EQUILIBRIUM MOISTURE CONTENT OF BEANS

by

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I wish to express also my sincere appreciation to my advisor, Dr. Harry H. Pfost, for his personal interest in the work of his students.

The deepest gratitude goes to Julie Meier for her encouragement throughout this work. It is to her that this thesis is dedicated.

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INTRODUCTION

A proper understanding of adsorption and desorption characteristics of hygroscopic substances such as grains and legumes is of a great practical importance during handling, storage, drying, and conditioning. Grains or legumes gain or lose moisture, depending on the vapor pressure of moisture in them and in air surrounding them. The process of losing moisture from the substance is called desorption, and gaining moisture is called adsorption.

Considerable effort has been made to obtain the sorption isotherms of grains; that is, the curves describing the equilibrium relationship between the moisture content of substance and relative humidity at a specified temperature. A sigmoid shape isotherm has been found for grains. It has also been found that a hysteresis effect is exhibited in sorption isotherms of grains; that is, the equilibrium moisture content for a given relative humidity is higher during desorption than adsorption.

Numerous attempts have been made in the past decades to derive the isotherm equations describing sorption phenomena of grains and also to study the hysteresis effect on grains. However, only limited data on the equilibrium moisture contents of beans is reported in the literature, and practically no work on the hysteresis effect has been done for beans. Therefore, we initiated this investigation to provide the isotherm data on various beans and to examine whether the hysteresis effect would exist on beans.

LITERATURE REVIEW

Isotherm Theories

Many sorption theories have been introduced to describe and explain sorption phenomena of hygroscopic materials.

Brunauer (1943) classified adsorption isotherms into five types. These types are shown in Figure 1. The Type I curve is the Langmuir adsorption isotherm monolayer. Type II is called the S-shape or sigmoid curve. This curve describes the adsorption of water vapor by cereal grains or other biological materials. Type III is closely related to Type II. Types IV and V result in the adsorption onto highly porous adsorbents, like water vapor onto carbon.

One of the oldest and most widely known theories of adsorption is the Langmuir equation. Langmuir (1918) assumed that, at equilibrium, the rate of adsorption was equal to the rate of evaporation. He further assumed that the probability of evaporation of a molecule is the same whether the neighboring positions on the surface are occupied by other molecules or not. He also assumed that every molecule coming from the gas phase which strikes a molecule already absorbed on the surface is elastically reflected.

The isotherm equation obtained by Langmuir is:

$$\frac{V}{Vm} = \frac{bP}{1 + bP} \qquad (1)$$

where V = The volume of gas adsorbed

Vm = The amount of gas adsorbed at surface saturation

b = constant

P = equilibrium pressure

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THIS IS AS RECEIVED FROM CUSTOMER.

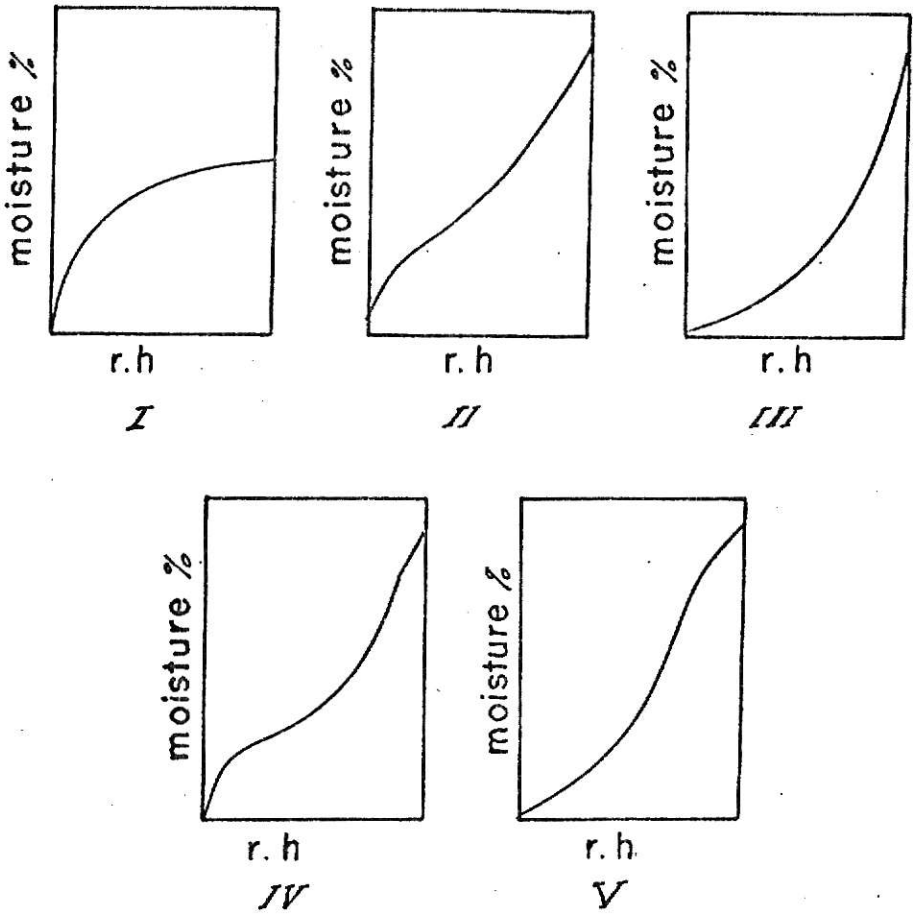


FIGURE 1. TYPES OF ADSORPTION ISOTHERMS ACCORDING TO THE CLASSIFICATION OF BRUNAUER (1943).

This equation represents a monolayer adsorption process.

Polanyi (1916) was the first to consider multimolecular adsorption. His potential theory stated that the surface potential for adsorption extends up through the first layer to bind another, forming multimolecular layers. These layers are under compression because each layer is compressed by all the layers adsorbed on top of it. The top layer would have the density of the gas. The forces attracting the molecules to the surface decrease with distance. Polanyi represented his potential theory by the following equation:

$$E_1 = \int_{dx}^{di} V \, dp \qquad (2)$$

where di = The density of the adsorbed substance

dx = The density of the gas phase

V = The adsorbed volume

DeBoer and Zwicker (1929) explained the adsorption 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. The polarization theory by DeBoer and Zwicker was the first to account for the sigmoid isotherm. DeBoer and Zwicker developed the following equation:

$$\ln\left(\frac{P}{K_3 P_0}\right) = K_2 K_1^{\,n} \qquad (3)$$

where P = the equilibrium pressure of the n'th layer

P_0 = the saturation vapor pressure

K_1, K_2, K_3 = constants

Brunauer, Emmett and Teller (1938) postulated the multimolecular adsorption theory. They derived an isotherm equation for multimolecular layers that is similar to Langmuir's derivation for unimolecular layer. They assumed that the rate of condensation on the bare surface is equal to the rate of evaporation from the first layer, and that the evaporation condensation properties of the molecules in the second and higher layers are the same as those of the pure liquid state. The derived equation is:

$$\frac{V}{Vm} = \frac{CP}{(P_0-P)\left[1 + (C - 1)\, P/P_0\right]} \qquad (4)$$

where P = an equilibrium pressure

P_0 = saturation vapor pressure at the same temperature

C = parameter varying with the gas and temperature

V = Volume adsorbed

Vm = Volume or amount of gas adsorbed when the entire adsorbent surface is covered with a monomolecular layer

This equation gives an S-shaped isotherm.

The BET equation is the most widely used in adsorption studies because of its rigorous theoretical approach and because surface areas and approximate heats of adsorption can be calculated from the equation. The constant C can be defined approximately as

$$C = (E_1 - E_L)/RT$$

where E_1 = The heat of adsorption of the adsorbate in the first adsorbed layer

E_L = The heat of condensation of the adsorbate

R = Universal gas constant

T = The absolute temperature

Smith (1947) considered the specific ease of water vapor sorption. He considered the sorbed water to be of two principal classes:

$$W = W_b + W_c \tag{5}$$

where W_b is the amount of water bound on the inner or outer surface of the absorbent by forces greater than those responsible for condensation of water to the liquid state. W_c is the amount of water normally condensed within the adsorbent. Smith defined W_c as:

$$W_c = - W' \ln (1 - P/P_o) \tag{6}$$

where W' is the amount of normally condensed vapor required to saturate the first layer of the W_c fraction thus,

$$W = Wb + Wc = Wb - W'\ln (1 - P/P_o) \tag{7}$$

Rodriguez-Arias (1956) and Becker (1956) found that the approximate region of applicability of the Smith equation was between 50 and 90 percent relative humidity for corn and wheat.

Hoover and Mellon (1950) found that the sorption of water at high relative humidity depends on the prior sorption on active sorptive groups such as the free amino and peptide groups. They showed that many isotherms between 30 to 90 percent relative humidity can be described by the simple relationship:

$$\log a = K\ P/P_o + b \tag{8}$$

where a is the amount absorbed, P/P_o is relative vapor pressure, and K, b are empirical constants.

An isotherm equation was developed by Henderson (1952) which is:

$$1 - P/P_o = \exp(-KTm^n) \quad (9)$$

where P/P_o = equilibrium relative humidity

T = absolute temperature

K, n = constants depending on temperature and materials

m = equilibrium moisture content, percent dry basis

Chung and Pfost (1967) developed a new isotherm equation that may be applicable to describe the isotherm of cereal grains and their products over a wider range of relative humidity. They determined that the adsorption potential function can be replaced by the free energy function or useful work function. By using thermodynamic relations they derived

$$\Delta F = RT \ln P/P_o \quad (10)$$

and then they assumed that the free energy function, or useful work decreases exponentially with increasing thickness of adsorbed layer, and it is variant with temperature. Mathematically this assumption was expressed

$$-\Delta F = A \exp(-Bm) \quad (11)$$

By equating equation 10 with equation 11 they finally developed the equation:

$$\ln P/P_o = -\frac{A}{RT} \exp(-Bm) \quad (12)$$

where P/P_o = equilibrium relative humidity

A, B = constants

T = absolute temperature

m = moisture content

R = universal gas constant

Strohman and Yoerger (1967) developed an equation from Othmer's linearity in comparison to the free energy approach used by Chung and Pfost (1967)

$$P/P_o = \exp\left[a \exp(bm) \ln P_o + C \exp(dm)\right] \qquad (13)$$

where a, b, c, and d are constants depending on the grain used and m is the equilibrium moisture content.

Chen (1971) developed the following equation under assumption that the diffusion is the rate controlling mechanism in the sorption process

$$y = \exp\left(K + me^{nx}\right) \qquad (14)$$

where k, m, and n are constants

y = relative humidity

x = equilibrium moisture content.

The drying of hygroscopic materials was considered as moisture migration in a diffusional field by Chen.

Hysteresis

Theoretically, adsorption-desorption curves should coincide, however, in practice, they do not, and the resulting phenomenon is termed hysteresis. No definitive theory to describe the hysteresis effect has been proposed, but investigators generally associated hysteresis with capillary condensation.

It has been found that the equilibrium moisture content of cereals and their products for desorption is higher than that for

adsorption. The equilibrium vapor pressure is lower during desorption than adsorption. Cohan (1941) classified the proposed theories as:

1. the incomplete wetting theory,
2. the ink-bottle theory, and
3. the open-pore theory.

The first explanation of hystereses was postulated by Zsigmondy (1911) in terms of capillary condensation. He stated that during adsorption incomplete wetting takes place in the capillaries of the absorbent because of impurities, mostly permanent gases absorbed on the walls of capillaries. This causes the adsorption moisture content to be lower than the desorption moisture content.

Kraemer and McBain (1935) suggested that cavities with constricted necks are responsible for hysteresis.

During adsorption the vapor pressure in these bottle cavities is determined by condensation in the portion with a relatively large diameter, during desorption, by condensation in the narrower neck.

Cohan pointed out that the gel structure may consist predominantly of pores which widen toward their bases and behave as though open.

Urguhart (1929) attributed the hysteresis in the sorption of water by cellulose to an irreversible uncoupling of hydroxyl groups within the cellulose structure, the uncoupling occurring during adsorption and recoupling occurring at a relatively delayed stage in the desorption process.

Hart (1964) found that as temperature increases, hysteresis effect decreases. He found that the initial rate at which high moisture wheat loses moisture is greater than the rate at which low moisture

wheat regains moisture.

Smith (1947) suggested that hysteresis is due to swelling which increases the surface area and due to the presence of rigid structural elements of much greater dimensions than those of the sorbate molecules.

Young and Nelson (1967) stated that hysteresis is subject to a wetting environment. Since a biological material is a combination of many biological cells, three mechanisms are hypothesized by which water is held by the material. a) There can be a unimolecular layer of water molecules bound to the surface of the cells. b) There can be multimolecular layers of molecules stacked on top of the first layer. c) There can be moisture within the cells. The surface molecules of the cell exert binding forces on the water molecules which prevent them from moving inward. As the amount of water builds up, the diffusional forces exceed the binding forces and allow some molecules to move into the cell. There is no force to pull the moisture out of the cells until all the moisture has been removed from the surface during desorption.

Chung and Pfost (1967) in the investigation of the cause of hysteresis effect, postulated the hypothesis that more sorption sites or polar sites on the surface of an adsorbent might be available to water vapor during the desorption process than during the adsorption process. They justified this hypothesis by showing the differences between the heats of desorption and heats of adsorption. They also explained that a reduced availability of polar sites on the surface of an adsorbent in the adsorption process is to be expected because

of the crack formation due to wetting. They concluded that the difference in the availability of sorptive sites or polar sites on the surface of the adsorbent to water vapor would cause the hysteresis. They also found that in the third cycle of desorption and adsorption of wheat, the hysteresis loop practically disappeared.

