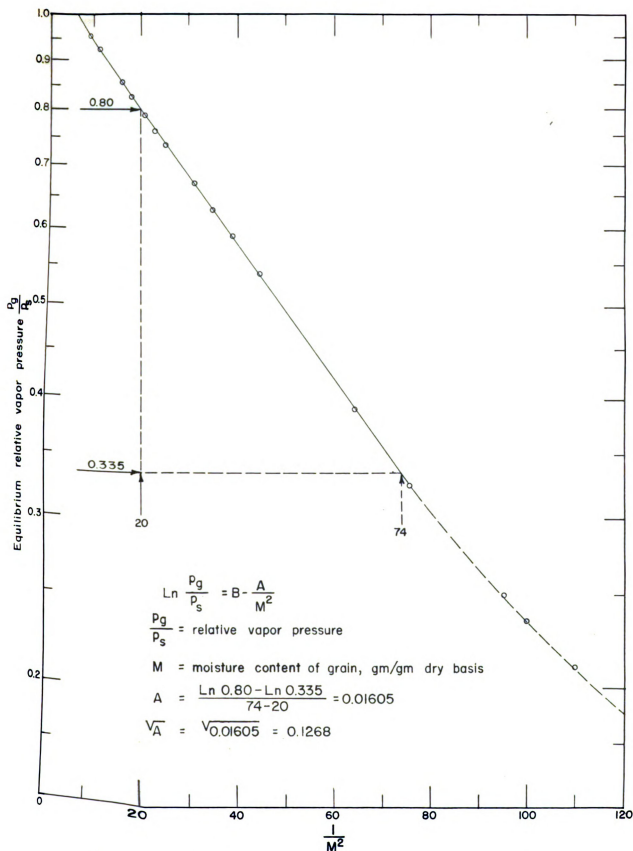


Figure 17 Determination of the H-J constants for the 40° desorption isotherm.

effect has been reported by other investigators. For instance, Hogan and Karon (26) found good agreement between the values of $A^{\frac{1}{2}}$ and v_m in their analysis of desorption equilibrium data of rough rice. Also Dunford and Morrison (15) obtained similar results in their work on the adsorption of water vapor by proteins. Yet an analysis of the H-J plots obtained for the desorption data of this investigation yielded values for $A^{\frac{1}{2}}$ corresponding in the average to values in the neighborhood of 10.35 percent dry basis. The order of magnitude of these values is approximately one and a half times that of the v_m values. It is interesting to note, however, that this average value of $A^{\frac{1}{2}}$ corresponds rather closely to the general order of magnitude of the values obtained from the range of linearity of the same H-J plots as marking the probable onset of two-dimensional condensation. It may be inferred from the foregoing that while the v_m -values do serve as a measure of a first unimolecular layer, this is not necessarily continuous over the whole internal surface, there remaining probably lesser active portions of the surface still available for adsorption. The molecules comprising this layer are probably characterized by a fairly uniform heat of adsorption. Then upon further adsorption on the remaining bare portions of the surface, and conceivably even on top of the first layer, a point is reached where enough lateral interaction between the water molecules themselves will develop to cause the formation of the condensed film as indicated by the analysis of the H-J plots. The heat of adsorption involved in this latter part of

the process is most probably of a lesser order of magnitude than that characterizing the initial adsorption, but still appreciably higher than the heat of liquefaction. In fact, referring back to Figure 12, which shows the variation with moisture content of the differential heats of desorption, it will be appreciated that probably even successive layers will involve heats of adsorption in excess of the heat of liquefaction even though decreasing in magnitude. It would appear then as if the influence of the surface forces of the grain could still reach outwards beyond the first unimolecular layer. It is conceivable that the principles underlying the polarization theory of adsorption postulated by de Boer and Zwikker may well play some role in this connection. This is all the more probable in view of the highly polar nature of the water molecules.

The Smith Equation

The Smith equation, which is applicable over the higher pressure region where the two-constant B-E-T equation breaks down, was also employed for correlating the experimental data. The Smith equation is

$$w = w_b - w' \ln(1 - p/p_g) \quad (42)$$

where, it will be recalled, w is the moisture content expressed on a wet basis. As a first step in applying the equation, the function $-\ln(1 - p/p_g)$ was computed for the relative pressures at intervals of 0.5 and at shorter intervals wherever it was convenient

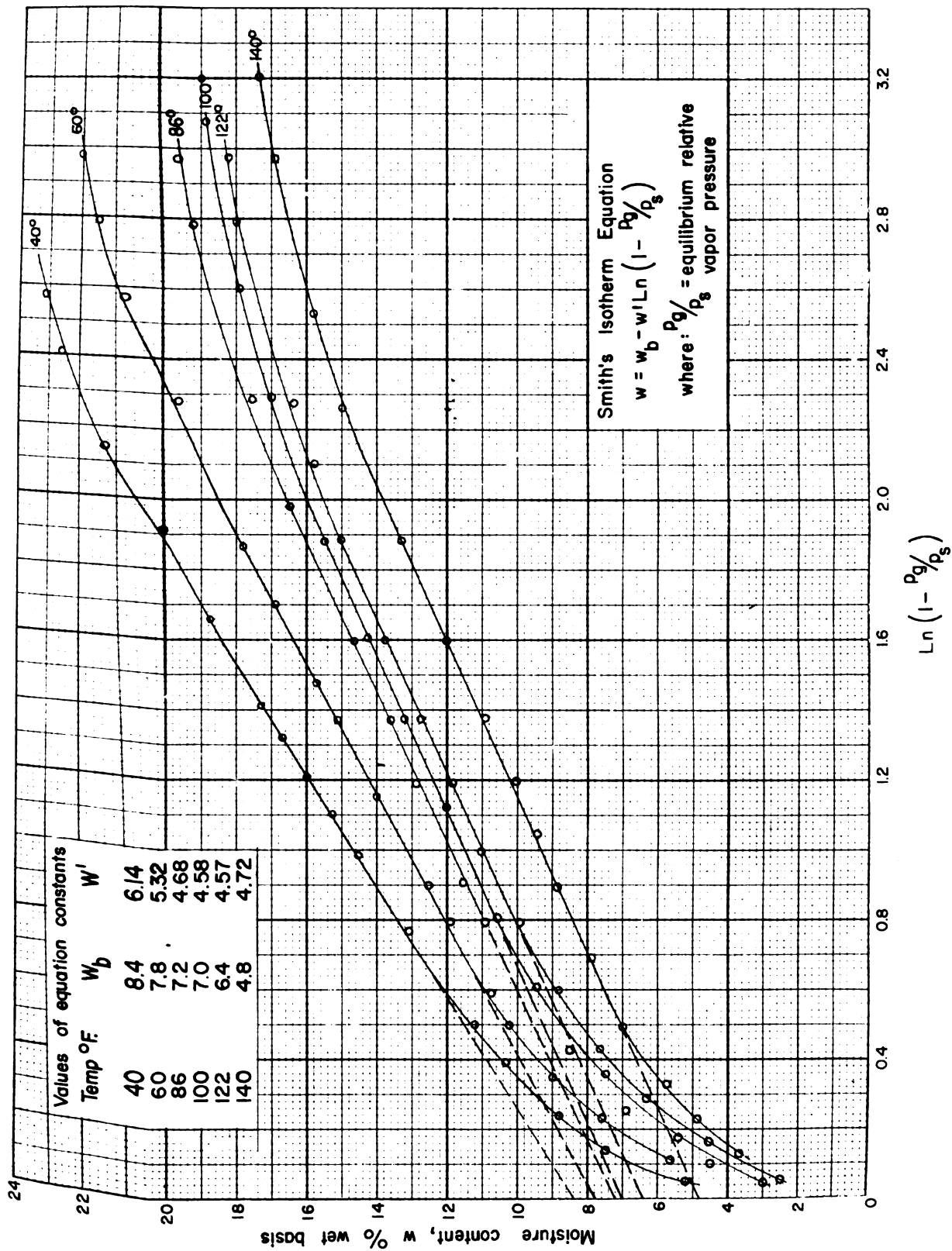


Figure 18 Smith plots of desorption isotherms for shelled corn

to define more accurately the limits of linearity in the plots. The corresponding moisture content values were then converted to the terms required by the equation, namely, on a wet basis. The same was done for each of the isotherms and the plots then constructed as shown in Figure 18. In columns 2 and 4 of Table XI, the computed point values for the 100°F isotherm are shown as an example of the above procedure.

An examination of Figure 18 will show that the plots gave good straight lines extending between values of the logarithmic function of about 0.6 on one end and 2.0 to 2.3 on the other. These values correspond to a range of relative pressures from about 0.45 up to about 0.90 which is very nearly the prescribed range of validity for Smith's equation. It has been mentioned that Becker and Sallans (4) found essentially similar results when applying the equation to their desorption isotherms of wheat. They also suggested a graphical method for defining the intermediate approximately linear region of the isotherm. This method consists of plotting the data according to both the B-E-T two-constant equation and the Smith equation on the same graph, and then drawing a straight line tangential to the Smith curve and intersecting the B-E-T curve at its point of inflection. Their method was tested on the experimental desorption isotherms for shelled corn with very satisfactory results. Prior to constructing the plots, an adequate number of point values was computed for each curve by using the values previously obtained for the respective constants of each equation. Figure 19 illustrates

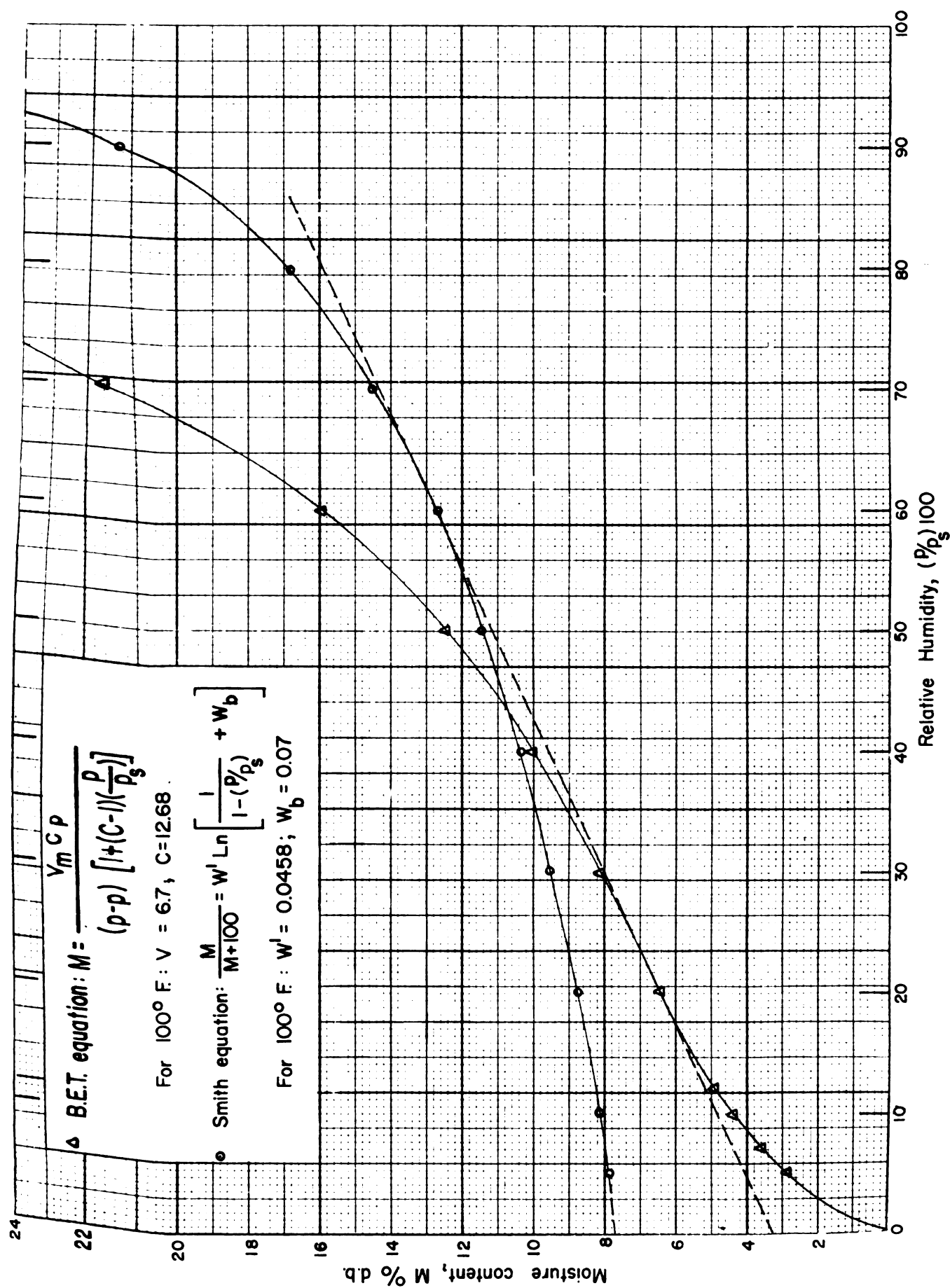


Figure 19 Desorption isotherm of shelled corn at 100°F plotted according to the B.E.T. and Smith equations, illustrating a method of obtaining the intermediate linear region.

the results of the plot for the 100°F isotherm. A comparison of the resulting composite curve with the 100°F experimental isotherm of Figure 7 showed nearly perfect agreement over the range of relative pressures from 0.15 up to about 0.82. It may therefore be concluded that the foregoing method is eminently successful in predicting the intermediate approximately linear region of the desorption isotherm.

Henderson's Equilibrium Equation

One objective of the investigation was to test the correctness of Henderson's equilibrium equation in describing the shape of the isotherm and in accounting for its temperature dependence. Henderson's equation involves two constants, k and n , which are held to depend only on the characteristics of the material; their values should entirely govern the shape of the curve at any given temperature. The equation is

$$1 - \frac{p}{p_s} = e^{-k T M_e^n} \quad (43)$$

If one evaluates the constants k and n from the experimental isotherm data and then calculates a complete isotherm from equation (43) on the basis of the values thus obtained for the constants, the extent to which the calculated curve agrees with the experimental isotherm may be considered a measure of the equation's validity in characterizing the shape of the isotherm. Moreover, if Henderson's equation accounts correctly for the temperature dependence of the isotherm one should be able to calculate the curve at any temperature on the basis of the values previously determined for

constants k and n . Conversely, the values for constants k and n should remain constant for any given material regardless of the isotherm temperature.

According to the foregoing criterion, the first step in testing equation (43) involves therefore the evaluation of the equation constants from the experimental data. This was accomplished for each experimental isotherm of Figure 7. by selecting two appropriate points on the approximately linear portion of the curve, and substituting the corresponding coordinate values in their respective places in the equation. The resulting equations were then solved simultaneously. To illustrate, the calculations involved in evaluating the constants for the 122°F isotherm are shown below.

