

ADSORPTION KINETICS OF WATER VAPOR
BY YELLOW CORN

by

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INTRODUCTION

The change of moisture content of grain with the environmental condition to which grain is exposed is not only of scientific interest but also, owing to the influence of moisture content on the keeping quality of grain, of great commercial importance. During the storage and handling of grain, the physical and chemical changes are continuously taking place in all grain. Of various factors influencing on the rate of these changes, moisture is by far the most important.

The change in moisture content of grain may be an adsorption or a desorption process depending on whether water is taken on or given off by the grain from the environment. Numerous attempts have been made to understand adsorption and desorption process of gases or water vapor on solid substances and in developing an expression relating the equilibrium state of the material to the environmental conditions. Although the adsorption isotherms of grain has been intensively studied for years, the adsorption kinetics of water vapor as well as many factors which influence the rate at which water vapor is adsorbed by grain has not been well explored.

Many investigators have studied the adsorption kinetics of industrial gases on solid substances, and some of them have been successful in developing the adsorption rate equations. Applications of those theories to the adsorption of water vapor by biological materials such as cereal grains may be very helpful to understand the nature of the adsorption phenomena as well as the effects of many factors which influence the rate of adsorption of water vapor by cereal grains. Moreover, the proper understanding of the

nature and those effects on the adsorption phenomena will give the fundamental informations about the grain drying, storage, and even about the grain quality evaluation.

The measurement system used in this adsorption kinetics study will be one of the most up to date methods to measure the rate of adsorption and to understand the nature of the adsorption phenomena.

OBJECTIVES

The objectives of this study were:

1. To study the nature of adsorption kinetics of water vapor by grain to provide useful information for grain storage and grain drying.
2. To investigate the effects of environmental condition, temperature and relative humidity, and initial moisture content of grain on the adsorption rate of water vapor by grain.
3. To develop the theoretical or semi-empirical equation which would describe the adsorption kinetics of cereal grains.
4. To investigate the possibility of using the adsorption rate constant as an index for determining the percentage of sound grain in a grain sample in order to eliminate individual analysis by visual method.

LITERATURE SURVEY AND THEORETICAL ASPECTS

General Concepts of Adsorption

When a gas or vapor is brought in contact with a solid, a part of it is taken up by the solid. The molecules that disappear from the gas phase remain on the outside attached to the surface. The concentration of gas molecules is greater in the immediate vicinity of the solid surface than in the bulk gas phase, regardless of the nature of the gas or surface. The process during which this surface excess is formed is called "adsorption".

Adsorption is to be distinguished from "absorption", which involves bulk penetration of the gas into the structure of the solid by some process of diffusion. The solid that takes up the gas or vapor is called the "adsorbent", the gas or vapor attached to the surface of the solid is called the "adsorbate".

The adsorbed particles are either held rigidly to the surface, or they can move over the surface freely into two dimensions. The concept of mobile and localized adsorbed films is well described in Ross and Oliver (31). Since prior to adsorption the gas molecules moved freely into three dimensions, the adsorption process is accompanied by a decrease in entropy, The change in heat content of the system is

$$\Delta H = \Delta F + T\Delta S$$

where ΔF = the change in the free energy of the system

ΔH = the change in heat content of system

ΔS = the entropy change

T = the absolute temperature

and since both ΔF and ΔS are negative, ΔH must also be negative. This means that all adsorption processes are exothermic, regardless of the nature of the forces involved. The change in the heat content of the system is called the "heat of adsorption". In van der Waals adsorption it is of the same order of magnitude as the heats of condensation of gases, in chemisorption as the heats of chemical reactions.

Physical Adsorption and Chemical Adsorption

It is customary to divide adsorption process into two categories, physical or chemical, depending on the nature of the forces involved. Physical adsorption, also termed van der Waals adsorption, is caused by molecular interaction forces (a weak interaction between solid and a gas); the formation of a physically adsorbed layer may be similar to the condensation of a vapor to form a liquid. The heat of physical adsorption is not only of the same order of magnitude as that of condensation but physically adsorbed layers, particularly those many molecular diameters thick, behave in many respects like two-dimensional liquids. On the other hand, chemical adsorption, usually abbreviated to chemisorption, involves transfer of electrons between the solid (or adsorbent) and the gas (or adsorbate). The process essentially involves the formation of chemical compound. The distinction between physical adsorption and chemisorption is well explained in Young and Crowell (39).

Free Water and Bound Water

Water may be held in the solid in three distinct ways. Some water may

be held in the intergranular spaces and within the pores of the material. This type of water, called "free water", exerts the same vapor pressure, and contains the same latent heat of vaporization as does pure water at the same temperature, and is more closely related to the structure of adsorbent than to the molecules of adsorbent.

Another portion of water may be adsorbed on the internal and external surfaces of the solid material by interaction between the water molecules and those of the solid material. This type of water, called "bound water" exerts a vapor pressure less than that of liquid water at the same temperature and is more closely associated with the adsorbent.

Finally some water may combine in a chemical union with the molecules of the adsorbent. This type of water may exist in the form of hydrates.

Energy Changes in Adsorption

Total energy evolved in the adsorption process is the sum of potential and kinetic energies. The consideration of potential energy changes on adsorption is required for the construction of a model that takes into account the translational, rotational, and vibrational states of the adsorbed molecule, as well as the nature and origin of the adsorptive forces.

A molecule in the gas phase has potential energy with respect to its possible adsorbed state at an interface. This potential energy is fixed by the nature of the gas-solid interface and is independent of any kinetic energy possessed by the particles either before or after the transition.

Suppose a molecule approaches and is adsorbed at a solid surface. The change of potential energy of the system follows the path ABC in Fig. 1 and

would then return along the reverse path CBA to its original value unless, by collision, some of the molecule's momentum in the component normal to the surface is lost, the energy appearing as heat. The molecule is detained in the two-dimensional phase until, by collision, it gains enough kinetic energy to escape from the potential well.

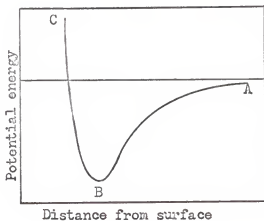


Fig. 1. Change of potential energy of a gas molecule on approaching a solid surface

Another factor that affects the energy change on adsorption is the attractive force exerted by molecules already adsorbed. The pressure of these molecules on the surface increases the potential energy for adsorption of molecules in the gas phase; the more that are present, the greater the effect, so that this factor is a function of the surface concentration.

Rate of Adsorption

The adsorption of pure gases and vapors is often very fast. In physical adsorption equilibrium is often established so quickly that the rate

cannot be measured. However, this is not always the case; the fast initial adsorption is frequently followed by a rate-determining transition over an energy barrier to the final stage of adsorption. In many cases the blocking of the adsorption by molecules already adsorbed slows down the rate; e.g., H. S. Harned(20) found that in the adsorption of chloropicrin by charcoal, adsorbed air acted as inhibitor. In still other cases foreign molecules in the gas phase slow down the adsorption by blocking diffusion of the gas to be adsorbed into narrow capillaries. Patric and Cohan(28) found that 1.0mm pressure of air, oxygen, or nitrogen slowed down the adsorption of water vapor by silica gel considerably.

In general, it seems safe to conclude that in physical adsorption for pure gaseous system the gas molecules are adsorbed as rapidly as they can reach the surface. The slow effects are either due to foreign molecules in the gas phase activated adsorption, chemisorption, chemical reaction, solution, or to the inability of the molecules to get in contact with the surface of the adsorbent.

Taylor(35) was the first to point out that the rate of activated adsorption increases exponentially with the temperature, just like the rates of chemical reactions, and he showed that the energy of activation can be calculated from the temperature coefficient of the rate. Because this type of adsorption possesses an energy of activation, he named it activated adsorption. The energies of activation obtained by adsorption rate measurements have been ascribed by various investigators to solution, diffusion, migration, or reaction on the surface. The determination of the rate of activated adsorption may be complicated by the simultaneous occurrence of chemical reaction or solution.

Adsorption Rate Theories and Their Application

Studies of the adsorption of gases on solids have been eminently successful in developing the characteristics and extent of solid surfaces. The monomolecular layer theory by Langmuir(25), the potential theory by Polani(7), the Brunauer-Emmett-Teller theory of multilayer adsorption(8), and numerous others suggested that it might be possible to deduce most of important properties of solid surfaces from adsorption data. The excellent description of the development and application of these theories was given by Brunauer(7), Young and Crowell(39), and many others(2, 18, 31).

The well-known adsorption rate theories will be described and their application will be discussed.

(a) McBain's Equation

The theory of adsorption rates was first investigated by McBain(27). He observed that the rate of hydrogen on charcoal consisted of two distinct phenomena. He called one of these phenomena adsorption and assumed that its rate was instantaneous; he believed that the other phenomenon was diffusion and derived an expression for its rate from Fick's diffusion law. The equation is

$$Q = \frac{4cL}{\pi^2} \left(\frac{\pi^2}{8} - \left(e^{-(D\pi^2/L^2)t} + \frac{1}{9} e^{-(9D\pi^2/L^2)t} + \frac{1}{25} e^{-(25D\pi^2/L^2)t} + \dots \right) \right) \quad (1)$$

where Q = the amount of gas that has diffused through unit surface at time t

c = the concentration in the gas phase (assumed to remain constant)

L = the total thickness of the solid

D = the diffusion constant

If a considerable fraction of the final amount is already dissolved in the solid, all terms but the first in the parenthesis can be neglected to a very good approximation. One obtains then

$$q = A\left(\frac{m^2}{8} - e^{-kt}\right) \quad (2)$$

where q = the amount dissolved at time t

A, k = constants

McBain did not test his equations, nor did any other investigator. Nevertheless, the rate determining step in physical adsorption may be a diffusion process finally led back to the adsorption equations identical in form with McBain's equation. To be sure, the diffusion is into the pores of the adsorbent and not to its body.

(b) Langmuir's Equation

The theory of the rate of adsorption on a free surface was also derived by Langmuir(25).

The experimentally measured rate is the difference between the rate at which the molecules condense on the surface and the rate at which they leave the surface. If the rate is determined at constant pressure it is given by

$$\frac{d\theta}{dt} = k_1(1 - \theta) - k_2\theta \quad (3)$$

where θ = the fraction of the surface covered with adsorbed gas

k_1, k_2 = constants (the constant k_1 includes the pressure)

Integrating with the boundary conditions that $\theta = 0$ when $t = 0$, $\theta = \theta_e$ when $t = \infty$

$$\theta = \theta_e(1 - e^{-kt}) \quad (4)$$

where θ = the fraction of the surface covered when equilibrium is reached.

Since $\theta = q/q_e$, equation(4) can be written in the form

$$q = q_e(1 - e^{-kt}) \quad (5)$$

i.e.

$$\ln \frac{q_e}{q_e - q} = kt \quad (6)$$

where q , q_e = the amounts adsorbed after time t and at equilibrium respectively. A plot of equation(6) on the left hand side against t should be a straight line.

Harned(20) tested Langmuir's rate equation for the rate of adsorption of chloropicrin and of carbon tetrachloride on charcoal at low pressures. He found that for charcoals with clean surface Langmuir's equation was actually obeyed (prior to these runs the charcoal was evacuated at 700° C for three hours). Unless adsorbed impurities are removed in some such manner the rate of adsorption becomes very slow.

A wide variety of experimental adsorption data has been found to fit the Langmuir equation fairly well(6, 16, 20). However, Chung and Pfost(9) demonstrated that adsorption data of agricultural products did not follow the Langmuir equation.

For very long runs, Bangham and Sever(?) used the equation

$$\ln \frac{q_e}{q_e - q} = kt^{1/m} \quad (7)$$

It should be noted that for $m = 1$ this equation becomes formally identical with Langmuir's equation.

