Adsorption Kinetics of Water Vapor by Yellow Corn.
I. Analysis of Kinetic Data for Sound Corn[1]

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ABSTRACT

Adsorption rates of water vapor by yellow corn samples at three initial moisture contents were examined under various environmental conditions by a continuous measurement system. In order of importance the factors influencing the adsorption rate were relative humidity, initial moisture content, and temperature. The kinetic data were well described by the Elovich adsorption kinetic equation. A semiempirical equation, based on the Elovich equation, was developed, and agreement between experimental data and data generated by this equation was remarkably close.

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Physical and chemical changes take place continuously in all grains during storage and handling. Of various factors influencing the rate of these changes, moisture and temperature are by far the most important (1).

Numerous attempts have been made to understand the adsorption and desorption processes of gases or water vapor on solid substances and to develop an expression relating the equilibrium state of the material to the environmental conditions. Although the adsorption isotherms of grain have been studied extensively (1,2,3), the adsorption kinetics of water vapor by grains have not been well explored.

Many investigators have studied the adsorption kinetics of industrial gases on solid substances, and some of them have developed adsorption-rate equations (4,5,6,7). Applying adsorption theories of these materials to the adsorption of water vapor by biological materials, such as cereal grains, may be helpful in understanding the nature of adsorption phenomena as well as the effects of factors which influence the rate of adsorption. Moreover, proper understanding of the adsorption kinetics will provide useful information on grain quality and a guide for grain conditioning, storing, processing, and fumigating.

The objectives of this investigation were: to study the nature of adsorption kinetics of water vapor by corn to provide useful information on grain storage and drying; to investigate the effects of environmental conditions (temperature and relative humidity), and of initial moisture content of corn on the adsorption rate of water vapor; and to develop an expression to describe the adsorption kinetics of corn.

MATERIALS AND METHODS

Yellow corn (Pioneer 3306) harvested in 1968 was used to determine the adsorption rate of water vapor under various environmental conditions. Ear corn samples, harvested at about 24% moisture and shelled by hand to eliminate damage to kernels, were kept under three environmental conditions, which gave moisture contents of approximately 9, 11, and 14% (dry basis).

To measure the weight change of a sample continuously at a specified environmental condition, the weighing unit of the CAHN electrobalance was mounted on the top of the test chamber, Aminco 3-B Climate-Lab, wherein the dry-bulb temperature was controlled to ±3/4°F. and the r.h. to ±1/2%. The electrobalance was connected to the strip-chart recorder for tracing the weight change of a sample with respect to time. The recording balance had 100 g. capacity and electrical indicating ranges from 0.2 mg. to 20 g. (readable and reproducible to 0.01% and accurate to 0.05% of the dial range). A schematic diagram of the experimental setup and equipment is shown in Fig. 1.

A sample (about 20 g.) was placed in a single layer on a pan made of 200-mesh brass-wire screen. The brass-wire pan containing the sample was suspended from the sample loop of the electrobalance inside the test chamber which was set to a specific environmental condition. The initial temperature of the sample was controlled to the same dry-bulb temperature of the test condition. The initial moisture content (M_0) was determined by placing the sample in an air-oven for 72 hr. at 217°F.

Three factors, initial moisture content (M_0) of the corn sample, temperature, and r.h. of the air surrounding the sample with three different levels of each factor,

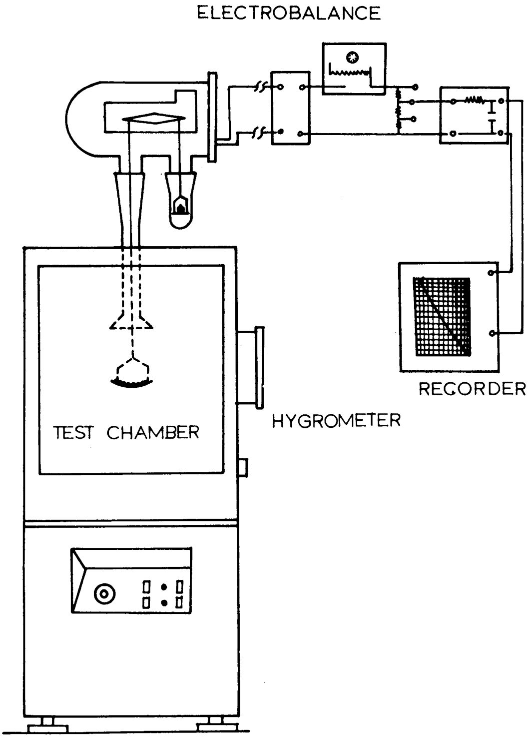

Fig. 1. Schematic diagram of experimental setup.

