

SIMULATION OF NUTRIENT STABILITY
IN DRY FOODS DURING STORAGE

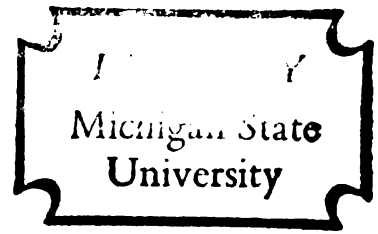
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ABSTRACT

SIMULATION OF NUTRIENT STABILITY IN DRY FOODS DURING STORAGE

By

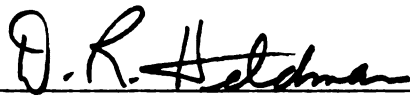
Hadi Karia Purwadaria

Determination of the vitamin content of dry foods during storage is essential for the processor to accomplish label claims. The objectives of this study were 1) to establish a mathematical model describing the rate of vitamin degradation (k) as a function of product water activity (a_w) and 2) to develop a computer-aided prediction of vitamin degradation and moisture uptake in dry foods during storage.

A model food system was used in this study with ascorbic acid as the observed nutritional quality index. Shelf-life tests were conducted at a temperature of 30°C, and at 10, 40, and 85% RH using cardboard boxes with waxed-paper liners as the packaging material.

The results showed that the relationship between k for ascorbic acid and a_w is linear at 10, 20, and 30°C. The predicted results provided good agreement with the experimental data. The simulation is applicable to predict the vitamin degradation for a one-year period.

Approved by:



Major Professor
and Department Chairman

SIMULATION OF NUTRIENT STABILITY
IN DRY FOODS DURING STORAGE

By

Hadi Karia Purwadaria

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INTRODUCTION

Dry foods can deteriorate during storage due to oxidative mechanisms resulting in nutrient degradation, off-flavor development, and color changes. Accurate determination of the vitamin content of dry foods during storage is essential to provide the processor with the assurance of meeting label claims.

Shelf-life tests for measurement of vitamin degradation are time consuming and costly. Computer simulation of vitamin destruction in dry foods represents an alternative approach to shelf-life testing which is worth considering. The development of acceptable computer simulation requires the incorporation of experimental kinetics data which describe the rate of vitamin degradation as a function of water activity and temperature along with appropriate moisture and oxygen transport coefficients for the product packaging material.

In this study, a computer simulation to predict the moisture gain and the vitamin degradation in dry foods during storage was developed. The simulation is useful for the manufacturer in selecting product packaging material and product storage conditions as well as meeting the labeled nutrition claim of the product.

Ascorbic acid was selected as the index of the nutrient quality for the purpose of this research because of its labile nature compared to the other vitamins in foods. A model food system was used to provide better control of the uniformity of initial food composition and

vitamin concentration. The mathematical model obtained in this study is for ascorbic acid in the model food system. However, the procedure described for establishing the mathematical model and for developing the computer simulation can be applied to other vitamins in dry foods with minor modifications.

The specific objectives of this research were:

1. To examine the rate of moisture adsorption as a function of storage relative humidity and moisture transport coefficient of the packaging film.
2. To develop a mathematical model to describe the rate of vitamin degradation as a function of product water activity.
3. To develop a computer-aided prediction of ascorbic acid degradation in the model food system during storage.
4. To examine the application of computer simulation to prediction of ascorbic acid stability in dry foods during storage under various storage conditions, various characteristics of the food product and various packaging materials.

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REVIEW OF LITERATURE

The Influence of Water Activity, Moisture Content and Temperature on Ascorbic Acid Degradation

Several researchers have recently conducted experiments on ascorbic acid degradation in different kinds of food products. Vojnovitch and Pfeifer (1970) carried out research on the stability of ascorbic acid in wheat flour, corn-soya-milk (CSM), and mixed infant cereal. Lee and Labuza (1975) worked on a model food system composed of corn oil, glycerol, cellulose, ascorbic acid, and water (model food system I). Kirk et al. (1976) used a different model food system containing protein, fat, carbohydrate, reducing sugar, sucrose, and salt (model food system II) into which ascorbic acid was added.

All of the above studies showed that the degradation of ascorbic acid at various water activities and storage temperatures follows the first order kinetic reaction. Table 1 illustrates that the rate of ascorbic acid degradation increases (half-life decreases) with increasing water activity (and thus moisture content), and with temperature.

Based on the activation energy (E) data, Lee and Labuza (1975) concluded that there was no change in the mechanism of the oxidation of ascorbic acid as a function of water activity in intermediate moisture foods.

Kirk et al. (1976) observed that the total ascorbic acid (TAA) stability is a function of storage temperature as well as a_w .

Table 1. The rate of ascorbic acid degradation in some food products.

Product	Moisture Content g H ₂ O/100 g solids	a _w	T, °C	Half-life, days	E, Kcal/mole
Mixed infant cereal ^{a)}	5.0	-	45	23.8	14.8
			37	45.3	
			26	103.2	
	7.0	-	45	14.3	12.5
			37	25.0	
			26	47.5	
	10.7	-	45	10.2	4.9
			37	15.0	
			26	19.4	
Model food system I ^{b)}	-	0.32	45	4.2	21.7
			40	6.9	
			35	12.2	
			23	52.5	
	-	0.51	45	1.7	20.8
			40	3.8	
			35	5.9	
			23	23.3	
	-	0.67	45	1.2	17.9
			40	2.0	
			35	3.5	
			23	10.6	
	-	0.75	45	0.6	17.1
			40	1.0	
			35	1.4	
			23	4.4	
	-	0.84	45	0.2	18.3
			40	0.3	
			35	0.6	
			23	1.9	
Model food system II ^{c)}	-	0.24	30	39	15.9
			20	73	
			10	187	
	-	0.40	30	22	17.6
			20	54	
			10	165	
	-	0.65	30	6	24.0
			20	48	
			10	139	

^{a)}Vojnovitch and Pfeifer (1970)^{b)}Lee and Labuza (1975)^{c)}Kirk et al. (1976)

None of the researchers, previously mentioned, established the relationship between the rate of ascorbic acid destruction and a_w .

The Effect of Sorption Hysteresis on the Degradation of Ascorbic Acid

Bach (1974) and Lee and Labuza (1975) found a hysteresis effect on the sorption isotherm of model food system II and model food system I, respectively.

A greater loss of ascorbic acid was reported on the desorption (DM) loop than on the adsorption (DH) loop of the model system. Table 2 shows the half-lives for the adsorption system are larger than those for the desorption system (Lee and Labuza, 1975). The possible reason for this phenomena is that the desorption system has a higher moisture content, and the degradation occurs rapidly due to lower viscosity and possible dilution in the aqueous phase.

Table 2. Half-life for ascorbic acid degradation in desorption (DM) and adsorption (DH) systems (Lee and Labuza, 1975).

a_w	Half-life, days							
	23 °C		35 °C		40 °C		45 °C	
	DM	DH	DM	DH	DM	DH	DM	DH
0.32	37.7	52.5	10.1	12.2	5.9	6.9	3.5	4.2
0.51	20.3	23.3	5.7	5.9	2.8	3.8	1.5	1.7
0.67	7.2	10.6	2.5	3.5	1.2	2.0	0.9	1.2
0.75	2.8	4.4	0.8	1.0	0.5	1.0	0.2	0.6
0.84	1.0	1.9	0.3	0.6	0.18	0.3	0.1	0.2

The Influence of Oxygen on Ascorbic Acid Degradation

It is generally known that the presence of oxygen increases the rate of ascorbic acid degradation, but no specific information of the role of oxygen on the kinetics or mechanism of ascorbic acid oxidation is available.

Labuza and Tannenbaum (1972) discussed the results of Jensen (1967) and Vojnovitch and Pfeifer (1970) as shown on Table 3. It was suggested that the mechanism predominating at high a_w might be nonenzymatic browning, while the low activation energy at low a_w and the loss of ascorbic acid below the monolayer moisture content might possibly be due to other oxidation mechanisms.

The Influence of the Packaging Film on Vitamin Degradation

A packaging film separates an internal environment wherein a food product containing vitamins is stored, from an external environment. Differences in oxygen partial pressure and water activity between the internal and external environment result in the potential transfer of oxygen and moisture through the packaging film.

The outside environment, the barrier properties of the packaging material, and the inside environment all influence the vitamin stability of the product (Karel, 1972a; Heldman, 1974).

Karel et al. (1959) studied the transfer rate of moisture vapor through several types of packaging film at various conditions of relative humidity and temperature. The results showed a linear relationship for both transfer rate versus relative humidity and transfer rate versus

temperature. An in-depth investigation resulted in a polynomial relationship between water vapor transfer and water activity (Karel et al., 1971).