At a relative pressure of 0.30 the equilibrium moisture content of shelled corn, as given by the 122°F isotherm of Figure 7, is 7.65 percent, 'dry basis. Substituting values in equation (43)

$$1 - 0.30 = e^{-k(122 + 460)(7.65)^n}$$

$$0.70 = \frac{1}{e^{k(582)(7.65)^n}}$$

Transposing and taking logarithms,

$$k(582)(7.65)^n = \ln 1.43 = 0.3577$$

$$k(7.65)^n = 6.146 \times 10^{-4}$$

Again taking logarithms

$$\ln k + n(\ln 7.65) = \ln 6.146 - 4(\ln 10)$$

$$\ln k + 2.0347 n = -7.3940 \quad (a)$$

Similarly, at a relative pressure of 0.70 the equilibrium moisture content given by the same isotherm is 13.62, and substituting pertinent values in equation (43)

$$1 - 0.70 = e^{-k (582) (13.62)^n}$$

Going through exactly the same steps as before, a new relationship is obtained as follows

$$\ln k + 2.6180 n = -6.1828 \quad (b)$$

Solving equations (a) and (b) simultaneously,

$$\ln k + 2.0347 n = -7.3940$$

$$\ln k + 2.6180 n = -6.1828$$

$$0.5833 n = 1.2112$$

$$n = 2.08$$

Substituting now the value of n in equation (a)

$$\ln k + (2.0347) (2.08) = -7.3940$$

$$\ln k = -11.6261$$

Converting to common logarithms:

$$\log k = -11.6261 \times 0.4343$$

$$\log k = -5.0492$$

By definition

$$k = 10^{-5.0492}$$

and

$$1/k = 10^{5.0492}$$

Taking common logarithms

$$\log (1/k) = 5.0492 \times \log 10 = 5.0492$$

$$1/k = \text{antilog } 5.0492$$

By referring to a table of common logarithms

$$1/k = 1.120 \times 10^5$$

Taking reciprocals

$$k = 8.93 \times 10^{-6}$$

The same procedure described above was followed for each of the remaining five isotherms. Table IX, columns 2 and 3, shows the values of constants k and n thus calculated. It will be seen that the values of the equation constants show a definite dependence on temperature. The variation with temperature appears to be particularly pronounced in the case of constant k which increased steadily from a value of 1.90×10^{-6} at 40°F to a value of 9.68×10^{-6} at 140°F . Constant n , on the other hand, decreased from a value of 2.47 to a value of 2.08 at 122°F , increasing again to 2.20 at 140°F . This behavior of the constant n of exhibiting a reversal of its change trend at the upper extreme of the temperature range may seem a little anomalous, and may reflect a certain degree of ambiguity in the values of equilibrium content obtained at this elevated temperature. A closer examination of Figure 7 will reveal that the 140°F isotherm exhibits an increased downward displacement as well as a slight deformation as compared with the family of isotherms as a whole. It is conceivable that too long an exposure of the grain samples at a temperature of 140°F may have resulted in abnormally high weight losses throughout the latter part of the equilibration period, due to changes other than normal water desorption. Such contingency would appear to be a definite

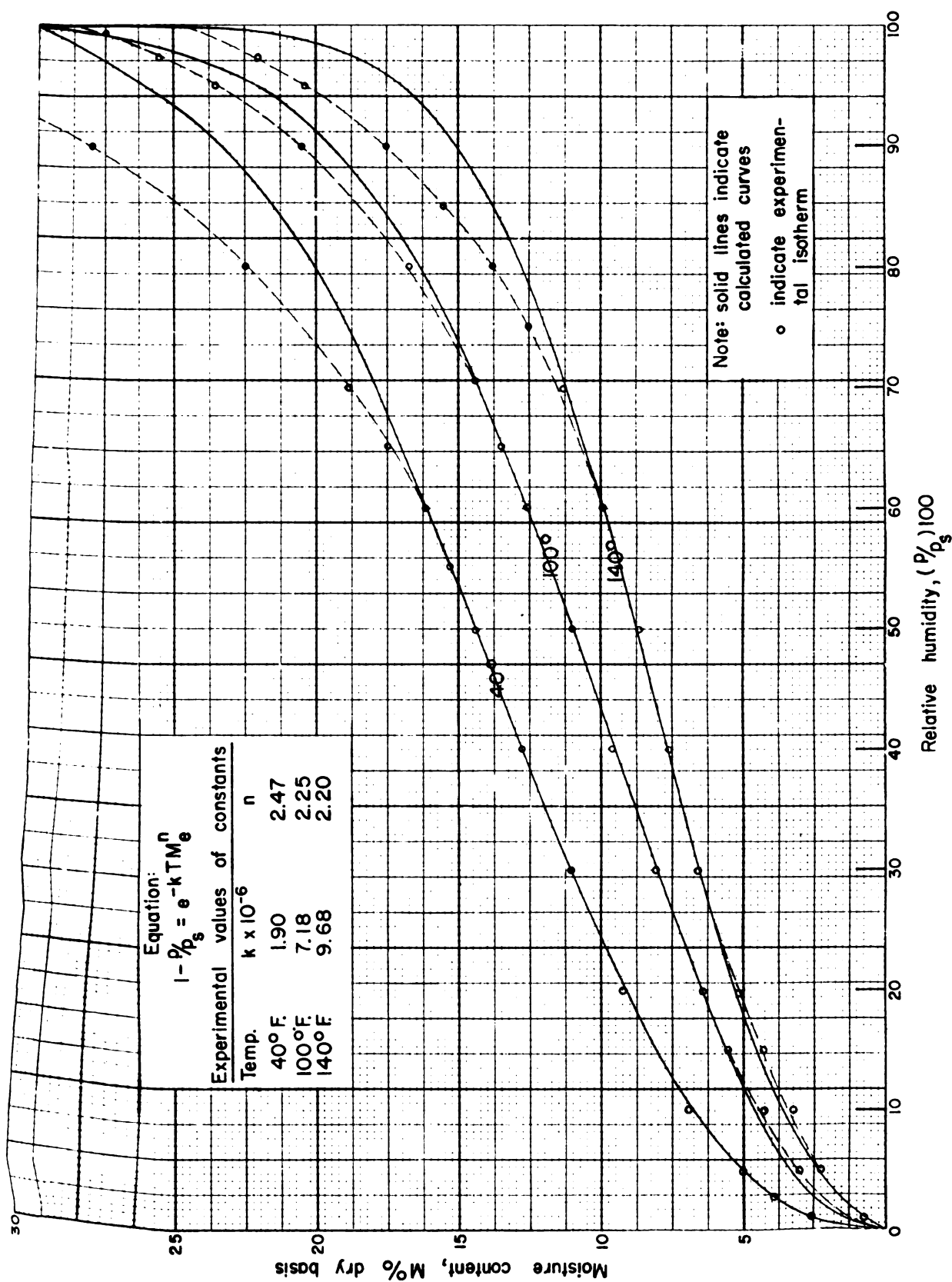


Figure 20 Comparison of curves plotted according to Henderson's equation with experimental desorption isotherms.

limitation of the static method in obtaining hygroscopic equilibria at elevated temperatures. It should be stressed, however, that the foregoing observation can not by itself be regarded as conclusive evidence against the reliability of the 140°F experimental isotherm. Nevertheless, it strongly suggests the advisability of inquiring into the matter further in order to decide upon the applicability of the static method to studies in hygroscopic equilibria at elevated temperatures.

In view of the results discussed above, concerning the variation of constants k and n with temperature, it can be concluded that Henderson's equation fails in accounting correctly for the temperature dependence of the isotherm. Some knowledge as to the behavior of these constants with varying temperature should be useful, however, in predicting the position of the isotherm at any temperature within the range of the investigation. When the values of both constants were plotted against temperature the smooth curves shown in Figure 21 were obtained. In the absence of more exact values for the equation constants, Figure 21 should therefore be helpful in providing suitable values for the calculation of isotherms at any temperature within the range of 40°F to 140°F .

As a rough check on the reliability of the foregoing procedure in calculating hygroscopic equilibrium data for intermediate temperatures, a comparison was made between values thus calculated for a temperature of 77°F and those reported by Coleman and Fellows (14) for yellow dent shelled corn at that same temperature

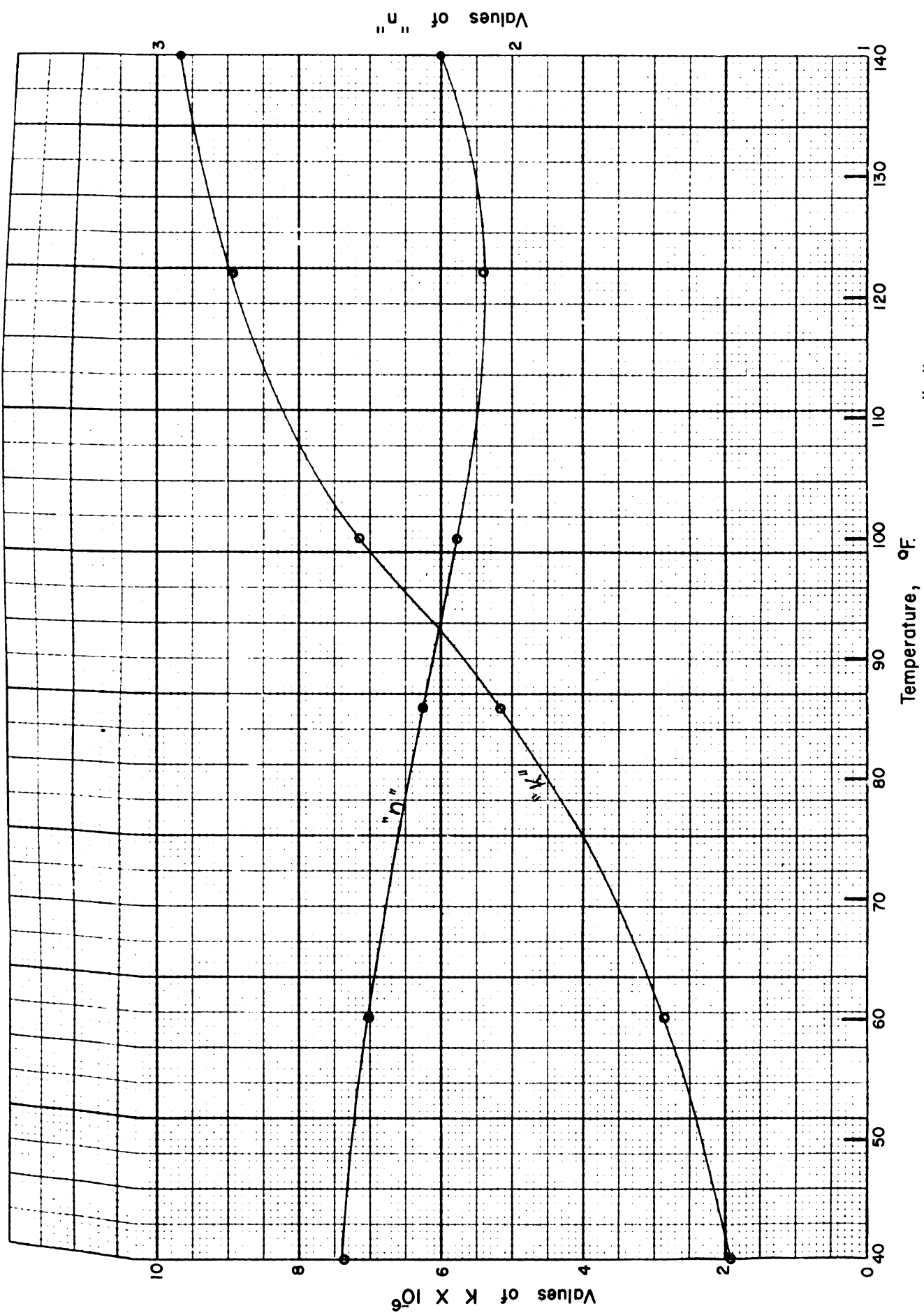


Figure 21. Temperature dependence of constants K and n of Henderson's equation for shelled corn.

for various relative humidities. The results of this comparison are tabulated in Table XII. The table shows the values reported by Coleman and Fellows (wet basis), the same values converted to a dry basis, the values calculated as explained above, and also, corresponding values which were visually interpolated from the experimental isotherms of Figure 7. It will be seen that up to a relative humidity of 60 percent the agreement between the calculated values and those reported by Coleman and Fellows was fairly satisfactory, with considerable deviation occurring at the higher relative humidities. These results are in accord with those discussed further below and afford proof of the adequacy of the method. On the other hand, the agreement between the reported values and those visually interpolated from the experimental isotherms was much closer throughout the whole range of relative humidities. This latter observation may be regarded as confirmatory evidence of the reliability of the experimental isotherms.

In order to determine whether Henderson's equation succeeds in describing the shape of the isotherm throughout its entire range, the isotherms were calculated by fitting equation (43) with the respective values of constants k and n . Enough points were calculated to enable following the course of the isotherm throughout the entire range of relative vapor pressures. These calculated curves were then compared with the experimental isotherms. Figure 20 shows such a comparison for three of the isotherms. It will be seen that for the relative humidity range

TABLE XII
COMPARISON OF DATA BY COLEMAN AND FELLOWS WITH CORRESPONDING
VALUES CALCULATED ACCORDING TO HENDERSON'S EQUATION
AND EXPERIMENTAL CONSTANTS¹

Equilibrium relative humidity, percent	Data by Coleman and Fellows ²		Calculated values ³ percent dry basis	Visually interpolated values from experimental isotherms ⁴
	Reported values percent wet basis	Converted values percent dry basis		
15	6.40	6.84	6.40	6.5
30	8.40	9.17	9.00	9.16
45	10.50	11.62	11.40	11.72
60	12.90	14.80	13.60	13.75
75	14.80	17.35	16.50	17.00
90	19.10	23.61	20.40	22.50
100	23.8	31.20	28.00	31.25

1/ Experimental constants obtained from Figure 21 , for 77°F as follows:
constant $K = 4.05 \times 10^{-6}$; constant $n = 2.31$

2/ Data by Coleman and Fellows for yellow dent shelled corn at 77°F,
taken from Table 1, Chapter IX of Reference (28).

3/ Calculated by substituting interpolated constants in Henderson's
equation.

4/ Obtained from Figure 7.

from 20 percent to 60 percent there is an excellent agreement between the calculated and the experimental isotherms. However, beyond that range the experimental isotherms generally deviate markedly in an upward direction from the calculated curves. It should also be noted that while the experimental curves show definite intersections with the vertical axis at saturation the calculated curves approach this axis asymptotically. Below a relative humidity of 0.15 to 0.20 the tendency of the experimental isotherms is towards slightly lower equilibrium moisture content values than the equation calls for, even though the extent of the deviation may be considered negligible. It is evident from the foregoing that Henderson's equilibrium equation can only be expected to yield good results in predicting hygroscopic equilibria of shelled corn when appropriate values of the equation constants are used according to the temperature, and then only below a relative pressure of about 0.70. It is also quite likely that varietal characteristics may introduce appreciable variations in the values of the constants as may be inferred from a comparison between the constants previously calculated by Henderson and those herein evaluated from the experimental isotherms. Henderson (23) gave two sets of values calculated from data of two different sources as follows:

<u>Value of k</u>	<u>Value of n</u>	<u>Temperature</u>
1.10×10^{-5}	1.90	77°F
1.59×10^{-6}	2.68	77-83°F

When compared with the values reported in Table IX it will be seen that while they appear to be of the same order of magnitude, the differences are such as to suggest appreciable influence of varietal characteristics.