Commonly used grain drying relationships developed by Sherwood(33) is:

$$\frac{M - M_e}{M_0 - M_e} = e^{-ut} \quad (8)$$

Equation(8) is identical with Langmuir's equation if it is assumed that some of the relationships which hold for drying may also hold for wetting. Under this assumption Young and others(41) developed the equation

$$\frac{M_e - M}{M_e - M_0} = \left(\frac{a}{a+t} \right)^b \quad (9)$$

where a, b = experimentally determined values
and they tested this equation with cured tobacco under the environmental condition of 80 percent relative humidity and 86° F.

(c) Damköhler's Equation

The rate equation for the diffusion of molecules in the pores of an adsorbent was derived by Damköhler(12).

For adsorption at constant pressure the equation is

$$\theta = 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-\delta(2n+1)^2}}{(2n+1)^2} \quad (10)$$

where θ = the fraction of the equilibrium amount adsorbed at time t

$$\delta = (2\pi/L)^2 Dt$$

L = the length of the capillary

D = the overall diffusion coefficient

In deriving equation(10), Damköhler believed that surface diffusion has an energy of activation even in physical adsorption because when a molecule

moves from one position of equilibrium to another over the surface it has to climb over a potential barrier, and energy of activation most necessarily be smaller than the heat of adsorption.

There is a strong resemblance between the Langmuir rate equation and the diffusion equation of Damkohler and McBain. Note, for example, the similarity between McBain and Langmuir equations. The only difference is that in the parenthesis one equation has $\frac{6}{\pi^2}$, which is equal to 1.23, the other has 1.00.

(d) Wicke's Diffusion Equation

Wicke(42) derived a diffusion equation for the rate of adsorption which is somewhat similar to Damkohler's. Wicke assumed that the adsorbent particles were spherical, and he set up a differential equation for the diffusion of the gas toward the center of a sphere. With the certain boundary conditions the solution of the equation is

$$\Theta = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-6n^2} \quad (11)$$

where Θ = the fraction of the equilibrium amount adsorbed at time t

R = radius of the sphere

A = a constant

D = the diffusion coefficient

$\delta = (\pi^2/RA)Dt$

(e) Zeldovich-Roginski (or Elovich-Zhabrova) Equation

Zeldovich and Roginski(30) found that the rate of adsorption of CO on

finely divided MnO_2 decreases exponentially with the increase of the amount of gas adsorbed,

$$dq/dm = a e^{-\alpha q} \quad (12)$$

where q = amount adsorbed

t = time

a, α = constants over the course of the process

The same equation was found by Elovich and Zhabrova(14) to study the slow adsorptions of H_2 and of C_2H_4 on Ni at low temperatures. These authors also have indicated the procedure for testing equation and for determining the parameters from the experimental data. The integrated form of equation(22) can be written in the form

$$q = \frac{1}{\alpha} \ln(t+t_0) - \frac{1}{\alpha} \ln(t_0) \quad (13)$$

i.e.

$$q = \frac{2.3}{\alpha} \log(t+t_0) - \frac{2.3}{\alpha} \log(t_0) \quad (14)$$

with $t_0 = 1/\alpha a$

This equation predicts that if t_0 is chosen correctly, a plot of q vs. $\log(t+t_0)$ should be a straight line.

Eley and Leslie(13) found in their investigation on adsorption of water on solid proteins that the adsorption time curves had been found to follow the Roginski-Zeldovich (or Elovich-Zhabrova) equation in a slightly modified form.

The derivation of this equation assumed that the rate of adsorption dm/dt

possesses an activation energy which increases linearly with the amount of adsorbed gas "m",

$$\frac{dm}{dt} = K_0 f(p) \exp\left(-\frac{E_0 + \alpha m}{RT}\right) = K' \exp(-\alpha m/RT) \quad (15)$$

K_0 , E_0 , α are constants, and $f(p)$ some function of the pressure in the system. This is integrated to give the equation for the dependence of "m" on "t", viz.,

$$m = \frac{RT}{\alpha} \ln\left(t + \frac{RT}{\alpha K'}\right) - \frac{RT}{\alpha} \ln \frac{RT}{\alpha K'} \quad (16)$$

i.e.

$$m = \frac{RT}{\alpha} \ln(t + t_0) + C \quad (17)$$

This equation predicts that if " t_0 " is chosen by empirical methods, a plot of "m" vs. $\ln(t + t_0)$ should be a straight line with a slope $= RT/\alpha$, $t_0 = RT/\alpha K'$. From experimental data, " t_0 " can be found by trial and error method; with " t_0 " too small, the curve is convex, with " t_0 " too large it is concave to the axis of $\ln(t + t_0)$. This is well illustrated in Taylor and Thon (37).

MATERIAL AND METHODS

Preparation of Samples

Yellow corn (variety: Pioneer 3306) harvested in 1968 was used in this investigation to determine the adsorption rate of water vapor at various environmental conditions. Harvested ear corn samples (moisture content of 24%) were shelled by hand to eliminate possible mechanical damage by combine and these shelled corn samples were kept under the environmental conditions, for several days, which would give the moisture content of approximately 9%, 11%, and 14% respectively. When samples reached the moisture content of approximately 9%, 11%, and 14% respectively, they were put into vinyl sacks and placed in a refrigerator for several days so that every yellow corn kernel in a vinyl sack would have the same moisture content. Homogeneity of moisture content between kernels and within kernels was assumed in this investigation. Initial moisture content of the sound sample used in this adsorption study was determined by the air-oven method, and results of initial moisture content of the corn sample used are tabulated in Table 1.

In addition to the sound corn samples, various kinds of damaged corn samples were also prepared to study the adsorption rate differences between sound and damaged samples. Moldy corn samples were obtained from the Department of Bacteriology, K.S.U. and heat-damaged, sprout, and broken samples were prepared by the investigator. Artificial heat-damage was produced by heating high-moisture (24%) corn in the air-oven at 125° C for a period of four hours. Sound corn samples were cracked, and broken by a Burrows Kernel Cutter. Type and level of damaged corn samples prepared for this

Table 1. The air-oven results of the initial moisture contents * of corn samples A, B, and C, used in the adsorption study

Environmental Condition	Sample A		Sample B		Sample C	
	rep 1	rep 2	rep 1	rep 2	rep 1	rep 2
80°F - 80%	9.25	9.28	11.15	11.20	13.70	13.94
- 70%	9.27	9.20	11.20	11.34	13.81	13.78
- 60%	9.32	9.18	11.33	11.14	13.78	13.82
70°F - 80%	9.21	9.33	11.16	11.20	13.89	13.76
- 70%	9.21	9.22	11.20	11.39	13.71	13.70
- 60%	9.28	9.33	11.40	11.17	13.75	13.85
60°F - 80%	9.39	9.22	11.43	11.16	13.79	13.77
- 70%	9.28	9.32	11.20	11.33	13.84	13.76
- 60%	9.19	9.20	11.19	11.18	13.92	13.68
Mean	9.26		11.24		13.80	
S ²	0.0036		0.0094		0.0063	
True Mean	9.26 ± 0.06		11.24 ± 0.10		13.80 ± 0.08	

* All moisture contents are expressed in "dry basis"

Table 2. Damaged corn samples

Initial moisture	Type of damage	Level of damage
10.62 %	Sprout	20 %
		100 %
	Broken	20 %
		100 %
	Heat-damage	10 %
		20 %

investigation are summarized in Table 2. Samples for various levels of a specified damage were prepared by blending the known amount of damaged kernels with sound kernels.

Equipment Used

To measure the continuous weight change of the samples under the specified environmental condition, the following instrumentation system was established.

AMINCO 3-B CLIMATE-LAB which provides a test chamber (3 cu. ft. of volume) wherein the dry-bulb temperature is controlled to $\pm 3/4^{\circ}$ F and the relative humidity is controlled to $\pm 1/2\%$. Temperature and humidity ranges are obtained by manual setting of bimetal thermo-regulators. Refrigeration operates continuously and is opposed by cycling Lo-lag heaters. Precise humidity and temperature control is achieved in the test chamber by conditioning the air before it enters the test chamber, thus eliminating sources of humidity and temperature differentials often encountered in systems using water sprays, pans, and salt solutions inside the test chamber. Air is continuously circulated from the test chamber to the conditioner, conditioned and return to the test chamber. Electric hygrometer records test chamber conditions continuously.

A CAHN Electrobalance, made for recording weight change in vacuum, controlled atmosphere and room air, was used in this investigation. The weighing unit of the CAHN Electrobalance was mounted on the top of the test chamber and used for recording the weight change of samples continuously in controlled environmental chamber by extending its sample loop through the top of the test

Explanation of Plate I

Schematic Diagram of Measurement System

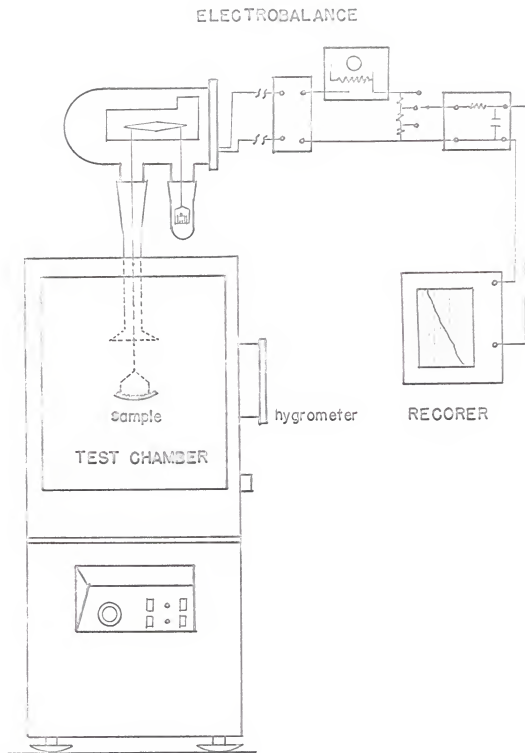
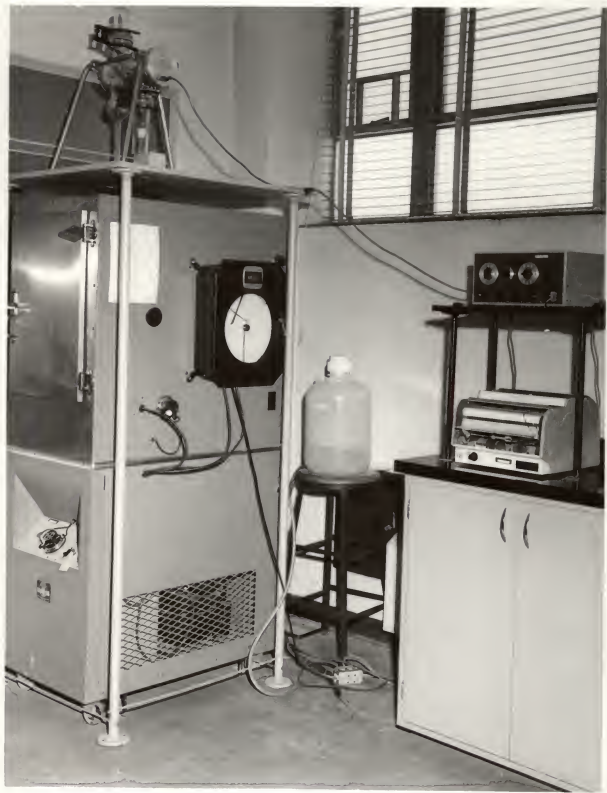


Plate I. Schematic Diagram of Equipment

Explanation of Plate II

View of the experimental equipment in the laboratory.



chamber. The recording balance used has 100 gm capacity, and electrical indicating ranges from 0.2 mg to 20 gms (readable and reproducible to 0.01% of the dial range and accurate to 0.05% of the dial range). A self-balancing potentiometric strip chart recorder manufactured by Texas Instrument Co. was used for accurate recording (accuracy of 0.1% of recording range or better) of the continuous weight change of the sample with respect to time.

Necessary modifications of the instrumental set-up were made in order to keep the test chamber and weighing unit of electrobalance in the same condition and to eliminate vibration effect on weighing mechanism. A schematic diagram of experimental set-up and equipment used are shown in Plates I and II.