Table 3. Ascorbic acid degradation in wheat flour and seaweed.

Product	Moisture Content, g H ₂ O/100 g solids	a _w	T, °C	k, days ⁻¹	E, Kcal/mole
Seaweed a)	11.1	-	25	6.6 x 10 ⁻³	8.8
			10	3.8	
			4	2.3	
	17.6	-	25	1.54 x 10 ⁻²	10.5
			10	5.78 x 10 ⁻³	
			4	2.89	
	33.3	-	25	7.21 x 10 ⁻²	22.0
			10	6.93	
			4	4.6	
Wheat flour b)	-	0.25	45	4.28 x 10 ⁻⁴	11.0
			37	2.86	
			26	1.43	
	-	0.55	45	1.86 x 10 ⁻³	16.0
			37	1.29	
			26	5.7 x 10 ⁻⁴	
	-	0.65	45	1.97 x 10 ⁻²	22.3
			37	7.0 x 10 ⁻³	
			26	2.1	

a) Jensen (1967)

b) Vojnovitch and Pfeifer (1970)

Quast and Karel (1973) pointed out that the quality degradation of food products is not only affected by moisture transfer into the package but by oxygen transfer as well. The moisture and oxygen transfer expressed as optimal permeability of packaging film, which is the ratio of oxygen permeability to moisture permeability (K_{O₂}/K_W), were found as a function of the bulk density of the food product and the outside relative humidity.

The barrier properties of packaging films are usually expressed as the moisture transport coefficient and oxygen transport coefficient, which are moisture and oxygen permeability per unit film thickness per unit area of the package, respectively (Heldman, 1974).

Computer Simulations and Mathematical Models for Food Quality

Kwolek and Bookwalter (1971) developed a mathematical model to predict storage stability of food as follows:

$$Y = a + t f(T_i) + u \quad (1)$$

where:

- Y: a measure of product quality
- a: initial product quality measurement
- t: time
- $f(T_i)$: the time rate change in Y
associated with the temperature
- u: random error because of the deviation of
observed Y

The functions $f(T_i)$ considered are:

$$f(T_i) = m + KT_i \quad (2)$$

$$f(T_i) = m T_i^K \quad (3)$$

$$f(T_i) = m/(K-T_i) \quad (4)$$

$$f(T_i) = m \exp(-K/T_i) \quad (5)$$

$$f(T_i) = m K^{T_i} \quad (6)$$

where:

m, K: constants

The functions applied to the mathematical model were equation (4) and (5). Equation (5) which is the Arrhenius model predicted flavor and peroxide value of the food product satisfactorily.

Karel (1972b) predicted the storage life of foods based on information gained by experimentally determining the properties of the food, the kinetics of food deterioration, and the package properties. The deterioration mechanism limiting shelf life of a food product and its dependence on the environmental parameters can be described by the following mathematical function:

$$dD/dt = f (RH, PO_2, T) \quad (7)$$

where:

- D: deteriorative index
- t: time
- RH: equilibrium relative humidity
- PO₂: oxygen pressure
- T: temperature

Changes in water activity can be related to the environmental parameters and the food and package properties:

$$a = f(a_0, t, RH, k_1 \dots k_n, T \dots) \quad (8)$$

where:

- a: water activity in the food at any time
- a₀: initial a
- k₁ ... k_n: constants characterizing sorptive and diffusional properties of the food and the package

Mizrahi et al. (1970) developed a simulation of browning in freeze-dehydrated cabbage stored in packages with films having different permeabilities to water vapor. The computer program was based on the

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browning reaction kinetics, the moisture transfer characteristics of the packaging films, and the product moisture contents.

Simon et al. (1971) presented a computer prediction describing the oxidative deterioration of freeze-dried shrimp. Organoleptic deterioration was correlated with absorption of oxygen and with loss of carotenoid pigment.

Labuza et al. (1972) established a mathematical model to calculate moisture gain by a dehydrated food in a package:

$$\ln(m_e - m_i)/(m_e - m_c) = (kH_2O/x)(A/w_s)(p_o/b)t \quad (9)$$

where:

- m_e : moisture content of food as predicted by the isotherm equation if exposed to the external package relative humidity
- m_i : initial moisture content of the food
- m_c : final moisture content
- kH_2O : permeability of the film
- x : film thickness
- A : area of the film
- w_s : weight of dry solids enclosed
- p_o : saturation vapor pressure of water at a given constant temperature, T
- b : barometric pressure

The equation was derived by assuming the sorption isotherm to be a linear function of relative humidity.

Quast et al. (1972) developed a mathematical model for oxidation of potato chips. The rate of oxygen uptake for potato chips was determined as a function of oxygen partial pressure, equilibrium relative humidity, and extent of oxidation. Quast and Karel (1972)

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developed a computer simulation for potato chips which deteriorate by two mechanisms simultaneously, i.e., by oxidation due to atmospheric oxygen and by textural changes due to moisture adsorption. The rate of accumulation of oxygen in the package, the rate of oxidation and the rate of change of moisture content were expressed as dimensionless variables:

$$\frac{dY1}{dt} = \frac{T.A.K02}{T0.V.X} (1 - Y1) - \frac{T.w.EMAX}{T0.V.P020.1000} \left(\frac{dY2}{dt}\right) \quad (10)$$

$$\frac{dY2}{dt} = \frac{[Y2.EMAX + \frac{P1 + P2 \cdot Y2 \cdot EMAX}{(Y3.RHMAX)^{\frac{1}{2}}}] \left[\frac{Y1.P020}{P3 + P4 \cdot Y1.P020}\right]}{EMAX} \quad (11)$$

$$\frac{dY3}{dt} = \frac{Y3.RHMAX}{-P5} \cdot \left[\ln \frac{Y3.RHMAX}{100}\right]^2 \cdot \frac{A.KW.PWS}{x.w} \left[\frac{RHO}{RHMAX} - Y3\right] \quad (12)$$

where:

$$Y1 = P02/P020$$

$$Y2 = EXT/EMAX$$

$$Y3 = RH/RHMAX$$

P02: oxygen partial pressure inside package

P020: outside oxygen partial pressure

EXT: extent of oxidation

EMAX: maximum allowable extent of oxidation

RHMAX: maximum allowable equilibrium relative humidity of the product

K02: oxygen permeability

T0: reference temperature

V: total headspace volume

w: weight of product

KW: water vapor permeability

PWS: pressure of saturated water vapor

P1,2,3,4,5: constants

The rate of change of moisture was found using the Kuhn isotherm for the moisture- a_w relationship which was considered as the best fit for potato chips (Quast and Karel, 1972).

Later, Quast and Karel (1973) used this computer simulation to calculate optimal permeabilities for minimizing the deterioration due to these two interacting mechanisms. The influence of packaging film size, bulk density of the product, and initial condition of oxygen concentration and relative humidity were studied.

Further developments have been concerned with nutritional stability in foods. Based on data published by Vojnovich and Pfeifer (1970), Wanninger (1972) established a mathematical model to predict the ascorbic acid stability during storage:

$$\ln k = -E/RT + a \ln H_2O + b \quad (13)$$

where:

k: rate constant of ascorbic acid degradation

E: activation energy

R: gas law constant

T: absolute temperature

H_2O : moisture content

a,b: constants

The model assumes that moisture content will modify the rate constant (k), but does not have a significant influence on the activation energy E while the oxygen content is constant. It was stated that the storage humidity might affect the rate of degradation.

Heldman (1974) proposed a basic computer simulation for storage conditions which influence vitamin stability. The mathematical model for the rate constant k as a function of oxygen and water activity is as follows:

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$$k = f(p^i, a^i) \quad (14)$$

where:

p^i : oxygen partial pressure inside the package

a^i : water activity inside the package

The oxygen uptake by the reaction, which results in vitamin loss, affects the oxygen partial pressure inside the package:

$$p^i = p_O^i \exp(-k't) \quad (15)$$

where:

p_O^i : initial oxygen partial pressure inside the package

k' : oxygen uptake rate constant

t : time

The water activity inside the package is influenced by the moisture transport through the packaging film. The moisture transport can be described as:

$$dM/dt = (K/x)(A/w_S)p_S(a^O - a^i) \quad (16)$$

where:

dM/dt : the rate of moisture transport through the packaging film

K : film transfer coefficient

A : packaging surface area

a^O : water activity outside the package

x : film thickness

w_S : mass of food product inside the package

p_S : absolute pressure of air in the storage

The water activity inside the package can be calculated by the Brunauer, Emmett, and Teller (BET) equation (Bach, 1974):

$$a^i/M(1-a^i) = 1/w_m c + (c-1) a^i/w_m c \quad (17)$$

M: equilibrium moisture content of the food product

w_m and c : BET constants of food product

Singh and Heldman (1975) presented a simulation of ascorbic acid degradation in a liquid infant food formula. The oxygen uptake by the liquid food was studied at different light intensities and effective depths of light penetration into the food product.