Drying Rate Data

The analysis and discussion of the preceding sections have dealt with the equilibrium aspects of the investigation. The time-rate relationships will now be considered.

Drying Curves

It has been explained that throughout the equilibration period of most samples, sufficiently detailed data were obtained to enable accurate construction of drying curves and subsequent correlation of the drying data. Upon termination of any given run the observational data were processed, as shown in Table III for one of the samples, so that the equilibrium moisture content as well as the values of moisture content at each time of observation were calculated. On the basis of these calculated data, drying curves were constructed for each sample by plotting the moisture content values (dry basis), against drying time in hours. The large number of curves so obtained precludes including them all here; however, Curve A of Figure 22 illustrates a typical example of this kind of curve. In general, very smooth curves were obtained by joining all experimental points with hardly any point deviating significantly from the curve. As is characteristic of drying in the falling-rate period, the curves exhibited continually decreasing slopes approaching asymptotically the corresponding equilibrium moisture content values. These drying curves enabled ascertaining what was the instantaneous moisture content of the samples at any time during the drying process.

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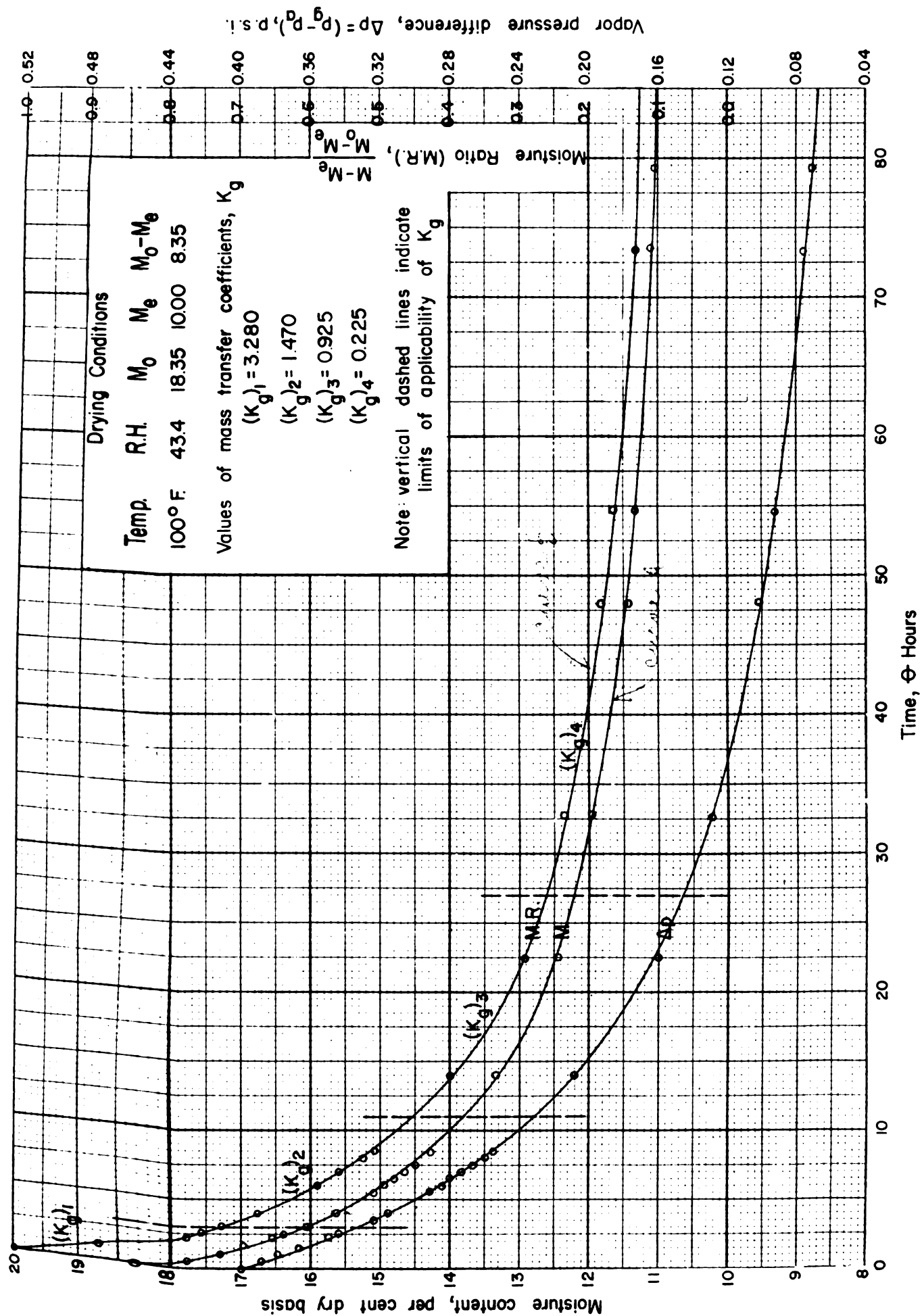


Figure 22 Variation with time of various parameters and mass transfer coefficients in thin layer drying of shelled corn.

For comparative purposes it was desirable to reduce the drying curves of the various samples—in which the initial moisture content showed some variation—to some common basis. This was accomplished by computing the values of the moisture content ratio, $(M - M_e)/(M_0 - M_e)$ dry basis and plotting these, instead of the moisture content values, as ordinates against the drying time. In this case, all points on the ordinate axis start at a value of 1.0 regardless of the initial moisture content of the sample. Curve B of Figure 22 shows such a curve as a result of plotting the same data of curve A according to this procedure. Also Figures 25, 27, 29, 31 and 33 give this type of curve for other drying conditions. These curves not only facilitated further correlation of the data but enabled the determination of half-response periods for each of the samples. It will be recalled that a knowledge of this factor for any given set of drying conditions is of great value in drying calculations. These values were obtained by reading from the drying curves the value of drying time corresponding to a value of the moisture ratio of 0.50. Table XIII shows the values thus obtained for various drying conditions.

Factors Affecting the Half-Response Period

A study of Table XIII reveals that the most important single factor affecting the length of the half-response period is temperature. The higher the temperature the shorter will be the period of half-response for any given set of conditions. Next in importance to the temperature factor in determining the length of the half-response period seems to be the initial moisture content, M_0 .

TABLE XIII
VALUES OF HALF-RESPONSE PERIODS FOR SHELLED CORN
UNDER DIFFERENT DRYING CONDITIONS

Rel. Hum. percent	p_a psia	M_o % d.b.	M_e % d.b.	$M_o - M_e$ % d.b.	$(\Delta p)_o$ psi	$\phi_{\frac{1}{2}}$ hr.
40°F						
14.0	0.0170	26.96	7.78	19.18	0.0967	26
34.6	0.0421	27.30	11.80	15.50	0.0724	20
53.4	0.0640	27.22	14.90	12.22	0.0504	29
59.3	0.0722	27.01	16.35	10.66	0.0417	18
75.1	0.0914	27.47	20.50	6.97	0.0236	26
60°F						
12.8	0.0328	27.20	6.35	20.85	0.2235	13
33.9	0.0869	26.80	10.52	16.28	0.1681	10.5
37.5	0.0861	27.50	11.10	16.40	0.1538	11
54.0	0.1385	27.50	13.30	14.20	0.1178	12.8
56.0	0.1451	27.50	14.10	13.40	0.1022	11
75.9	0.1945	27.20	18.20	9.00	0.0618	13.5
86°F						
11.2	0.0689	20.77	4.86	15.91	0.4817	11.2
32.4	0.1993	21.75	9.02	12.73	0.3619	7.0
43.5	0.2676	21.14	10.50	10.64	0.2860	7.5
56.3	0.3464	20.08	12.35	7.73	0.1944	7.0
63.6	0.3894	17.86	13.57	4.29	0.1169	11.5
75.2	0.4626	20.92	15.83	5.09	0.0050	5.5
86.3	0.5309	21.20	19.28	1.92	0.0284	6.50
100°F						
11.1	0.1054	18.60	4.78	13.82	0.7081	17.0
31.9	0.3038	18.44	8.46	9.98	0.5088	10.0
43.4	0.4129	18.35	9.95	8.40	0.3958	9.0
50.0	0.4746	27.79	10.86	16.93	0.4717	6.0

TABLE XIII (Cont.)

Rel. Hum. percent	P_a psia	M_o % d.b.	M_e % d.b.	$M_o - M_e$ % d.b.	$(\Delta p)_o$ psi	$\phi_{\frac{1}{2}}$ hr.
61.8	0.5866	18.49	12.78	5.71	0.2250	9.5
75.1	0.7128	32.82	15.35	17.47	0.2364	5.25
79.1	0.7508	28.85	16.53	12.32	0.1984	8.75
85.6	0.8125	34.54	18.60	15.94	0.1367	18.0

122°F						
11.4	0.2039	44.00	3.83	40.17	1.5849	3.0
11.4	0.2039	37.48	3.83	33.65	1.5849	3.25
20.4	0.3649	38.10	5.97	32.13	1.4239	3.0
28.4	0.5080	36.79	7.48	29.31	1.2808	3.0
47.1	0.8425	32.26	9.88	22.40	0.9463	3.75
74.7	1.3362	37.66	14.78	22.88	0.4526	5.5

140°F						
11.2	0.3235	42.70	3.39	29.31	2.5651	2.0
21.0	0.6066	43.80	5.21	38.59	2.2820	2.0
25.3	0.7308	44.03	6.12	37.91	2.1578	2.0
49.9	1.4443	43.70	8.59	35.11	1.4443	3.0
74.9	2.1635	16.52	12.63	3.89	0.4825	4.5
55.2	1.5945	43.70	8.59	34.66	1.2938	2.75

It was evident that under the same external drying conditions, the higher the initial moisture content the shorter the half-response period tends to be. This behavior may at first seem rather anomalous in view of the fact that the free moisture content corresponding to the higher M_0 -value must also be higher, thus increasing the amount of water that should desorb within the half-response period. However, it should be noted that as the moisture content of the grain increases, the additional amounts of water involved in the desorption or drying process are apt to be bound by ever-decreasing forces and are therefore more easily desorbed. Thus the increased initial drying rate that results from a higher initial moisture content more than compensates for the increased amount of water to be removed. It follows from the foregoing that both the equilibrium moisture content and the free moisture content also have an important bearing in determining the extent of the half-response period. For instance, as the equilibrium moisture content approaches the lower-most values—where the binding forces of the grain exert the strongest influence—the desorption rate becomes slower and slower with a consequent increase of the half-response period. It would appear then as if the important factor concerning the free moisture content is the moisture range over which it occurs. Referring to Figure 12, which shows the variation of the Othmer latent heat ratios with moisture content, it may be inferred that beyond a moisture level of 18 percent, dry basis, the binding forces are more nearly uniform and therefore the latter effect may become less noticeable. Other factors which may

come into play as the moisture level is lowered, to account for the foregoing behavior, are the increase in overall diffusion resistance and the probable decrease in the diffusivity of the grain.

Determination of Drying Rates

In an attempt to obtain a simple analytical expression for the drying rate which may obviate the need for graphically differentiating the drying curves, the same data used in obtaining the last mentioned type of curves were plotted on semilogarithmic graph paper. The values of moisture content ratio, $(M - M_e)/(M_0 - M_e)$ were plotted as ordinates on the logarithmic scale against drying time on the arithmetic scale. The plots yielded excellent straight lines over restricted regions of the curve with sharp changes in slope occurring at more or less regular intervals between the linear portions. This behavior is shown in Figure 23 which represents the semilogarithmic plot of the drying curve of Figure 22. Figures 26, 28, 30, 32 and 34 also illustrate the same type of curves for other drying conditions. The foregoing results prove conclusively that the exposed drying behavior of shelled corn obeys an exponential law analogous to Newton's law of cooling, but with rate constants which are only valid over restricted ranges of moisture content. This relationship may be formulated thus

$$M - M_e = (M_0 - M_e) e^{-k\theta} \quad (57)$$

or

$$\frac{M - M_e}{M_0 - M_e} = e^{-k\theta} \quad (58)$$

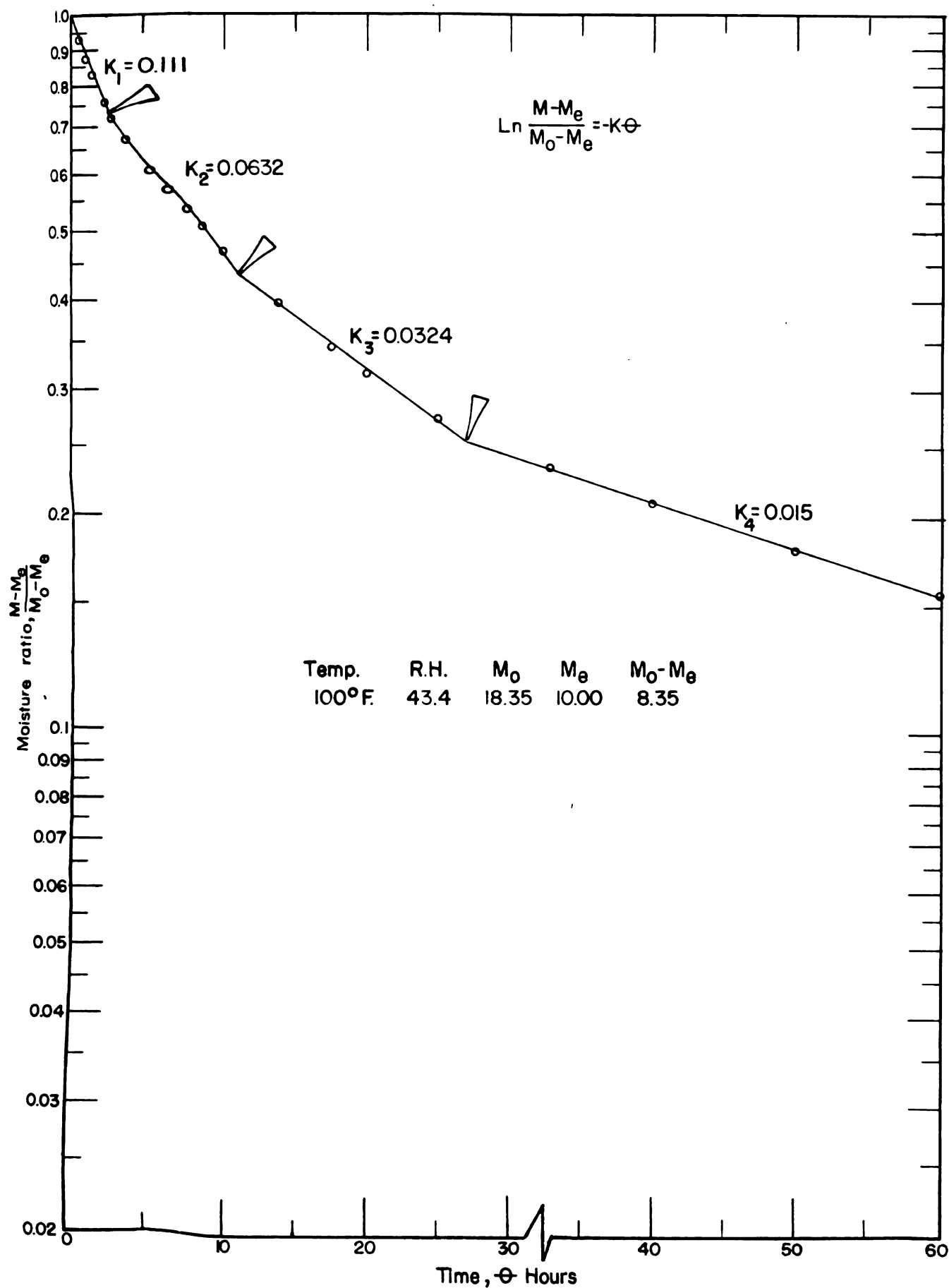


Figure 23 Semilogarithmic plot of moisture ratio vs. time curve of Figure 22 showing behaviour of rate constant K .