Procedures

The adsorption rate of water vapor by corn was studied by placing corn in an atmosphere of constant temperature and relative humidity.

Samples (20 gm) were placed on 4 1/2 inch diameter pan made from fine brass wire screen (200 mesh) in a single layer so that no superimposing corn was present to restrict the movement of water vapor to the corn. This brass wire pan with samples was hung from the sample loop of the electrobalance so that the weight change of samples could be measured continuously under the specific environmental condition provided by the test chamber; the weight change of a sample was recorded continuously for 11 hours (see Plate I).

The empty brass wire basket was tested under the experimental conditions to obtain the weight increase or decrease during the investigation. The

results were found to be insignificant. However, the empty basket was kept in the test chamber of the experimental condition for one hour before samples were placed in it.

Initial weight of the sample was measured by Mettler Type H analytical balance to the accuracy of ± 0.1 mg. Initial temperature of the sample was controlled to the same as the dry-bulb temperature of the test condition under which its adsorption rate was investigated. Initial moisture content of the sample was determined by the air-oven method.

Experimental Design

Twenty seven series of tests were conducted for studying the effects of three factors; initial moisture content, temperature, and relative humidity, on the adsorption rate and the nature of the adsorption. Samples having initial moisture content of about 9.2%, 11.2%, and 13.8% were tested under the nine different environmental conditions. Factors and their levels investigated are summarized in the following Table 3.

Table 3 Factors and their levels

Sample initial moisture content*	Temperature	Relative humidity
9.0%	60°F	60%
11.0%		70%
		80%
14.0%	70°F	60%
		70%
		80%
	80°F	60%
		70%
		80%

* Approximate values

Two replications of each series were conducted, and their results were averaged.

RESULTS AND DISCUSSION

Adsorption rate data of corn having initial moisture contents of 9.26%, 11.24%, and 13.8% were obtained at various temperatures and relative humidities to study the effects of these factors on adsorption rate. The influences of temperature, relative humidity, and initial moisture content on adsorption rate present a number of interesting phenomena which are yet unexplained. In this section, analysis of the experimental data, application of Elovich adsorption rate equation, development and test of the semi-empirical equation, and adsorption rate difference between sound and damaged grain will be discussed.

Experimental Data

The experimental data of integral rate of adsorption of water vapor by corn with three different initial moisture content levels at nine different environmental conditions are tabulated in Table 4. The results obtained from the experiments are reproduced in Figures 2, 3, and 4. The amount of water adsorbed by yellow corn with respect to time was reported based on the weight of dry matter.

In order to investigate the reproducibility of adsorption rate data, three adsorption rate replications with corn samples were conducted at 80° F and 80% relative humidity. The results are plotted in Fig. 5. The results of the three adsorption rate replications showed a good reproducibility of data. The statistical tests also showed (Tables 7, 8) there are no significant differences between pairs of replications of experimental data.

Table 4. Amount of water vapor adsorbed
by corn, g H₂O/100g dry corn

Initial moisture	Time (hrs)	Environmental Condition					
		60% - 60°F		60% - 70°F		60% - 80°F	
		REP 1	REP 2	REP 1	REP 2	REP 1	REP 2
9.26 %	1	0.218	0.213	0.301	0.301	0.333	0.312
	2	0.344	0.339	0.440	0.432	0.519	0.499
	3	0.459	0.442	0.574	0.568	0.693	0.668
	4	0.562	0.530	0.690	0.683	0.841	0.827
	5	0.650	0.617	0.799	0.792	0.977	0.959
	6	0.743	0.694	0.925	0.918	1.119	1.096
	7	0.825	0.775	1.018	1.011	1.228	1.227
	8	0.912	0.852	1.128	1.120	1.338	1.342
	9	0.994	0.918	1.232	1.224	1.458	1.458
	10	1.059	0.989	1.325	1.306	1.556	1.573
	11	1.136	1.054	1.401	1.393	1.671	1.622
11.24 %	1	0.155	0.155	0.222	0.223	0.211	0.223
	2	0.244	0.244	0.344	0.367	0.350	0.374
	3	0.327	0.327	0.444	0.479	0.461	0.485
	4	0.421	0.393	0.550	0.584	0.560	0.591
	5	0.493	0.460	0.627	0.662	0.649	0.686
	6	0.571	0.526	0.716	0.751	0.744	0.764
	7	0.632	0.592	0.777	0.829	0.832	0.847
	8	0.693	0.653	0.844	0.902	0.910	0.920
	9	0.754	0.714	0.933	0.974	0.982	0.992
	10	0.859	0.758	0.980	1.035	1.049	1.059
	11	0.865	0.819	1.049	1.102	1.100	1.121
13.80 %	1	0.096	0.096	0.125	0.125	0.148	0.148
	2	0.142	0.142	0.177	0.177	0.205	0.205
	3	0.193	0.193	0.234	0.234	0.268	0.268
	4	0.226	0.226	0.268	0.268	0.306	0.306
	5	0.260	0.260	0.302	0.302	0.336	0.336
	6	0.294	0.294	0.331	0.331	0.370	0.370
	7	0.317	0.317	0.353	0.353	0.404	0.404
	8	0.340	0.340	0.382	0.382	0.433	0.433
	9	0.362	0.362	0.405	0.405	0.461	0.461
	10	0.385	0.385	0.433	0.433	0.490	0.490
	11	0.408	0.408	0.456	0.456	0.518	0.518

Table 4 (cont.)

Initial moisture	Time (hrs)	Environmental Condition					
		70% - 60°F		70% - 70°F		70% - 80°F	
		REP 1	REP 2	REP 1	REP 2	REP 1	REP 2
9.26 %	1	0.383	0.383	0.427	0.426	0.580	0.582
	2	0.612	0.618	0.710	0.700	0.960	0.960
	3	0.809	0.821	0.926	0.929	1.241	1.251
	4	0.990	1.007	1.128	1.131	1.526	1.500
	5	1.154	1.166	1.320	1.323	1.772	1.777
	6	1.302	1.324	1.501	1.508	2.015	2.029
	7	1.444	1.477	1.670	1.667	2.245	2.264
	8	1.586	1.631	1.827	1.831	2.461	2.483
	9	1.723	1.762	1.983	1.989	2.686	2.685
	10	1.865	1.893	2.147	2.148	2.844	2.866
	11	1.985	2.025	2.298	2.295	3.030	3.035
11.24 %	1	0.311	0.318	0.361	0.384	0.441	0.457
	2	0.501	0.502	0.605	0.646	0.724	0.738
	3	0.673	0.675	0.810	0.858	0.976	0.986
	4	0.812	0.825	0.994	1.031	1.190	1.206
	5	0.946	0.959	1.171	1.198	1.387	1.397
	6	1.074	1.082	1.327	1.354	1.559	1.578
	7	1.196	1.210	1.471	1.499	1.747	1.747
	8	1.307	1.316	1.610	1.627	1.911	1.916
	9	1.424	1.428	1.746	1.750	2.058	2.063
	10	1.519	1.522	1.868	1.867	2.194	2.174
	11	1.619	1.628	1.993	1.984	2.327	2.310
13.80 %	1	0.262	0.221	0.285	0.256	0.256	0.301
	2	0.382	0.346	0.416	0.404	0.427	0.448
	3	0.468	0.454	0.518	0.518	0.564	0.550
	4	0.547	0.545	0.632	0.614	0.669	0.647
	5	0.627	0.616	0.706	0.705	0.746	0.743
	6	0.684	0.693	0.769	0.779	0.826	0.823
	7	0.741	0.744	0.831	0.847	0.906	0.885
	8	0.798	0.812	0.888	0.916	0.974	0.959
	9	0.855	0.880	0.945	0.972	1.039	1.010
	10	0.912	0.920	0.997	1.029	1.094	1.067
	11	0.969	0.965	1.036	1.081	1.145	1.112

Table 4 (cont.)

Initial moisture	Time (hrs)	Environmental Condition					
		80% - 60°F		80% - 70°F		80% - 80°F	
		REP 1	REP 2	REP 1	REP 2	REP 1	REP 2
9.26 %	1	0.592	0.608	0.739	0.778	0.922	0.944
	2	0.980	1.002	1.221	1.251	1.527	1.552
	3	1.304	1.336	1.626	1.686	2.024	2.063
	4	1.588	1.631	2.004	2.040	2.498	2.523
	5	1.857	1.916	2.354	2.393	2.929	2.961
	6	2.120	2.184	2.683	2.725	3.333	3.350
	7	2.366	2.430	3.006	3.040	3.715	3.749
	8	2.607	2.682	3.307	3.350	4.080	4.110
	9	2.843	2.928	3.597	3.639	4.380	4.461
	10	3.062	3.164	3.865	3.921	4.719	4.787
	11	3.242	3.344	4.133	4.200	5.019	5.085
11.24 %	1	0.545	0.537	0.651	0.668	0.875	0.886
	2	0.901	0.896	1.074	1.064	1.389	1.402
	3	1.184	1.186	1.430	1.403	1.859	1.873
	4	1.484	1.448	1.747	1.698	2.268	2.271
	5	1.723	1.677	2.020	1.976	2.634	2.632
	6	1.951	1.904	2.287	2.226	2.979	2.975
	7	2.174	2.127	2.534	2.471	3.288	3.296
	8	2.379	2.333	2.771	2.705	3.574	3.590
	9	2.574	2.516	2.999	2.916	3.848	3.856
	10	2.757	2.706	3.210	3.133	4.088	4.100
	11	2.924	2.895	3.410	3.339	4.332	4.321
13.80 %	1	0.400	0.399	0.481	0.487	0.617	0.634
	2	0.645	0.632	0.817	0.808	1.002	0.999
	3	0.879	0.877	1.094	1.093	1.304	1.290
	4	1.084	1.076	1.307	1.315	1.576	1.587
	5	1.244	1.247	1.493	1.525	1.810	1.821
	6	1.398	1.401	1.675	1.713	2.014	2.049
	7	1.541	1.540	1.829	1.878	2.199	2.231
	8	1.678	1.663	1.971	2.049	2.373	2.420
	9	1.798	1.788	2.105	2.202	2.524	2.574
	10	1.912	1.902	2.230	2.333	2.670	2.722
	11	2.026	2.016	2.341	2.447	2.822	2.854

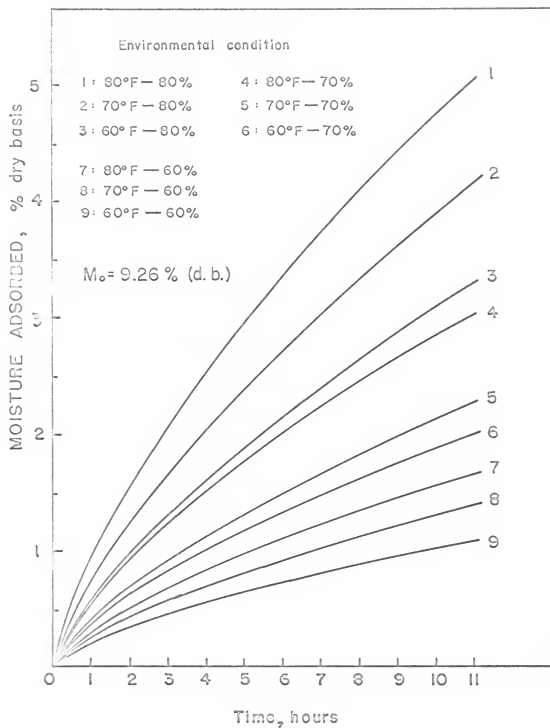


Fig. 2 Adsorption of water vapor by corn ($M_0 = 9.26\%$) at various environmental conditions