Lee (1976) established a computer simulation to predict ascorbic acid degradation in canned tomato juice during storage. The effect of pH, copper ion, and storage temperature were the parameters in the mathematical model.

THEORETICAL CONSIDERATIONS

The Kinetics of Vitamin Degradation

For the purpose of this study, model food system II was prepared using ascorbic acid destruction as the quality index. In the presence of oxygen, the reaction scheme is as follows:



The reaction undergoes first order kinetics (Kirk et al., 1976), so that the reaction rate can be described as:

$$dC/dt = -k C \quad (19)$$

where:

C: concentration of the vitamin

t: time

k: first order rate constant

Integrating and substituting the initial condition $C = C_0$ at $t = t_0$ yields:

$$C = C_0 \exp(-kt) \quad (20)$$

The Role of Oxygen and Moisture Vapor Transfer into the Package

The other factors influencing the vitamin degradation rates at a constant temperature are oxygen and moisture. Assuming oxygen is a non-limiting factor, then k is only a function of water activity inside the package (a^1):

$$k = f(a^i) \quad (21)$$

In this study, the relationship between the rate constant (k) and water activity for each temperature condition was obtained from the results of shelf-life tests.

The change of water activity inside the package due to increasing moisture content of the model food system was calculated from the BET equation (5). The BET constants were found experimentally by Bach (1974) using the Paltnikar and Heldman method (1971).

The increasing moisture content of the model food system was obtained from equation (16) assuming all the moisture transport through the packaging film was absorbed by the model food system.

The computer simulation flow sheet at a constant temperature can be expressed as shown in Figure 1.

The Influence of Temperature on the Rate Constant

The degradation rate of the vitamin at any temperature at a constant a_w can be expressed by the well-known Arrhenius equation:

$$k = k_o \exp (-E/RT) \quad (22)$$

or:

$$\ln k = (-E/RT) + \ln k_o \quad (23)$$

where:

- k_o : Arrhenius constant, time^{-1}
- E: activation energy, cal/mole
- R: gas constant, 1.987 cal/ $^{\circ}\text{K}$ -mole
- T: absolute temperature, $^{\circ}\text{K}$

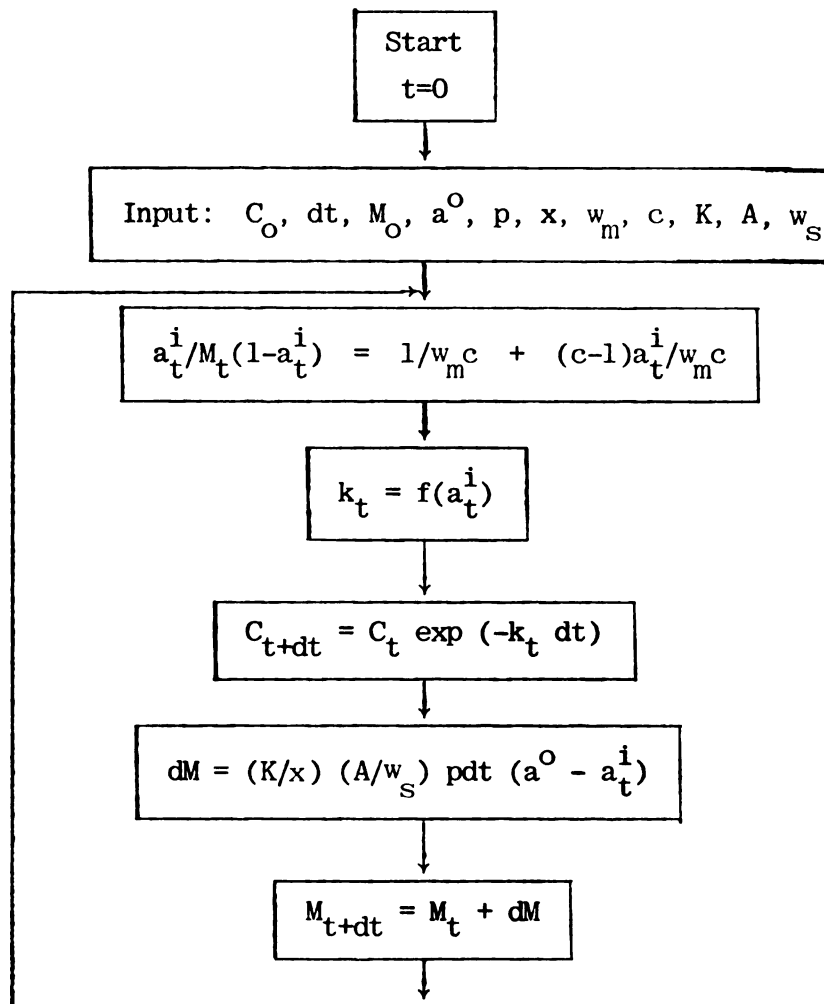


Figure 1. The computer simulation flow sheet at a constant temperature.

Based on equation (23), the Arrhenius curve can be plotted using the results of shelf-life tests for the rate constant of ascorbic acid degradation at various temperatures.

By obtaining the Arrhenius equation for three or more different water activities, a computer simulation using a least square fitting method can be developed to calculate k at various a_w values and to establish the relationship of k as a function of a_w at any temperature. The computer simulation flow sheet for k as a linear function of a_w is illustrated in Figure 2.

This program, incorporated into the previous computer simulation (Figure 1) as a subroutine, makes the simulation capable to predict the ascorbic acid degradation at any temperature.

The Influence of Temperature and Relative Humidity Fluctuation on the Rate Constant

The product temperature and moisture content are influenced by the changes of environmental temperature and relative humidity during storage and transportation in the marketing channel.

Lee (1976) developed a computer simulation to calculate the temperature fluctuation throughout a year using the Fourier series:

$$f(x) = (a_0/2) + \sum_{n=1}^{\infty} (a_n \cos(n\pi x/L) + b_n \sin(n\pi x/L)) \quad (24)$$

where:

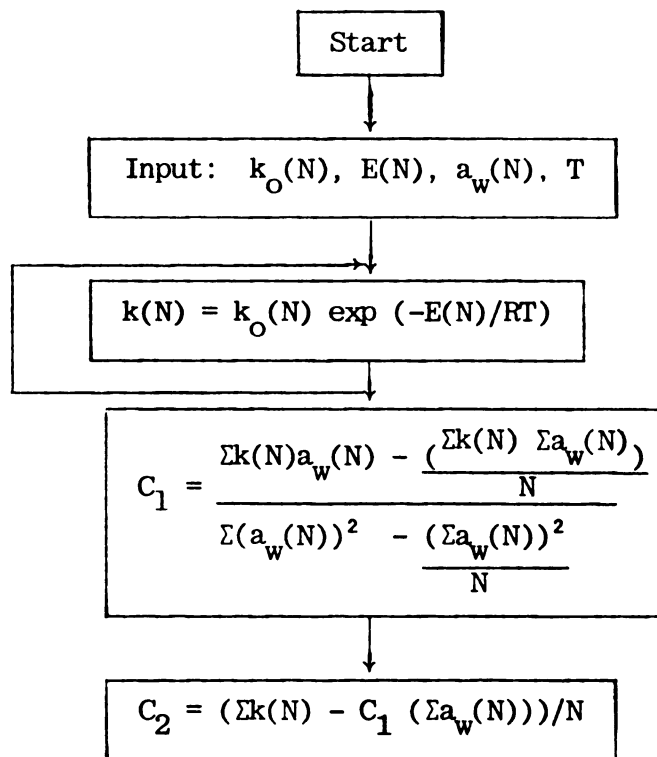
$$a_0 = (1/L) \left(\int_{-L}^L f(x) dx \right)$$

$$a_n = (1/L) \left(\int_{-L}^L f(x) \cos(n\pi x/L) dx \right)$$

$$b_n = (1/L) \left(\int_{-L}^L f(x) \sin(n\pi x/L) dx \right)$$

L : limit of cycle

x : time, days



N : number of Arrhenius equation
1,2,3, . . . , N

C_1 : slope of the linear curve for $k=f(a_w)$

C_2 : intercept of the linear curve

Figure 2. The computer simulation flow sheet to establish the relationship of k as a function of a_w at any temperature.