were studied for adsorption rates. The levels of each factor were 9.2, 11.2, and 13.8% (M_0); 60°, 70°, and 80°F. (dry-bulb temperature); and 60, 70, and 80% r.h. Thus there were 27 combinations of tests, which were replicated once at each combination. In addition to the above experiments, three more experiments were conducted with 12.46% initial moisture corn at 90°F. and 60% r.h.; 90°F. and 70% r.h.; and 70°F. and 90% r.h.

RESULTS AND DISCUSSION

Adsorption Kinetics

Figures 2, 3, and 4 show the effect of temperature and relative humidity on adsorption of water in corn with time. Average values of the moisture adsorbed (percent dry basis) for two replications are plotted against time because the two replications did not differ significantly. At a constant r.h., the adsorption rate increased with air temperature. At a constant temperature, the adsorption rate increased with r.h. The adsorption rate increased when both r.h. and temperature increased, but was not in the order of partial pressure of water vapor in air. At a given temperature, however, the adsorption rate was found to be in the order of the partial pressure of water vapor. This result was expected, because the r.h. was proportional to the partial pressure of water vapor at constant temperature. At constant temperature and r.h., adsorption rate of water vapor increased rapidly when M_0 decreased. This effect can be explained by the fact that, at a lower

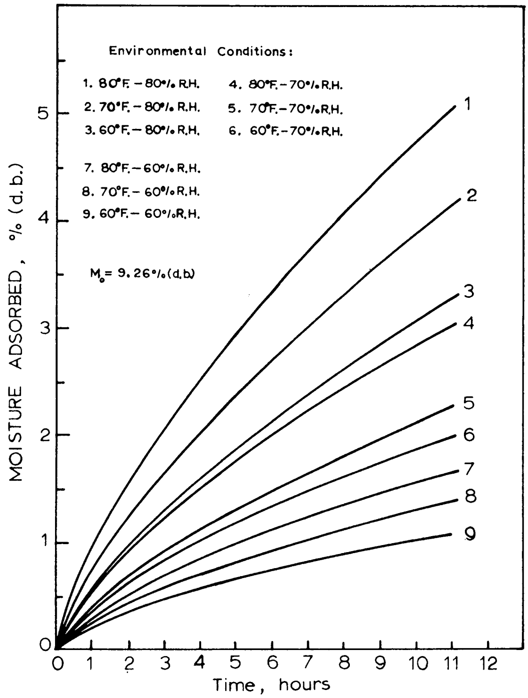

Fig. 2. Adsorption of water vapor by corn (M_0 = 9.26%) at various environmental conditions.

moisture content of corn, there exists a greater potential difference (concentration or vapor pressure) between corn and air, which is a driving force for the adsorption process.

Analysis of variance showed that among the factors studied, the order of importance influencing the adsorption rate was, first, r.h.; second, M_0; and third, temperature. Significant interactions on the adsorption rate were also observed. Interactions between temperature and r.h., and between temperature and M_0, had the most pronounced effects on adsorption rate. The interaction between temperature and r.h. can be considered as the partial pressure of water vapor in air, and the interaction between temperature and M_0 as the partial pressure, or concentration, of water in the original corn.

The adsorption rate of water vapor by yellow corn was slow compared to the physical adsorption of industrial gases on solids (4). For example, yellow corn having 9.26% M_0 adsorbed only 5% of its original weight at 80°F. and 80% r.h. in 11 hr. This slow adsorption process was probably due to the following physical aspects: 1) the blocking effect on the further adsorption by water molecules already adsorbed (thin film of water molecules on the surface of the kernels); 2) resistance of air to the movement of water vapor; and 3) diffusion of water vapor into some of the fine pores of yellow corn. Patrick and Cohan (8) showed that if there are impurities present either in the gas phase or in the adsorbed phase, the adsorption rate is slowed down considerably.