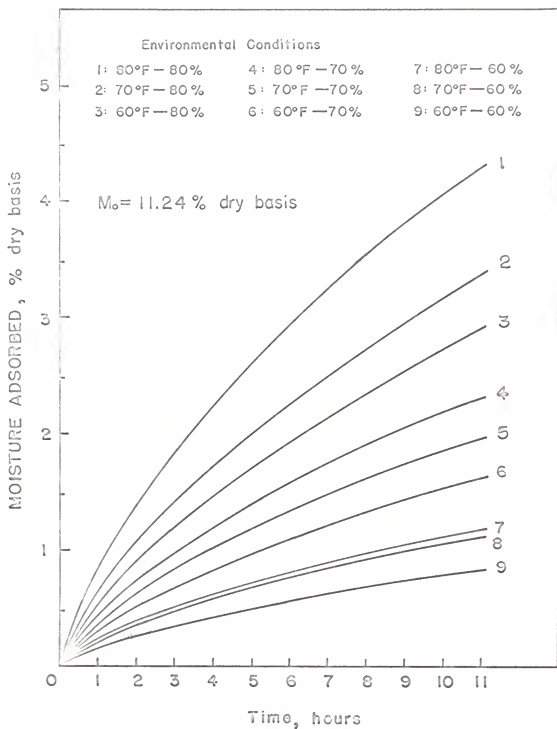


Fig. 3 Adsorption of water vapor by corn ($M_0 = 11.24\%$) at various environmental conditions

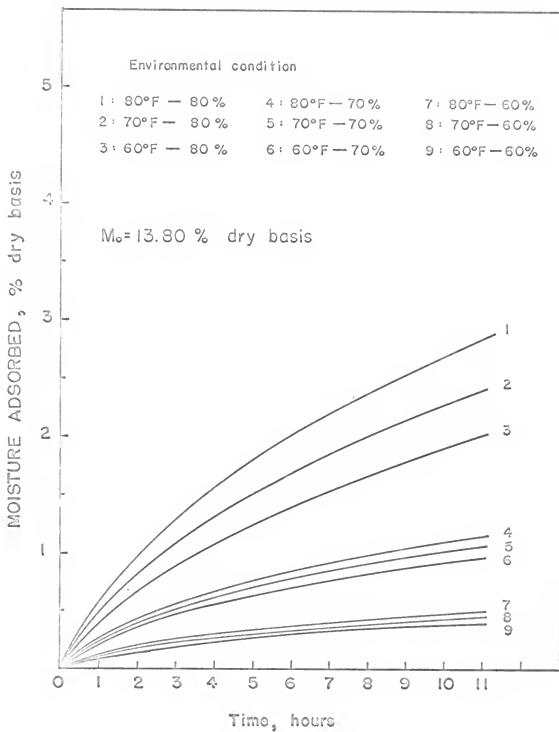


Fig. 4 Adsorption of water vapor by corn ($M_0 = 13.80\%$) at various environmental conditions

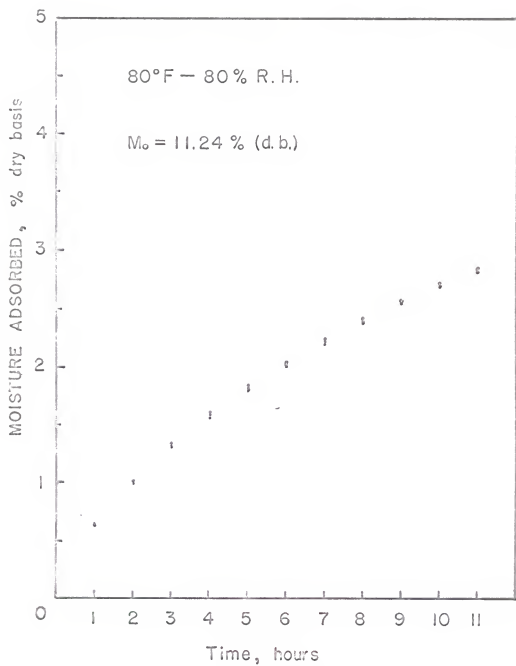


Fig. 5 Three replications of the adsorption of water vapor by corn ($M_o=11.24\%$) at 80°F—80% relative humidity

Effects of Temperature

Effects of temperature on adsorption rate can be observed in Figures 2 through 4. The adsorption rate of corn at a constant relative humidity increased by increasing temperature of the environmental chamber. Frazer and Heard(16) also found in their adsorption study of oxygen by a cobalt chromite catalyst that the rate of adsorption increased with temperature. According to the principle of Le Chatelier, the amount adsorbed at equilibrium state must always decrease with increasing temperature since the adsorption process is always exothermic. The studies by many investigators (9, 19, 39) show that the equilibrium moisture content of corn and other biological materials decreased with increasing temperature.

From the foregoing analysis, it can be predicted that some of the adsorption rate curves in Figures 2, 3, and 4 might cross each other after a considerable amount of time so that the equilibrium moisture content of corn at a constant relative humidity decreases with increasing temperature. Taylor and Sickman(36), in their adsorption rate study of hydrogen by a zinc oxide catalyst, found some rate curves cross each other. The reason for the crossing is that the amount adsorbed when equilibrium is reached decreases with temperature. Thus, it can be expected that rate curve of yellow corn cross each other because the initial rate is higher but the final amount adsorbed is less than that at the lower temperatures.

Effects of Relative Humidity

The effect of relative humidity on the adsorption rate is seen in Figures 2, 3, and 4, showing that the adsorption rate of corn at a constant

temperature increases with increasing relative humidity. The same effect was found for the absorptive capacity of corn (equilibrium moisture content) from the studies made by several investigators(1, 9, 19, 22).

It is interesting to note that the rate of adsorption increases with the increasing of both relative humidity and temperature but not with increasing order of water vapor pressure in the environmental chamber. The order of adsorption rate (from the highest to the lowest) with a specific initial moisture content of corn is summarized in the following table:

Table 5 The ordered environmental conditions according to the adsorption rate and their corresponding water vapor pressures

Environmental condition		Vapor pressure *
<u>R.H. (%)</u>	<u>Temp. (°F)</u>	<u>in Hg</u>
80	80	0.8257
80	70	0.5914
80	60	0.4174
70	80	0.7225
70	70	0.5174
70	60	0.3654
60	80	0.6193
60	70	0.4435
60	60	0.3131

* Values of water vapor pressure were obtained from Thermodynamic Properties of Steam by Keenan and Keys(24).

This table shows that the adsorption rate observed in this study is not in the order of vapor pressure. However, at a given temperature, the adsorption rate is found to be proportional to the vapor pressure of water. This result can be expected because the relative humidity is proportional to the vapor pressure at a constant temperature. A similar result was observed in the

adsorption study of bovine plasma albumin by Eley and Leslie(13).

Effects of Initial Moisture Content

To show the effects of initial moisture content adsorption rate curves of corn of three different initial moisture content levels at 70° F and 80% relative humidity are reproduced in Figure 6. Note in Figure 6 that the rate of adsorption of corn at a constant temperature and relative humidity increases rapidly with decreasing initial moisture content. Similar results are observed in all the other environmental conditions. Such an effect can be explained by the fact that, at a lower moisture content of corn, there exists a greater potential difference between corn and the environment (concentration or vapor pressure difference) which is a driving force for the adsorption process.

Statistical Analysis

For the statistical analysis, adsorption rate data at 5 and 10 hours of adsorption time were analyzed by the factorial design in order to study the effects of main factors and their interactions on the adsorption rate. In this adsorption study there are three main factors; initial moisture content of the sample (M), relative humidity (R), and temperature (T), with three different levels for each factor. At each treatment combination, the experiment was replicated once. Thus, the experiment can be described as a 3x3x3 factorial experiment(10) consisting of 27 treatment combinations per replication.

Since the experimental data tabulated in Table 4 are expressed as the

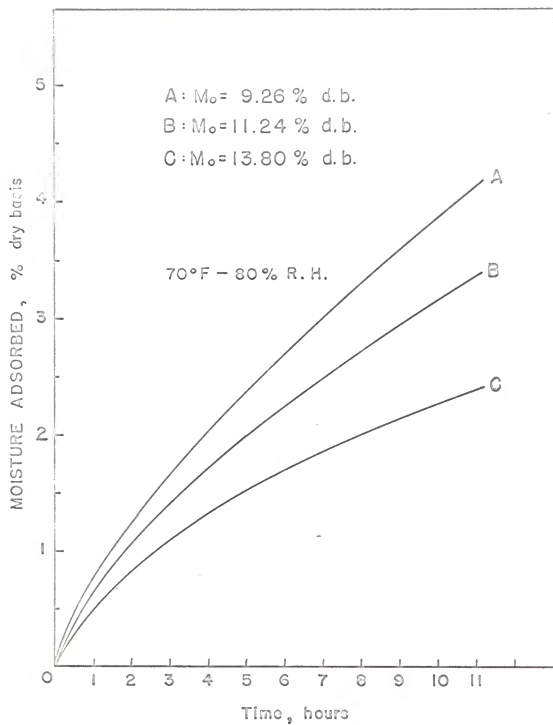


Fig. 6 Adsorption of water vapor by corn at 70°F-80%, showing the effect of initial moisture content

Table 6. Arcsine transformed data of the amount of water vapor adsorbed by corn after five hours and ten hours

Initial moisture	R.H.	Temp.	After 5 hours		After 10 hours	
			rep 1	rep 2	rep 1	rep 2
9.26 %	60%	60°F	4.62	4.51	5.90	5.71
		70°F	5.13	5.11	6.61	6.58
		80°F	5.67	5.62	7.17	7.20
	70%	60°F	6.16	6.20	7.85	7.90
		70°F	6.60	6.61	8.43	8.43
		80°F	7.66	7.67	9.71	9.73
	80%	60°F	7.82	7.94	10.08	10.23
		70°F	8.92	8.82	11.34	11.42
		80°F	9.87	9.93	12.55	12.65
11.24 %	60%	60°F	4.02	3.89	5.15	4.99
		70°F	4.54	4.61	5.68	5.75
		80°F	4.66	4.75	5.88	5.91
	70%	60°F	5.58	5.61	7.09	7.09
		70°F	6.21	6.28	7.86	7.86
		80°F	6.77	6.79	8.52	8.48
	80%	60°F	7.54	7.44	9.56	9.48
		70°F	8.17	8.09	10.33	10.21
		80°F	9.34	9.33	11.67	11.68
13.80 %	60%	60°F	2.92	2.92	3.55	3.56
		70°F	3.15	3.15	3.77	3.77
		80°F	3.32	3.32	4.01	4.01
	70%	60°F	4.54	4.52	5.48	5.48
		70°F	4.82	4.82	5.74	5.83
		80°F	4.96	4.96	6.01	5.94
	80%	60°F	6.41	6.42	7.94	7.92
		70°F	7.03	7.09	8.57	8.59
		80°F	7.73	7.75	9.41	9.50

proportion (ratio), the distribution of such data may tend to be binominal in form(34), and such data may not satisfy the assumptions for the analysis of variance. Therefore, the data are transformed into arcsine of \sqrt{x} where x is the measurement actually taken(17), before performing the analysis of variance.

The arcsine transformed data of amount adsorbed after 5 hours and amount adsorbed after 10 hours are tabulated in Table 6.

Tables 7 and 8 summarize the results of analysis of variance for the data of Table 6. The analyses results show highly significant effects of main factors, namely, initial moisture content, relative humidity, and temperature, and all of the first and the second order interactions between main factors on the adsorption rate of water by yellow corn ($\alpha=0.01$). Although the effects of interactions are found to be all significant, their effects are relatively small compared with the effects of main factors.

Among main factors studied, the order of importance influencing the adsorption rate is first relative humidity, second, initial moisture content, and third, temperature. Such a result can also be seen in Figures 2, 3, and 4. The coupled effects between temperature and relative humidity, and between temperature and initial moisture content are most pronounced among the interactional effects on influencing the adsorption rate. It can be considered that the coupled effect between temperature and relative humidity may be the vapor pressure of water in air, and the coupled effect between temperature and initial moisture content may be the vapor pressure or concentration of water in the original corn. The analysis also shows no significant difference between replications which implies a good reproducibility and reliability of our adsorption data.