Since relative humidity is a function of temperature and dew point, it is possible to predict the relative humidity fluctuation throughout a year using the same equation.

The computer simulation flow sheet in Figure 1 can be modified to predict the vitamin retention in the product as the temperature and relative humidity fluctuates during a year. The modified flow sheet is shown in Figure 3.

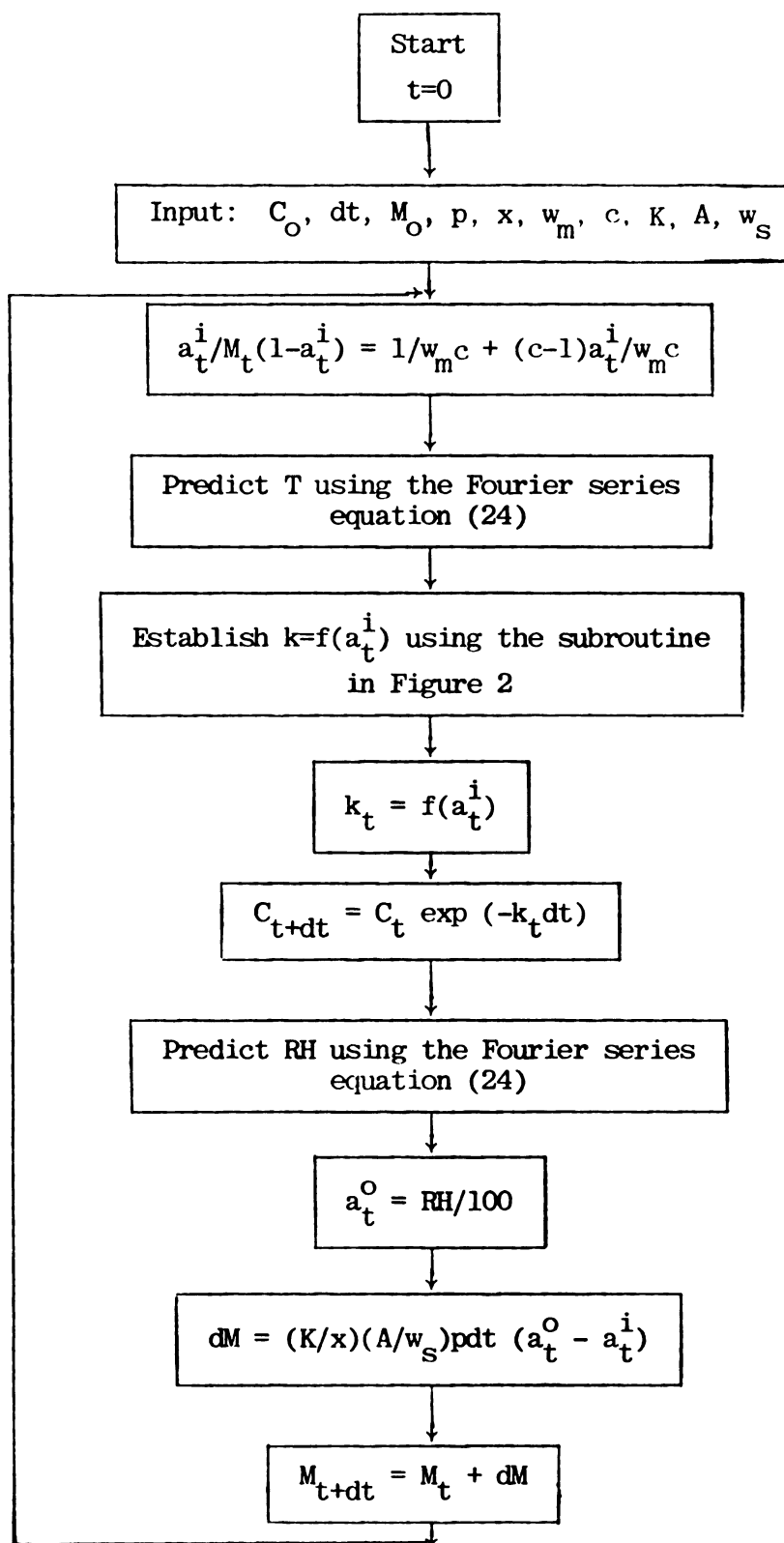


Figure 3. Computer simulation flow sheet at fluctuating temperature and relative humidity.

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EXPERIMENTAL CONSIDERATIONS

Materials

A model food system was prepared in order to get an accurate and uniform initial vitamin concentration. Its composition was modeled after cereal products and illustrated in Table 4. The preparation method described by Kirk et al. (1976) was followed. The ingredients were dry-mixed by a ribbon blender and water was added to obtain 40% total solids. The slurry was heated to 60°C and homogenized in a Manton-Gaulin homogenizer at 103.4×10^5 Newton/m² gage (1500 psig) in the first stage and 34.5×10^5 Newton/m² gage (500 psig) in the second stage. Ascorbic acid was added to the model as USP reduced ascorbic acid at a level of 25% RDA per 100g of model system on a dry weight basis. Then, the model system was freeze-dried in a Virtis Model FFD 42 WS Freeze-Dryer, frozen at a temperature of -40°C and dried at 110°C and an absolute pressure of 5 μ Hg.

The measurement of the packaging film moisture transfer coefficient was carried out with anhydrous calcium chloride as the desiccant in 8-mesh granulars which were free of 30-mesh fines as suggested by ASTM Standard E 96 (1975).

To find the relationship between k and a^i , a relatively large can of 303 x 406 size was used for a 15g sample in order to establish the condition where oxygen is a non-limiting factor.

Table 4. Composition of model food system.

Component	Percent
Protein	10.2
Fat	1.0
Carbohydrate	76.6
Reducing Sugar	5.1
Sucrose	5.1
Salt	2.0

To determine the water diffusion into the product and to verify the computer simulation results, 21g (3/4 oz.) breakfast cereal boxes containing a waxed paper film were used. The boxes were supplied by General Foods, Post Division, Battle Creek, Michigan.

Procedures

Measurement of the moisture transfer coefficient

The anhydrous calcium chloride was reactivated by heating at 200°C for one hour. Fifty grams of desiccant were placed in the waxed paper film liners with and without cardboard boxes. The packages were stored for seven days in cubicles at 30°C and 10, 40 and 85% relative humidities. The cubicle conditions were controlled by a humidistat. The mass difference after seven days was recorded as moisture transfer through the packaging film.

Measurement of the rate of ascorbic acid degradation as a function of water activity

Thin slabs of the model food system were equilibrated to 0.10, 0.24, 0.40, 0.50 and 0.65 water activities in an equilibrium chamber. The air condition in the equilibrium chamber was regulated using an Aminco-Aire unit which maintains constant humidity and temperature.

Ten grams of equilibrated samples were put into 303 x 406 cans. The cans were sealed and stored in cubicles at 10, 20 and 30°C. The ascorbic acid degradation history was recorded for each water activity until the half-life was reached, and the rate constant of vitamin degradation was calculated by equation (20). The functional relationship between the rate constant and water activity was then obtained by plotting the rate constant at each water activity.

Shelf-life test for the model food system

Fifteen grams of the model food system was packed into the boxes containing waxed paper film liners. The waxed paper was heat-sealed. The boxes were stored in cubicles at 30°C and 10, 40, and 85% RH. The moisture content on a dry weight basis was recorded until the equilibrium condition was achieved to get the water adsorption history during storage. The ascorbic acid degradation history was also recorded until the half-life was achieved.

Measurement of the product moisture content

The moisture content was determined as described by Kirk et al. (1976). Samples of 2g were dried in a vacuum oven at pressure less than

4.6×10^3 Newton/m² and at the same temperature as the product was stored. A cold trap was inserted between the vacuum oven and the vacuum pump to maintain a temperature differential between the inside and outside of the vacuum chamber in order to aid in the water vapor transfer from the chamber. The samples were dried until they achieved constant weight. Then, dried air at a rate of 15–20 ml/min was admitted into the chamber to expell the remaining water vapor.

Measurement of the ascorbic acid degradation

The ascorbic acid retained during the storage was determined by the semi-automated O-phenylenediamine microfluorometric procedure as described by Kirk and Ting (1975). The total ascorbic acid was measured as dehydro ascorbic acid following oxidation of reduced ascorbic acid with 2,6 dichloroindophenol. Dehydro ascorbic acid was detected by fluoronephelometer as the fluorescence product after reaction with O-phenylenediamine.