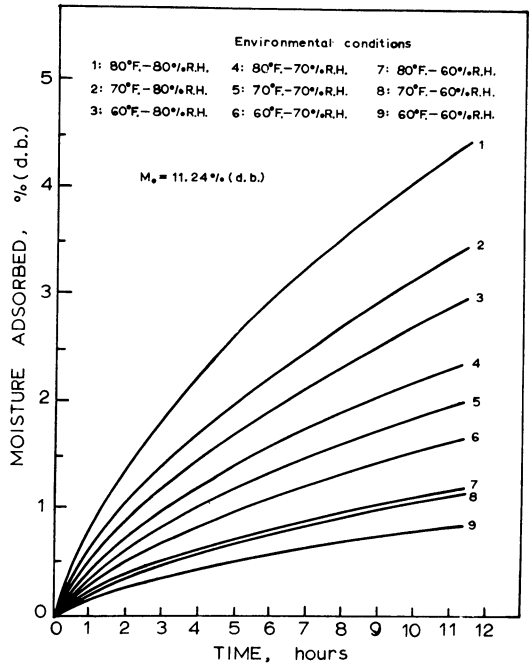

Fig. 3. Adsorption of water vapor by corn (M_0 = 11.24%) at various environmental conditions.

Analysis of Kinetic Data

Roginski and Zeldovich (7) found that the rate of adsorption decreases exponentially with the amount of gas adsorbed,

$$\frac{dM}{dt} = a \exp(-\alpha M) \qquad (1)$$

where M is the amount of gas adsorbed, t is time, and a and α are constants over the course of the process. The same equation was also found by Elovich and Zhabrova (6). The investigation on the adsorption of water vapor on a protein by Eley and Leslie (5) showed that their data followed the Elovich equation in a slightly modified form.

Integrating eq. 1 with the initial condition that M = 0 or $m - M_0 = 0$ when t = 0, where m is moisture content (percent dry basis) of the material at time, t, and M_0 is initial moisture content (percent dry basis), we obtain:

$$M = \frac{2.303}{\alpha}\log\left(t + \frac{1}{\alpha a}\right) - \frac{2.303}{\alpha}\log\left(\frac{1}{\alpha a}\right) \qquad (2)$$

that is,

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

$$\frac{2.303}{\alpha},\ t_0 = \frac{1}{\alpha a} \text{ and } C = A\log(t_0).$$

A plot of M vs. log $(t + t_0)$ should yield a straight line with slope A and intercept $-C$ if t_0 is chosen correctly by trial and error method (9). In the present

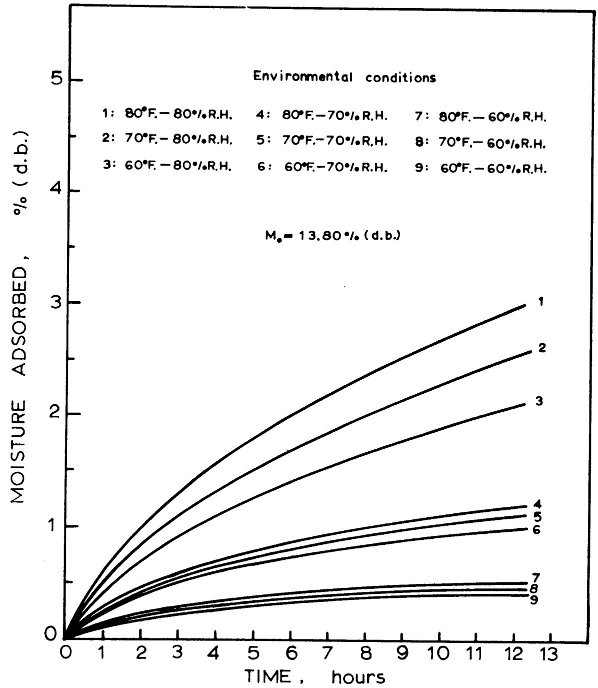

Fig. 4. Adsorption of water vapor by corn (M = 13.80%) at various environmental conditions.

investigation, t_0 was found to be a constant for a given M_0 of a sample. Figure 5, based on the data in Fig. 2, shows that eq. 2 describes the adsorption rate of water vapor by yellow corn. The data in Figs. 3 and 4 also followed eq. 2. Constants A and C in eq. 2 were evaluated by using the method of least squares.