It will be seen from the semilogarithmic plots that as many as four or five different and ever-decreasing values for the rate constant took place in governing the drying process over the first 72 hours of drying. Interestingly, there appears to be some correlation between the number of values for the rate-constant occurring over the drying period and the theoretical number of molecular layers estimated by application of the B-E-T three-constant equation as constituting the adsorbed water. It might well be inferred that the value of the rate constant is to a certain extent related to the particular layer of molecules that is being desorbed, and hence to the particular intensity of the binding forces that oppose the process. The changes in value of the rate constant may also reflect changes in the moisture diffusivity of the kernels as drying proceeds.

The values of the drying rate constants were determined for the various drying conditions and are given in Table XIV along with their corresponding ranges of applicability. The latter are expressed both in terms of moisture content, percent dry basis. The drying rate values were obtained by measuring directly the slopes of the linear semilogarithmic plots, while the limits of the corresponding ranges of validity were determined from the values which marked the beginning and end of each linear portion of the curve.

The expression for the drying rate is obtained by differentiation with respect to time of equation (59), thus

TABLE XIV
DRYING RATE CONSTANTS, k , FROM SEMILOGARITHMIC PLOTS OF DRYING CURVES

Curve and Figure	T_a °F	l.H. %	k_1	k_2	k_3	k_4
Ranges of applicability, percent moisture content, dry basis						
Figure 26						
A	40	14.0	0.075	0.0315	0.016	0.0072
			26.96 - 24.79	24.79 - 20.50	20.50 - 16.25	16.25 -
B	60	12.8	0.125	0.0510	0.0214	0.0104
			27.20 - 23.30	23.30 - 17.50	17.50 - 13.20	13.20
C	122	11.4	0.1845	0.0742	0.0289	0.020
			37.50 - 16.30	16.30 - 10.00	10.00 - 7.75	7.75 - 5.5
D	140	11.2	0.338	0.149	0.0503	0.0184
			47.00 - 19.00	19.00 - 11.50	11.50 - 7.30	7.30 - 5.90
Figure 30						
A	40	59.3	0.0622	0.0325	0.0231	0.0149
			27.01 - 25.20	25.20 - 20.20	20.2 - 18.00	18.00 -
B	60	56.6	0.0738	0.0526	0.0224	0.0143
			27.50 - 23.84	23.84 - 19.84	19.84 - 16.00	16.00 -
C	100	50.0		0.1047	0.0424	0.0143
				23.50 - 18.00	18.00 - 13.00	13.00 -

TABLE XIV (Cont.)

Curve and Figure	T _a °F	R.H. %	k ₁	k ₂	k ₃	k ₄
Ranges of applicability, percent moisture content, dry basis						
D	122	47.1	0.259	0.1275	0.0672	0.0109
			32.3 - 21.40	21.40 - 15.40	15.40 - 10.2	10.2 -
E	140	55.2	0.271	0.139	0.074	0.0522
			43.60 - 13.00	13.00 - 10.4	10.40 - 9.70	9.70 -
<u>Figure 34</u>						
A	40	75.1	0.0313	0.0238		
			27.47 - 25.20	25.2 - 21.9		
B	60	75.9	0.0583	0.0396	0.0291	
			27.20 - 25.20	24.50 - 20.5	20.5 -	
C	86	75.2	0.1240	0.0585	0.0243	
			20.92 - 17.9	17.9 - 16.7	16.75 - 15.83	
D	100	75.1	0.1385	0.0886		
			32.82 - 17.4	17.15 - 15.35		

TABLE XIV (Cont.)

Curve and Figure	T _o °F	R.H. %	k ₁	k ₂	k ₃	k ₄
Ranges of applicability, percent moisture content, dry basis						
<u>Figure 32</u>						
A	100	61.8	0.0800	0.0375	0.0133	0.00685
-	-	-	18.50 - 16.0	16.00 - 14.75	14.75 - 14.15	14.15 - 12.83
B	122	59.8	0.172	0.086	0.0286	0.0084
-	-	-	38.35 - 15.78	15.78 - 13.18	13.18 - 12.75	12.75 - 11.51
C	140	59.3	0.245	0.114	0.0657	0.0121
-	-	-	43.12 - 12.9	12.9 - 11.35	11.35 - 10.74	10.74 - 9.35
<u>Figure 28</u>						
A	40	34.6	0.0612	0.0334	0.0198	0.0115
-	-	-	27.30 - 25.50	25.50 - 20.30	20.3 - 16.14	16.4 -
B	60	33.9	0.0925	0.0402	0.0267	0.0171
-	-	-	26.80 - 22.8	22.8 - 15.8	15.8 - 13.5	13.5 -
C	86	32.4	0.1865	0.0690	0.0358	0.0237
-	-	-	21.75 - 18.5	18.50 - 14.75	14.75 - 11.95	11.95 - 10.80

TABLE XIV (Cont.)

Curve and Figure	T _a °F	R.H. %	Ranges of applicability, percent moisture content, dry basis			
			k ₁	k ₂	k ₃	k ₄
A	122	68.7	0.1435	0.0723	0.00105	
			32.11 - 16.9	16.9 - 14.15	14.15 -	
B	122	20.4	0.333	0.151	0.061	
			38.1 - 29.05	29.05 - 14.97	14.97 - 10.32	
C	86	63.3	0.0423	0.0164		
			17.86 - 14.5	14.5 -		

$$\frac{d(M - M_e)}{d\theta} = \frac{d}{d\theta} (M_o - M_e) e^{-k\theta} \quad (59)$$

Since both M_e and $(M_o - M_e)$ are constant for any given sample of grain equation (59) becomes

$$dM/d\theta = (M_o - M_e) (e^{-k\theta}) (-k) \quad (60)$$

But substituting from (58) one obtains

$$dM/d\theta = -k (M - M_e) \quad (61)$$

Equation (61) states that the rate of drying is a direct function of the free moisture content at any time and of the rate constant, k . It will be seen from equation (58) that taking logarithms of both sides, the equation for the semilogarithmic plots of the drying curves is obtained thus

$$\ln \frac{M - M_e}{M_o - M_e} = -k \theta \quad (48)$$

The drying rate constant k corresponds to the slope of the linear plots.

According to the foregoing procedure, the values for the instantaneous drying rates governing the process at each time of observation were calculated for all samples. Table XIV shows the characteristic drying rates obtained directly from the slopes of the semilogarithmic drying curves of Figures 26, 28, 30, 32 and 34. The corresponding ranges of applicability are also indicated in terms of moisture content, dry basis.

The results show that the drying rates are definitely an increasing function of temperature. In general the drying rate constants were found to increase in value about four times when the temperature increased from 40° to 140°F , under any given condition of relative humidity.

It will also be noted that under the same temperature conditions an increase in relative humidity tends to slow the process. However, a careful study of Table XIV and the corresponding drying curves will reveal that the drying rate appears to be less sensitive to changes in relative humidity than it is to variations in temperature or moisture content, at least in the range of relative humidities below seventy percent. For instance, it will be seen from Figure 26 and the corresponding section of Table XIV that keeping the relative humidity relatively constant at a level of about twelve percent an increase in temperature from 40° to 140°F caused the drying rate constant k_1 to increase by four and a half times. On the other hand, by referring to Figure 30 and its corresponding section of Table XIV it will be noticed that keeping the temperature constant at 40°F an increase in relative humidity from 14.0 percent to 59.3 percent brought about only a slight drop in the value of the drying rate constant from 0.075 to 0.0622. The effect of relative humidity on the drying rate, however, seems to become more pronounced at the higher relative humidities.

Testing the Vapor Pressure Theory of Drying

According to a generally accepted concept of the vapor pressure theory of drying, the driving force in any drying process is furnished by the difference between the aqueous vapor pressure of the material and the partial aqueous vapor pressure of the drying air. Furthermore, the theory is generally regarded as maintaining that under identical conditions of vapor pressure potentials the instantaneous drying rates should be the same regardless of the drying conditions, i.e., temperature and relative humidity of the drying air. As a rule the aqueous vapor pressure p_g of the material at any instant is assumed to be given by the equilibrium vapor pressure corresponding to the instantaneous mean moisture content of the material at any instant corresponding to the instantaneous mean moisture content of the material at the temperature under consideration. Accordingly, the p_g -values could be obtained from the desorption isotherm corresponding to the drying temperature, by multiplying the appropriate equilibrium vapor pressure by the saturation vapor pressure of water at the given temperature. The values thus obtained are shown in Table IIIA column 7. By subtracting from each of these values those of the aqueous partial vapor pressure, p_a , corresponding to the drying conditions the values of the instantaneous vapor pressure potentials $(p_g - p_a)$ were likewise calculated and recorded in column 8 of the same table. By plotting the values of $(p_g - p_a)$ ordinates against drying time as abscissae in ordinary graph paper

very satisfactory smooth curves were obtained which enabled determining the vapor pressure potential at any instant during the process. This type of curve is illustrated by curve B of Figure 22 and was drawn for each one of the grain samples. By referring to curve B of Figure 22 and to the semilogarithmic plot of Figure 23, the instantaneous drying rate and vapor pressure potential could be readily determined for any given instant. It was thus possible to check the correctness of the vapor pressure theory by comparing the drying rates thus determined for identical values of vapor pressure potential under different drying conditions. In practice, a certain value of vapor pressure potential was selected which would be common to several different drying conditions. By referring to the vapor pressure potential-versus-drying time curve, the time at which this value occurred for that particular sample was determined. This value of time was next entered on the corresponding semilogarithmic plot of moisture-ratio against time and both the value of the rate constant k , and of the moisture ratio occurring at that particular time determined. The rate constant was given by the slope of the plot. By multiplying the moisture ratio by the corresponding value of initial moisture content for the sample in question, the free moisture content, $M - M_e$, was obtained. From equation (61) the drying rate could be calculated. The same procedure was repeated with as many samples as possible which would yield drying rate values for identical magnitudes of vapor pressure potential and the calculated values tabulated in Table XV. It will be seen that no two single values were found

TABLE XV
 DRYING RATES OF SHELLLED CORN AT EQUAL VALUES OF Δp
 UNDER DIFFERENT DRYING CONDITIONS

Temp. °F	Rel. Hum. percent	Δp psia	M % d.b.	M - M _e % d.b.	k hr. ⁻¹	dM/d ϕ % d.b.-hr. ⁻¹
86	75.2	0.0800	19.75	3.92	0.1240	0.4860
60	12.8	0.0800	12.00	5.65	0.0120	0.0678
100	75.1	0.0800	15.46	0.11	0.0886	0.0097
60	33.9	0.0800	15.36	4.86	0.0358	0.1740
40	14.0	0.0810	21.90	14.12	0.0315	0.4510
100	43.4	0.0800	11.19	1.19	0.0150	0.0179

86	75.2	0.0762	20.00	4.17	0.1240	0.5180
60	12.8	0.0762	11.80	5.45	0.0120	0.0654
140	80.7	0.0760	14.95	0.92	0.3370	0.3100
100	43.4	0.0762	11.12	1.12	0.0132	0.0148

86	75.2	0.0512	18.80	2.97	0.1240	0.3690
40	34.6	0.0512	20.70	8.90	0.0334	0.2975
40	14.0	0.0512	10.75	7.97	0.0092	0.0735

140	55.2	0.5120	12.20	3.28	0.1390	0.4550
140	11.2	0.5120	6.50	3.11	0.0199	0.0619
140	21.0	0.5120	7.60	1.40	0.0198	0.0278

40	59.3	0.0330	25.74	9.59	0.0622	0.5960
60	75.9	0.0320	23.70	5.50	0.0390	0.2140

100	61.8	0.12	15.10	2.27	0.0375	0.085
86	11.2	0.12	8.60	3.92	0.0101	0.040
60	37.5	0.12	20.50	9.40	0.0430	0.425
60	12.8	0.12	14.70	8.35	0.0196	0.166
60	33.9	0.12	19.80	9.30	0.0402	0.374

TABLE XV (Cont.)

Temp. °F	Rel. Hum. percent	Δp psia	M % d.b.	M - M _e % d.b.	k hr. ⁻¹	$\frac{dM}{d\theta}$ % d.b.-hr. ⁻¹
122	68.7	0.12	14.70	1.40	0.0728	0.102
100	75.1	0.12	18.82	3.48	0.1385	0.483
100	43.4	0.12	11.82	1.82	0.0150	0.027

140	20.1	1.40	11.50	6.30	0.0835	0.545
140	11.2	1.400	9.90	6.50	0.0635	0.412

86	32.4	0.301	17.60	8.58	0.0690	0.592
122	63.7	0.304	17.90	4.09	0.1435	0.596
100	43.4	0.302	13.84	3.84	0.0632	0.249

122	47.1	0.767	18.90	9.02	0.1275	1.240
122	11.4	0.762	10.82	6.89	0.0638	0.440
140	49.9	0.767	12.40	5.80	0.1110	0.645
100	75.1	0.135	19.45	4.10	0.1385	0.568
122	47.1	0.139	10.90	1.02	0.0672	0.069
122	68.7	0.135	14.90	1.59	0.0728	0.1160
60	33.9	0.136	22.82	12.32	0.0402	0.4970
60	12.8	0.135	15.80	9.45	0.1960	1.8500
100	61.8	0.135	15.45	2.62	0.0375	0.0983
86	11.2	0.135	9.20	4.52	0.0138	0.0624
100	43.4	0.135	11.96	1.96	0.0158	0.0310

40	59.3	0.026	22.75	6.60	0.0325	0.2140
140	80.7	0.026	14.30	0.27	0.0337	0.0090

to coincide in any given group corresponding to the same vapor pressure difference, and that on the contrary, widely divergent drying rates were obtained under identical conditions of vapor pressure potential. The foregoing results tend to indicate that the instantaneous vapor pressure potential, as generally determined from desorption isotherms and instantaneous values of mean moisture content, is not the most important single factor governing the drying rate of such hygroscopic materials as shelled corn and other cereal grains.