Description of Computer Program

Based on the flow sheet presented previously, a computer program was developed in order to predict:

1. The moisture content of the food product at any time during storage.
2. The water activity inside the package.
3. The vitamin degradation at any time during storage.

The input necessary to operate the program is as follows:

1. BET constants of the food product.
2. Initial moisture content, initial vitamin concentration, and the mass of the food product.
3. Relationship of the rate constant of vitamin degradation as a function of product water activity.
4. Moisture transport coefficient, film thickness, and surface area of the package.
5. Temperature, relative humidity, and absolute pressure of the air in the storage.
6. Time increment.

The computer simulation was used to evaluate the influence of the following operational parameters:

1. Initial moisture content.
2. Moisture transfer coefficient and film thickness of the packaging material.
3. Mass of product per unit surface area of the packaging material.
4. Storage temperature and relative humidity.

RESULTS AND DISCUSSIONS

Measurement of Moisture Transfer Coefficient

The experimental moisture transfer coefficients at various relative humidities for waxed paper with and without cardboard boxes are presented in Table 5. These data indicate that the cardboard box does not have a significant influence on the moisture transfer. This might be attributed to the sealing of the cardboard box which does not maintain a different environment inside the box when compared to the outside storage condition.

The moisture transfer coefficient increases as the vapor pressure differential increases. However, the increasing value which is in the range of $0.25\text{--}0.83 \times 10^{-5} \text{ gH}_2\text{O-cm/m}^2\text{-hr-mmHg}$ has a small influence in calculating dM in equation (16). If the average of all K values in Table 5 is taken, the error is equal to $\pm 0.36 \times 10^{-5} \text{ gH}_2\text{O-cm/m}^2\text{-hr-mmHg}$ for K values from 10 to 85% RH. The average value, which is $7.25 \times 10^{-5} \text{ gH}_2\text{O-cm/m}^2\text{-hr-mmHg}$, was used as the moisture transfer coefficient in the computer simulation.

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Table 5. Moisture transfer coefficient (K) for waxed paper with and without cardboard box at various relative humidities.

Waxed Paper	Vapor Pressure Differential (% RH)	K ($\text{gH}_2\text{O-cm})/(\text{m}^2\text{-hr-mmHg})$
Without cardboard box	10	7.00×10^{-5}
	40	7.25
	85	7.67
With cardboard box	10	6.75×10^{-5}
	40	7.13
	85	7.58

Water Diffusion into the Product

Influence of relative humidity

The results of computer prediction and experimental data on the increases of moisture content of the model food systems stored at 10, 40, and 85% RH and 30°C are shown in Figure 4. The predicted moisture contents are in good agreement with the experimental data. The standard deviations between the computer-predicted results and experimental data are 0.22, 0.20, and 0.78 $\text{gH}_2\text{O}/100\text{g}$ solids at 10, 40, and 85% RH, respectively. However, at 85% RH, the computer results predicted lower moisture contents than the experimental data. This may be attributed to the BET equation used in the computer simulation to predict water adsorption.

The BET model assumed that (1) the heat of adsorption for the first layer is constant, (2) the heat of adsorption in all layers above the first is identical and equal to the latent heat of condensation, and (3) adsorption occurs only on specific sites. Unfortunately, these

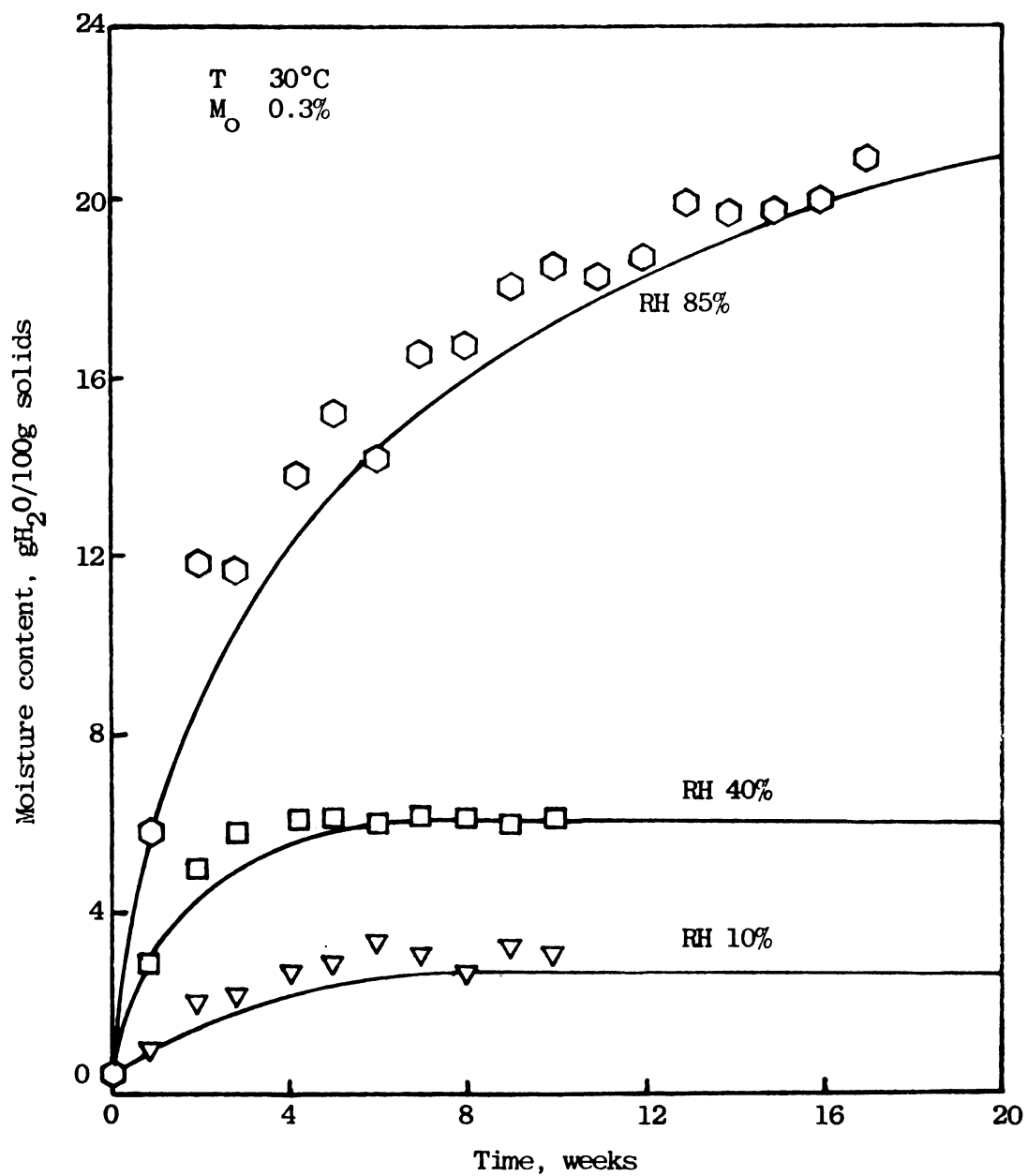


Figure 4. Computer prediction and experimental data for the product moisture content during storage at various relative humidities.

assumptions are not entirely true. Labuza (1968) stated that the BET equation usually holds only between water activities of 0.1 to 0.5, arguing that the water surface area in most foods (100 to 250 m²/g) is much larger than nitrogen surface area (0.2 to 2.0 m²/g) which is the predicted adsorption BET value.

The BET model neglects horizontal interactions between the molecules within the layer and vertical interactions, normal to the surface. At higher humidities as many layers are adsorbed, the horizontal forces between the adsorbate molecules can scarcely remain negligible because their average separation is much less than a single diameter (Gregg and Sing, 1967).

Figure 4 also illustrates that a longer time is required to reach the equilibrium condition at 85% RH. Since the water adsorption occurs in the capillary region at this high humidity, the completion of water condensation in the pores of food may take more time than in the monomolecular and multilayer region.

Influence of temperature

The influence of temperature on the moisture gained by the model food system is illustrated in Figure 5. At lower temperature conditions, the food product will adsorb water at a slower rate. The product will tend to achieve a higher equilibrium moisture content at the lower temperature. This is indicated by the sorption isotherm curves at various temperatures in Appendix 1.