Examination of slope A indicated that it was directly related to r.h. If slope A is plotted against r.h. and temperature as a parameter in a logarithmic graph for a given M_0, a series of parallel straight lines is found. That is, there is a functional relation between slope A and r.h. for a given M_0:

$$A = A' (\text{r.h.})^n \tag{3}$$

where r.h. is expressed as a decimal, n is a constant for a given M_0, and A' is a constant for fixed M_0 and temperature.

A', when plotted against temperature for various M_0, is linearly related to temperature. That is,

$$A' = BT - b$$

that is,

$$A' = B(T - T_0) \tag{4}$$

where T is dry-bulb temperature in °R., and B, b, and T_0 are constant for a given M_0. Furthermore, the plot of B in eq. 4 vs. the reciprocal of initial moisture

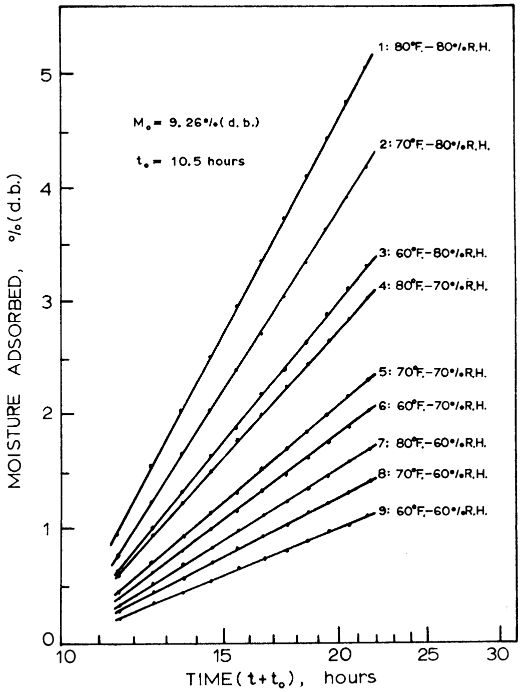

Fig. 5. Plot of data in Fig. 2 according to equation 2.

content showed that B can be expressed by the equation

$$B = \frac{12.96}{M_0} - 0.78 \qquad (5)$$

Therefore, from eqs. 3, 4, and 5, the slope A in eq. 2 can be expressed as follows:

$$A = (\frac{12.96}{M_0} - 0.78)\,(T-T_0)\,(r.h.)^n \qquad (6)$$

According to eq. 2, the intercept C, defined as "A log t_0," should be automatically fixed with known A and t_0 if the adsorption rate data satisfy eq. 2. The intercepts evaluated agreed with the expected theoretical value A log t_0. However, they were consistently lower than the expected theoretical value, and the deviation between the two corresponding values became greater as the M_0 of a sample increased. This deviation might be caused primarily by the inherent error which resulted in evaluating t_0. It should be noted again that since t_0 was evaluated by a trial and error method, it would be almost impossible to find the true t_0. Therefore, we introduced a correction factor λ so that the intercept C could be evaluated by the expression:

$$C = \lambda\, A \log t_0 \qquad (7)$$

From the foregoing analysis, eq. 2 can be written:

$$M = A \log (t + t_o) - \lambda A \log t_o \qquad (8)$$

in which M is expressed as a percent moisture adsorbed (d.b.), and A is eq. 6. The values of t_o, T_o, n, and λ for a given M_o are summarized in Table I. Equation 8 was tested with data at 90°F. and 60% r.h.; 90°F. and 70% r.h.; and 70°F. and 90% r.h. with 12.46% M_o, which were not used in the analyses. In generating data by equation 8, parameters t_o, T_o, n, and λ were interpreted from the data in Table I. The values interpreted were: t_o = 5.8 hr., T_o = 459 R., n = 5.0, and λ = 0.958. Experimental data and the curves generated by eq. 8, as seen in Fig. 6, agreed well. The average deviations of calculated data from corresponding experimental data were 1.49% for 90°F. and 60% r.h.; 4.54% for 90°F. and 70% r.h.; and −3.69% for