It was considered possible, however, that the drying rate was still a function of the vapor pressure potential but probably owing to such factors as uneven moisture distribution within the individual kernels, varying diffusivity throughout the kernel, or peculiarities in the distribution of the water-binding forces involved, the use of a single proportionality factor was not warranted over extended ranges of moisture content. Such concept may be formulated thus

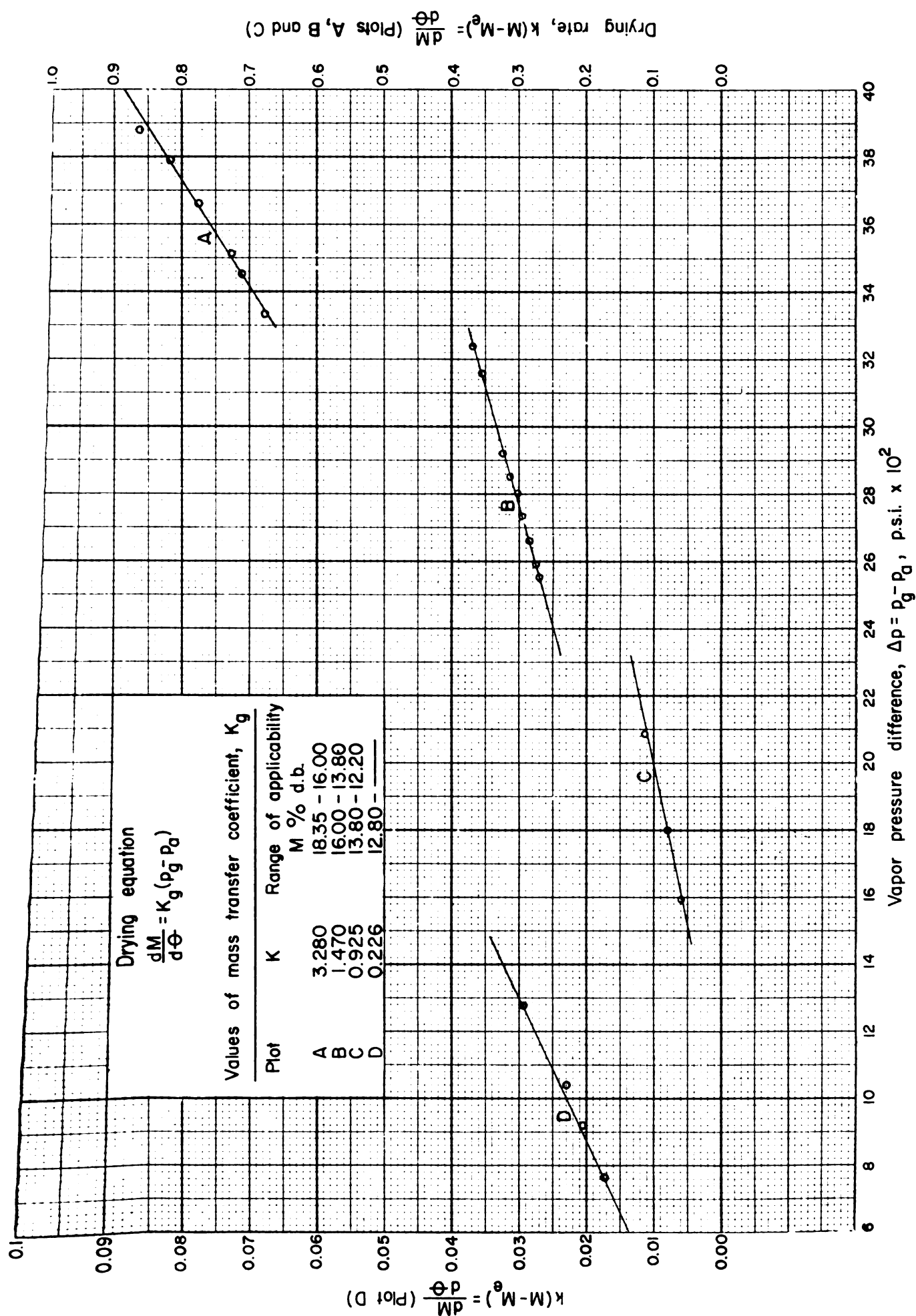
$$dM/d\theta = K_g (p_g - p_a) \quad (62)$$

where K_g is a constant of proportionality intended to express the combined effect on the drying rate of all other influential factors aside of the vapor pressure potential. If the drying rate is expressed in terms of percent (dry basis) per hour, i.e., grams of water per 100 grams of dry grain per hour, and the vapor pressure in terms of pounds per square inch, then K_g is expressed in units of percent of water content (dry basis) per hour per unit

difference in vapor pressure in pounds per square inch, and may be termed the mass transfer coefficient.

Mass Transfer Coefficients

From equation (62) the value of mass transfer coefficient K_g at any given instant could be obtained by dividing the drying rate by the corresponding vapor pressure potential. Similarly by plotting the values of drying rate as ordinates against the corresponding values of vapor pressure potential as abscissae the behavior of the mass transfer coefficient throughout the drying process could be determined. Accordingly, these plots were constructed for the various samples representing exposure to different drying conditions in order to determine the correctness of the foregoing concept. An example of these plots is shown in Figure 24. It will be seen that the plots were essentially linear over the same ranges of validity obtained for the corresponding drying rate constants. The values of mass transfer coefficient for the various samples were calculated in the foregoing manner and are given in Table XVI along with their corresponding ranges of applicability. These results show that equation (62) successfully characterizes the drying process, provided appropriate values of the mass transfer coefficient be employed over different ranges of moisture content. The limiting factor governing the drying rate seems to be the mass transfer coefficient which in turn, appears to be primarily a function of the moisture content for any given set of drying conditions.

Figure 24 Method for computing mass transfer coefficients, K_g from data of Figures 22 and 23.

The pronounced effect that the moisture level appears to have on the magnitude of the mass transfer coefficient is undoubtedly related to the relative intensity of the binding forces acting on the water molecules. In view of the sharp stepwise changes that occur in the values of both the drying rate constant k and in the mass transfer coefficient K_g as drying proceeds it seems logical to infer that the resistance to desorption stems essentially from the tenacity of the binding forces, and that the relative intensity of these remains relatively constant as long as the molecules of one particular layer are being desorbed, falling off abruptly as desorption from another layer begins. It would appear from the above considerations that the law of exponential decay governs throughout the entire drying process with the proviso that the rate constant assumes a correspondingly lower value for each of the adsorbed layer molecules. The exceedingly low drying rates that are observed at very low moisture levels are most probably due to the very high adsorptive forces acting on molecules which are adsorbed on particularly active centers of the internal surface and perhaps also on the sharpest cracks or crevices of the porous structure. The general behaviour of the heats of adsorption at the various moisture levels appears to lend support to the above concept.

TABLE XVI

MASS TRANSFER COEFFICIENTS, K_g , FOR SHELLED CORN UNDER VARIOUS DRYING CONDITIONS

Temp. °F	R.H. %	P_a psi	M_o % d.b.	M_e % d.b.	K_g % M, d.b./hr. per psi	Ranges of applicability	
						M, % d.b.	p, psi
40	14.0	0.0170	26.96	8.09	50.00 11.07 3.02 1.05	26.96 - 24.80 24.80 - 20.50 20.50 - 16.25 16.21 - 13.75	0.090 - 0.087 0.087 - 0.074 0.074 - 0.056 0.056 - 0.040
40	75.1	0.0914	27.47	20.6	14.9 9.0	27.47 - 25.20 25.20 -	0.0176 - 0.0136 0.0125 -
40	59.3	0.0722	27.01	16.15	64.70 11.50 7.72	27.01 - 25.25 24.95 - 20.15 19.65 -	0.0356 - 0.0326 0.0317 - 0.0178 0.0158 -
60	33.9	0.0869	26.80	10.5	7.37 4.28 2.44	22.82 - 18.80 18.8 - 15.9 15.9 - 13.1	0.1360 - 0.0712 0.112 - 0.086 0.086 - 0.045
60	75.9	0.1945	27.20	18.20	1.64 0.77 0.10	27.2 - 24.80 24.5 - 20.40 19.78 -	0.0445 - 0.0365 0.0355 - 0.0158 0.0145 - 0.0077
60	12.8	0.0328	27.20	6.35	4.93 1.57	18.8 - 17.2 17.2 - 13.5	0.19 - 0.15 0.15 - 0.12

TABLE XVI (Cont.)

Temp. °F	R.H. %	p _a psi	M _o % d.b.	M _e % d.b.	K g % M, d.b./hr. per psi	Ranges of applicability		
						M, % d.b.	p, psi	
122	20.4	0.3644	38.10	5.97	6.5 2.75 0.61 0.19	25.3 - 20.3 20.3 - 15.31 15.31 - 10.52 10.14 -	1.395 - 1.27 1.27 - 0.90 0.90 - 0.55 0.55 - 0.200	
-	-	-	-	-	-	-	-	-
140	55.2	1.5945	43.58	8.92	5.05 2.18	21.21 - 16.0 16.0 - 11.0	1.193 - 0.96 0.96 - 0.38	
-	-	-	-	-	-	-	-	-
140	11.2	0.3235	42.70	3.39	0.256 0.076	10.4 - 7.85 7.8 -	1.60 - 0.85	
-	-	-	-	-	-	-	-	-
140	80.7	2.334	44.58	14.03	3.63 2.55 0.418	22.49 - 18.20 18.20 - 15.70 15.70 - 14.10	0.496 - 0.304 0.304 - 0.136 0.136 - 0.064	
-	-	-	-	-	-	-	-	-
140	49.9	1.4443	43.70	8.59	3.3 0.375 0.006	23.11 - 16.31 14.50 - 12.09 11.25 - 9.75	1.397 - 1.076 0.936 - 0.556 0.556 - 0.269	
-	-	-	-	-	-	-	-	-
100	43.4	0.4129	18.35	10.00	3.280 1.470 0.925 0.226	18.35 - 16.00 16.00 - 13.80 13.80 - 12.20 12.20 -	0.409 - 0.328 0.328 - 0.236 0.236 - 0.132 0.132 -	

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TABLE XVI (Cont.)

Temp. °F	R.H. %	P _a psi	M _o % d.b.	M _e % d.b.	K g % M, d.b./hr. per psi	Ranges of applicability	
						M, % d.b.	p, psi
86	75.2	0.4632	20.92	15.83	8.5 2.88	20.34 - 17.9 17.75 - 16.36	0.09 - 0.055 0.055 - 0.03
86	32.4	0.1993	21.75	9.02	5.53 2.75 0.627	21.75 - 16.6 16.6 - 14.02 13.6 - 10.50	0.361 - 0.279 0.279 - 0.207 0.191 - 0.069
100	75.1	0.7128	32.82	15.35	14.00 7.25 2.45	28.7 - 23.2 22.1 - 17.4 17.2 - 15.6	0.24 - 0.18 0.18 - 0.07 0.07 - 0.008
100	31.9	0.3025	18.44	8.46	2.02 0.394 0.122	18.44 - 13.5 13.1 - 10.6 10.45 - 9.6	0.51 - 0.316 0.301 - 0.143 0.133 - 0.077
122	68.7	1.2289	32.11	13.31	5.25 2.94 1.02	24.6 - 20.2 20.2 - 17.4 17.4 - 14.0	0.5 - 0.38 0.38 - 0.25 0.25 - 0.04
122	59.8	1.0697	38.35	11.54	6.0 3.4	23.93 - 19.0 19.0 - 15.8	0.66 - 0.53 0.53 - 0.35
122	47.1	0.8425	32.28	9.88	12.0 2.67 0.742	25.01 - 22.57 19.61 - 16.13 14.55 - 10.90	0.909 - 0.857 0.762 - 0.592 0.482 - 0.137

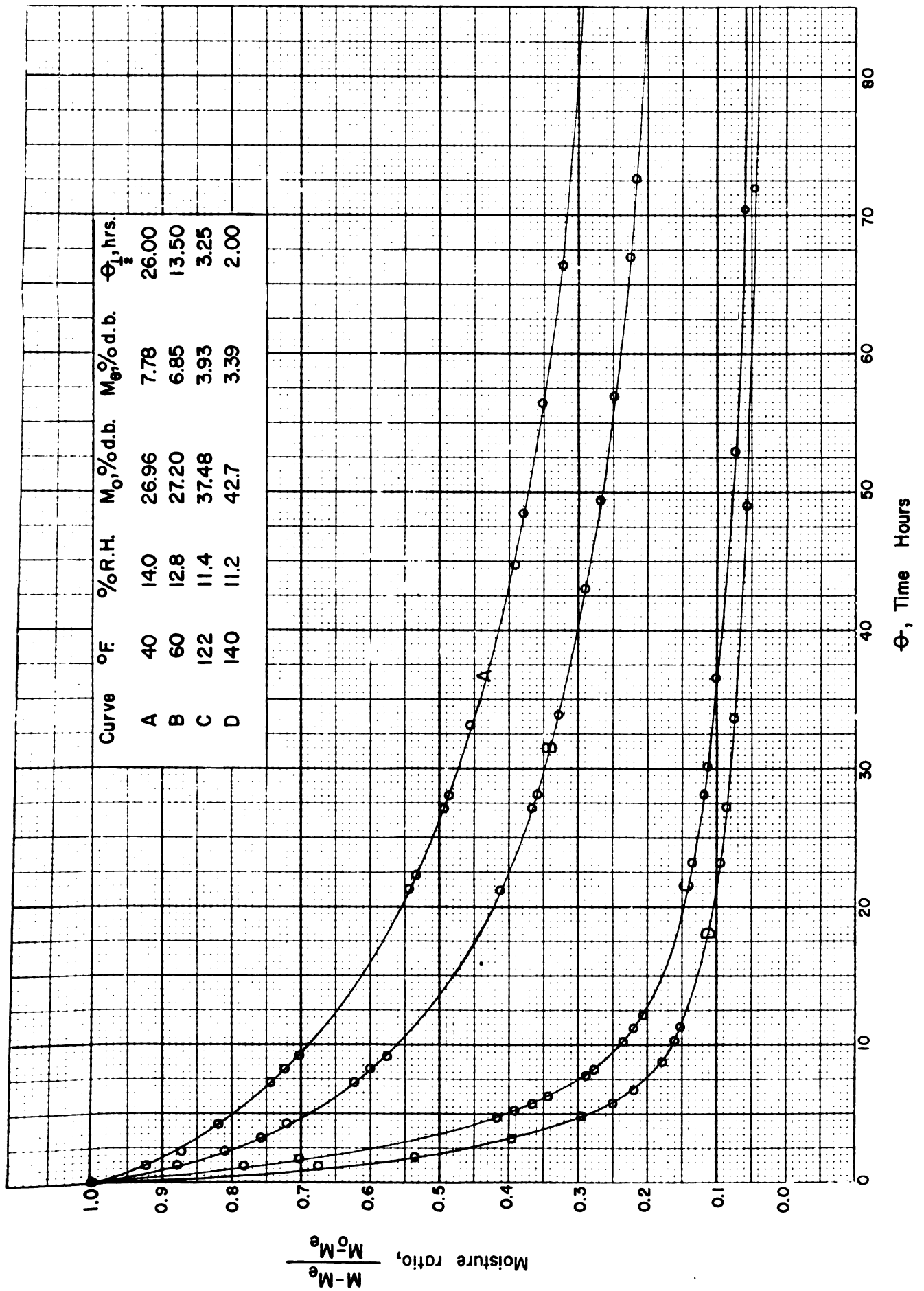


Figure 25 Drying curves for shelled corn fully exposed to various drying conditions