Investigation

Objectives

The objectives of this investigation were:

1. To find adsorption and desorption isotherms of red beans, baby lima beans, and pinto beans at 70° F, 80° F, 90° F, and 100° F, over a range of relative humidity from 10 to 90 percent.
2. To study the rate of desorption in beans.
3. To test the fitness of the results in Chung and Pfost equation.
4. To determine the heats of desorption and adsorption of water by various types of beans.

MATERIALS AND METHODS

Three different kinds of dry beans; small red field beans (phaseolus vulgaris), baby lima beans (phaseolus lunarus), and pinto field beans (phaseolus vulgaris) obtained from a grocery store were used to obtain desorption and adsorption isotherms at 70° F, 80° F, 90° F, and 100° F temperatures. Samples for obtaining the desorption isotherms were wetted to about 25 percent moisture content. Samples for obtaining the adsorption isotherms were oven dried at 120° F temperature to 5-10 percent of initial moisture content, dry basis. Sample sizes from 4.0 to 6.0 grams were placed in baskets made from fine wire screen. The relative humidity, depending on the temperature, was controlled by solutions of sulfuric acid. The concentration ranged from 10 to 60 percent of sulfuric acid. Perry's Chemical Engineer Handbook (1950) was used to determine relative humidities at different solution concentrations. The range of relative humidity of 10 to 90 percent was used. The container used for relative humidity control was a 500 ml flask, which was filled with 200 ml of sulfuric acid solution. The basket containing a sample was suspended above the solution in the container, and then the flask was sealed with a rubber stopper. The flask containing the sample was placed in the temperature control chamber for three weeks. Then the equilibrium moisture contents of samples were determined by an oven method (72 hours at 103° C).

In addition, the rates of desorption for red bean were examined at 20, 50, and 80 percent relative humidities with 70° F and 100° F

temperatures. These samples were taken out of the temperature control chambers every 48 hours and weighed until the weights of samples remained constant. Also during this test a possible change in the solution concentration was studied. Densities of concentrations of sulfuric acid for 20, 50, and 80 percent of relative humidities were calculated and checked periodically every 48 hours.

RESULTS AND DISCUSSION

Rate of Desorption

In Figure 2 we can observe the rates approaching to the moisture equilibrium at different relative humidities for red beans. As we can see in Figure 2 the rate of desorption is a function of the relative humidity and temperature. For an example at 20 percent of relative humidity the rate of desorption decreased sharply while at 80 percent of relative humidity the rate of desorption gradually decreased. As the equilibrium was approached the rates of desorption decreased considerably. The rates of desorption did appear significantly higher in the first two days of storage period. We also observed that at higher temperatures for a given relative humidity the rates of desorption were faster. At 100^{o} F for a given relative humidity the rate of change in moisture was greater than at 70^{o} F but the actual equilibrium moisture content was less. At higher temperatures the period of time to reach equilibrium was also less.

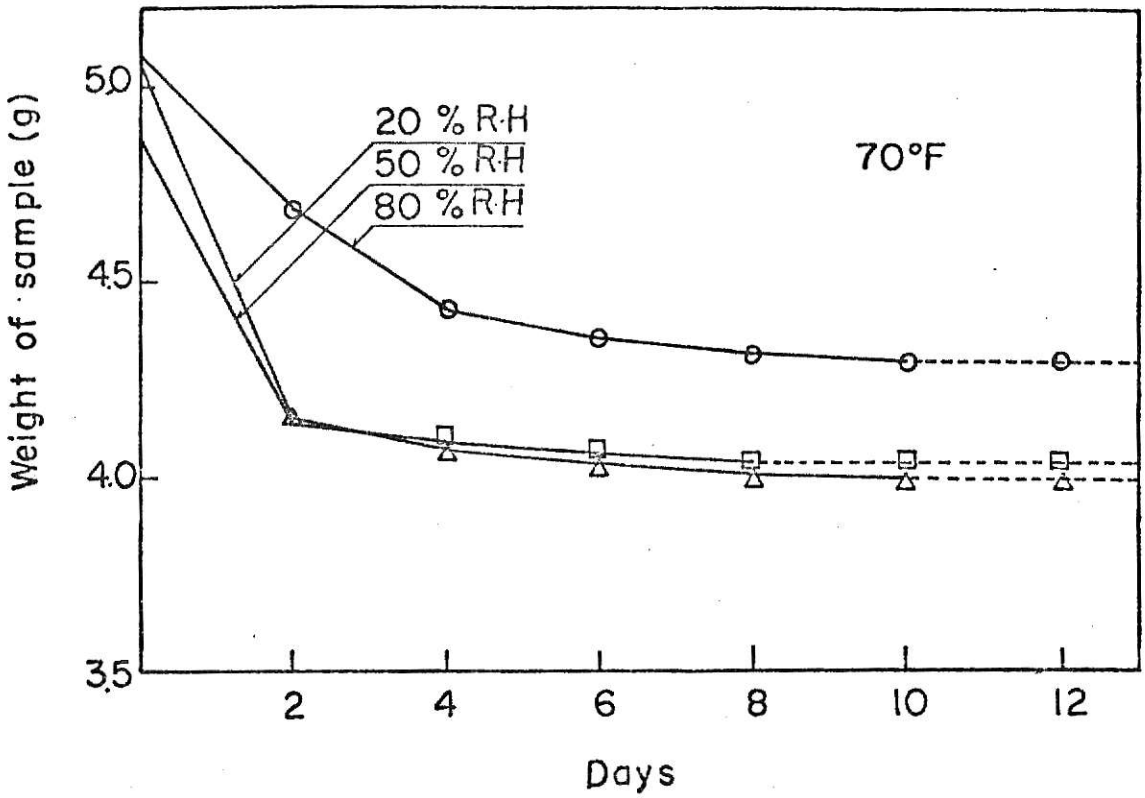
The Change in the Solution Concentration

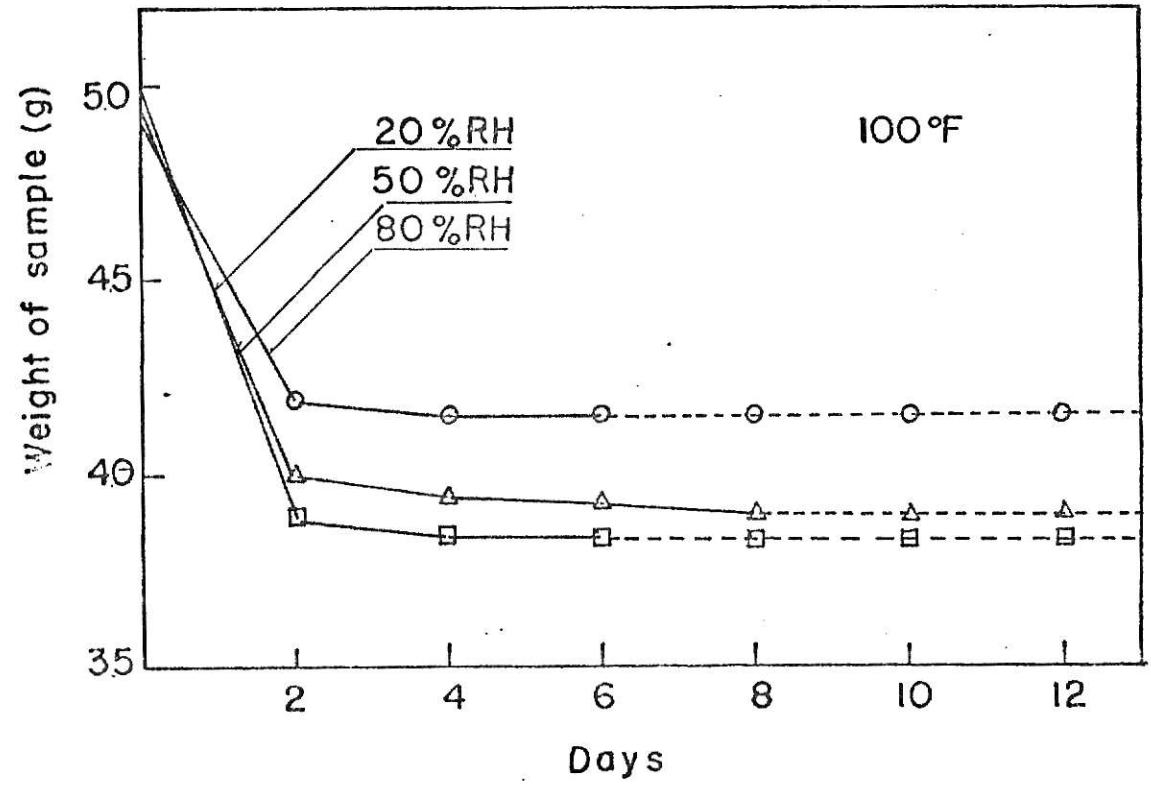
In this investigation densities of 1.460 gr/cc and 1.193 gr/cc of concentration of sulfuric acid for 20 and 80 percent of relative humidity respectively, were checked periodically every 48 hours. The values of densities remained constant. The results showed no change in the sulfuric acid concentration during a test period.

Experimental Isotherms

The equilibrium moisture contents for desorption and adsorption

FIGURE 2. Rates of desorption for red beans at 70° F and 100° F.





process of beans are given in Table 1. Isotherm curves of beans for desorption and adsorption at various temperatures are shown in Figures 3 through 14. It can be seen in these curves that for both adsorption and desorption the equilibrium moisture content increases with an increase in relative humidity. At equilibrium the vapor pressure of the water in the grain is the same as the pressure of water in it environment. As the environmental pressure increases, or relative humidity increases, the pressure of the water in the grain must increase to reach equilibrium.

Figures 3 through 14 show that the equilibrium moisture content decreases with an increase in temperature. This can be explained by the principle of "Lechatlier". The principle states that if a stress is applied to a system at equilibrium, the system will readjust to decrease the stress. The stress in this case is a temperature. As the temperature increases the kinetic energy increases, causing an increase in stress. To reduce this stress some of the molecules escape to the environment, thus decreasing the moisture content. A diagramatic representation of the influence of temperature for red beans is shown in Figure 15.

Desorption and adsorption curves for beans investigated are sigmoid in shape, like other cereal grains and belong to the Type II isotherms according to the classification of Brunauer (1938). Each isotherm consists of three regions: the low pressure region concave to the relative humidity axis, the intermediate linear portion and the high pressure region convex to the relative humidity axis.

Table 1. Experimental isotherm data at 70, 80, 90, and 100° F for various beans.

Material	Temperature (deg. Fahr)	Relative Humidity (%)	Desorption E.M.C. %(d.b)	Adsorption E.M.C. % (d.b)
Red beans	70	89.40	---	---
		79.15	22.35	21.50
		69.46	18.88	17.50
		59.07	14.05	13.65
		48.57	12.79	11.00
		38.89	10.76	9.35
		30.13	9.91	8.89
		20.38	8.66	7.50
		11.62	7.53	---
	80	89.17	---	---
		78.62	---	19.52
		69.04	17.59	16.93
		58.99	14.29	13.61
		48.62	12.06	11.06
		39.02	10.00	9.68
		30.16	8.69	8.35
		20.73	7.78	7.14
		12.11	6.53	---
	90	89.51	---	---
		78.95	---	21.77
		69.39	18.28	17.90
		59.34	14.33	14.04
		49.00	11.66	11.56
		39.44	10.11	10.07
		30.59	8.81	8.46
		21.16	7.33	7.19
		12.29	6.43	---
	100	89.81	---	---
		79.24	---	---
		69.75	18.37	17.78
		59.79	14.24	13.39
		49.55	11.95	11.48
		40.07	9.44	9.35
		31.19	8.91	8.15
		21.65	6.39	7.74
		12.66	5.59	---

Table 1 (continued)

Material	Temperature (deg. Fahr)	Relative Humidity (%)	Desorption E.M.C. % (d.b)	Adsorption E.M.C. % (d.b)
Baby lima bean	70	89.40	---	---
		79.15	23.34	21.75
		69.46	19.69	17.96
		59.07	15.01	14.00
		48.57	13.21	11.40
		38.89	11.20	9.80
		30.13	10.79	9.05
		20.38	9.54	8.05
		11.62	7.50	---
	80	79.17	---	---
		78.62	---	21.50
		69.04	18.71	17.50
		58.99	15.09	13.96
		48.62	12.39	11.40
		39.02	9.69	9.61
		30.16	8.85	8.57
		20.73	7.95	---
		12.11	6.79	---
	90	89.51	---	---
		78.95	---	---
		69.30	18.55	18.20
		59.34	15.63	13.90
		49.00	12.14	11.26
		39.44	10.14	9.65
		30.59	9.04	8.53
		21.16	7.34	---
		12.29	---	---
	100	89.81	---	---
		79.24	---	---
		69.75	18.08	17.42
		59.79	14.52	14.16
		49.55	12.36	11.25
		40.07	10.06	10.02
		31.19	9.14	8.33
		21.65	8.15	---
		12.66	---	---

Table 1 (continued)

Material	Temperature (deg. Fahr)	Relative Humidity (%)	Desorption E.M.C. % (d.b)	Adsorption E.M.C. % (d.b)
Pinto beans	70	89.40	---	---
		79.15	23.23	22.95
		69.46	18.70	17.77
		59.07	15.61	14.12
		48.57	12.93	11.61
		38.89	11.68	10.22
		30.13	9.38	8.38
		20.38	8.61	7.32
		11.62	7.73	---
	80	89.17	---	---
		78.62	---	22.69
		69.04	18.46	17.60
		58.99	15.06	14.08
		48.62	12.43	11.51
		39.02	10.32	10.12
		30.16	9.04	8.27
		20.73	7.86	7.28
		12.11	6.89	---
	90	89.51	---	---
		78.95	---	22.53
		69.39	18.33	17.29
		59.34	14.96	14.00
		49.00	12.00	11.44
		39.44	10.23	10.08
		30.59	8.94	8.17
		21.16	7.73	---
		12.29	6.74	---
	100	89.81	---	---
		79.24	---	22.08
		69.75	18.29	17.16
		59.79	14.40	14.00
		49.55	11.84	11.35
		40.07	10.16	9.43
		31.19	8.80	8.07
		21.65	7.65	7.05
		12.66	6.29	---