The following fixed model was used for statistical analysis of the experimental data.

$$X_{ijkl} = \mu + M_i + R_j + T_k + (MR)_{ij} + (MT)_{ik} + (RT)_{jk} + (MRT)_{ijk} + \epsilon_{ijkl}$$

where X_{ijkl} = the amount of moisture adsorbed under i initial moisture, j relative humidity, k temperature, and l replication

μ = the grand average of all X_{ijkl} conceivable for these specific temperature, relative humidities, and initial moisture contents.

M_i = the true average effect of i initial moisture content relative to μ , R and T . $\Sigma(M_i) = 0$ and $E(M_i) = M_i$

R_j = the true average effect of j relative humidity relative to μ , M and T . $\Sigma(R_j) = 0$ and $E(R_j) = R_j$

T_k = the true average effect of k temperature relative to μ , M and R . $\Sigma(T_k) = 0$ and $E(T_k) = T_k$

$(MR)_{ij}$ = the true average effect of combining the i initial moisture and j relative humidity relative to μ and T . $\Sigma(MR)_{ij} = 0$

$(MT)_{ik}$ = the true average effect of combining the i initial moisture and k temperature relative to μ and R . $\Sigma(MT)_{ik} = 0$

$(RT)_{jk}$ = the true average effect of combining the j relative humidity and k temperature relative to μ and M . $\Sigma(RT)_{jk} = 0$

$(MRT)_{ijk}$ = the true average effect of combining M_i , R_j , and T_k relative to μ . $\Sigma\Sigma(MRT)_{ijk} = 0$

ϵ_{ijkl} = the random error of observation associated with the l th observation within M_i , R_j , and T_k . It is assumed that the ϵ_{ijkl} are NID $(0, \sigma^2)$ variates.

The following hypotheses are tested against their corresponding alternative hypotheses.

$$H_0 (\text{all } M_i = 0), \quad H_0 (\text{all } R_j = 0), \quad H_0 (\text{all } T_k = 0),$$

$$H_0 (\text{all } (MR)_{ij} = 0), \quad H_0 (\text{all } (MT)_{ik} = 0), \quad H_0 (\text{all } (RT)_{jk} = 0),$$

$$H_0 (\text{all } (MRT)_{ijk} = 0), \quad H_0 (\text{all replications are same})$$

Table 7. Analysis of variance for the data
in Table 6 (After 5 hours)

Source of variation	DF	Sum of squares	Mean squares	F
Replication	1	0.00001	0.00001	0.0053
Treatments	26	186.4697	7.1719	3794.6
Initial moisture (M)	2	35.5103	17.7559	9394.3 *
R.H. (R)	2	135.5798	67.7899	35867.6 *
Temperature (T)	2	12.3042	6.1521	3255.1 *
M x R	4	0.1205	0.0301	15.9 *
T x R	4	1.6364	0.4091	216.5 *
M x T	4	1.0657	0.2667	141.1 *
M x R x T	8	0.2528	0.0315	16.7 *
Error	26	0.0492	0.0019	
Total	53	186.5189		

* significant with any reasonable α

Table 8. Analysis of variation for the data
in Table 6 (After 10 hours)

Source of variation	DF	S.S	M.S	F
Replication	1	0.00004	0.00004	0.0134
Treatments	26	311.4389	11.9784	4000.8
M	2	73.4937	36.7469	12273.5 *
R	2	215.9829	107.9915	36069.3 *
T	2	17.4643	8.7321	2916.6 *
M x R	4	0.1591	0.0398	13.3 *
T x R	4	2.2323	0.5581	186.4 *
M x T	4	1.7435	0.4359	145.6 *
M x R x T	8	0.3631	0.0454	15.2 *
Error	26	0.0779	0.0030	
Total	53	311.5167		

The adsorption of water vapor by yellow corn in this investigation is very slow compared to the physical adsorption of industrial gases on solids investigated by many researchers. For example, yellow corn ($M_0 = 9.26\%$) adsorbs only 5% of its own weight at 80°F - 80% relative humidity for 11 hours. The slow adsorption process on yellow corn is probably due to the following physical aspects:

- (1). The blocking of the adsorption by water vapor molecules already adsorbed since the corn samples investigated have already had a considerable amount of initial moisture (9.26%, 11.24%, and 13.80%).
- (2). Resistance of air to the movement of water vapor. The effect of gaseous impurities on the rate of adsorption was studied by Patrick and Cohan(28) who found that if there are impurities presented either in the gas phase or in the adsorbed phase, the rate of adsorption is slowed down considerably.
- (3). Diffusion of water vapor into some of the fine pores of the yellow corn after the fast initial adsorption process.

According to the adsorption rate data obtained in this investigation, the adsorption of water vapor by yellow corn may not be considered as a pure physical adsorption alone, but considered as a combination of physical adsorption and diffusion process. At the initial stage, the adsorption of water vapor takes place in yellow corn forming multi-molecular layers of water; the slow diffusion of water vapor follows at the later stage.

Application of Elovich-Zhabrova (or Zeldovich-Roginski) Equation

Zeldovich and Roginski(30) found that the rate of adsorption of CO on N_2O_2 decreases exponentially with the increase of the amount m of gas adsorbed,

$$dm/dt = a \exp(-\alpha m) \quad (18)$$

where a and α are constants over the course of the process. The same equation was found by Elovich and Zhabrova(14).

Integrating the equation(18) with the boundary condition that $m=0$ when $t=0$, we obtain

$$\begin{aligned} m &= (2.303/\alpha) \log(t+1/\alpha a) - (2.303/\alpha) \log(1/\alpha a) \\ \text{i.e.} \quad m &= A \log(t+t_0) - C \end{aligned} \quad (19)$$

where $A = 2.303/\alpha$, $t_0 = 1/\alpha a$ and $C = A \log(t_0)$

A plot of m vs. $\log(t+t_0)$ should yield a straight line with a slope A and intercept $-C$ if " t_0 " is chosen correctly by trial and error methods(37).

Thus, the analysis involves first to evaluate a disposable parameter, " t_0 ". With " t_0 " too small, the curve is convex, and with " t_0 " too large it is concave to the axis of $\log(t+t_0)$. This is illustrated in Fig. 7, drawn from the data in Table 4. It was found in this investigation that " t_0 " is a constant with very good approximation if initial moisture content of a sample is fixed.

Elovich plots for the data in Table 4 are shown in Figures 8, 9, and 10. Elovich equations were obtained by using the method of least squares to evaluate the slope and the intercept, and those values are tabulated in Table 9.

The effects of temperature and relative humidity on the slope of Elovich

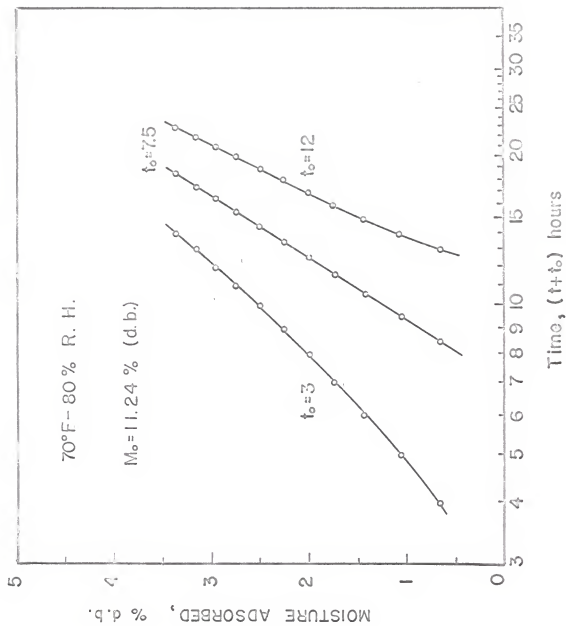


Fig. 7 Dependence of t_0 on Elovich plot of adsorption rate data of corn at 70°F - 80% relative humidity

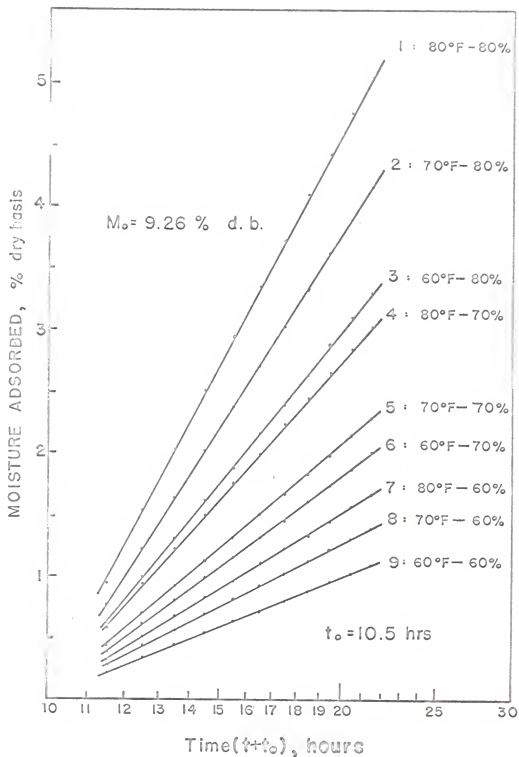


Fig. 8 Elovich plots of adsorption of water vapor by corn ($M_0 = 9.26\%$) at various environmental conditions

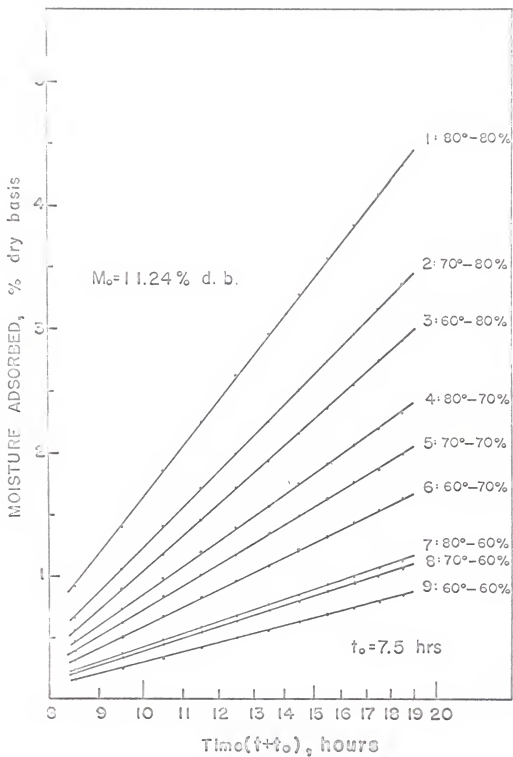


Fig. 9 Elovich plots of adsorption of water vapor by corn ($M_0=11.24\%$) at various environmental conditions

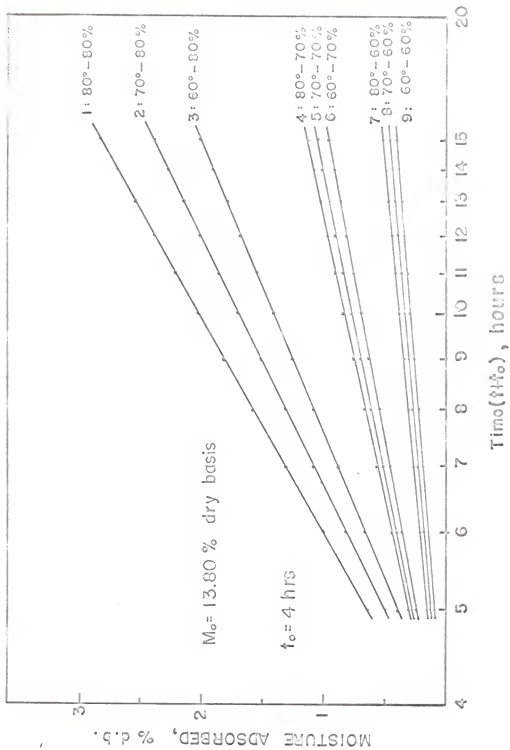


Fig. 10 Elovich plots of adsorption of water vapor by corn
 ($M_0=13.80\%$) at various environmental conditions

Table 9. Tabulation of the slope, A, and the intercept, C, in Equ.