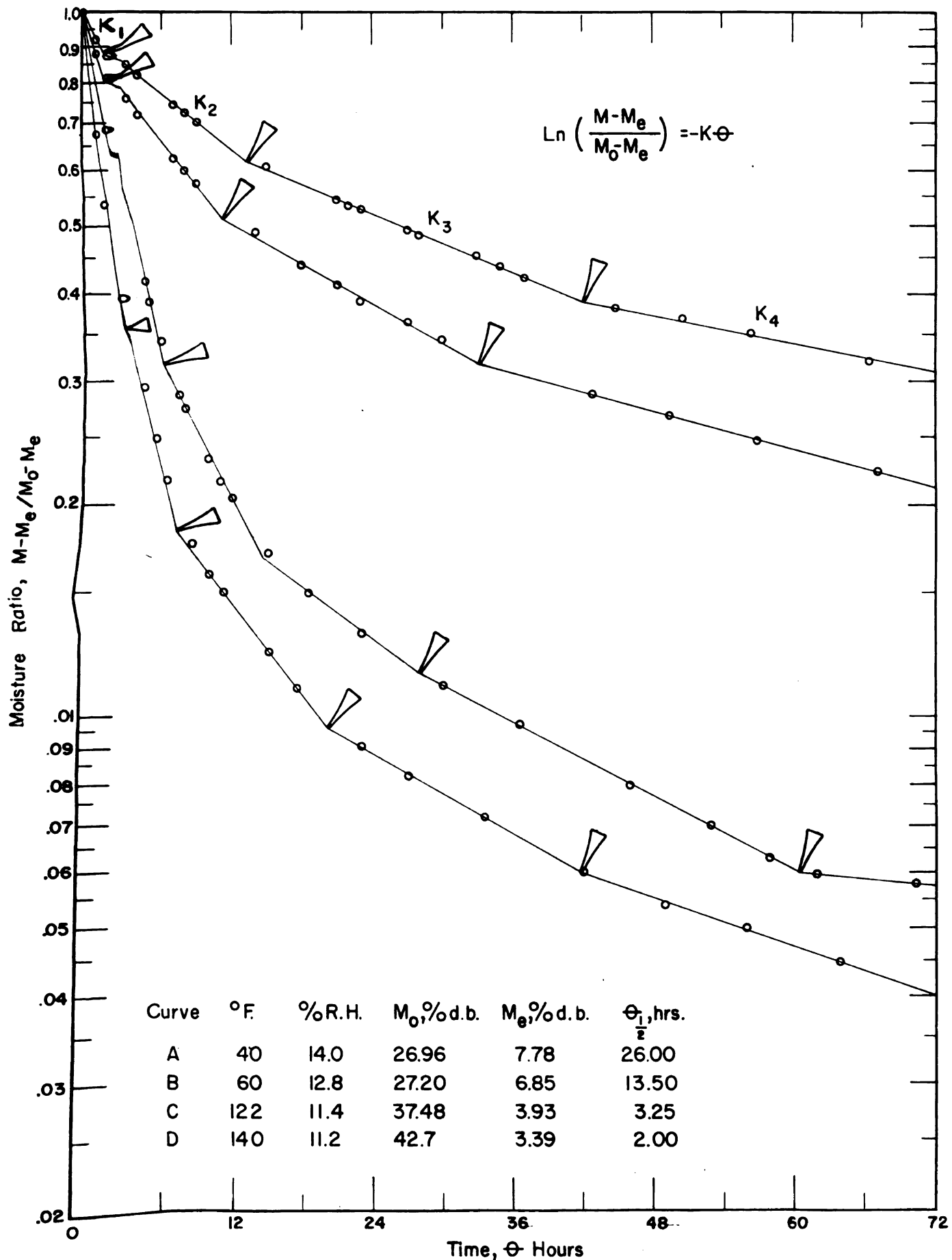


Figure 26 Semilogarithmic plots of drying curves of Figure 25 showing slope breaks with corresponding changes of rate constant K .

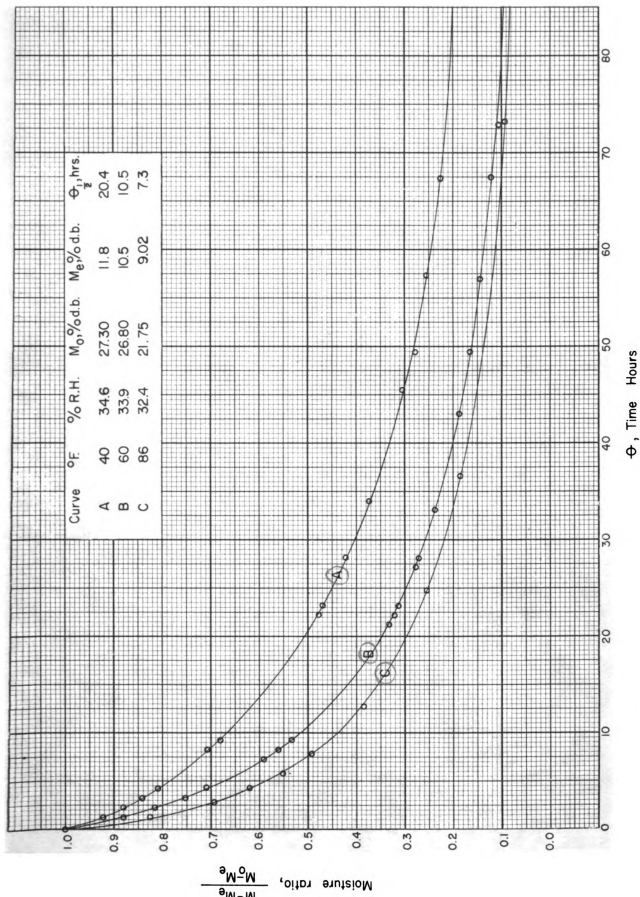


Figure 27 Drying curves for shelled corn fully exposed to various drying conditions

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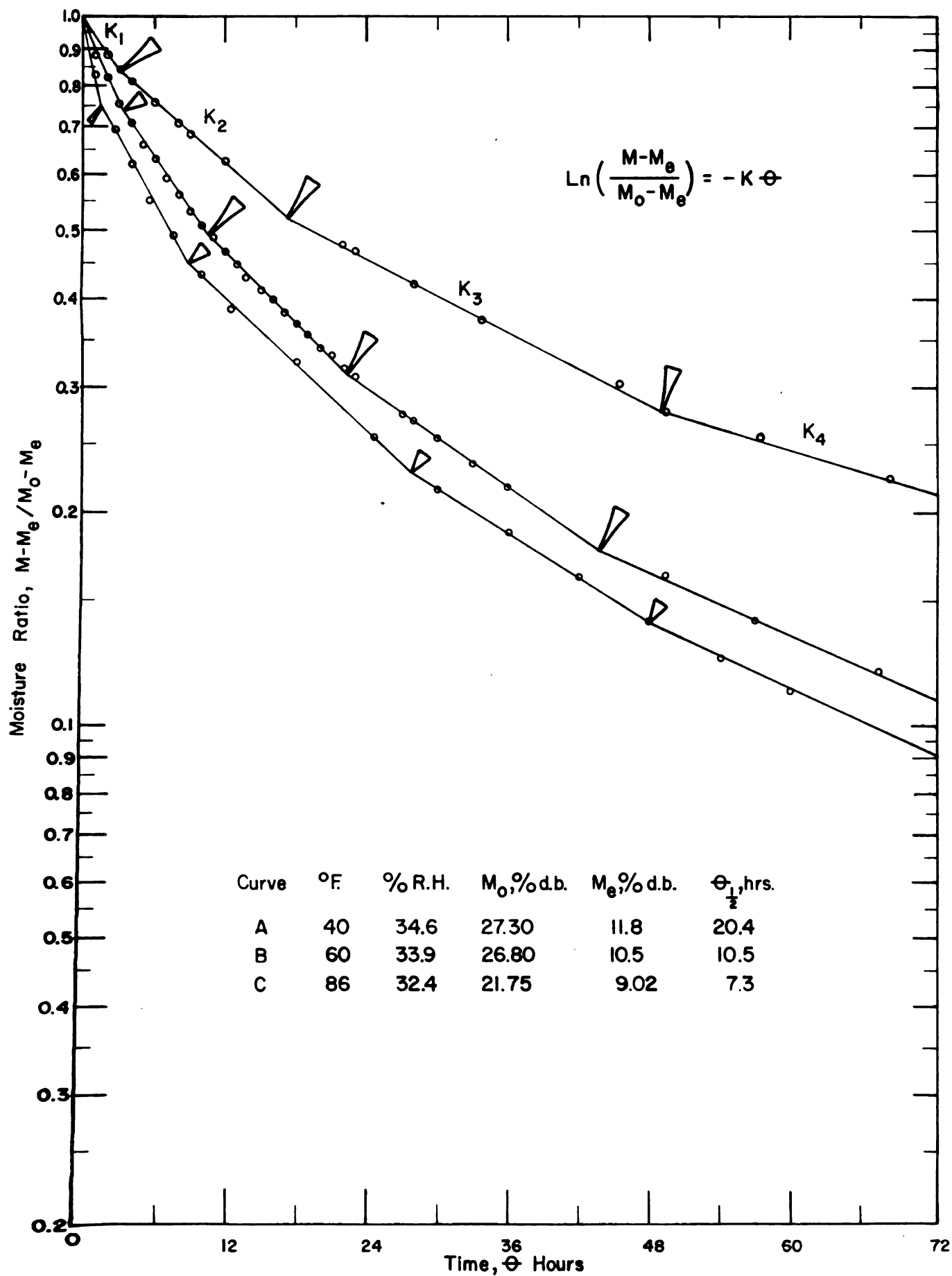


Figure 28 Semilogarithmic plots of drying curves of Figure 27 show-

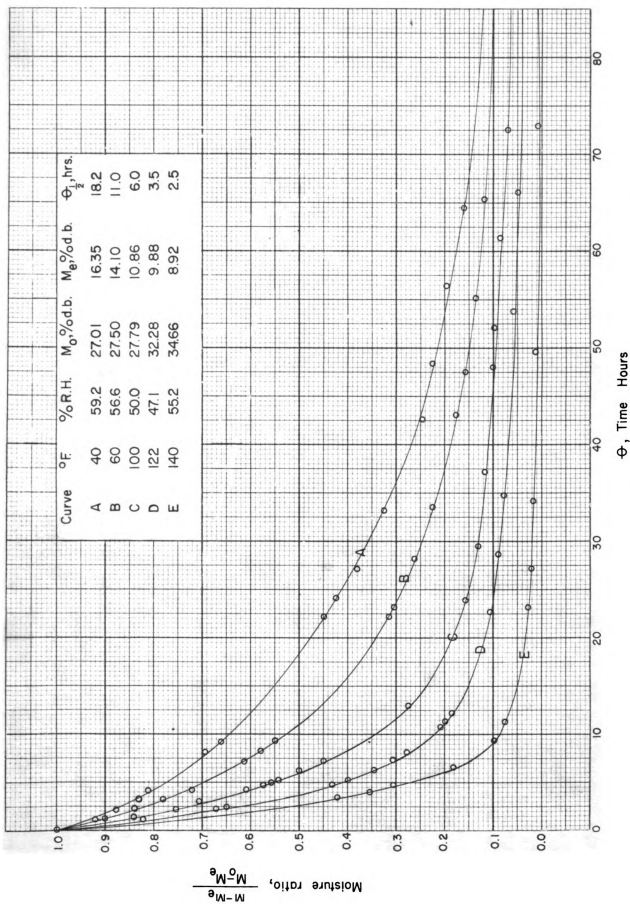


Figure 29 Drying curves for shelled corn fully exposed to various drying conditions

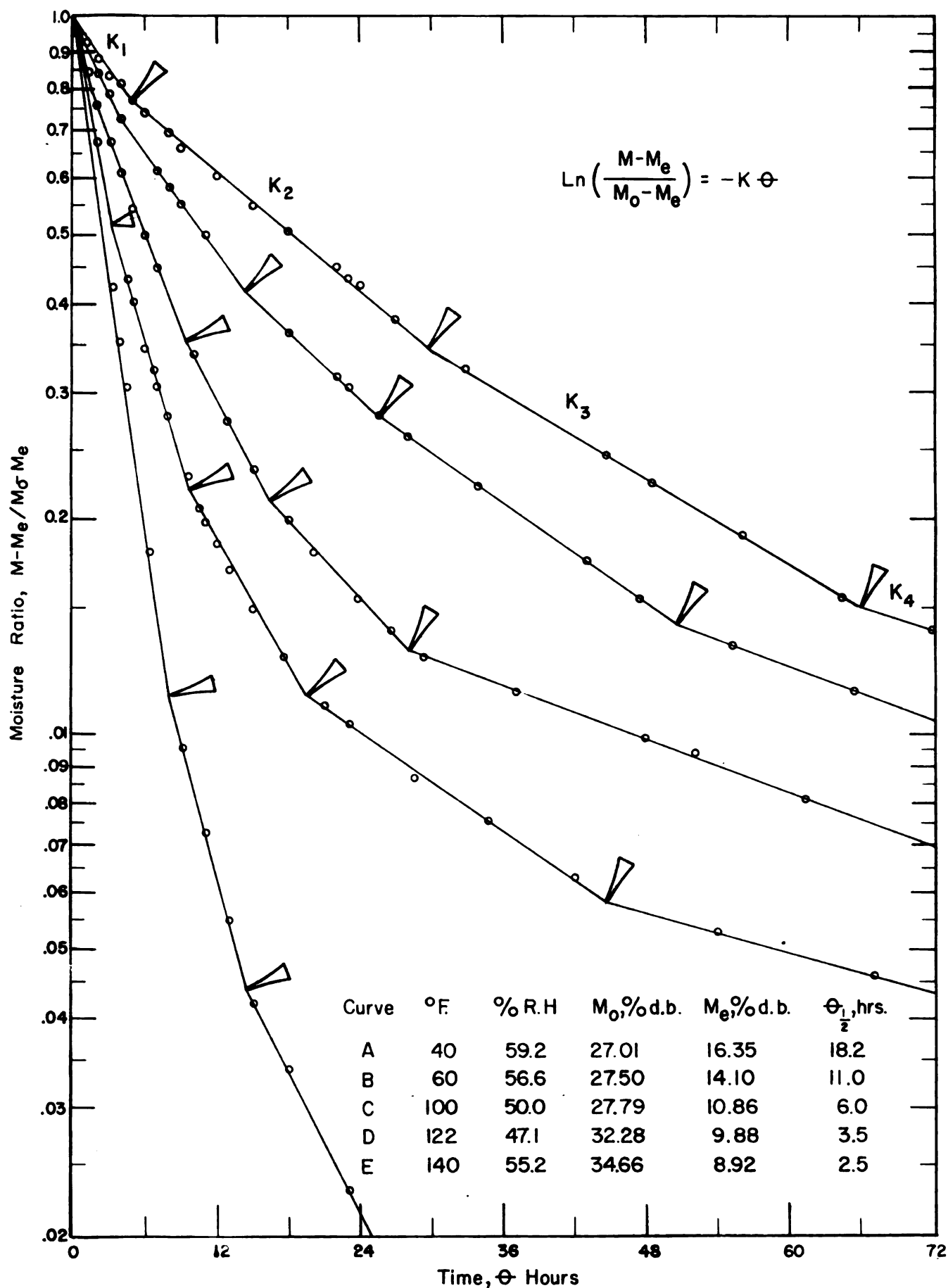


Figure 30 Semilogarithmic plots of drying curves of Figure 29 showing slope breaks with corresponding changes of rate constant K