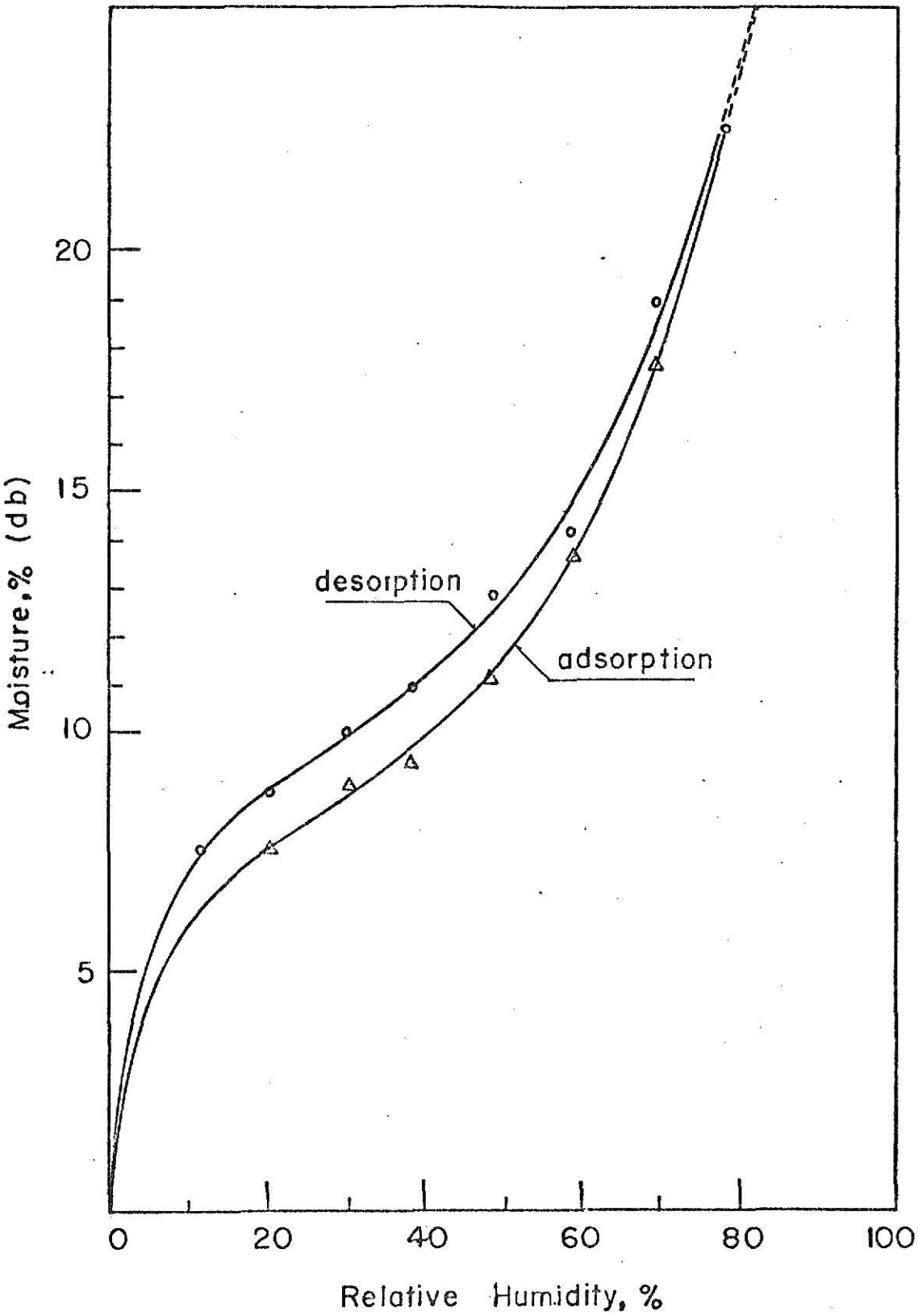


FIGURE 3. ADSORPTION-DESORPTION ISOTHERMS OF RED BEANS AT 70° F SHOWING HYSTERESIS EFFECT.

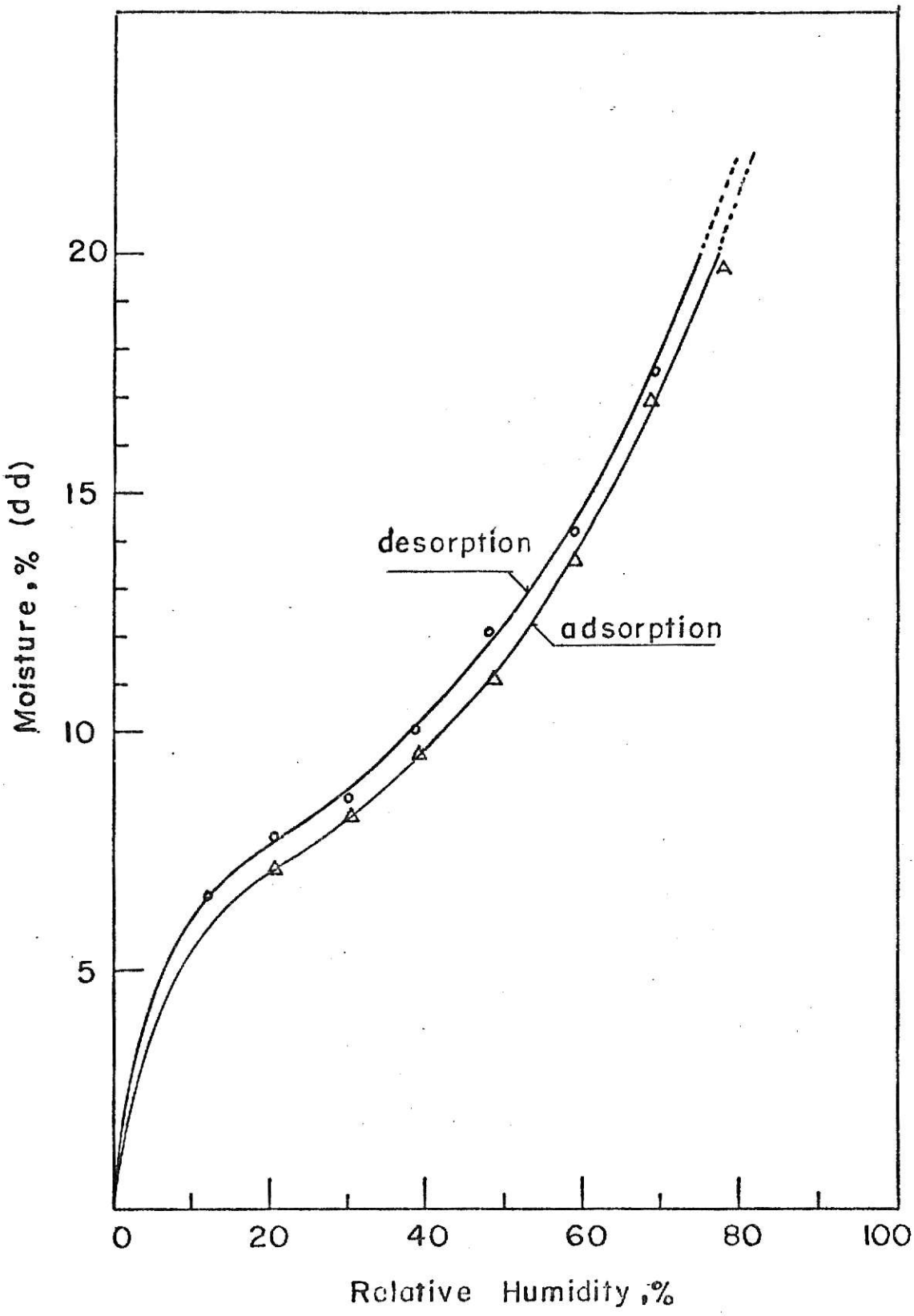


FIGURE 4. ADSORPTION-DESORPTION ISOTHERMS OF RED BEANS AT 80° F SHOWING HYSTERESIS EFFECT.

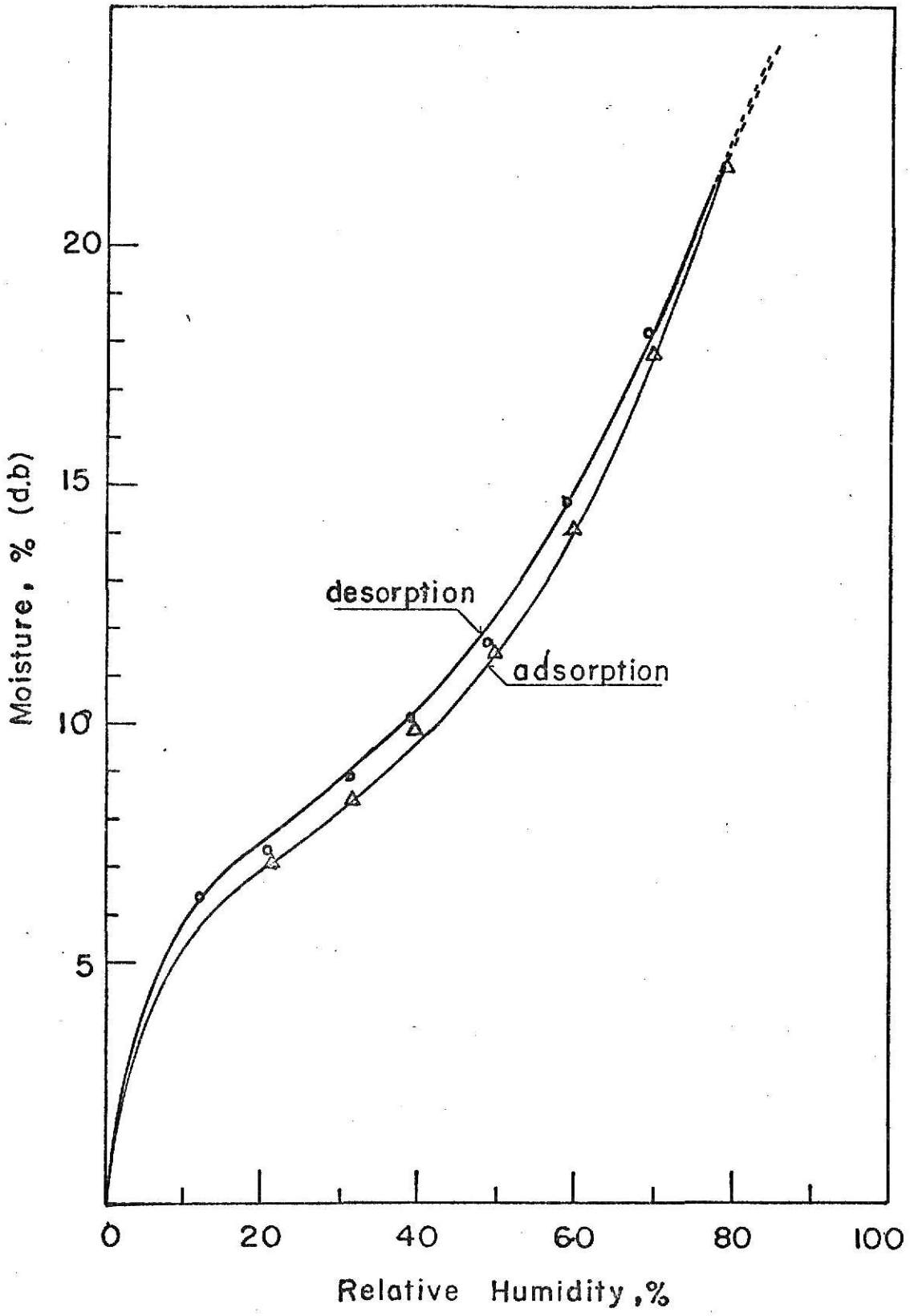


FIGURE 5. ADSORPTION-DESORPTION ISOTHERMS OF RED BEANS AT 90° F SHOWING HYSTERESIS EFFECT.