The sorption isotherm curves at 20, 25, 30, and 37°C were established by Bach (1974). The sorption isotherm curve at 10°C was developed by measuring the moisture content of the model food system at various water

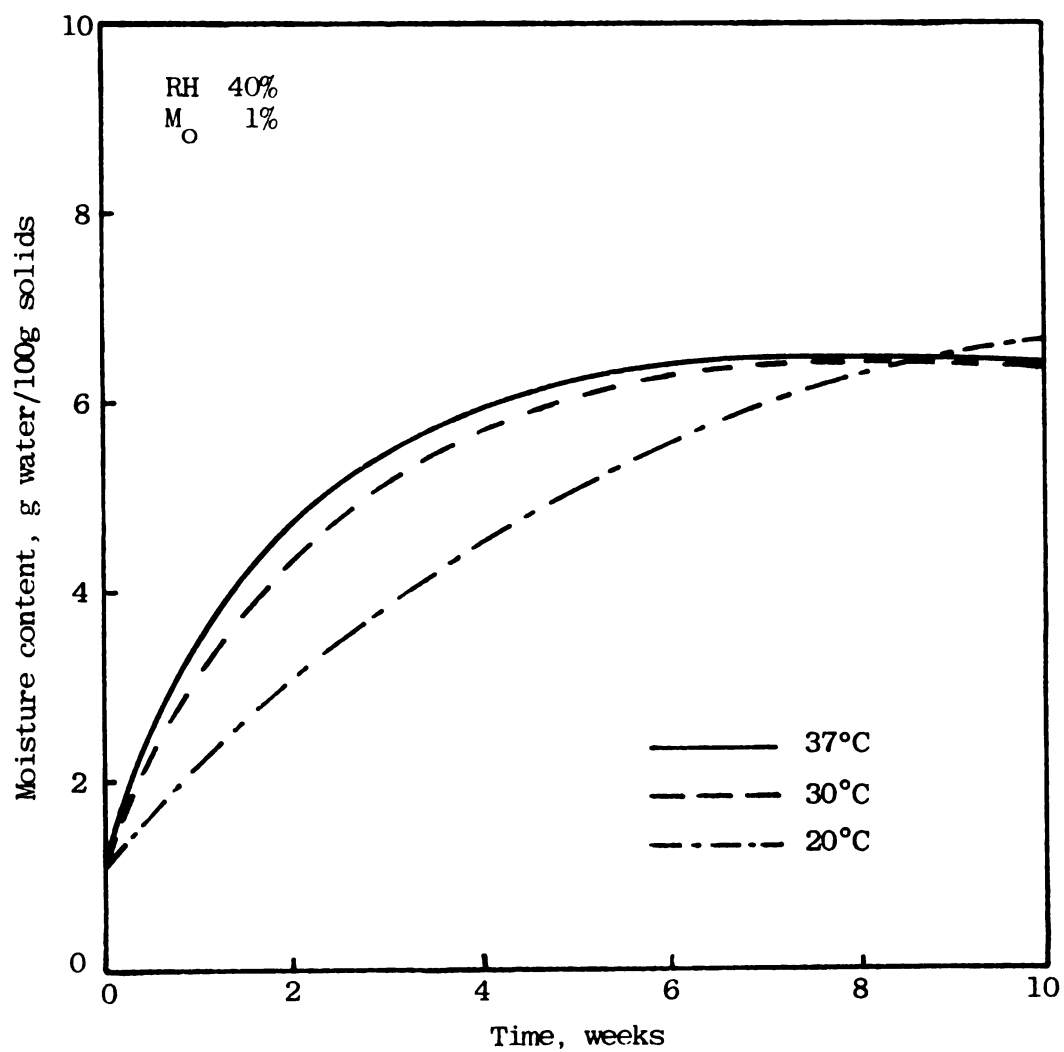


Figure 5. Computer prediction of the model food system moisture content during storage at various temperatures.

activities using the same method described by Bach (1974). The energy constant (c) and the monomolecular moisture content (w_m) were calculated for each temperature (Appendix 2) and were plotted as a function of temperature (Figures 6 and 7).

The energy constant (c) decreases from 10°C to 22.5°C and then increases to 37°C following a polynomial function, while the monomolecular moisture content (w_m) decreases as an exponential function.

The adjusted curves were developed based on the modification of c and w_m at 30°C in order to get acceptable agreement between the computer-predicted moisture content and experimental data. The adjusted functions were used in the simulation to calculate the c and w_m of the model food system at any temperature.

Influence of packaging film

Film thickness and the moisture transfer coefficient (K) of the package will affect the water diffusion to the product. An increase in the film thickness will cause slower moisture transfer into the package (Figure 8) so that the water diffusion into the product will be reduced. An increase in the moisture transfer coefficient results in greater moisture transfer rates into the package (Figure 9) and the food product will reach equilibrium moisture conditions more rapidly.

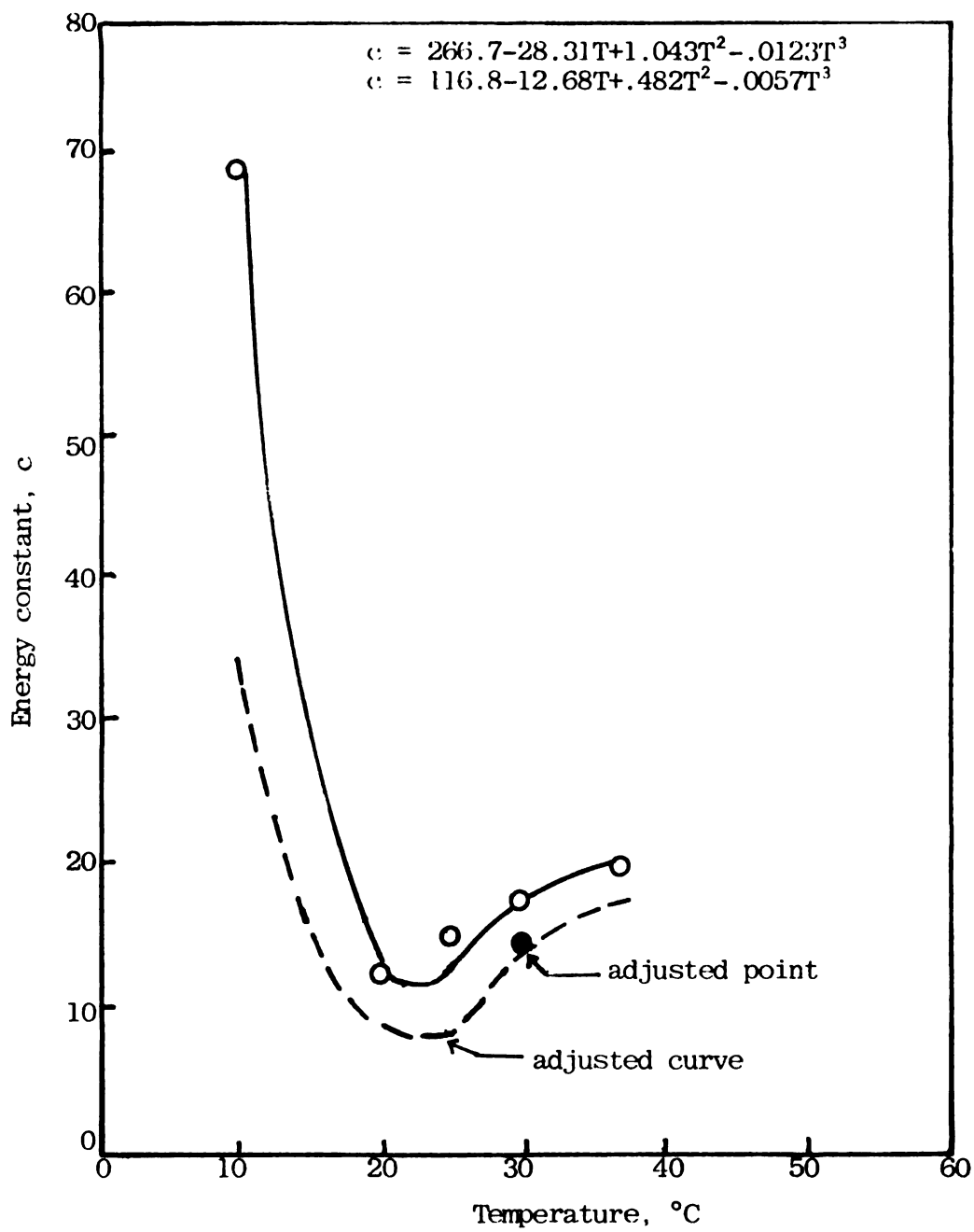


Figure 6. Energy constant (c) of BET equation as a function of temperature.