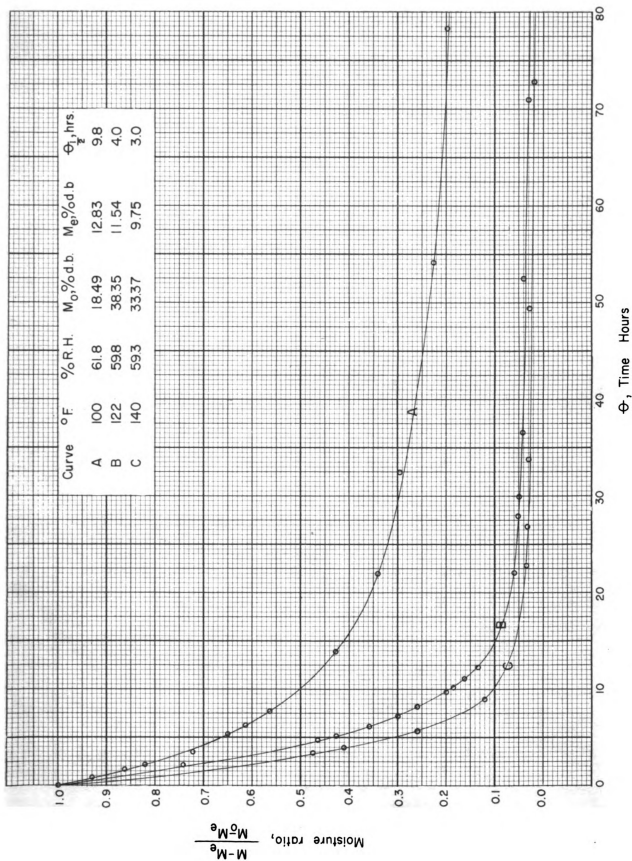


Figure 31 Drying curves for shelled corn fully exposed to various drying conditions

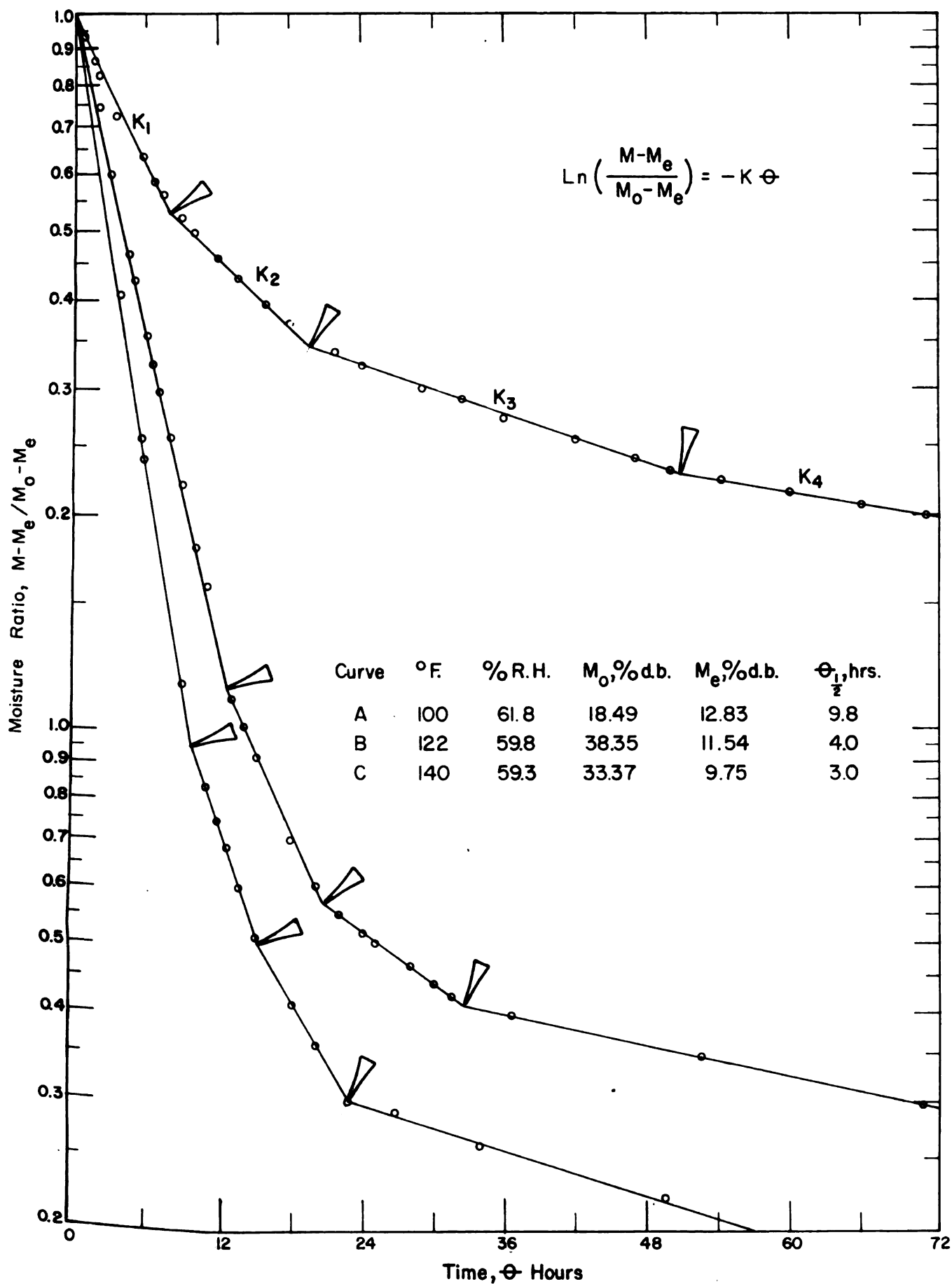


Figure 32 Semilogarithmic plots of drying curves of Figure 31 showing slope breaks with corresponding changes of rate constant K

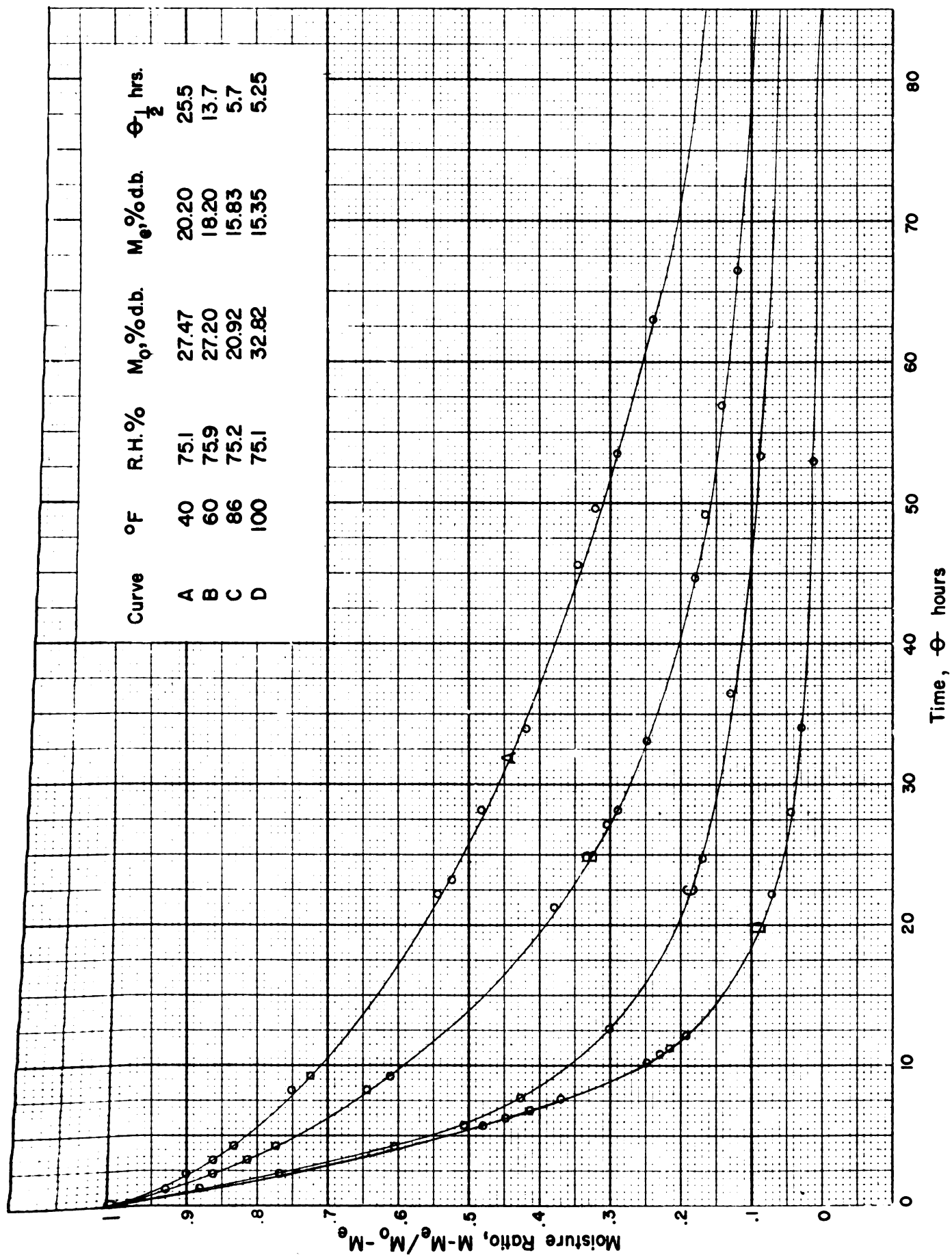


Figure 33 Drying curves for shelled corn

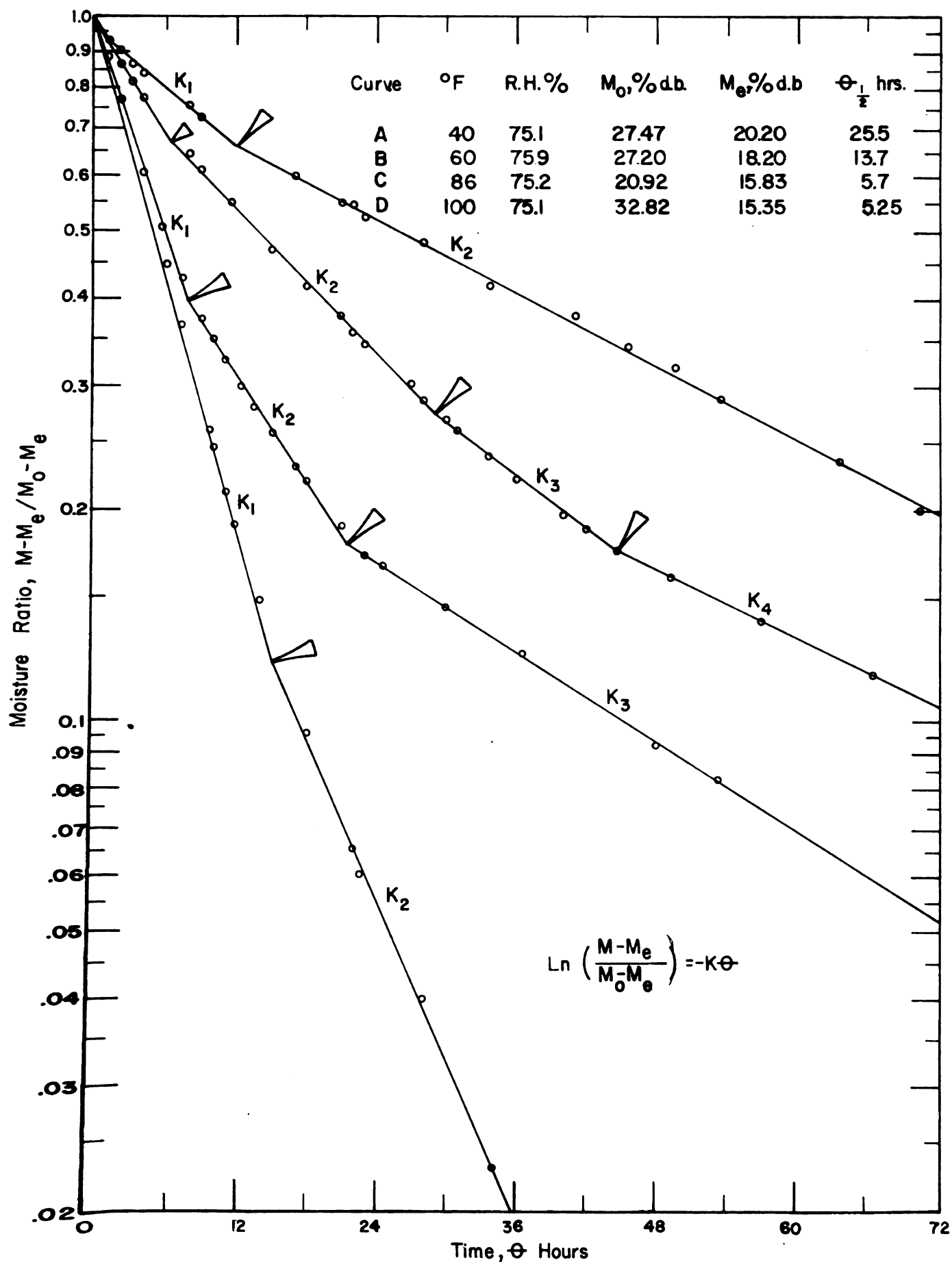


Figure 34 Semilogarithmic plots of drying curves of Figure 33 showing slope breaks with corresponding changes of rate constant K

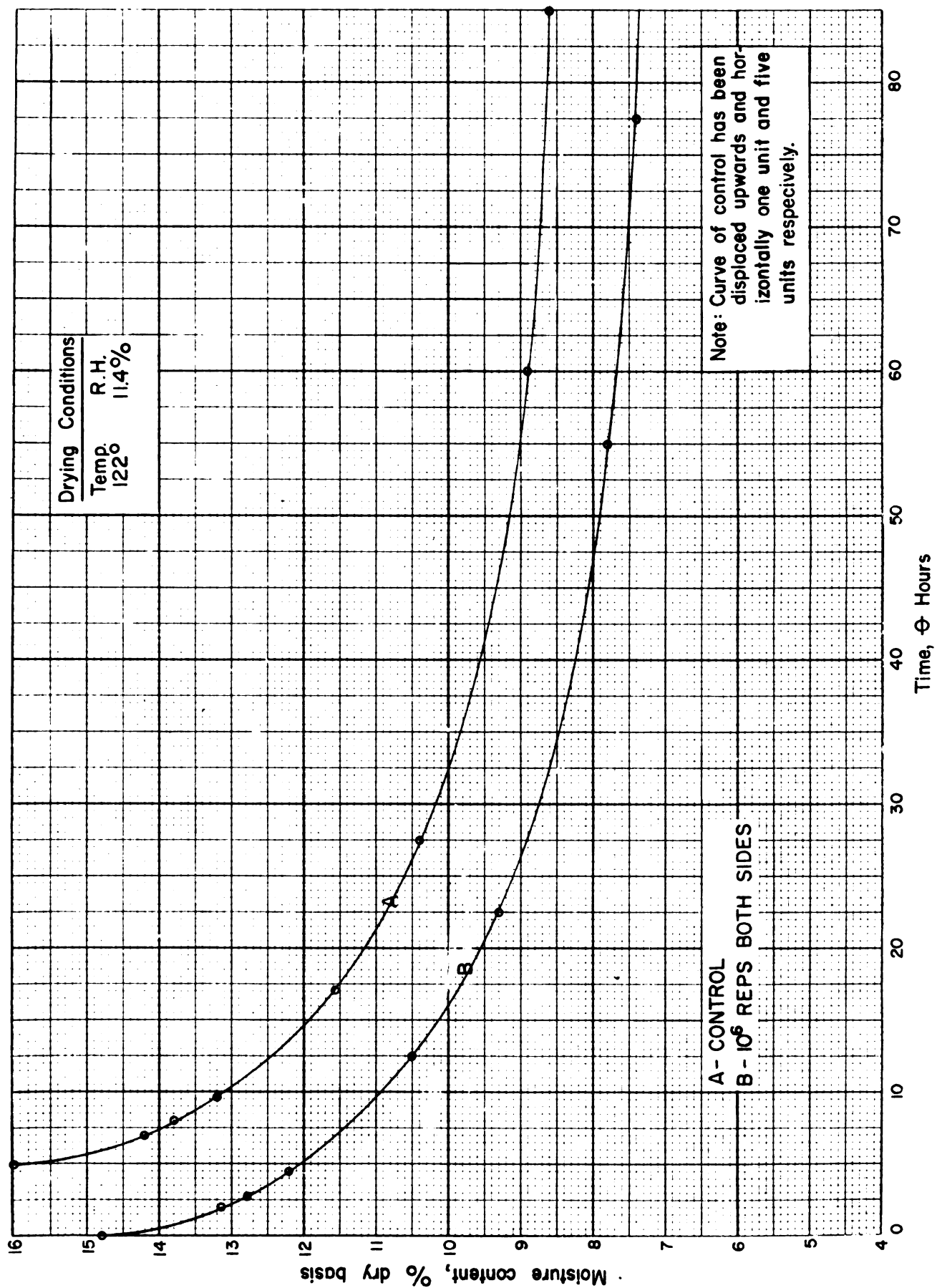


Figure 35 Drying curves of irradiated and control samples of shelled corn.