$$m = A \log(t+t_0) - C$$

Initial moisture	Relative humidity	Temp.	A		C	
			rep 1	rep 2	rep 1	rep 2
9.26%	60%	60°F	3.355	3.053	3.338	3.023
		70°F	4.095	4.055	4.057	4.017
		80°F	4.866	5.013	4.817	5.003
	70%	60°F	5.836	5.984	5.797	5.953
		70°F	6.787	6.787	6.753	6.756
		80°F	8.935	9.023	8.864	8.961
	80%	60°F	9.722	10.061	9.704	10.053
		70°F	12.429	12.491	12.434	12.464
		80°F	14.997	15.182	14.948	15.121
11.24%	60%	60°F	2.215	1.963	1.833	1.681
		70°F	2.434	2.567	2.040	2.150
		80°F	2.649	2.623	2.247	2.199
	70%	60°F	3.854	3.864	3.273	3.276
		70°F	4.799	4.673	4.095	3.932
		80°F	5.572	5.484	4.726	4.622
	80%	60°F	7.042	6.901	5.988	5.874
		70°F	8.106	7.845	6.866	6.622
		80°F	10.232	10.207	8.605	8.571
13.80%	60%	60°F	0.645	0.645	0.355	0.355
		70°F	0.681	0.681	0.350	0.350
		80°F	0.769	0.769	0.393	0.393
	70%	60°F	1.433	1.553	0.750	0.861
		70°F	1.569	1.706	0.802	0.927
		80°F	1.823	1.695	0.993	0.877
	80%	60°F	3.399	3.388	1.946	1.941
		70°F	3.847	4.107	2.178	2.385
		80°F	4.563	4.676	2.552	2.638

plot can be observed in Figures 8, 9, and 10. The slope of Elovich plot at a constant relative humidity increases with increasing temperature and the slope at a constant temperature increases with increasing relative humidity.

Elovich transformation of Fig. 6 is reproduced in Fig. 11 to show the initial moisture content effects on the slope of Elovich plot. It was also found from Fig. 11 that the slope at a constant temperature and relative humidity increases rapidly with decreasing initial moisture content of corn.

Analysis of variance based on the slope of Elovich plot is performed and the results are tabulated in Table 10.

Table 10 Analysis of variance for the slope, A , in Elovich equation:

$$m = A \log(t + t_0) - A \log(t_0)$$

Source of variation	DF	Sum of squares	Mean squares	F
Replication	1	0.0035	0.0035	0.3133
Treatment	26	721.599	27.7538	2484.7
M	2	304.915	152.4576	13648.8*
R	2	321.3236	160.0618	14383.3*
T	2	32.7799	16.3900	1467.3*
M x R	4	39.5145	9.8786	884.4*
T x R	4	9.1242	2.2811	204.2*
M x T	4	11.8276	2.9569	264.7*
M x R x T	8	2.1135	0.2642	23.7*
Error	26	0.2905	0.0112	
Total	53	721.8890		

* Significant with any reasonable α .

Inferences drawn from the result of analysis of variance based on the slope of Elovich plot are exactly the same as those drawn from the result based on the original rate data.

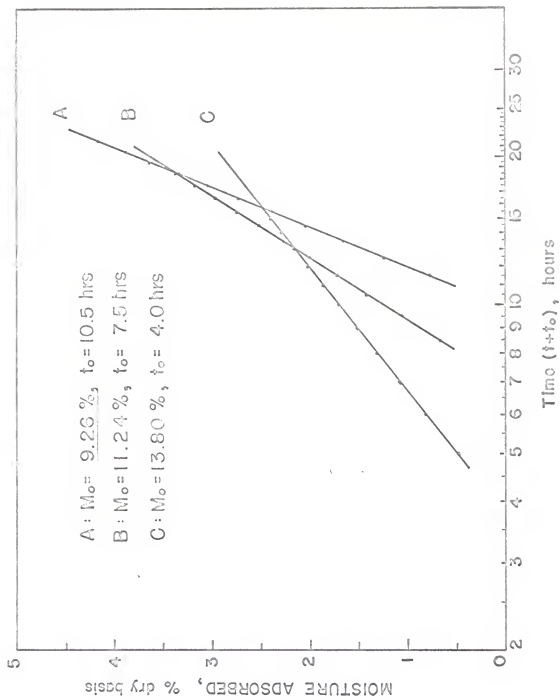


Fig. 11 Elovich plots of the adsorption of water vapor by corn at 70°F-80% R.H., showing the effect of initial moisture content

Indeed, the analysis shows that the adsorption rate of water vapor by yellow corn or other cereal grains can be well described by Elovich equation.

Analysis of the Slope, A, in Elovich Plot

The examination of slope, A, indicates that the slope is directly related to the relative humidity (see Figs. 8, 9, and 10). If the slope, A, is plotted against relative humidity in logarithmic scale for various initial moisture contents and temperatures, a series of parallel straight lines was found at a constant initial moisture content as shown in Fig. 12 (a) and (b). These figures show that there is a functional relationship between the slope, A, and relative humidity. That is,

$$A = A'(R.H.)^n \quad (20)$$

where R.H. = relative humidity, a decimal

A' and "n" are constants

Values of "n" were evaluated by using the method of least squares, and the results are tabulated in the following table.

Table 11 The values of "n" in equation:

$$A = A'(R.H.)^n$$

M ₀	Temperature (°F)			
	60°F	70°F	80°F	Avg.
9.26%	3.918	3.872	3.884	3.890
11.24%	4.261	4.038	4.710	4.340
13.80%	5.960	6.127	6.214	6.100

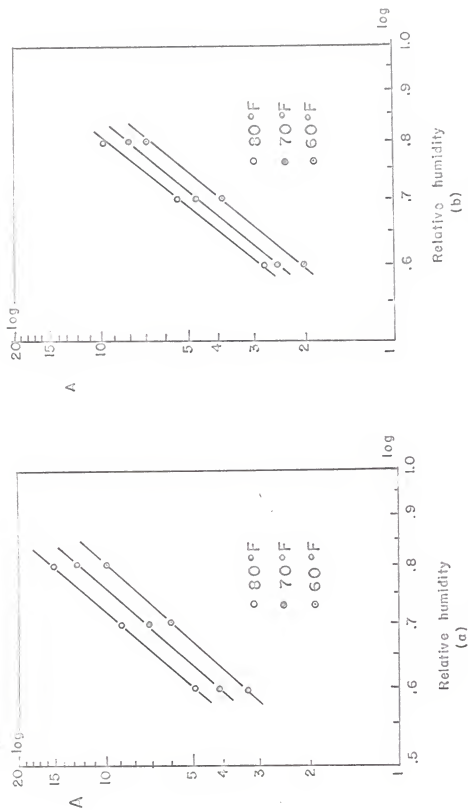


Fig. 12 Relationship between the slope, A , in Equ. (19) and relative humidity at 9.26% (a) and 11.24% (b) initial moisture content

The above table shows that "n" remains almost constant for a given initial moisture content, regardless of temperature. Therefore, "n" is just a function of initial moisture content alone. That is,

$$n = f(M_0) \quad (21)$$

Values of A' were calculated using the average values of "n" in Table 11 and are summarized in Table 12. It can be noted that the value of A' is a constant if initial moisture content and temperature are fixed so that $A' = f(T, M_0)$.

Table 12 Calculated value of A' in the equation:

$$A = A' (R.H.)^n$$

Environmental condition	Initial moisture content		
	9.26%	11.24%	13.80%
60°F - 60%	23.388	18.770	14.037
- 70%	23.668	18.143	12.825
- 80%	23.562	18.361	13.032
70°F - 60%	29.723	22.961	14.821
- 70%	27.181	22.266	14.068
- 80%	29.681	21.055	15.273
80°F - 60%	36.028	24.206	16.735
- 70%	35.951	25.980	15.111
- 80%	35.944	26.915	17.740

If A' is plotted against temperature for various initial moisture contents (Fig. 13), it was found that there is a linear functional relationship between A' and temperature. That is,

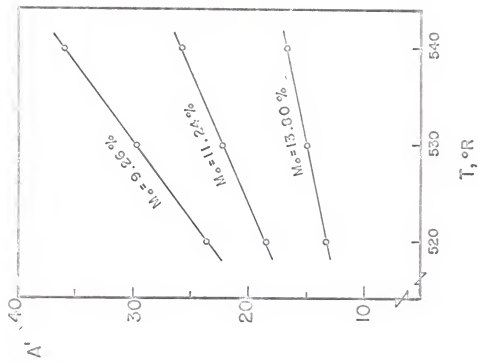


Fig. 13 Plot of A' in Equ(20) against temperature for various initial moisture contents

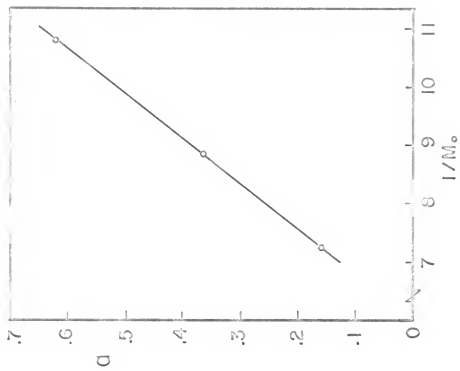


Fig. 14 Plot of " a " in Equ.(22) against the reciprocal of initial moisture contents

$$\Lambda' = aT - b$$

i.e.

$$\Lambda' = a(T - T_0) \quad (22)$$

where $T = t + 460$, $^{\circ}\text{R}$ and $T_0 = b/a$

The values of "a" and T_0 were evaluated by the method of least squares and are tabulated in Table 13.

Table 13 Values of "a" and T_0 in equation:

$$\Lambda' = a(T - T_0)$$

M_0 (% d.b.)	"a"	T_0 ($^{\circ}\text{R}$)
9.26%	0.6215	482
11.24%	0.3645	470
13.80%	0.1615	436

Furthermore, the plot of "a" against the reciprocal of initial moisture content (Fig. 14) indicates that the value "a" can be expressed in terms of initial moisture content by the equation:

$$a = (12.961/M_0) - 0.781 \quad (23)$$

where M_0 = initial moisture content, % dry basis

From equations (20), (22), and (23), the slope, Λ , in Elovich plot can be expressed as follows;

$$\Lambda = a(T - T_0)(\text{R.H.})^n \quad (24)$$

where T = absolute temperature, °R

$$a = (12.961/M_0) - 0.781$$

T_0 and n = constants depending on initial moisture content as shown in Tables 11 and 13.

Using this developed equation (24), the values of A were calculated and these calculated values (Table 14) were found to be very close to the experimental data to a very good approximation.

Table 14 Calculated value of the slope, A , in Elovich rate equation (19)

M_0	R.H.	Temperature		
		60°F	70°F	80°F
9.26%	60%	3.223	4.071	4.919
	70%	5.870	7.414	8.959
	80%	9.868	12.465	15.062
11.24%	60%	1.985	2.390	2.795
	70%	3.877	4.668	5.460
	80%	6.921	8.334	9.746
13.80	60%	0.589	0.659	0.729
	70%	1.507	1.687	1.866
	80%	3.405	3.810	4.216

Analysis of the Intercept in Elovich Plot

According to the integrated form of Elovich equation (Eq. 19), the intercept, C , which is defined as " $A \log(t_0)$ ", should be automatically fixed with known A and " t_0 " if the adsorption rate data satisfy the theory

and assumption involved in Elovich equation. The intercept, C, evaluated by Elovich plot fairly well agrees with the expected theoretical value of C, "A log (t₀)". However, the intercept, C is consistently lower than the corresponding expected value of intercept by a certain factor, and the deviation between two corresponding values becomes greater as the initial moisture content of corn increases. It appears that this deviation is mainly caused by the inherent error which results in evaluating "t₀". It should be noted again that since "t₀" is evaluated by the trial and error method, it is almost impossible to find the true "t₀". Perhaps, the value of "t₀" can be refined by the iteration method with the aid of a computer.