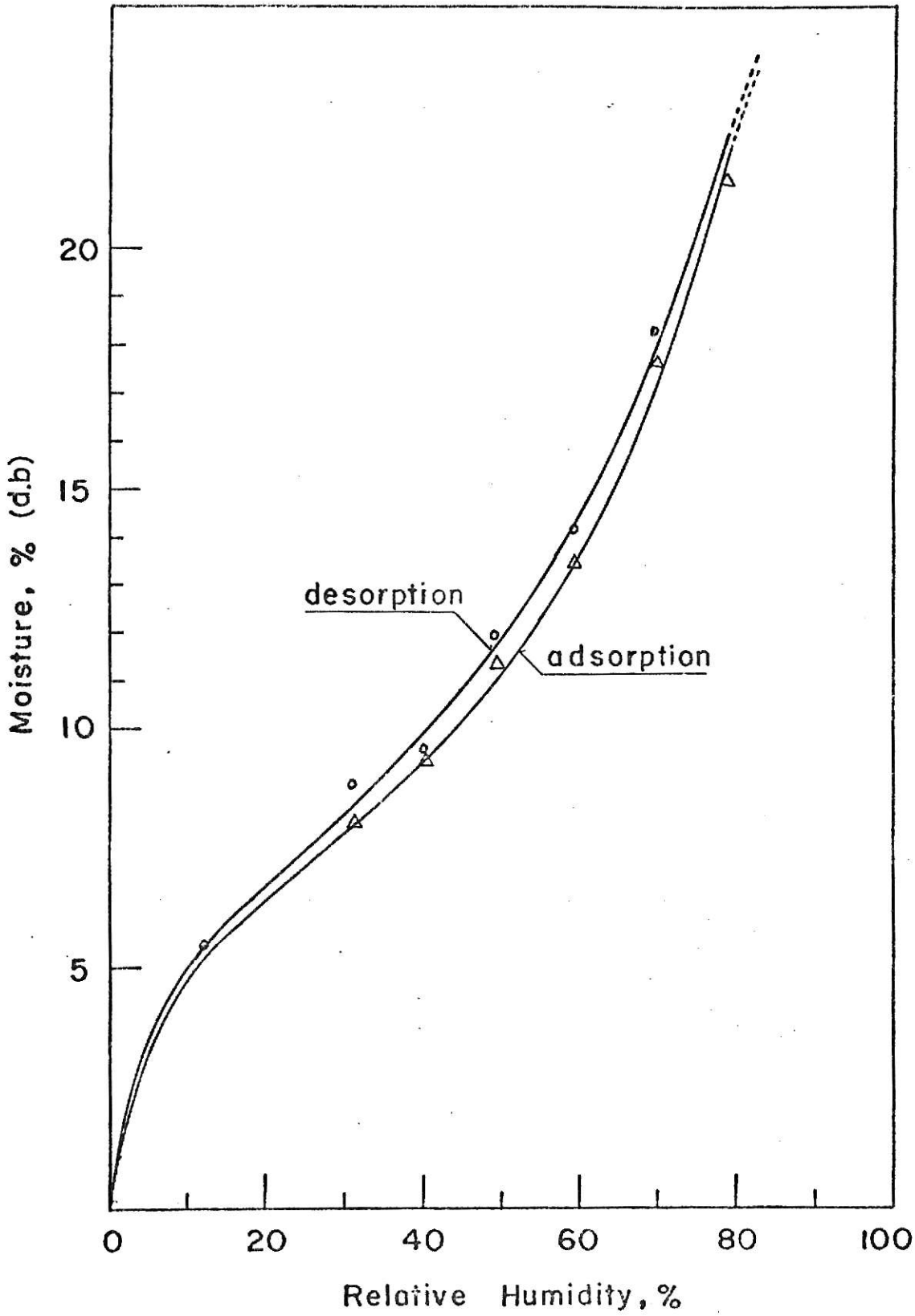


FIGURE 6. ADSORPTION-DESORPTION ISOTHERMS OF RED BEANS AT 100° F SHOWING HYSTERESIS EFFECT.

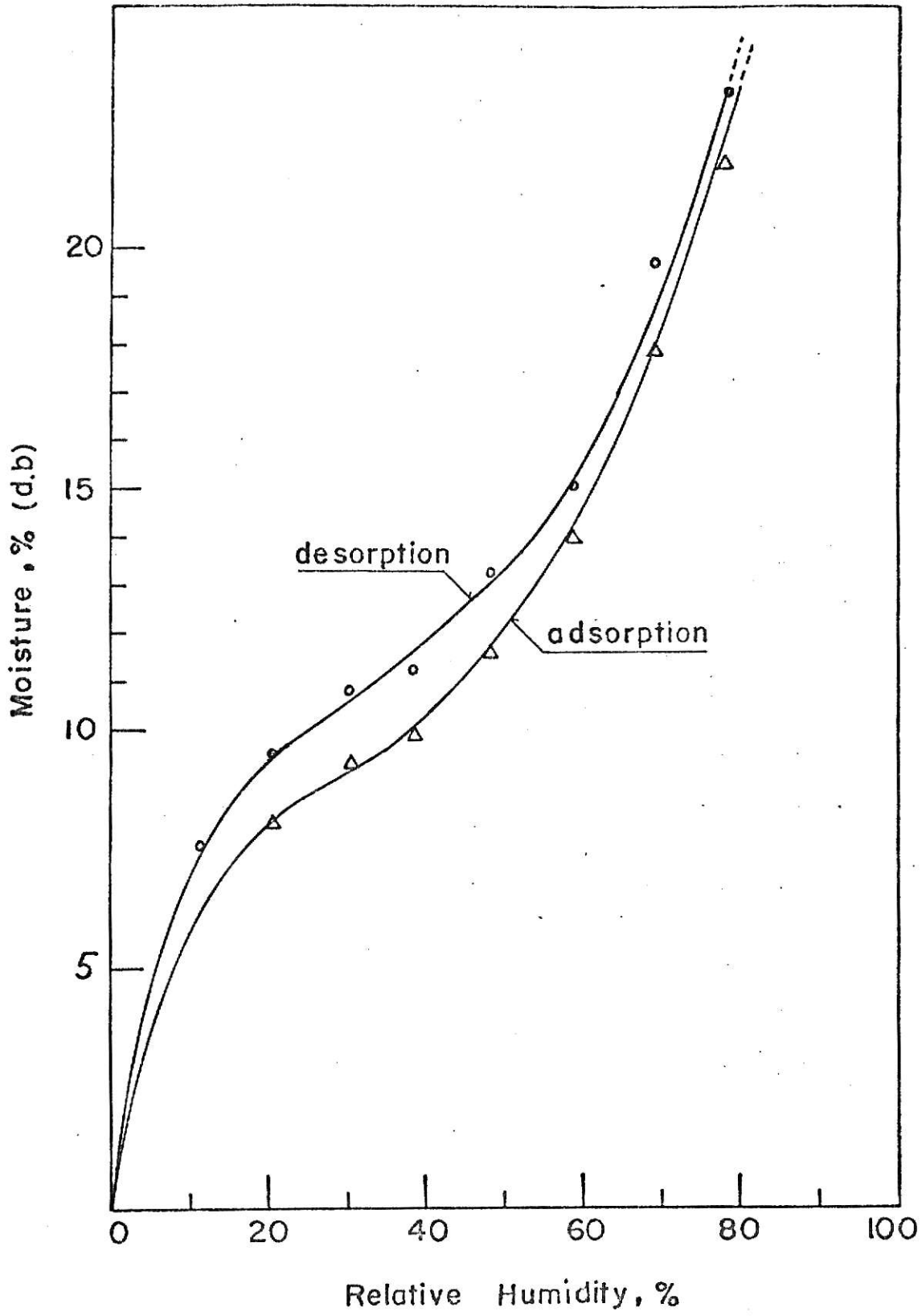


FIGURE 7. ADSORPTION-DESORPTION ISOTHERMS OF BABY LIMA BEANS AT 70° F SHOWING HYSTERESIS EFFECT.

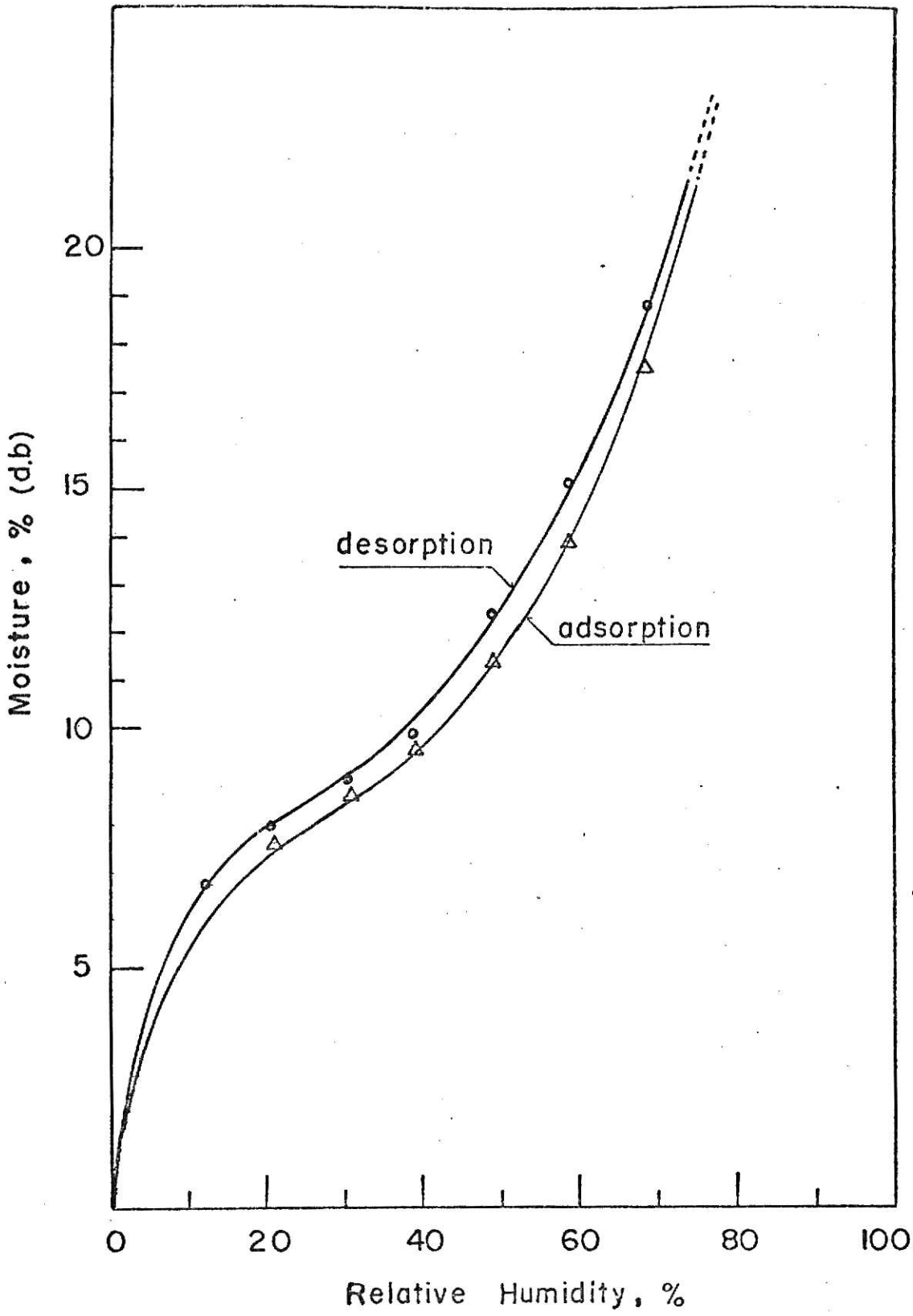


FIGURE 8. ADSORPTION-DESORPTION ISOTHERMS OF BABY LIMA BEANS AT 80° F SHOWING HYSTERESIS EFFECT.

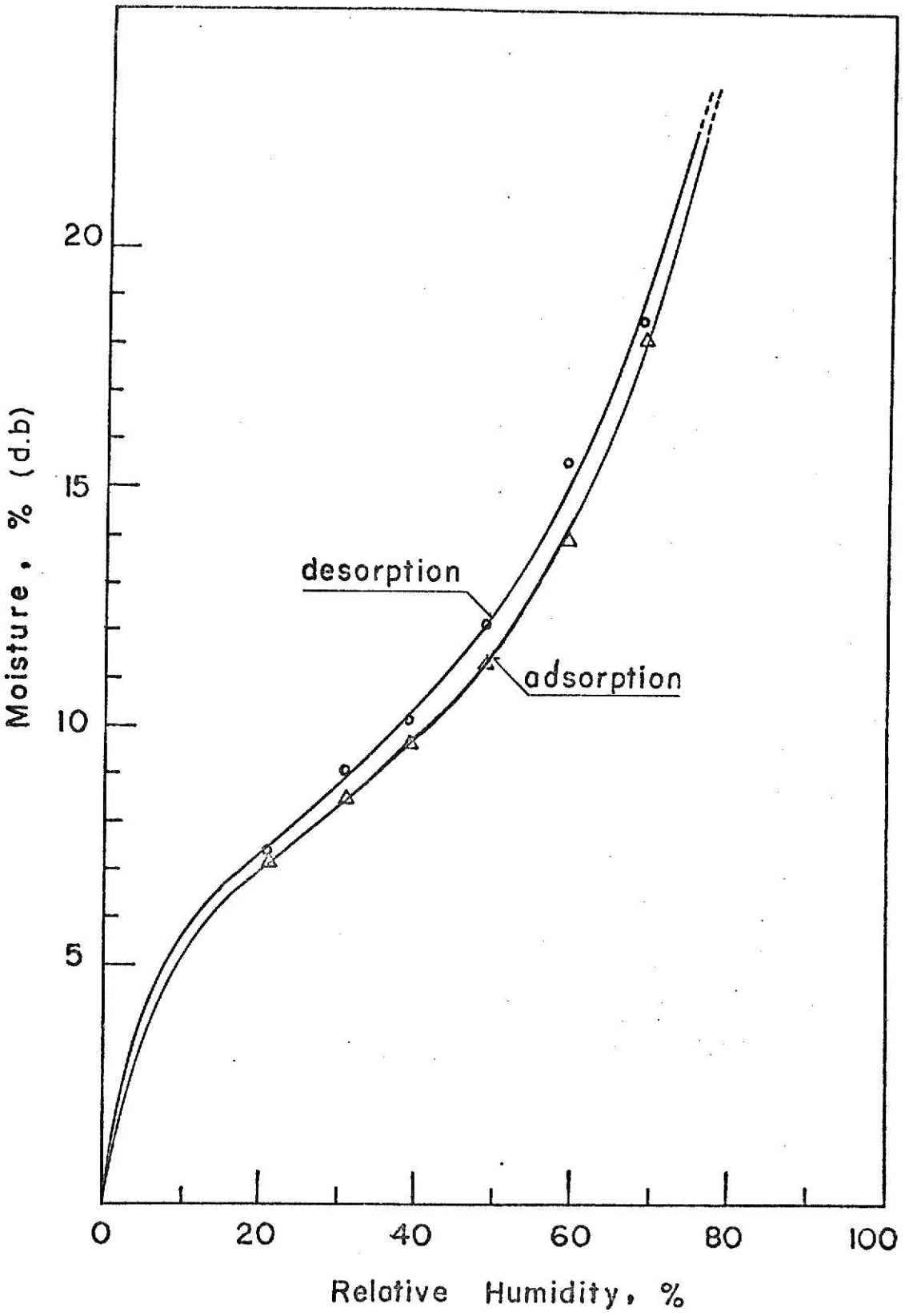


FIGURE 9. ADSORPTION-DESORPTION ISOTHERMS OF BABY LIMA BEANS AT 90° F SHOWING HYSTERESIS EFFECT.