SUMMARY AND CONCLUSIONS

An experimental inquiry into the theoretical aspects of grain drying was undertaken with the broad objective of gaining basic information pertaining both to the equilibrium and to the rate relationships of the drying process, with particular reference to shelled corn.

The experimental phase was directed toward obtaining hygroscopic equilibrium data over a range of constant drying conditions to permit the accurate construction of desorption isotherms for temperatures of 40°, 60°, 86°, 100°, 122°, and 140°F. A static method was employed whereby thin layer samples of grain were equilibrated above saturated aqueous solutions of chemically pure salts maintained in thermostatically controlled constant-temperature cabinets. Weighing data were obtained at sufficiently close intervals throughout the equilibration period to allow accurate construction of drying curves corresponding to the various testing conditions.

The experimental data concerning the equilibrium relationships are presented in the form of equilibrium moisture content values corresponding to the various constant drying conditions of the investigation, and also in the form of a family of desorption isotherms for the temperatures of test. The extensiveness of the data pertaining to rate relationships precludes their presentation here but enough drying curves are presented to amply illustrate all relationships discussed.

The desorption isotherms obtained were characteristic B-E-T Type II or sigmoid isotherms. Subsequent analysis of the experimental data on hygroscopic equilibria was aimed primarily at applying some of the most promising adsorption theories and equations to the desorption isotherms, in an attempt to elucidate the exact nature of the water-binding mechanism in shelled corn. The drying data were analyzed with the objective of testing the validity of the vapor pressure of drying as applied to cereal grains and in an attempt to determine basic relationships concerning the characteristic drying rates of fully exposed grain.

The results of the analyses justify the following statements concerning the most significant findings and conclusions of the investigation.

1. The average isosteric net heats of desorption for shelled corn over the temperature range of 86° to 122° , as calculated by the integrated Clausius-Clapeyron equation, were found to decrease from a value of 244 BTU per pound at a moisture level of six percent dry basis (5.4 percent wet basis) to a value of fifty-five BTU per pound at twenty-six percent moisture content dry basis (20.6 percent wet basis). These results were in good agreement with heats of desorption obtained according to three other methods, namely, Othmer's graphical method of vapor pressure correlation; from isosteric semi-logarithmic plots of the equilibrium vapor pressure values against the reciprocals of the absolute temperature; and from the energy constant of the B-E-T two-constant equation.

2. A test of Henderson's equation by its application to the experimental isotherms revealed that while it successfully describes the course of the isotherms in the range of relative pressures between 0.10 and 0.60 it tends to considerably understate the moisture content values beyond that range and to slightly overstate them at the lower relative pressures. Furthermore, the conclusion may be drawn that the equation fails to account correctly for the temperature dependence of the isotherm. Over the range of temperatures of the investigation, the values of constant k were found to increase steadily from 1.9×10^{-6} at 40°F to 9.68×10^{-6} at 140°F ; on the other hand, the values of constant n decreased from 2.47 at 40°F to 2.08 at 122°F slightly increasing again to 2.20 at 140°F . Smooth curves representing the foregoing variations are presented as a useful device for obtaining suitable approximate values of the constants for use in the calculation of isotherms at intermediate temperatures within the range.

3. The hygroscopic equilibrium data of shelled corn were examined with the B-E-T two-constant equation and found to yield very satisfactory linear plots in the range of relative pressures between 0.05 and 0.35. Furthermore, the surface constants v_m as evaluated from the intercepts of the linear plots were found to agree closely with the experimental values; likewise, the heats of desorption for the first unimolecular layer as evaluated from the energy constants c were found to be of the right order of magnitude. The foregoing results justify the conclusion that

multimolecular adsorption is the predominant water-binding mechanism in shelled corn. The effective internal surface area available for adsorption was calculated and found to be in the order of 0.262 square meters per milligram of dry grain.

4. When examined by means of Smith's equation, the hygroscopic equilibria of shelled corn were found to yield good straight lines in the range of relative pressures between 0.45 and 0.90, which corresponds closely to the prescribed region of validity of the equation. Smith's equation describes the isotherm adequately in the above-mentioned region of relative pressures.

5. A graphical method for defining the intermediate linear region of the isotherm, recently proposed by Becker and Sallans, was found to result in excellent agreement with the experimental data. The method consists essentially in plotting the isotherm according to both the B-E-T two-constant equation and the Smith equation, and then drawing a straight line tangent to the Smith curve to intersect the B-E-T curve at its point of inflection.

6. Treatment of the data by means of the Harkins-Jura equation yielded very good straight lines in the range of relative pressures from about 0.45 up to about 0.90, showing that in this region the adsorbed water occurs as a condensed film.

7. When the isotherm data were examined by means of the B-E-T three-constant equation a value of five for the size constant n resulted in an excellent fit up to a relative pressure of 0.70, while a value of six gave a satisfactory fit at a relative pressure

of 0.90. These results strongly suggest that despite its heterogeneous character, shelled corn possesses a fairly uniform porous structure involving micropores of an average width in the order of thirty Angstroms and requiring from five to six molecular layers to become completely filled with water.

8. In the light of the foregoing analyses the following simplified mechanism of water adsorption by shelled corn is postulated: in the region from zero pressure to around 0.20 relative pressure, the water is adsorbed as a unimolecular layer involving heats of adsorption in the order of 670 calories per gram; the average amount of water comprising this first layer is around 7.14 grams per 100 grams of dry grain over the temperature range of the investigation. Upon adsorption of additional molecules corresponding to an amount of about 3.25 grams per 100 grams dry basis (corresponding to relative pressures between 0.30 and 0.45, depending on the particular temperature) enough lateral interaction between the adsorbed molecules develops to cause the formation of a condensed film. At a relative pressure of around 0.90 all micropores of an average width of thirty Angstroms are completely filled with five to six molecular layers, with capillary condensation in increasingly larger capillaries setting in beyond that relative pressure up to saturation. The heats of adsorption diminish for each successive layer but remain above the heat of liquefaction throughout the whole range up to saturation.

9. The analysis of the drying data indicated that the instantaneous vapor pressure potential, as given by the difference between

the vapor pressure corresponding to the instantaneous moisture content and the aqueous partial vapor pressure of the drying air, is not the most important single factor influencing the drying rate of shelled corn; under identical vapor pressure potentials but different drying conditions, widely divergent drying rates were obtained. However, over restricted ranges of moisture content, the drying rate could be characterized by an equation analogous to Ohm's law with the vapor pressure potential as the driving force and the reciprocal of a mass transfer coefficient as the resistance. Values of the mass transfer coefficient for shelled corn, under various constant drying conditions, in terms of percent moisture content dry basis per hour per unit vapor pressure potential in pounds per square inch are presented together with their corresponding regions of applicability in terms of moisture percent dry basis.

10. There was ample evidence to indicate that the main factors affecting the drying rate of shelled corn, listed in order of their relative importance, are as follows: (1) moisture content level at any instant, (2) temperature, (3) free moisture content, and (4) relative humidity. As a general rule, other conditions being equal, the higher the moisture content, or the higher the temperature the greater will be the drying rate. An increase in relative humidity, particularly beyond seventy five percent, tends to slow down the drying process; however the drying rate appears to be less sensitive to a change in relative humidity than it is to a change in any of the other factors.

11. The fully exposed or thin layer drying behavior of shelled corn was found to obey closely an exponential drying law analogous to Newton's law of cooling. However, the drying rate constant was found to vary in stepwise fashion according to sudden drops in value occurring at various intervals throughout the drying process. There appears to be a correlation between the number of different values of the drying rate constant for a given set of drying conditions and the number of molecular layers that can be adsorbed on each wall of the capillaries as determined by the B-E-T three-constant equation. This behavior of the drying constant is related to that of the mass transfer coefficient previously described, and seriously hinders the general applicability of the simple equation based on the drying law. Nevertheless, the observation that the applicability range for the rate constant seems to be long enough (in the order of thirty percent at 140°F for initial moisture content levels around forty-five percent dry basis) at temperatures above 100°F suggests the feasibility of using the simple equation to characterize fully exposed drying rates when heated air is used for the drying process.

12. Values for the half-response period, the time required for fully exposed grain to reach a moisture content ratio of 0.50, are presented for the various drying conditions. The same factors affecting the drying rate have the opposite effect on the length of the half-response period.

13. Other valuable data presented include values of all constants involved in the various isotherm equations for each of the temperatures of the investigation; Othmer latent heat ratios for various moisture contents; isosteric heats of desorption for various moisture levels; family of isosteres for moisture levels from six to twenty-two percent dry basis at intervals of two percent, representing the variation of the equilibrium vapor pressure of shelled corn in pounds per square inch absolute with relative humidity.

14. While the extent of the experiments along this line was limited in scope, the results obtained appear to justify the conclusion that irradiating shelled corn at a moisture level of fifteen percent dry basis with either a dose of 10^6 reps or of 10^7 reps applied on each of both flat sides of the kernel, has no noticeable effect on the drying rate.

SUGGESTIONS FOR FURTHER WORK

1. Determination by a dynamic method of hygroscopic equilibria of shelled corn over a temperature range from 140° to 260°F, which represents the limit of current practice in commercial drying of grains; treatment of the data in a similar manner as done in this investigation with the objective of defining the temperature dependence of the isotherm.

2. Similar investigations as above but with other cereal grains and related products as the experimental material.

3. Determination of characteristic fully exposed drying rates by a static method over the same temperature range as indicated above for other grains. While a static method has definite limitations for determination of hygroscopic equilibria it does present advantages over dynamic methods for determination of drying rates. Further work along this line should be aimed at establishing suitable statistical values for the rate constant which may be applicable to practical drying problems under various drying conditions.

4. Obtain hygroscopic equilibrium data for the various cereal grains and related materials in the temperature range from -20° to 40°F.

5. Knowledge in the field of physical adsorption is being continuously enriched by the results of current research. Examination and reexamination of hygroscopic equilibrium data in the light of

the newest developments in the field of adsorption afford a valuable tool for elucidating the water-grain relationships.

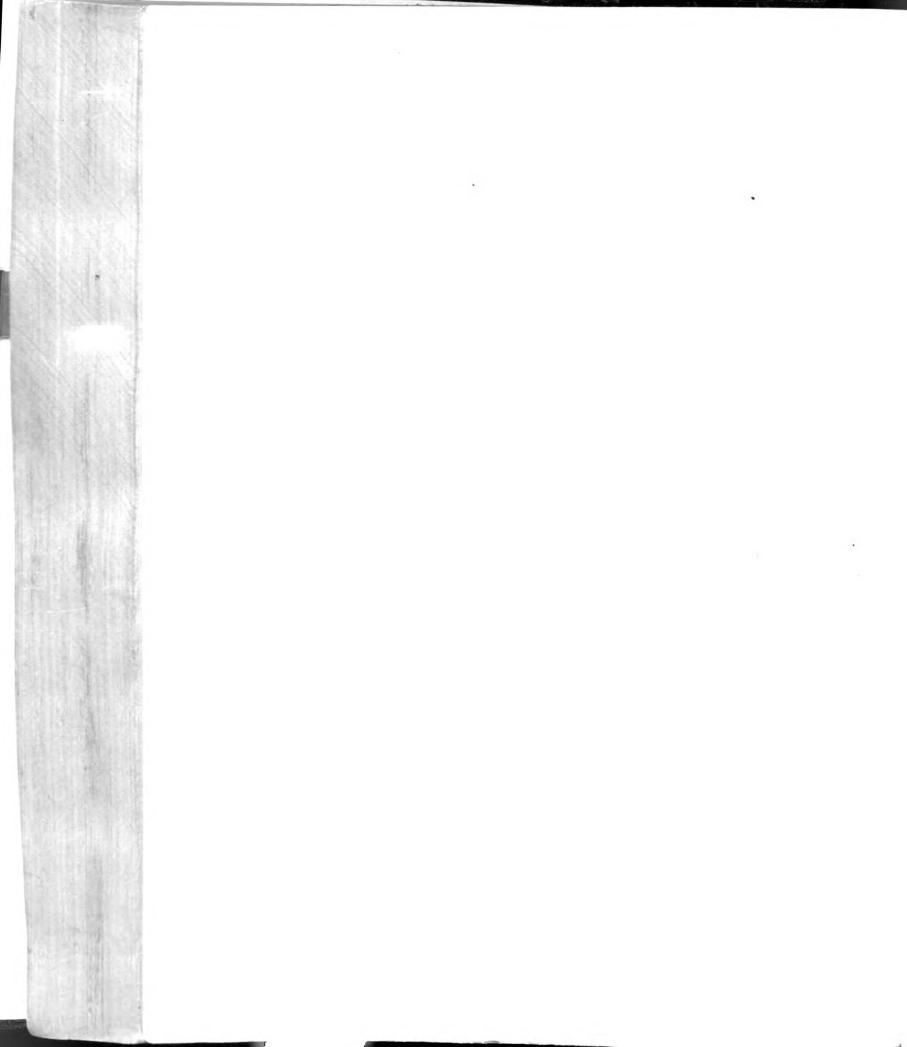
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