TABLE I. VALUES OF CONSTANTS IN EQUATION 8 FOR DIFFERENT INITIAL MOISTURE CONTENTS

M_o pct.	t_o hr.	T_o °R.	n	λ
9.26	10.5	482	3.89	0.975
11.24	7.5	470	4.34	0.967
13.80	4.0	436	6.10	0.900

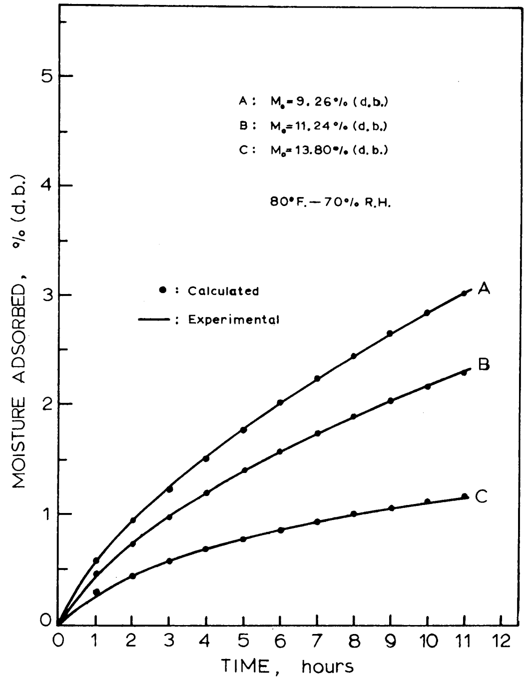

Fig. 6. Comparison between experimental adsorption data and data generated by equation 8.

70°F. and 90% r.h. Thus, the change in moisture content of corn for a certain environmental condition can be approximated by eq. 8. Equation 8, however, would not satisfy the limiting condition (equilibrium state). To describe the adsorption rate approaching the equilibrium state, the diffusion model equation might be introduced.

Literature Cited

1. CHUNG, D. S., and PFOST, H. B. Adsorption and desorption of water vapor by cereal grains and their products, Parts I, II, III. Trans. Am. Soc. Agr. Engr. 10(4): 549 (1967).
2. HALL, C. W., and RODRIGUEZ-ARIAS, J. H. Equilibrium moisture content of shelled corn. J. Am. Soc. Agr. Engr. 39(8): 466 (1958).
3. HENDERSON, S. M. A basic concept of equilibrium moisture. J. Am. Soc. Agr. Engr. 33: 29 (1952).
4. BRUNAUER, S. The adsorption of gases and vapors. I. Physical adsorption. Princeton University Press: Princeton, N.J. (1943).
5. ELEY, D. D., and LESLIE, R. B. Adsorption of water on solid proteins with special reference to haemoglobin. Advan. Chem. Phy. 7: 238 (1963).
6. ELOVICH, S. Y., and ZHABROVA, G. M. Mechanism of catalytic hydrogenation of ethylene on nickel. I. Kinetics of the process. Zh. Fiz. Khim. (U.S.S.R.) 13: 1761 (1939).
7. ROGINSKI, S., and ZELDOVICH, Y. The catalytic oxidation of carbon monoxide on manganese dioxide. J. Acta Physiochimica (U.S.S.R.) 1: 554 (1934).
8. PATRICK, W. A., and COHAN, L. H. The rate of sorption of water vapor on silica gel and iron silica gel. J. Phys. Chem. 41: 437 (1937).
9. TAYLOR, H. A., and THON, N. Kinetics of chemisorption. J. Am. Chem. Soc. 74: 4169 (1952).

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