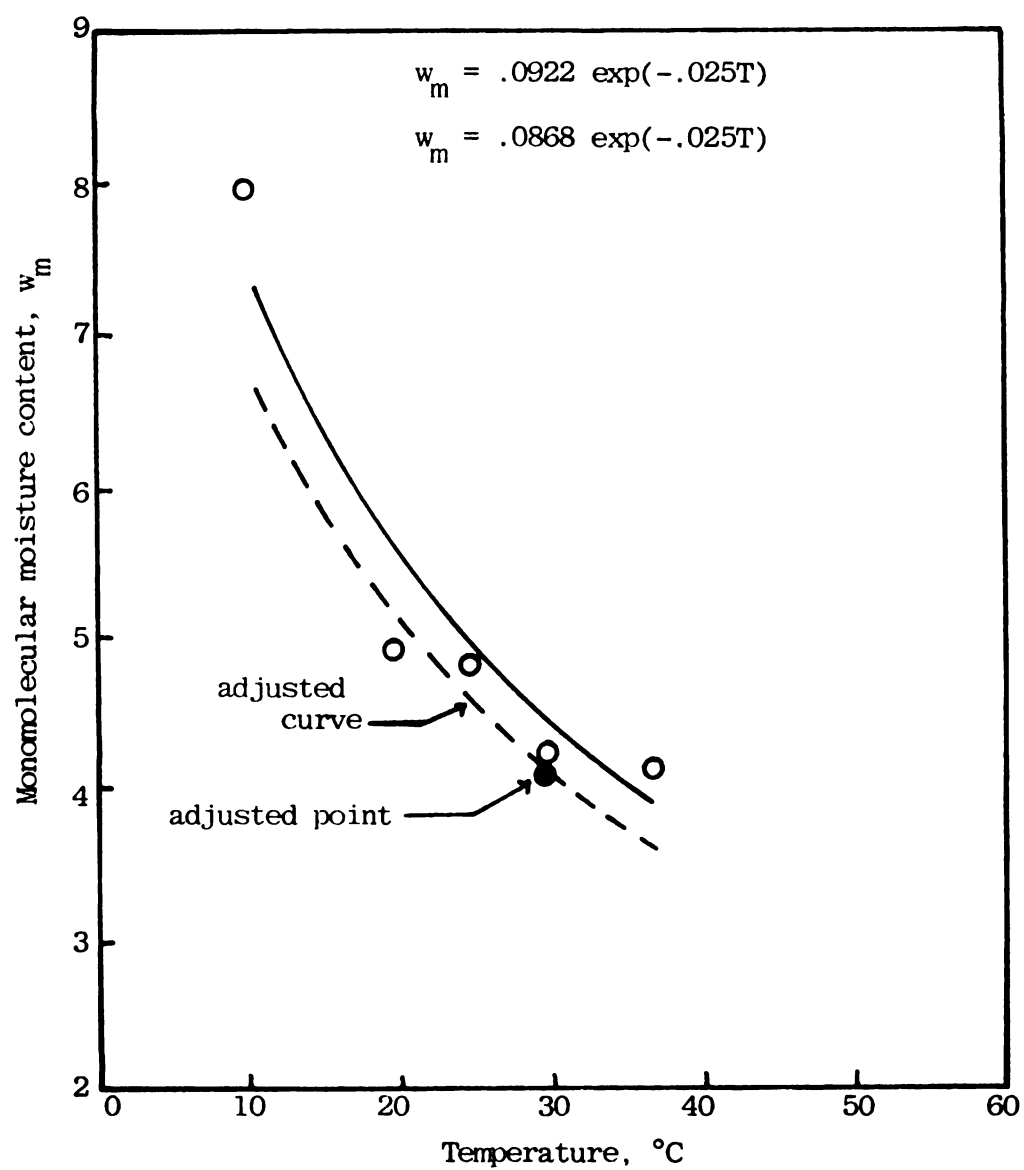


Figure 7. Monomolecular moisture content (w_m) of BET equation as a function of temperature.

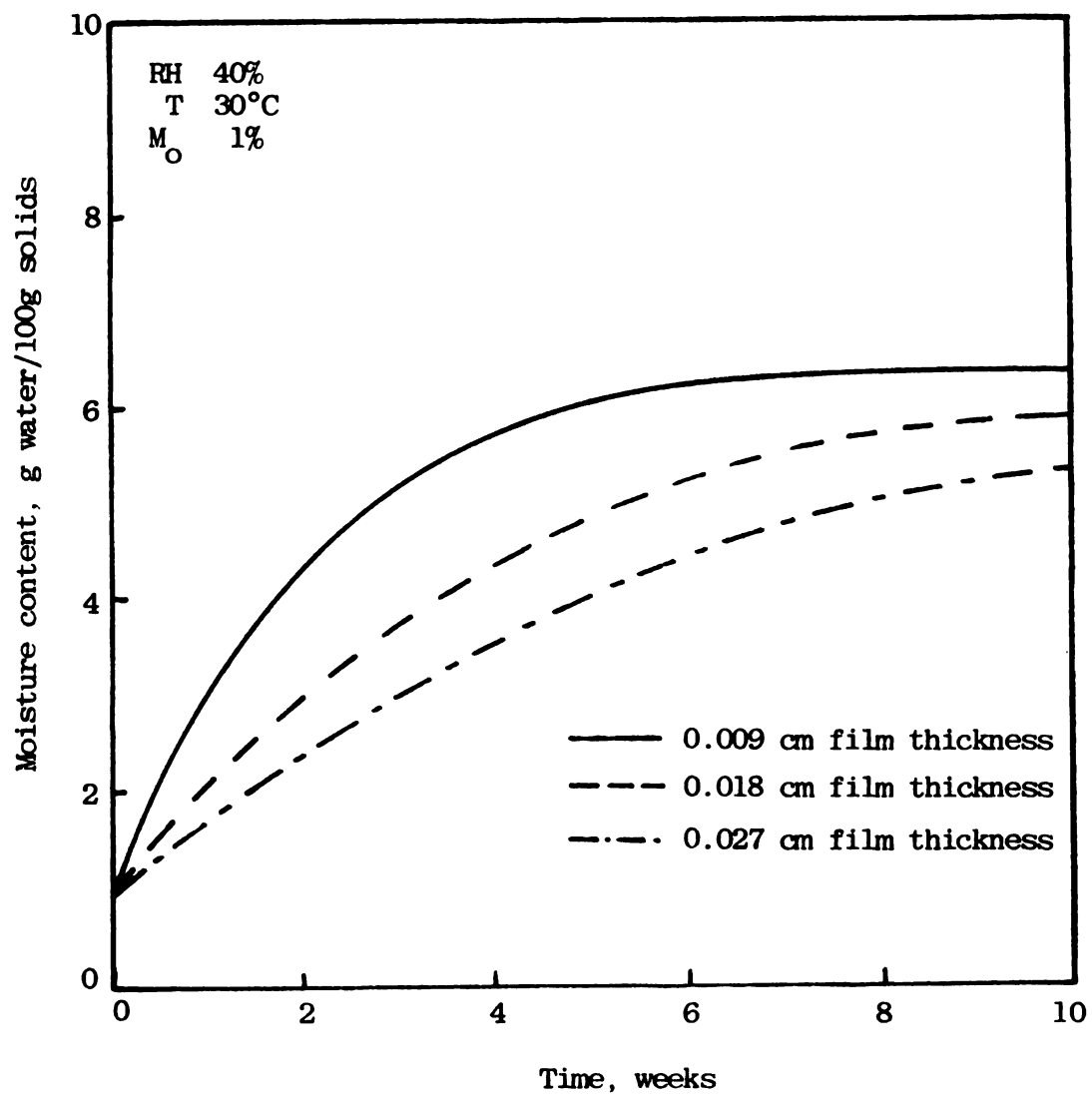


Figure 8. Computer prediction of the model food system moisture content during storage at various packaging film thicknesses.