The rate of the difference, which will be called correction factor hereafter, by which the experimental data of the intercept differed from the "A log (t₀)" were calculated using the relationship;

$$\text{correction factor, } \lambda = \frac{\text{the intercept, C}}{A \log (t_0)}$$

The correction factor is found to be the same at a specified initial moisture content regardless of the relative humidity and temperature of air. The correction factors evaluated are tabulated in the following Table 15.

Table 15 Tabulation of correction factor, λ , for refinement of the integrated Elovich equation

M ₀ (% d.b.)	t ₀ (hrs)	λ
9.26	10.5	0.975
11.24	7.5	0.967
13.80	4.0	0.900

Then, the intercept, C, can be given by the expression:

$$C = \lambda A \log(t_0) \quad (25)$$

From the foregoing analysis, the semi-empirical equation developed can be written as follows:

$$m = (12.96/M_0 - 0.78) (T - T_0) (R.H.)^n \log(t + t_0) - \lambda A \log(t_0) \quad (26)$$

where T_0 , n , and λ for a given initial moisture content are summarized in the following Table 16.

Table 16 Tabulation of T_0 , n , and λ for different initial corn moistures

M_0	T_0	n	λ
9.26%	482	3.89	0.975
11.24%	470	4.34	0.976
13.80%	436	6.10	0.900

The Applicability of Adsorption Kinetics Equation Developed

The semi-empirical equation developed was tested with samples from three different levels of initial moisture content with environmental conditions 70° F - 80% R.H. and 80° F - 70% R.H. The calculated values are tabulated in Table 17 together with experimental data for comparison and are reproduced in Figures 15 and 16. A remarkably close agreement between experimental data and the semi-empirical equation developed is seen in

Table 17. Comparison of calculated and experimental adsorption rate data

Initial moisture	Time (hrs)	Environmental Condition			
		80°F - 70%		70°F - 80%	
		cal.	exp.	cal.	exp.
9.26%	1	0.583	0.581	0.778	0.759
	2	0.907	0.960	1.262	1.236
	3	1.206	1.246	1.678	1.656
	4	1.484	1.513	2.065	2.022
	5	1.744	1.775	2.426	2.374
	6	1.987	2.022	2.765	2.704
	7	2.216	2.255	3.083	3.023
	8	2.432	2.472	3.384	3.329
	9	2.637	2.672	3.669	3.618
	10	2.831	2.855	3.939	3.893
	11	3.017	3.030	4.204	4.167
11.24%	1	0.454	0.449	0.693	0.660
	2	0.718	0.731	1.096	1.069
	3	0.955	0.981	1.458	1.417
	4	1.171	1.198	1.787	1.723
	5	1.369	1.392	2.088	1.998
	6	1.551	1.569	2.367	2.257
	7	1.721	1.747	2.625	2.503
	8	1.879	1.914	2.866	2.738
	9	2.027	2.061	3.092	2.958
	10	2.166	2.184	3.305	3.172
	11	2.298	2.319	3.506	3.375
13.80%	1	0.294	0.279	0.598	0.484
	2	0.440	0.438	0.900	0.813
	3	0.565	0.557	1.155	1.094
	4	0.673	0.658	1.376	1.311
	5	0.769	0.745	1.571	1.509
	6	0.854	0.825	1.745	1.694
	7	0.932	0.900	1.903	1.854
	8	1.002	0.967	2.047	2.010
	9	1.067	1.025	2.179	2.154
	10	1.127	1.081	2.302	2.282
	11	1.183	1.129	2.416	2.394

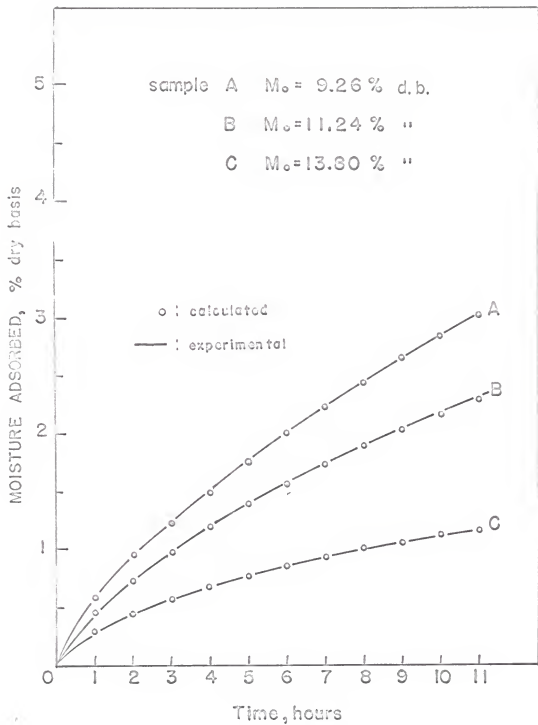


Fig. 15 Comparison between experimental adsorption rate data and corresponding calculated rate data at 80°F-70% R.H.

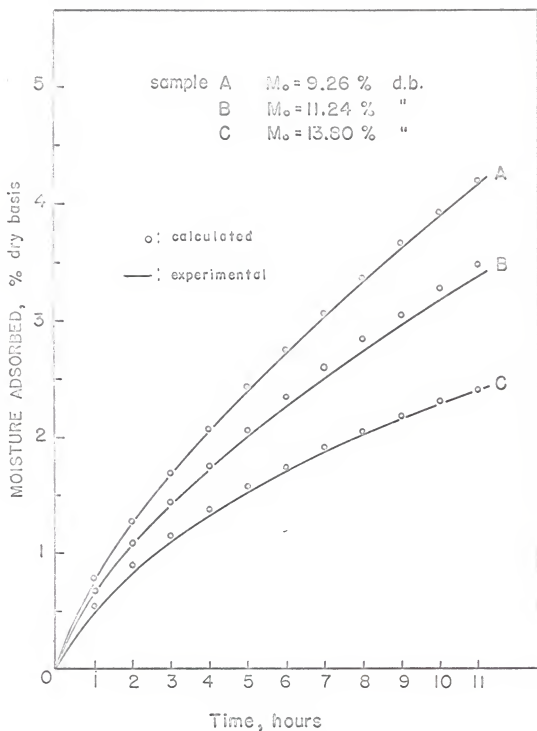


Fig. 16 Comparison between experimental adsorption rate data and corresponding calculated data at 70°F-80% relative humidity

Figures 15 and 16.

In order to further test the applicability of the semi-empirical equation to experimental data, statistical tests of the comparison of two groups (the calculated and experimental data) were performed. The "t" distribution furnishes a test of the hypothesis:

$$H_0(\mu_1 = \mu_2) \text{ against } H_a(\mu_1 \neq \mu_2)$$

where μ_1 and μ_2 are population means of group 1 (calculated) and group 2 (experimental).

$$t = \frac{(\bar{x}_1 - \bar{x}_2) - (\mu_1 - \mu_2)}{S_{\bar{x}_1 - \bar{x}_2}}$$

where \bar{x}_1 and \bar{x}_2 are sample means of group 1 and group 2 respectively, and $S_{\bar{x}_1 - \bar{x}_2}$ is the sample standard error of difference between means.

The value of "t" was calculated with experimentally obtained data and calculated data. For example, means and sums of squares, calculated for the adsorption data at 70° F - 80% R.H. with the sample of 11.24% initial moisture contents are:

$$\bar{x}_1 = 2.262 \text{ at } n = 11, \Sigma x^2 = 8.555$$

$$\bar{x}_2 = 2.170 \text{ at } n = 11, \Sigma x^2 = 7.807$$

Then,

$$S_{\bar{x}_1 - \bar{x}_2}^2 = \frac{8.555 + 7.807}{11(11 - 1)} = 0.0091$$

$$S_{\bar{x}_1 - \bar{x}_2} = 0.094$$

Therefore $t = (2.262 - 2.170)/0.0954 = 0.092/0.0954 = 0.965$

Let α , the probability of a Type I error, be 0.10, the corresponding value of "t" from a table of the "t" distribution (34) is 1.725 at $DF = 20$. This indicates that the calculated value of "t" is in the region of acceptance.

Therefore the null hypothesis, $H_0(\mu_1 = \mu_2)$ is accepted. Thus, it can be concluded that there is no difference between the group of experimental data and the group of calculated data. In testing this hypothesis for other samples at different environmental conditions, the same conclusion was drawn.

In addition to the visual comparison of two groups of data, the statistical tests performed definitely support the excellent applicability of the semi-empirical equation developed to describe the adsorption rate over the entire range of factors investigated.

However, the equation developed would not satisfy the limiting condition of the equilibrium state. To develop the equation which will satisfy the limiting condition of equilibrium state we might have to introduce the concept of equilibrium moisture content (21).

Several investigators (3,4) have attempted to correlate the adsorption rate approaching to equilibrium state by the diffusion model equation. This model assumes that the moisture diffuses into the grain according to Fick's law (11). Those equations were discussed in the literature review section. In the application of the diffusion model equations to adsorption process, the diffusion coefficient, D , assumed to remain constant throughout the adsorption process but the observed results always have indicated that D increases as the moisture content of the grain increases (see reference(3) for further details). With the expression of D as a function of moisture content, the diffusion model equation would become a very complicated form.

Adsorption Rates of Water Vapor by Damaged Corn Samples

The present official method for determining damage involves individual analysis for damaged and heat-damaged kernels by hand separation. This method

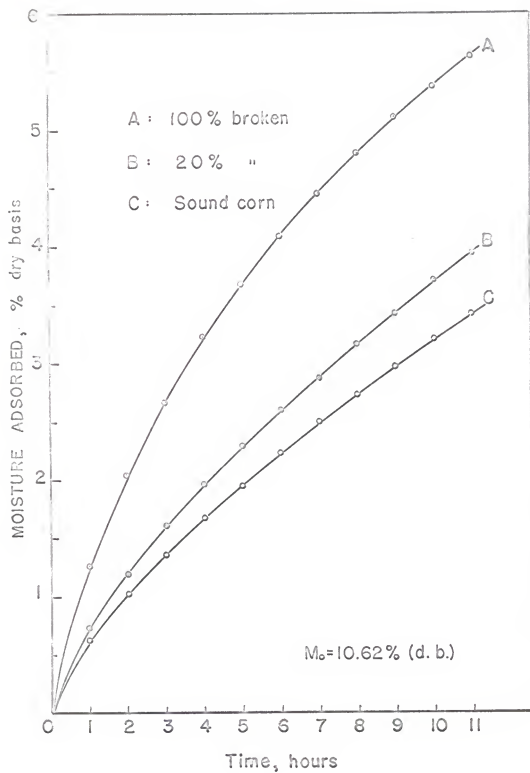


Fig. 17 Adsorption of water vapor by sound and broken corn samples at 70°F-80% R. H.

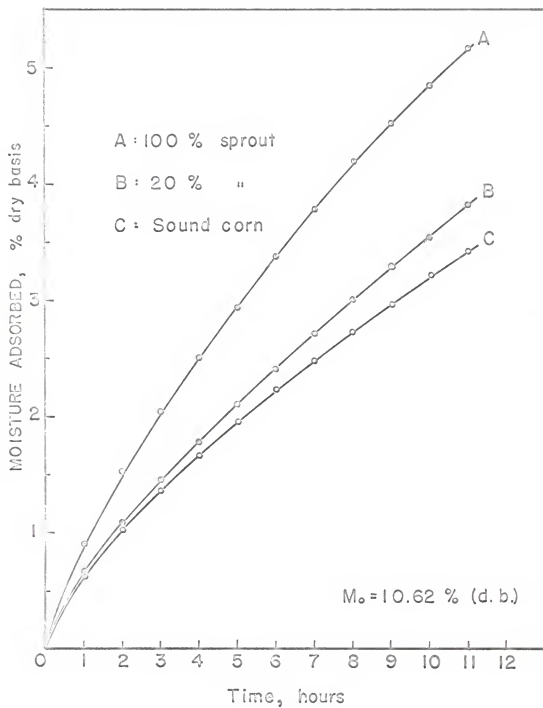


Fig. 13 Adsorption rate of water vapor by sound and sprout corn samples at 70°F-80% R. H.