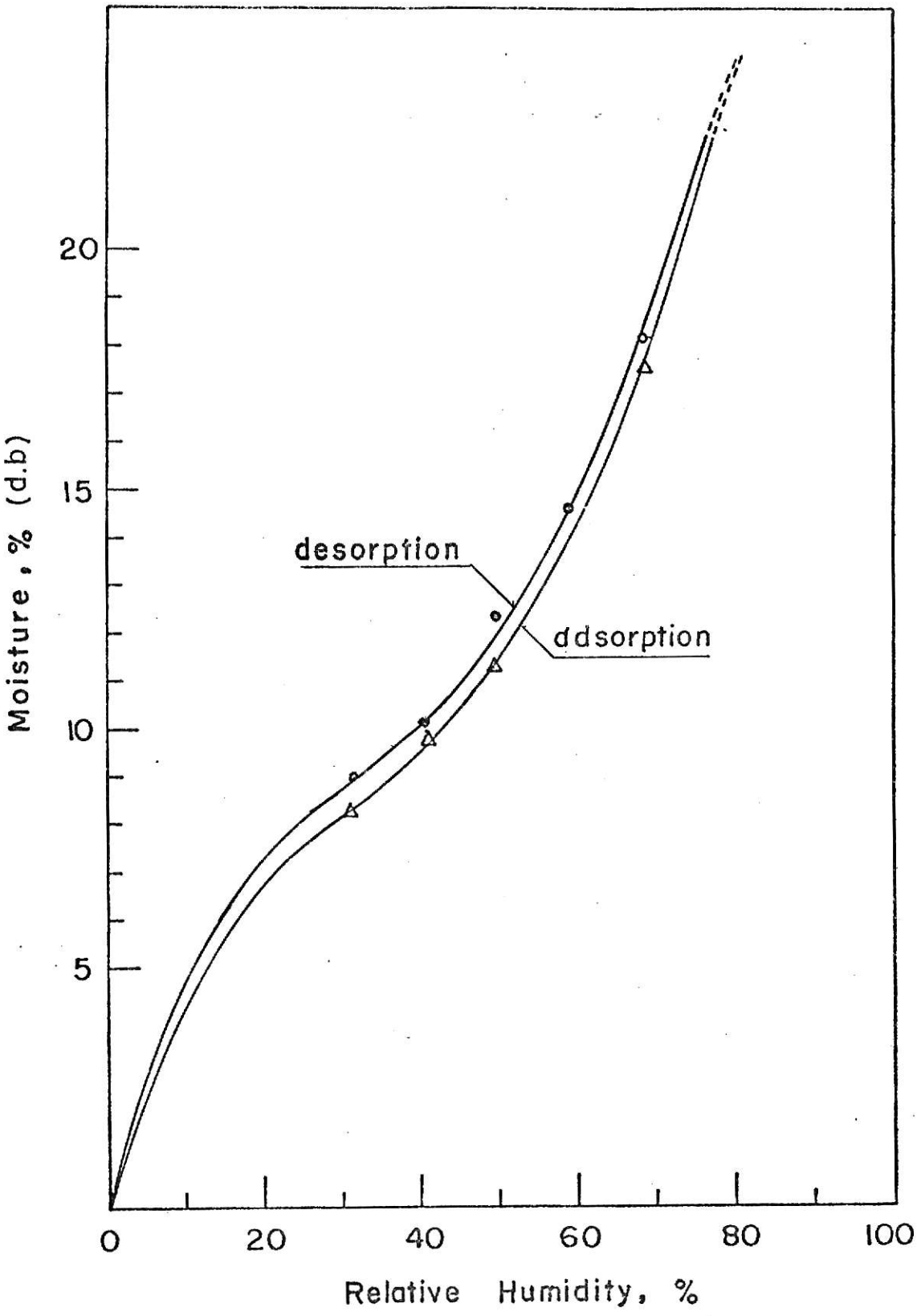


FIGURE 10. ADSORPTION-DESORPTION ISOTHERMS OF BABY LIMA BEANS AT 100° F SHOWING HYSTERESIS EFFECT.

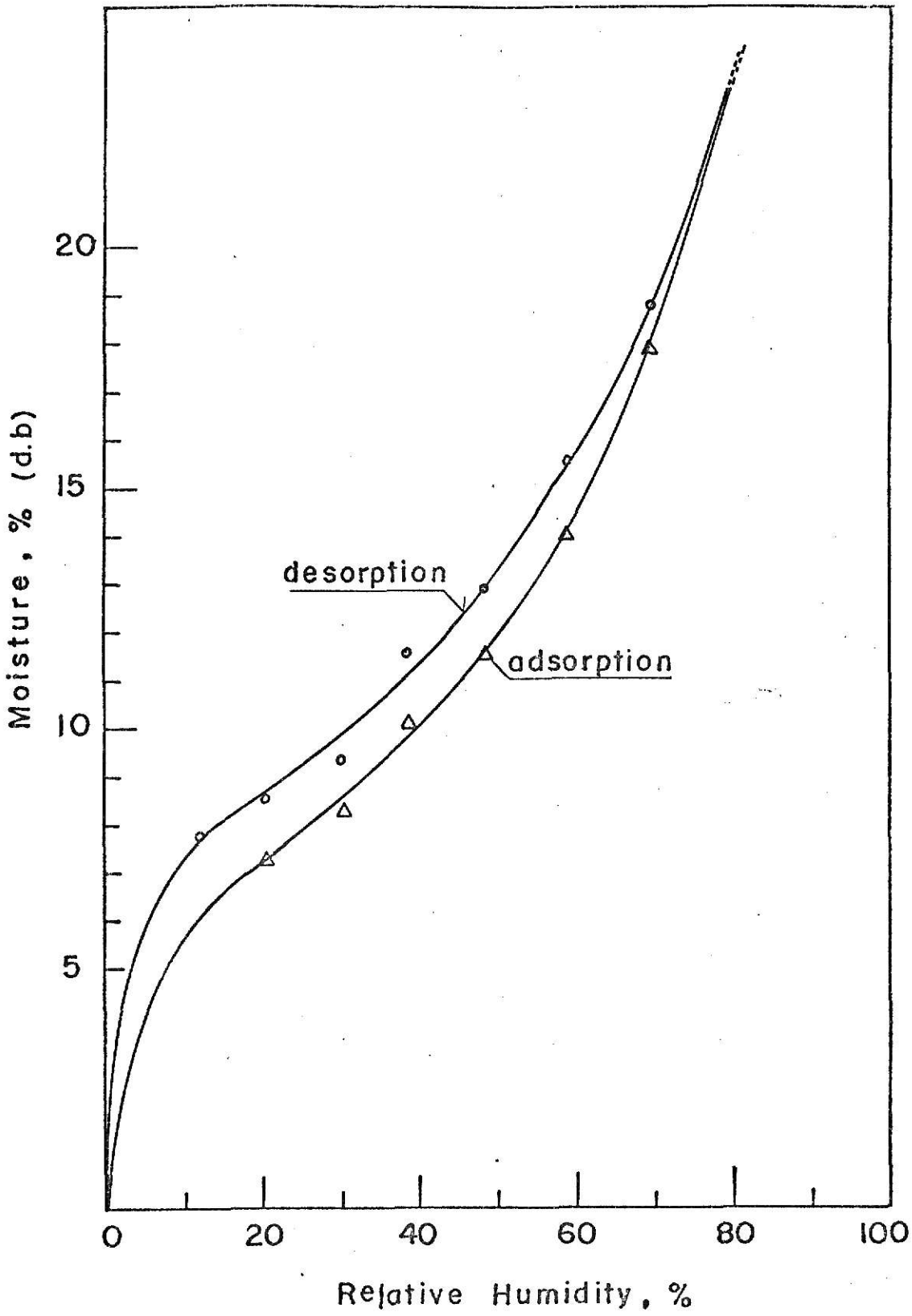


FIGURE 11. ADSORPTION-DESORPTION ISOTHERMS OF PINTO BEANS AT 70° F SHOWING HYSTERESIS EFFECT.

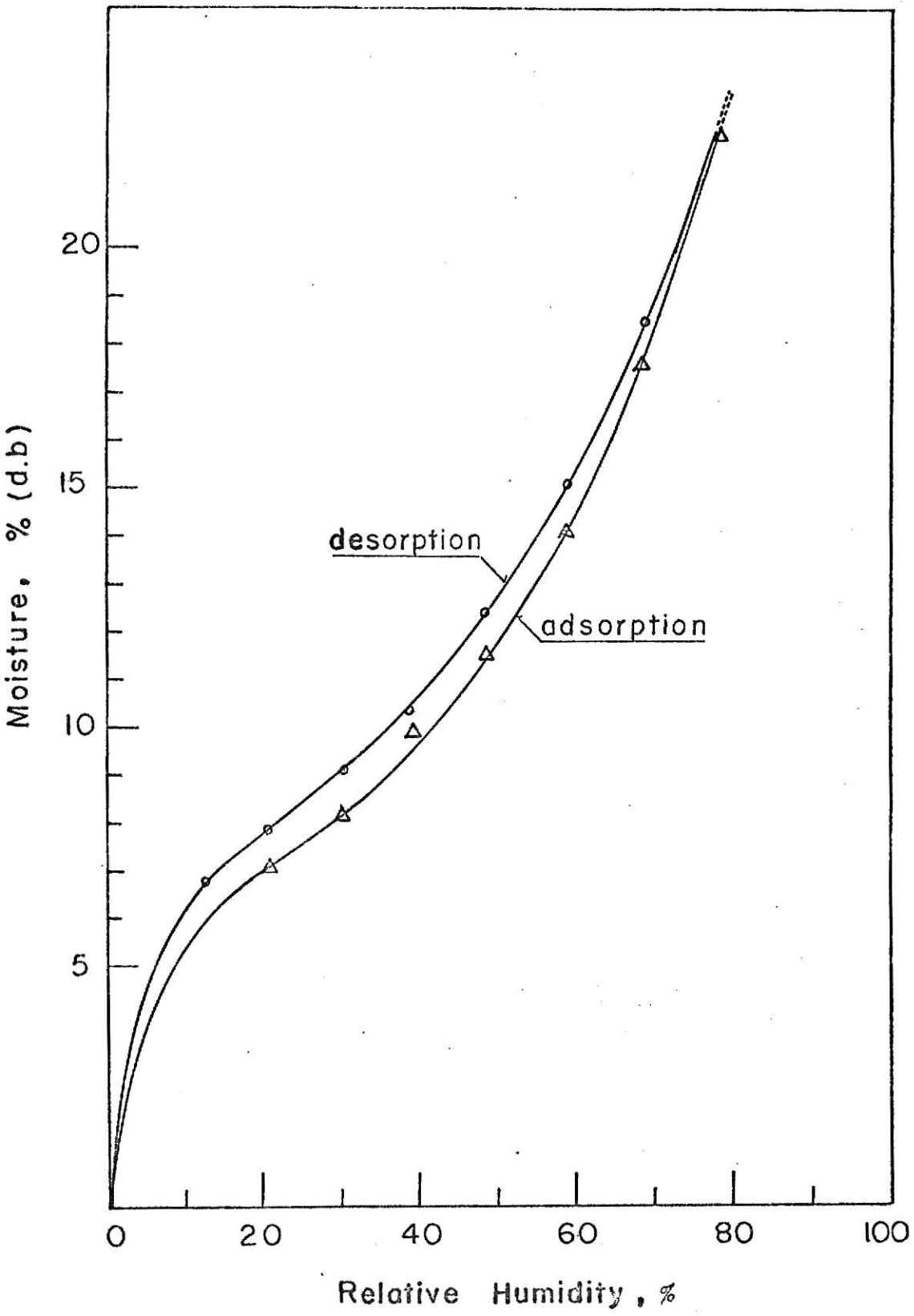


FIGURE 12. ADSORPTION-DESORPTION ISOTHERMS OF PINTO BEANS AT 80° F SHOWING HYSTERESIS EFFECT.