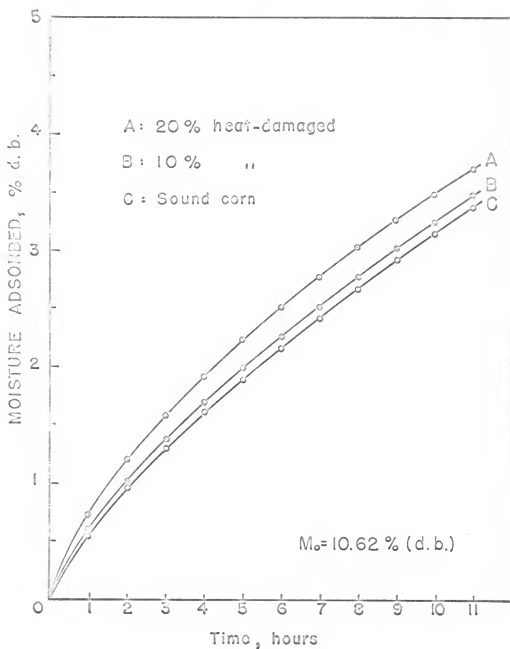


Fig. 19 Adsorption of water vapor by sound and heat-damaged corn samples at 70°F-80% relative humidity

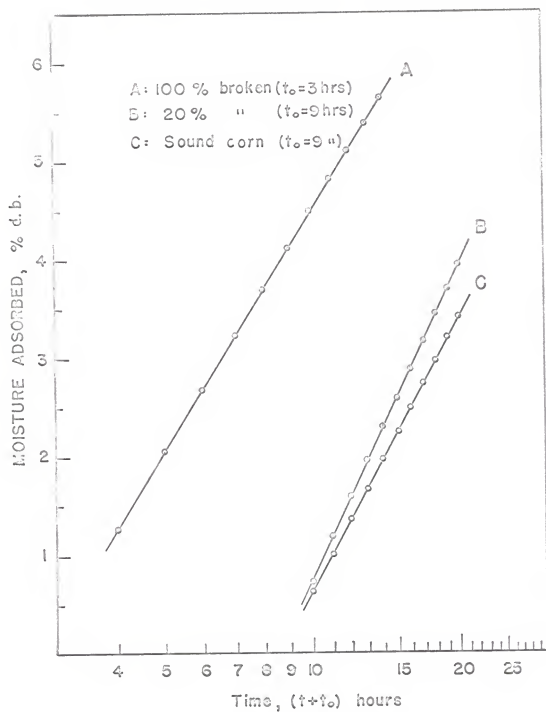


Fig. 20 Elovich plots of the adsorption of water vapor by sound and broken corn samples at 70°F-80% relative humidity

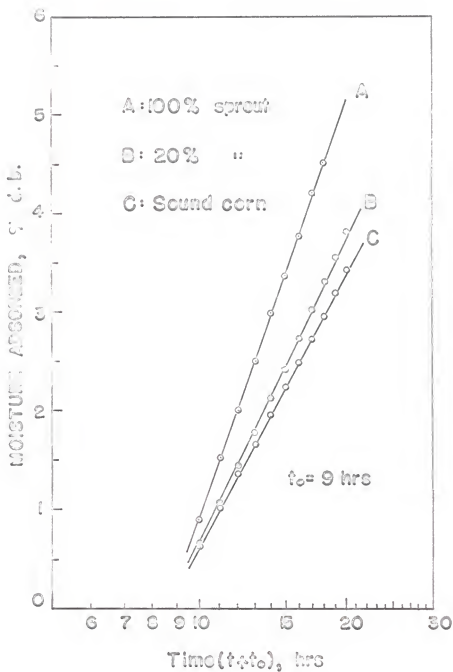


Fig. 21 Elovich plots of the adsorption rate of water vapor by sound and sprout corn samples at 70°F — 80% relative humidity

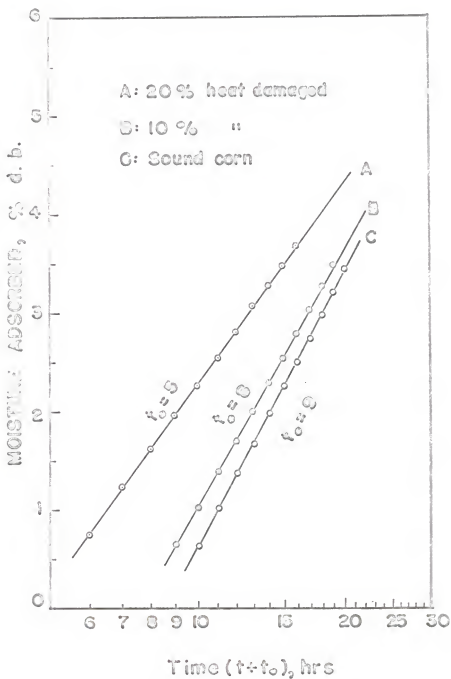


Fig. 22 Elovich plots of the adsorption of water vapor by sound and heat-damaged corn samples at 70°F - 80% relative humidity

is indeed tedious and time-consuming. Numerous investigations on methods of evaluating damaged grain have been attempted in order to eliminate individual analyses for damaged and heat-damaged kernels. In reviewing various investigation methods used in determining damage, a definite method, applicable to various conditions of different kinds of grains, has not been established. Thus, one of the purposes of this adsorption rate study with damaged yellow corn is to investigate the possibility of damage detection from the rate of adsorption.

adsorption rate of water vapor by sound and damaged corn samples at 70° F - 80% relative humidity was conducted to find out if it was possible to detect the difference between sound and damaged samples. The results are shown in Figures 17, 18, and 19.

Analyses of the results showed there were distinct differences in adsorption rates between different types of damage and between different levels of a specified damage. Elovich plots for broken, sprout, and heat-damaged samples are shown in Figures 20, 21, and 22, respectively. These plots showed distinct rate differences between different types and levels of a specified damage.

The adsorption rate of a broken sample was much higher than that of a sound sample because of higher specific conductance of broken kernels compared with kernels whose endosperm is not exposed. In other words, the resistance to movement was considerably reduced in the broken kernels. More adsorptive sites are readily available in the broken kernels than the sound ones. Several workers(9, 38) have pointed out that the hygroscopic properties of corn change significantly during the artificial drying at high temperature. The adsorption rate difference between a heat-damaged sample and

a sound sample may be explained in terms of hygroscopic properties of corn. The molecular shrinkage on the high temperature drying of yellow corn would cause the difference in availability of active site to water vapor in adsorption process, compared with that of sound grain. The adsorption rate of sprout sample was much higher than that of sound sample. This rate difference may be caused by the adsorptive potential difference and the difference in specific volume between sprout and sound grain.

The results of this preliminary investigation showed a possibility of evaluating the damage in a grain sample with the adsorption rate method.

Further detailed adsorption study of damaged grains will be left for future study.

CONCLUSIONS

The following conclusions were drawn from the analyses and data presented:

1. The adsorption rate data obtained in this investigation showed a good reproducibility and reliability of data. This indicates that a corn sample of a particular variety with same history will produce the same adsorption rate at a specific environmental condition.
2. Temperature, relative humidity, and initial moisture content have very significant effects on the rate of adsorption. The adsorption rate at a specific environmental condition increases with decreasing initial moisture content. The rate of adsorption increases with increasing relative humidity and with increasing temperature over the entire range of environmental condition investigated.
3. The coupled effects between temperature and relative humidity (the water vapor pressure of the air), and between temperature and initial moisture content (the vapor pressure or concentration of water of the yellow corn) are most pronounced among the interactional effects on influencing the adsorption rate.
4. In general, the adsorption of water vapor by yellow corn is a slow process, in contrast with that of pure gas by organic or inorganic adsorbents. The mechanism of adsorption kinetics of yellow corn is such that, at the initial stage, the adsorption of water vapor takes place in yellow corn, forming multi-molecular layers of water, and at the later stage, the slow diffusion of water follows.
5. The adsorption rate data obtained in this study correlated very well with

the Elovich-Zhabrova (or Roginskii-Zoldovich) adsorption kinetics equation;

$$dm/dt = a e^{-\alpha m}$$

with the exponent α remaining constant over the course of the adsorption process.

6. The semi-empirical equation developed in this adsorption study is,

$$m = A \log(t+t_0) - \lambda A \log(t_0)$$

where $A = (12.96/M_0 - 0.78)(T - T_0)(R.H.)^n$

λ = correction factor

The above developed semi-empirical equation conformed very well with the experimental rate data.

7. The experimental data did show distinct differences in adsorption rates between different types of damage and between different levels of a specified damage, compared with that of sound grain. It is possible to predict the percentage of sound grain in a grain sample from the adsorption rate data.
8. The optimum environmental condition to conduct the adsorption rate test, under which sound and damaged grain are investigated, will be 70° F - 80% relative humidity.

SUGGESTIONS FOR FUTURE RESEARCH

The following suggestions are recommended for future research:

1. Study the effects of temperature, relative humidity, and initial moisture content on the rate of adsorption at two more levels of those three factors other than those investigated in this work and test the semi-empirical equation developed.
2. Study the effect of initial moisture content on constants, T_0 , n , and λ in the semi-empirical equation developed such that the functional relationship between constants and initial moisture content may be obtained.
3. Study the effect of initial temperature of the sample, which is different from that of the testing environmental condition, on the rate of adsorption.
4. Conduct the similar adsorption kinetics study with other cereal grains such as wheat, grain sorghum, barley, and rye.
5. Conduct the comprehensive investigation of the adsorption rate differences between different types of damage and between different levels of a specified damage of cereal grains, compared with that of sound grains.

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ADSORPTION KINETICS OF WATER VAPOR
BY YELLOW CORN

by

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AN ABSTRACT OF A MASTER'S THESIS

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The nature of the relation existing between cereal grains and the molecules of water vapor that are adsorbed on its surface is not only of great practical importance in grain storage and trades, but a knowledge of it is fundamental for a proper understanding of the phenomenon of adsorption and its application.

The purposes of this investigation were, first, to investigate the effects of three factors, temperature, relative humidity, and initial moisture content on the adsorption rate of water vapor by yellow corn; second, to develop an adsorption rate equation which would be applicable for cereal grains; third, to find the possibility to detect the percentage of sound grain in a grain sample from the adsorption rate data.

Corn samples of three different levels of initial moisture content were used in this investigation to obtain the adsorption rate data at three different levels of dry-bulb temperature and relative humidity, respectively. The continuous weight change of the sample in the environmental chamber, which was maintained at constant temperature and relative humidity, was recorded by an electrobalance.

It was found that the adsorption rate of water vapor by corn increases with decreasing initial moisture content and increases with increasing temperature and relative humidity of the environmental condition.

Statistical analysis showed significant effects of initial moisture content, relative humidity, and temperature, and the first and second order interactional effects involved. However, the interactional effects on the adsorption rate was relatively small compared with effects of main factors investigated.

The adsorption rate data obtained in this investigation very well followed

the Elovich-Zhabrova (or Roginskii-Zeldovich) adsorption kinetics equation. The semi-empirical equation was developed based on the Elovich-Zhabrova adsorption kinetics equation. That is,

$$m = A \log(t + t_0) - \lambda A \log(t_0)$$

where $A = (12.96/M_0 - 0.78)(T - T_0)(R.H.)^n$

λ = correction factor

The above semi-empirical equation very well described the experimental adsorption rate data of yellow corn.

Adsorption rate study with damaged corn samples was conducted to find out if it was possible to detect the differences between sound and damaged samples. All adsorption curves obtained for various damaged corn also followed the Elovich-Zhabrova adsorption kinetics equation. The Elovich-Zhabrova plots for samples tested indicated distinct differences in adsorption rates between different types of damage and between different levels of a specified damage, compared with that of sound samples. The results suggested that it is possible to predict the percentage of sound grain in a grain sample from the adsorption rate data.