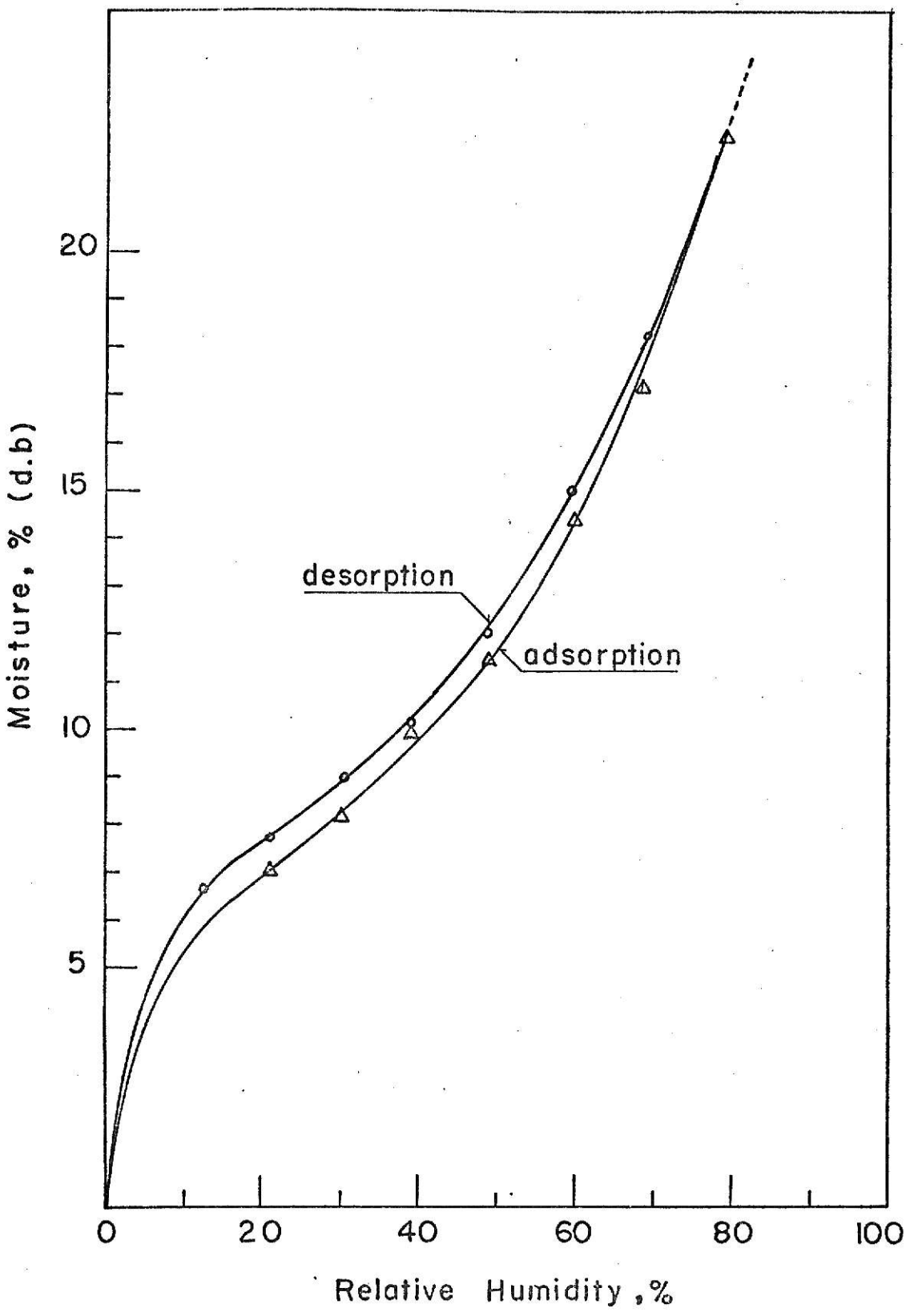


FIGURE 13. ADSORPTION-DESORPTION ISOTHERMS OF PINTO BEANS AT 90° F SHOWING HYSTERESIS EFFECT.

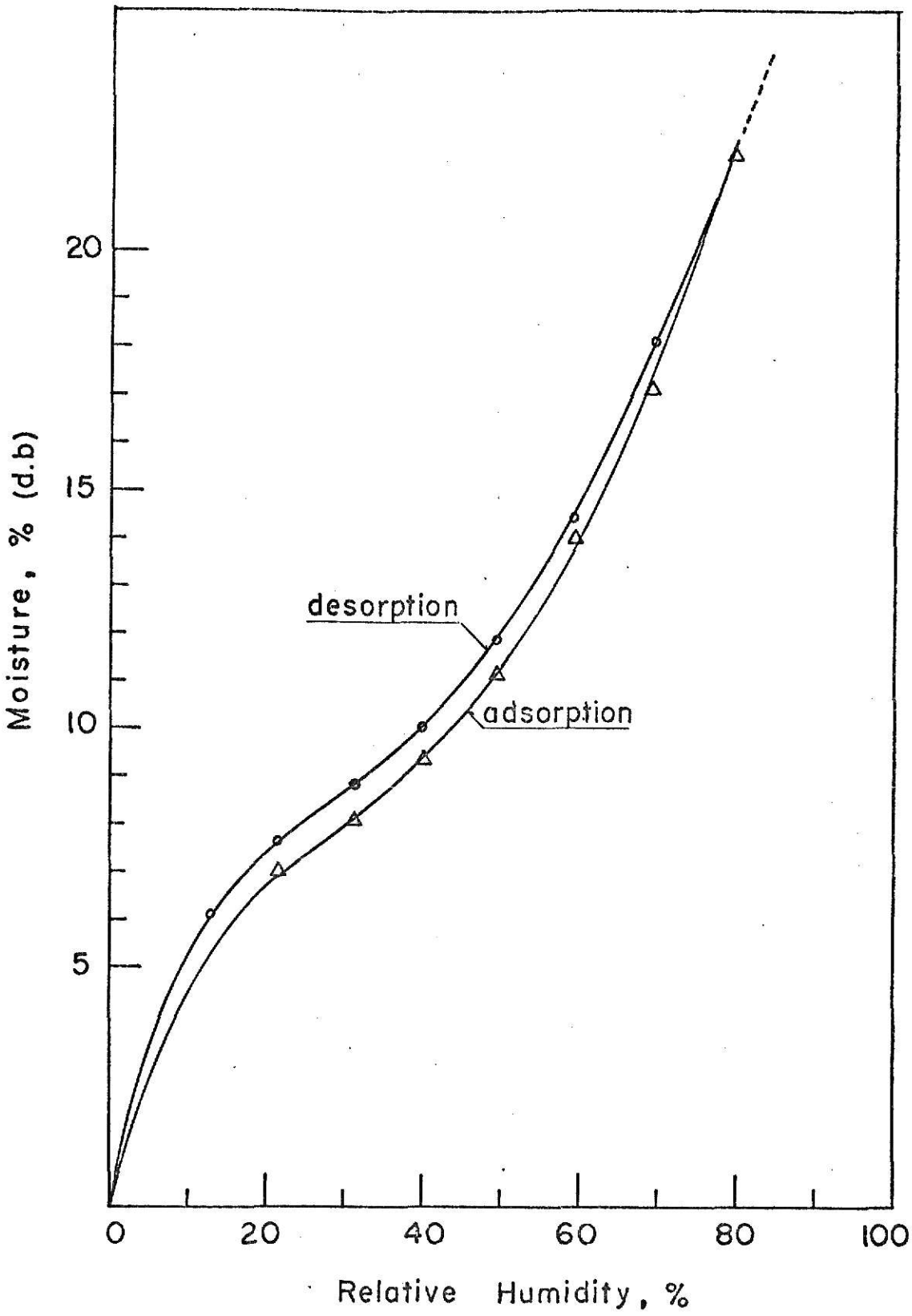


FIGURE 14. ADSORPTION-DESORPTION ISOTHERMS OF PINTO BEANS AT 100° F SHOWING HYSTERESIS EFFECT.

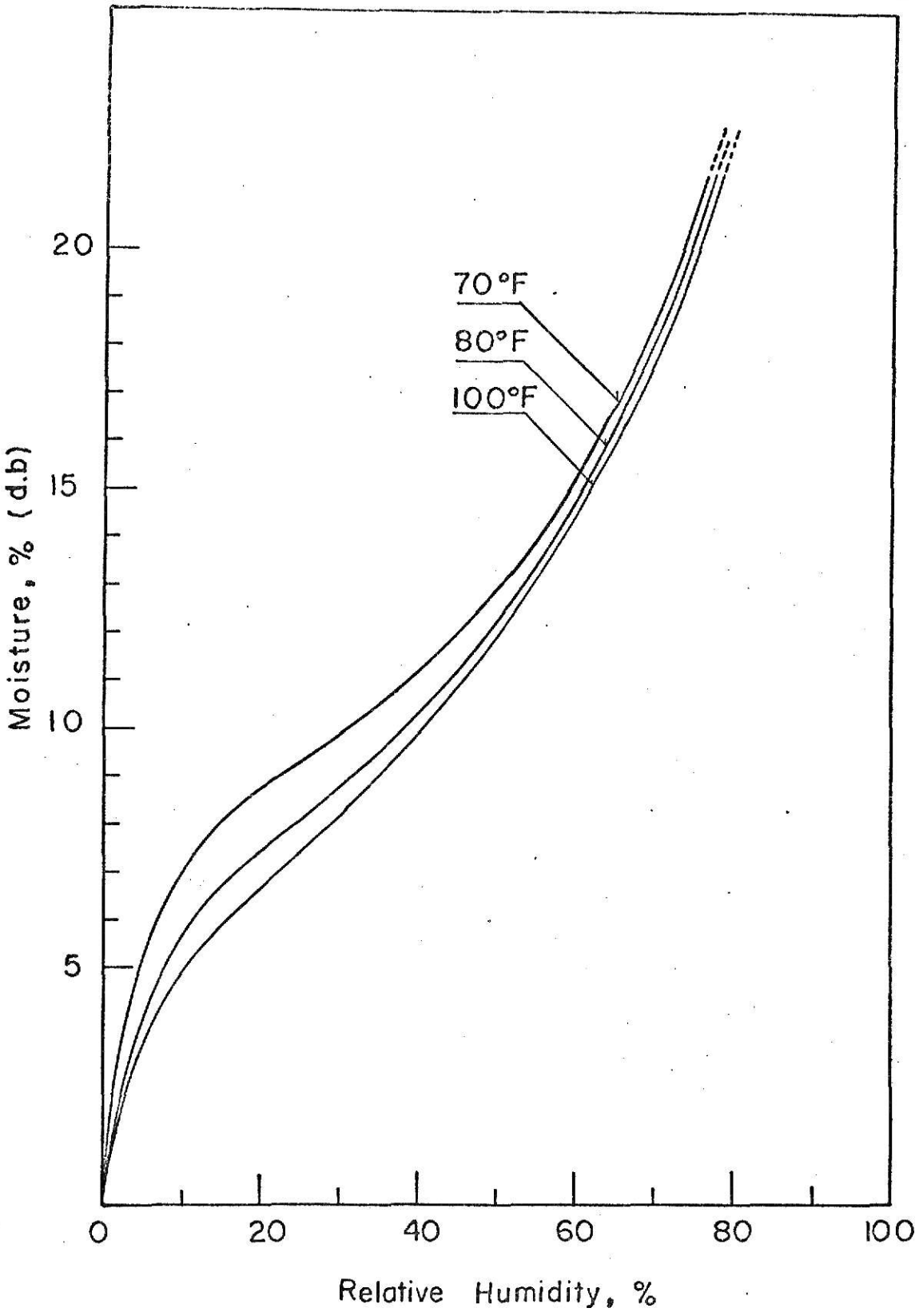


FIGURE 15. DESORPTION ISOTHERMS OF RED BEANS AT 70° F, 80° F, and 100° F SHOWING TEMPERATURE EFFECT.

A small difference in the value of equilibrium moisture content among various beans examined at a specified environment condition was observed.

For each kind of bean the phenomenon, commonly referred to as hysteresis, was present as shown in Figures 3 through 14. The results showed that hysteresis decreases with an increase in temperature. For the purpose of illustration isotherms curves for red bean at 70° F and 100° F temperature were plotted in Figure 16. Agreement in the hysteresis effect for the different kinds of beans at a given condition of relative humidity and temperature was observed. Molecular shrinkage during desorption is believed to reduce the availability of sorption sites on sorbent surface. Chung (1966) postulated that the difference in the availability of sorptive sites or polar sites on the surface of the adsorbent to water cause the hysteresis phenomenon.

Attention has been called repeatedly to the difference in the moisture contents of various cereal grains at different relative humidities, and the relationship of these values to allowable moisture content in storage. It is quite generally agreed that the critical moisture level for any cereal is the percentage moisture at which the seed is in equilibrium with a humidity of about 70 percent. Thus, the moisture contents at 70 percent relative humidity of barley, oats and wheat are about 14.5, 13.9, 14.6 percent respectively, whereas flax seed and other oil seeds are lower in equilibrium moisture content, at 75 percent relative humidity. We found that beans are higher with a value about 17% moisture. Thus, the storage of beans at high levels of moisture from 16 to 17%, dry basis can be considered safe.

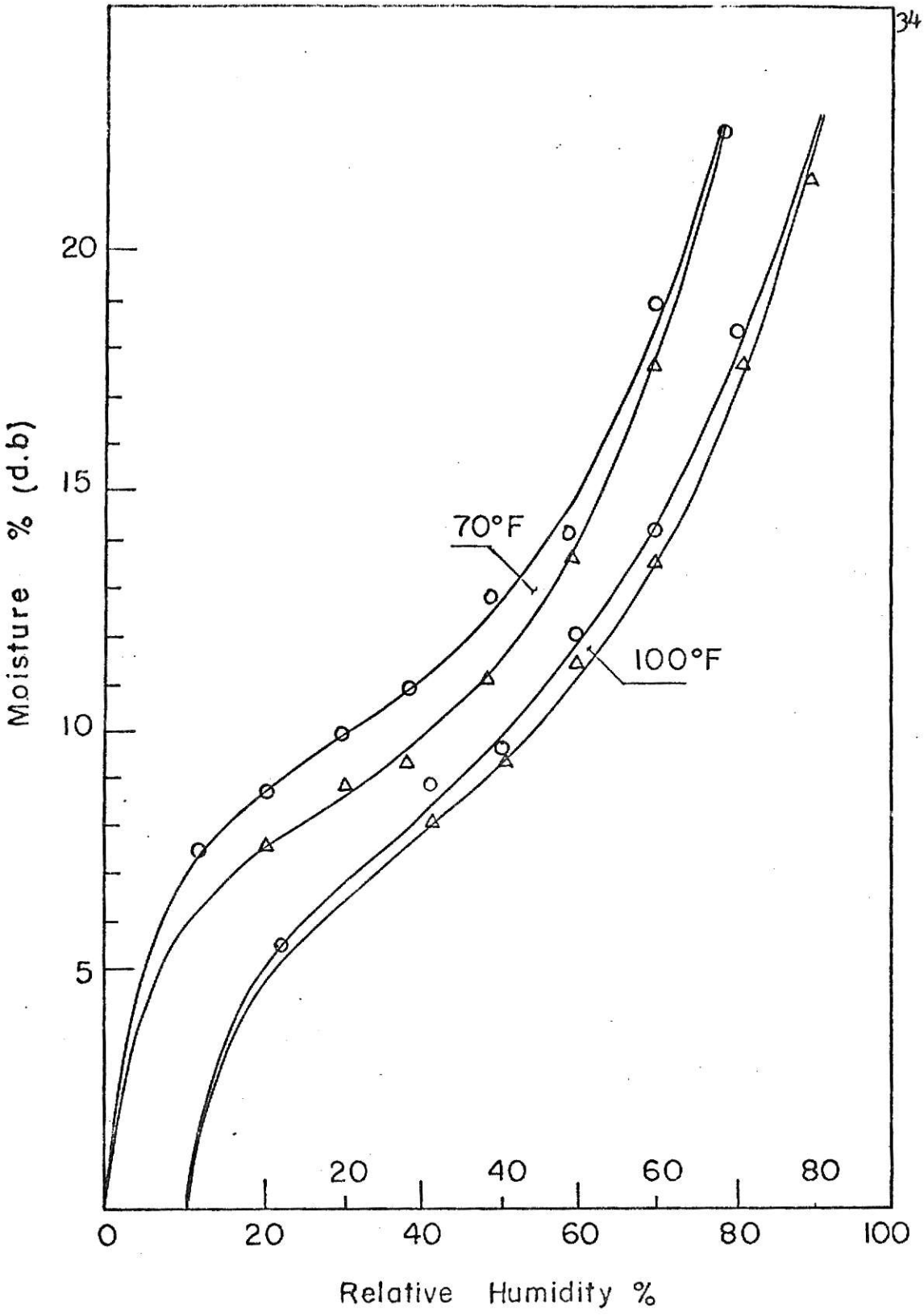


FIGURE 16. ADSORPTION-DESORPTION ISOTHERMS OF RED BEANS AT 70° F AND 100° F SHOWING HYSTERESIS EFFECT.

Application of Chung and Pfost Equation

The Chung and Pfost equation as explained in the review of literature, was tested to find its applicability to the results of this investigation.

In order to apply this equation, first, the values of $-\triangle F$ of desorption and adsorption at 70° F, 80° F, 90° F, and 100° F for each kind of bean were calculated using the equation (10). The values P/P_o of this equation were taken from curves 3 through 14 using the experimental data for constant values of m. These values are tabulated in Table 2. For the purpose of illustration, semiloganthmic paper values of $-\triangle F$ against moisture for red beans at different temperatures were plotted. The plotting of the values of $-\triangle F$ against moisture yielded a straight line as shown in Figure 17 which supports the assumption expressed by Chung and Pfost in their equation, namely, $-\triangle F = Ae^{-Bm}$ (11). Then the equation was transformed into a linear form $\ln(-\triangle F) = \ln A - Bm$ (15), and the constants A and B were evaluated by the least square method. The values of A, B and the values of the correlation coefficient are tabulated in Table 3.

For the Chung and Pfost equation the linear portion found and shown in Figure 17 has a correlation coefficient of +0.97 or better. The entire range of data is linear for this equation. For baby lima beans and pinto beans similar results were found at all temperatures of desorption and adsorption.

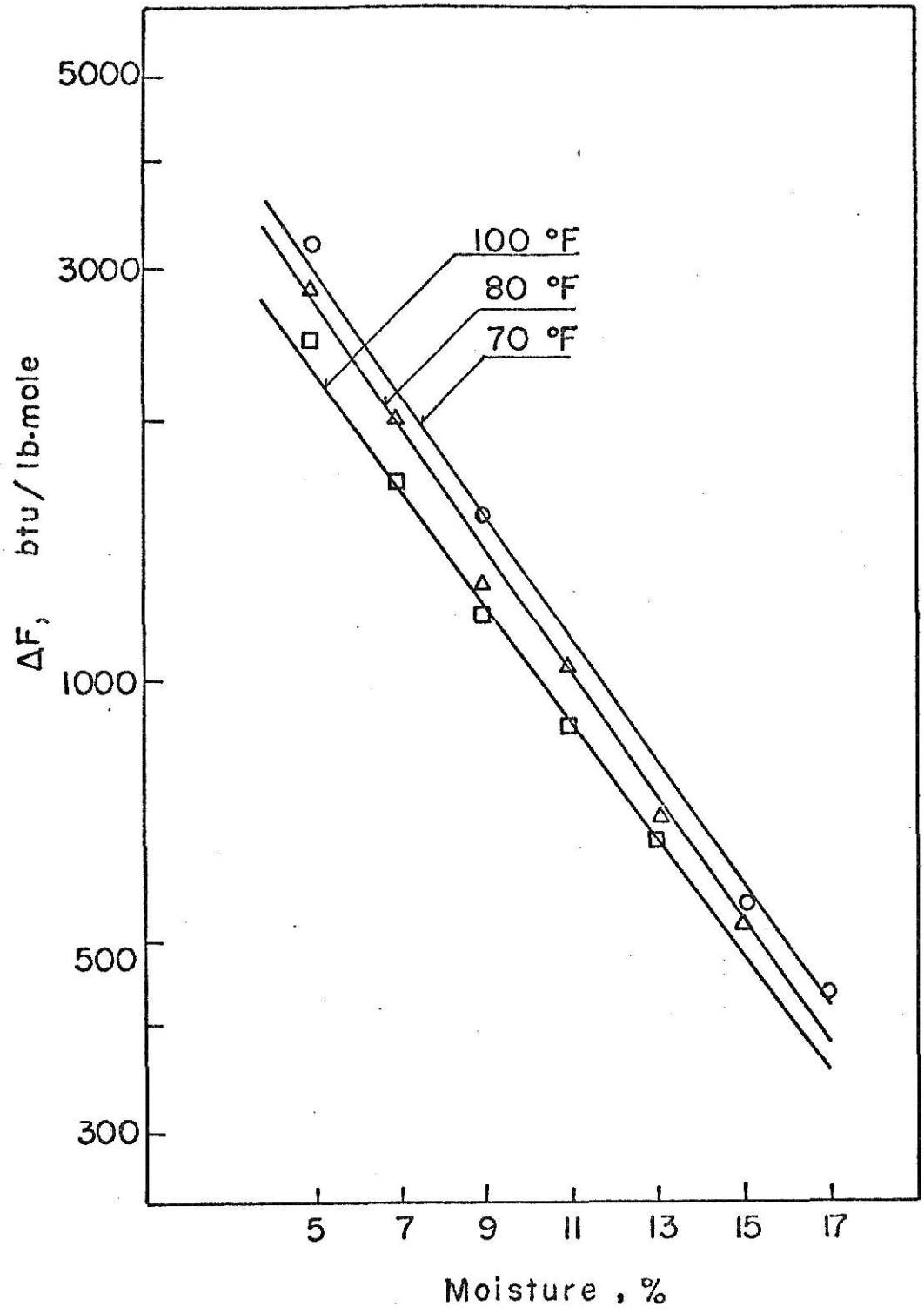


FIGURE 17. THE CHANGE IN FREE ENERGY OF DESORPTION FOR RED BEANS AT 70° F, 80° F, and 100° F.

Table 2. The free energy change of desorption and adsorption for various beans.

Material	Temperature (deg. Fahr)	m	Desorption $-\Delta F$, BTU/lb-mole	Adsorption $-\Delta F$, BTU/lb-mole
Red bean	100	5	2559.55	2453.60
		7	1683.10	1563.46
		9	1166.98	1075.56
		11	863.18	792.95
		13	664.55	605.51
		15	522.45	478.85
		17	420.55	396.47
		19	334.70	327.22
	90	5	2827.92	2691.27
		7	2000.72	1757.10
		9	1243.97	1129.62
		11	871.77	812.74
		13	672.72	623.31
		15	539.64	487.23
		17	437.22	421.04
		19	351.08	343.58
	80	5	3015.69	2707.32
		7	2033.52	1780.13
		9	1221.35	1125.30
		11	1071.90	809.30
		13	670.47	621.50
		15	529.83	486.78
		17	429.27	413.39
		19	344.70	344.70
	70	5	3262.50	2875.63
		7	2422.43	1927.96
		9	1546.17	1134.96
		11	985.23	794.32
		13	687.96	609.99
		15	537.41	477.76
		17	437.14	405.73
		19	352.93	338.32

Table 2 (continued)

Material	Temperature (deg. Fahr)	m	Desorption $-\Delta F$, BTU/lb-mole	Adsorption $-\Delta F$, BTU/lb-mole
Baby lima beans	100	5	2453.60	2311.50
		7	1875.71	1734.81
		9	1199.20	1105.21
		11	875.33	839.28
		13	684.95	644.52
		15	558.60	522.45
		17	461.88	428.70
		19	396.47	372.91
	90	5	2827.92	2628.87
		7	1902.88	1757.10
		9	1261.17	1146.14
		11	921.40	835.97
		13	693.12	642.80
		15	557.69	521.89
		17	478.73	437.22
		19	413.04	381.62
	80	5	2929.89	2642.34
		7	2107.47	1899.36
		9	1255.39	1140.72
		11	929.87	820.77
		13	680.52	640.82
		15	556.52	521.08
		17	461.75	429.27
		19	397.74	
	70	5	3100.33	2797.67
		7	2422.43	2068.44
		9	1804.05	1266.63
		11	1166.36	840.07
		13	772.17	638.56
		15	564.04	511.43
		17	453.20	429.20
		19	375.23	375.23

Table 2 (continued)

Material	Temperature (deg. Fahr)	m	Desorption $-\Delta F$, BTU/lb-mole	Adsorption $-\Delta F$, BTU/lb-mole
Pinto beans	100	5	2676.67	2404.19
		7	1937.48	1713.84
		9	1242.54	1075.56
		11	875.33	792.95
		13	674.70	628.75
		15	549.45	518.90
		17	445.17	428.70
		19	365.16	349.83
	90	5	2951.06	2691.27
		7	2108.19	1714.28
		9	1278.63	1100.32
		11	896.30	821.97
		13	699.32	642.80
		15	566.82	514.87
		17	453.63	432.34
		19	373.91	358.64
	80	5	3033.71	2694.01
		7	2122.89	1725.15
		9	1312.19	1095.10
		11	924.78	809.30
		13	711.30	640.82
		15	565.56	512.40
		17	465.05	429.27
		19	374.69	359.59
	70	5	3468.43	2782.75
		7	2657.19	1804.05
		9	1501.39	1150.54
		11	990.61	828.44
		13	750.47	628.95
		15	591.37	502.91
		17	469.51	421.32
		19	375.23	355.88

Table 3. Tabulation of constants A, B and correlation coefficient for various beans

Material		Temperature	A	B	r
Red beans	desorp	70° F	5591.48	14.72	0.998
	desorp	80° F	5229.11	15.27	0.981
	desorp	90° F	4717.33	14.27	0.960
	desorp	100° F	4272.69	13.69	0.830
	adsorp	70° F	3781.96	13.21	0.995
	adsorp	80° F	4424.88	14.77	0.999
	adsorp	90° F	4230.18	13.86	0.994
	adsorp	100° F	4242.89	14.14	0.994
Baby lima beans	desorp	70° F	5655.06	14.09	0.996
	desorp	80° F	4909.85	14.22	0.985
	desorp	90° F	4101.05	12.91	0.997
	desorp	100° F	5049.27	14.71	0.999
	adsorp	70° F	4054.16	13.35	0.992
	adsorp	80° F	3349.61	12.23	0.999
	adsorp	90° F	3359.00	12.22	0.987
	adsorp	100° F	3553.18	12.73	0.994
Pinto beans	desorp	70° F	5329.43	13.96	0.992
	desorp	80° F	5112.78	14.46	0.983
	desorp	90° F	5334.78	14.99	0.988
	desorp	100° F	4895.14	14.48	0.982
	adsorp	70° F	3494.69	12.18	0.992
	adsorp	80° F	3388.01	11.88	0.984
	adsorp	90° F	3010.90	11.30	0.991
	adsorp	100° F	3408.40	12.18	0.988

The theoretical desorption and adsorption isotherms of beans were obtained by substituting the corresponding constants A and B from Table 3 into equation 15. The isotherm data of various beans calculated by the theoretical Chung and Pfost equation are given in Table 4. In this table we can see a close agreement between experimental and theoretical isotherm data for the entire range of relative humidity.

As a conclusion, the isotherm equation developed by Chung and Pfost is very useful to determine the sorption of beans for a wide range of relative humidity at a given temperature.

Table 4. Comparison of calculated moisture contents and experimental moisture contents for isotherms of beans.

Material	Temp.	P/P_o	Desorption m(exp)	Desorption m(calc)	Adsorption m(exp)	Adsorption m(calc)
Red beans	70° F	0.8940				
		0.7915	22.35	21.21	21.50	20.69
		0.6946	18.88	18.20	17.50	17.33
		0.5907	14.05	15.70	13.65	14.55
		0.4857	12.79	13.56	11.00	12.16
		0.3889	10.76	11.73	9.35	10.12
		0.3013	9.91	10.11	8.89	8.32
		0.2038	8.66	8.19	7.50	6.18
		0.1162	7.53	6.13		
	80° F	0.8917				
		0.7862			19.52	19.24
		0.6904	17.59	16.87	16.93	16.32
		0.5899	14.29	14.56	13.61	13.92
		0.4862	12.06	12.51	11.06	11.81
		0.3902	10.00	10.77	9.68	10.01
		0.3016	8.69	9.19	8.35	8.37
		0.2073	7.78	7.41	7.14	6.53
		0.1211	6.53	5.48		
	90° F	0.8951				
		0.7895				
		0.6939	18.28	17.31	17.90	17.04
		0.5934	14.33	14.81	14.04	14.46
		0.4900	11.66	12.62	11.56	12.21
		0.3944	10.11	10.76	10.07	10.29
		0.3059	8.81	9.07	8.46	8.55
		0.2116	7.33	7.17	7.19	6.60
		0.1229	6.43	5.07		
	100° F	0.8981				
		0.7924				
		0.6975	18.37	17.28	17.78	16.69
		0.5979	14.24	14.68	13.39	14.17
		0.4955	11.95	12.41	11.48	11.97
		0.4007	9.44	10.48	9.35	10.10
		0.3119	8.91	8.71	8.15	8.39
		0.2165	6.39	6.73	7.74	6.47
		0.1266	5.59	4.53		

Table 4 (continued)

Material	Temp.	P/P_o	Desorption m(exp)	Desorption m(calc)	Adsorption m(exp)	Adsorption m(calc)
Pinto beans	70° F	0.8940				
		0.7915	23.23	22.03	22.95	21.78
		0.6946	18.70	18.85	17.77	18.14
		0.5907	15.61	16.22	14.12	15.13
		0.4857	12.93	13.96	11.61	12.53
		0.3889	11.68	12.03	10.22	10.32
		0.3013	9.38	10.32	8.38	8.36
		0.2038	8.61	8.30	7.32	6.05
		0.1162	7.73	6.13		
	80° F	0.8917				
		0.7862			22.69	21.68
		0.6904	18.46	17.67	17.60	18.04
		0.5899	15.06	15.22	14.08	15.06
		0.4862	12.43	13.06	11.51	12.44
		0.3902	10.32	11.22	10.12	10.20
		0.3016	9.04	9.55	8.27	8.16
		0.2073	7.86	7.66	7.28	5.88
		0.1211	6.89	5.63		
	90° F	0.8951				
		0.7895			22.53	21.74
		0.6939	18.33	17.31	17.29	17.89
		0.5934	14.96	14.92	14.00	14.73
		0.4900	12.00	12.84	11.44	11.97
		0.3944	10.23	11.06	10.08	9.61
		0.3059	8.94	9.45	8.17	7.48
		0.2116	7.73	7.65		
		0.1229	6.74	5.65		
	100° F	0.8981				
		0.7924			22.08	21.17
		0.6975	18.29	17.29	17.16	17.58
		0.5979	14.40	14.83	14.00	14.66
		0.4955	11.84	12.67	11.35	12.10
		0.4007	10.16	10.85	9.43	9.93
		0.3119	8.80	9.18	8.07	7.94
		0.2165	7.65	7.30	7.05	5.71
		0.1266	6.29	5.23		

Table 4 (continued)

Material	Temp.	P/P_o	Desorption m(exp)	Desorption m(calc)	Adsorption m(exp)	Adsorption m(calc)
Baby lima bean	70° F	0.8940				
		0.7915	23.34	22.24	21.75	20.98
		0.6946	19.69	19.09	17.96	17.65
		0.5907	15.01	16.49	14.00	14.91
		0.4857	13.21	14.25	11.40	12.54
		0.3889	11.20	12.34	9.80	10.53
		0.3013	10.79	10.64	9.05	8.74
		0.2038	9.54	8.64	8.05	6.63
		0.1162	7.50	6.49		
	80° F	0.8917				
		0.7862			21.50	20.94
		0.6904	18.71	17.68	17.50	17.42
		0.5899	15.09	15.19	13.96	14.52
		0.4862	12.39	13.00	11.40	11.97
		0.3902	9.69	11.13	9.61	9.80
		0.3016	8.85	9.43	8.57	7.83
		0.2073	7.95	7.51		
		0.1211	6.79	5.45		
	90° F	0.8951				
		0.7895				
		0.6939	18.55	18.05	18.20	17.44
		0.5934	15.63	15.29	13.90	14.52
		0.4900	12.14	12.87	11.26	11.96
		0.3944	10.14	10.81	9.65	9.78
		0.3059	9.04	8.94	8.53	7.82
		0.2116	7.34	6.84		
		0.1229				
	100° F	0.8981				
		0.7924				
		0.6975	18.08	17.22	17.42	17.14
		0.5979	14.52	14.80	14.16	14.35
		0.4955	12.36	12.68	11.25	11.90
		0.4007	10.06	10.89	10.02	9.83
		0.3119	9.14	9.24	8.33	7.92
		0.2165	8.15	7.40		
		0.1266				

Heats of adsorption and desorption for various beans

The heat of adsorption or desorption is indicative of the intermolecular force between the molecules of water vapor and the molecules of water vapor and the surface of absorbent. If water vapor is adsorbed on a surface, a quantity of heat has to be released which is known as the heat of adsorption. In the same way if water vapor is desorbed, a quantity of heat is taken up, which is called the heat of desorption.

The method of determining the heats of desorption is based on thermodynamic principles. The isosteric heat of sorption is expressed by the following equation

$$\Delta Hst = R\left(\frac{T_1 T_2}{T_2 - T_1}\right) \quad \ln P_2/P_1 \qquad (16)$$

where P_1 and P_2 are equilibrium vapor pressures at the absolute temperatures T_1 and T_2, respectively. In the evaluation of isosteric heats of adsorption and desorption of beans, relative humidities P_1/P_o and P_2/P_o were obtained from Figures 3 through 17 at constant values of m. The relative humidities were converted to the equilibrium vapor pressure P_1 and P_2. The values of Δ Hst finally were calculated by equation 16 with substitution of P_2 and P_1 at corresponding constant m.

For each kind of beans the isosteric heat of adsorption and desorption was calculated. The values of isosteric heats of adsorption and desorption that were calculated ranged from 2,000 BTU/lb to 1,000 BTU/lb as shown in Table 5. From these tables we can see that the values of heats of desorption are greater than those of heat of adsorption. This means that the energy involved in the desorption process of beans

Table 5. Values of heats of desorption and adsorption for various beans

Material	m %	Desorption Δ Hst BTU/lb.	Adsorption Δ Hst BTU/lb.
Red beans	5	1889.18	1568.42
	7	1676.03	1461.34
	9	1186.85	1174.56
T_1 = 80° F	11	1111.55	1106.92
and	13	1095.94	1083.54
T_2 = 100° F	15	1077.94	1076.36
	17	1074.35	1073.05
	19	1072.00	1071.58
	5	1864.50	1474.63
	7	1798.88	1402.10
	9	1574.24	1112.84
T_1 = 70° F	11	1265.23	1060.45
and	13	1089.15	1057.73
T_2 = 90° F	15	1070.01	1056.05
	17	1067.62	1043.45
	19	1065.77	1054.49
Baby lima beans	5	1914.64	1680.49
	7	1502.16	1389.77
	9	1191.45	1154.08
T_1 = 80° F	11	1170.89	1067.26
and	13	1068.60	1065.48
T_2 = 100° F	15	1065.22	1064.33
	17	1062.89	1062.13
	19	1061.42	1060.92
	5	2068.82	1447.38
	7	1942.92	1616.73
	9	1942.92	1291.21
T_1 = 70° F	11	1468.89	1096.15
and	13	1202.71	1072.67
T_2 = 90° F	15	1084.14	1066.46
	17	1057.03	1055.49
	19	1048.63	1054.89

Table 5 (continued)

Material	m %	Desorption Δ Hst BTU/lb.	Adsorption Δ Hst BTU/bl.
Pinto beans	5	1741.53	1621.83
	7	1433.49	1150.25
	9	1214.81	1127.58
T_1 = 80° F	11	1162.97	1106.92
and	13	1131.84	1091.13
T_2 = 100° F	15	1093.02	1066.15
	17	1093.00	1062.13
	19	1072.54	1060.00
	5	1999.82	1332.71
	7	1997.32	1275.83
	9	1454.81	1181.30
T_1 = 70° F	11	1237.33	1099.00
and	13	1160.45	1059.99
T_2 = 90° F	15	1112.44	1057.78
	17	1092.90	1053.78
	19	1066.24	1050.63

is greater than that in the adsorption process. For the purpose of illustration in Figure 18 we can observe that the heats of adsorption and desorption decrease continually with increasing moisture content and also that the heats of desorption and adsorption of beans are higher than heat of vaporization of pure water.

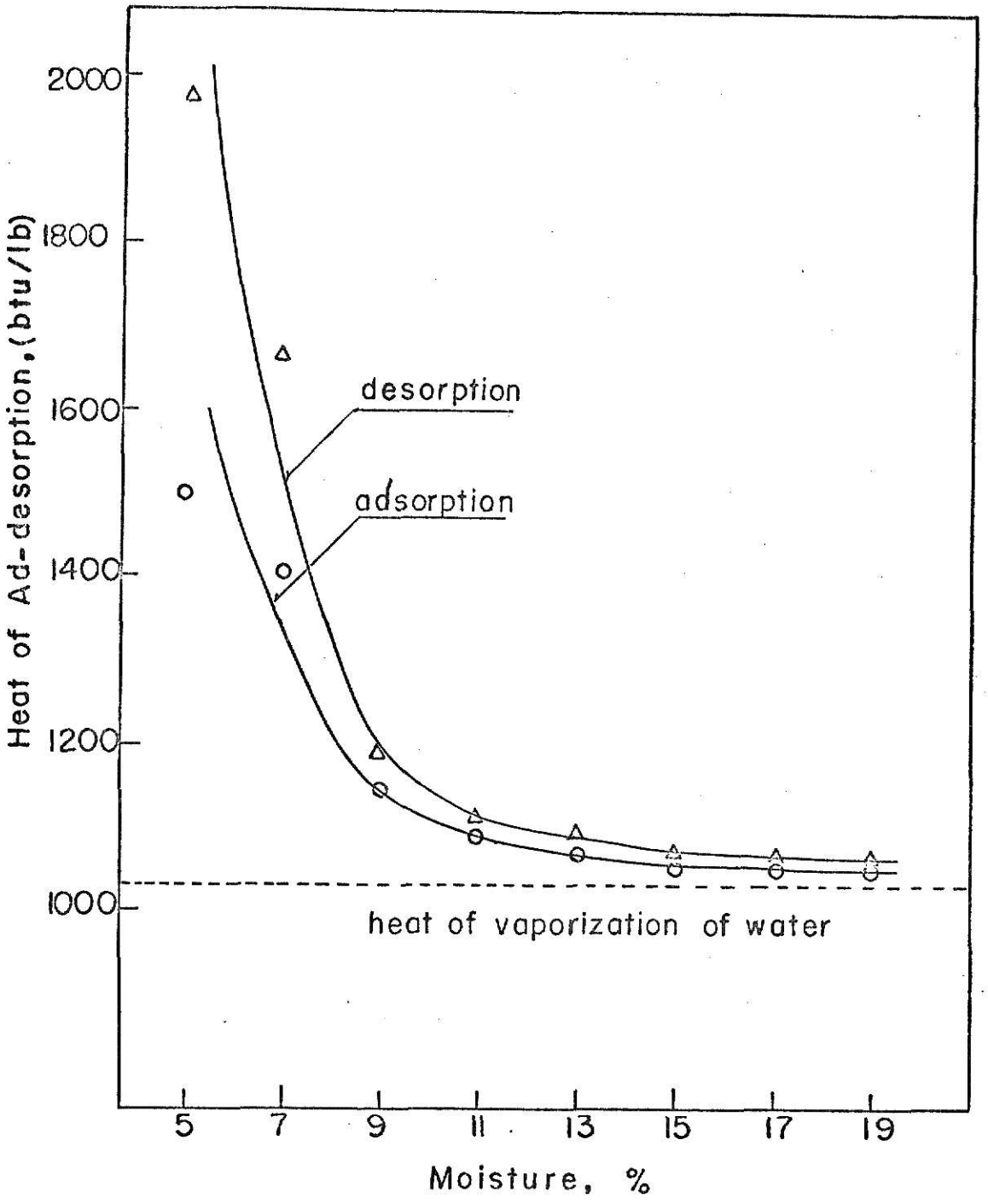


FIGURE 18. HEATS OF ADSORPTION AND DESORPTION FOR RED BEANS.

CONCLUSIONS

From the results of this investigation, the following conclusions were made:

1. The equilibrium moisture content for beans investigated decreases with an increase in temperature.

2. The Type II isotherm or sigmoid isotherm for beans is consistent with those for other grains found by earlier investigators.

3. The equilibrium moisture content for beans increases with an increase in relative humidity.

4. Hysteresis, for beans, decreases with an increase in temperature.

5. The rate of desorption for beans is a function of the relative humidity and temperature.

6. The rates of desorption for beans were higher in the first two days of storage period.

7. The isotherm equation developed by Chung and Pfost will predict the equilibrium moisture of beans for a wide range of relative humidity at a given temperature.

8. Isosteric heats of desorption and adsorption continually decrease with increasing moisture content, and the values of $\triangle$Hst for desorption are greater than those of adsorption.

9. The heat of desorption for beans was found to be greater than that of the latent heat of vaporization of pure water.

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EQUILIBRIUM MOISTURE CONTENT OF BEANS

by

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AN ABSTRACT OF A MASTER'S THESIS

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The moisture content of hygroscopic materials, such as beans, is very important to agricultural engineers because of its direct relationship to storage and drying problems. In order to provide proper moisture conditions for a particular material, it is often necessary to add moisture to or extract moisture from the material. This wetting or drying process requires a knowledge of the equilibrium moisture content of the grain for the environment to which it is subjected. Thus, the over-all purpose of this investigation was to find the adsorption and desorption isotherms of red beans, baby lima beans and pinto beans at 70° F, 80° F, 90° F, and 100° F for a range of relative humidity from 10 to 90 percent, and to test the fitness of the results in the Chung and Pfost equation. The investigation also dealt with the rate of desorption in red beans and heat of sorption of water by various types of beans.