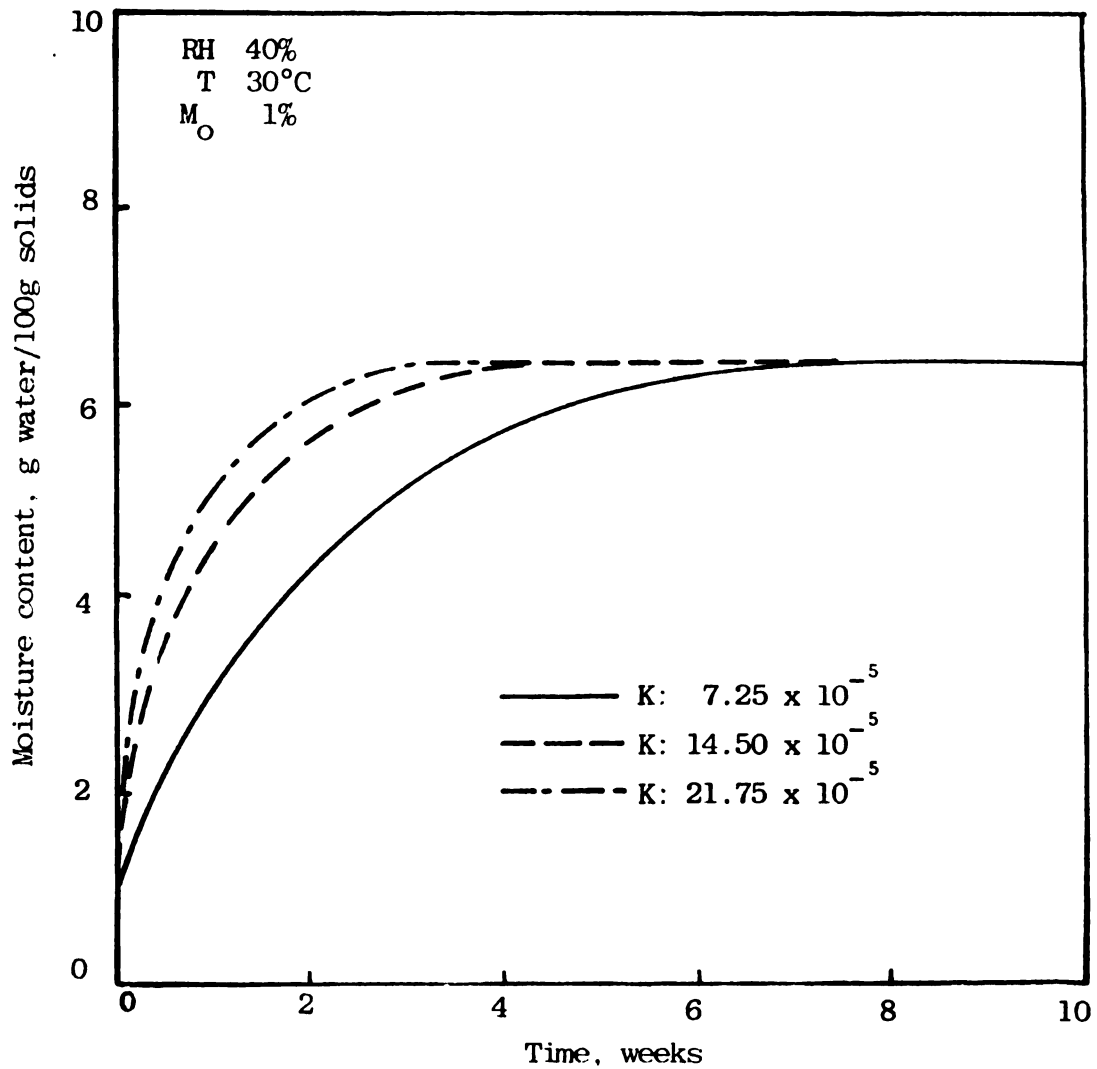


Figure 9. Computer prediction of the model food system moisture content during storage at various moisture transfer coefficients, K ($\text{gH}_2\text{O-cm/m}^2\text{-hr-mmHg}$).

Vitamin Retention During Storage

The relationship between the rate constant (k) and water activity (a_w)

The results from the experiments indicated that the rate constant (k) increases as a linear function as water activity (a_w) increases for large cans (303 x 406 can) at 10, 20 and 30°C (Figures 10-12). Vitamin retention data for small cans (TDT can), provided by Kirk et al. (1976), were plotted in the same figures. All the experiments take into account the range of 0.1 to 0.65 water activities which include only the monomolecular and multilayer region and not the capillary region.

Lee and Labuza (1975) presented the half-life of ascorbic acid in another model food system at various water activities and temperatures. Calculating and plotting the rate constants (k) against a_w gave the relationship of k with a_w as illustrated in Figure 13. The rate constant (k) begins to increase exponentially as a_w reaches the range of 0.6 - 0.7. This point is in the capillary region rather than in the multilayer region, while the starting point is 0.32 a_w which is, most likely, in the multilayer region. On the other hand, the model food system used by Lee and Labuza (1975) has a different composition (10g corn oil, 40g glycerol, 50g cellulose, 300mg ascorbic acid, and water) than the model food system used in this study (Table 4).

Lee and Labuza's model food system shows sorption isotherms of type III (Figure 14) while the sorption isotherms of the model food system used in this experiment indicates type II or a sigmoid isotherm according to the classification by Brunauer et al. (1940). A type III isotherm is characterized by its being convex to the water activity axis (Gregg and Sing, 1967). This suggests that the attractive forces

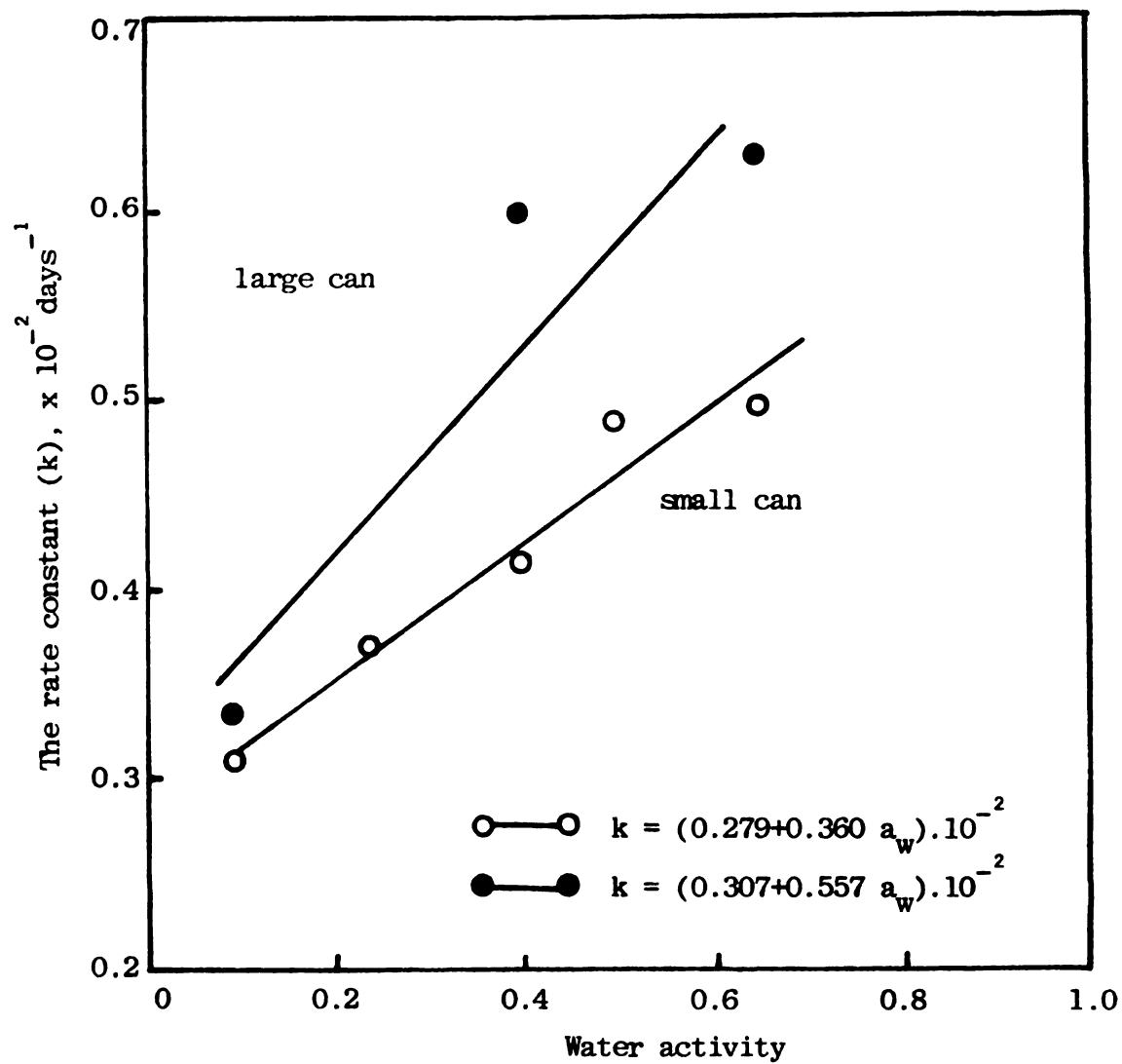


Figure 10. The rate constant of ascorbic acid degradation (k) as a function of a_w at 10°C.

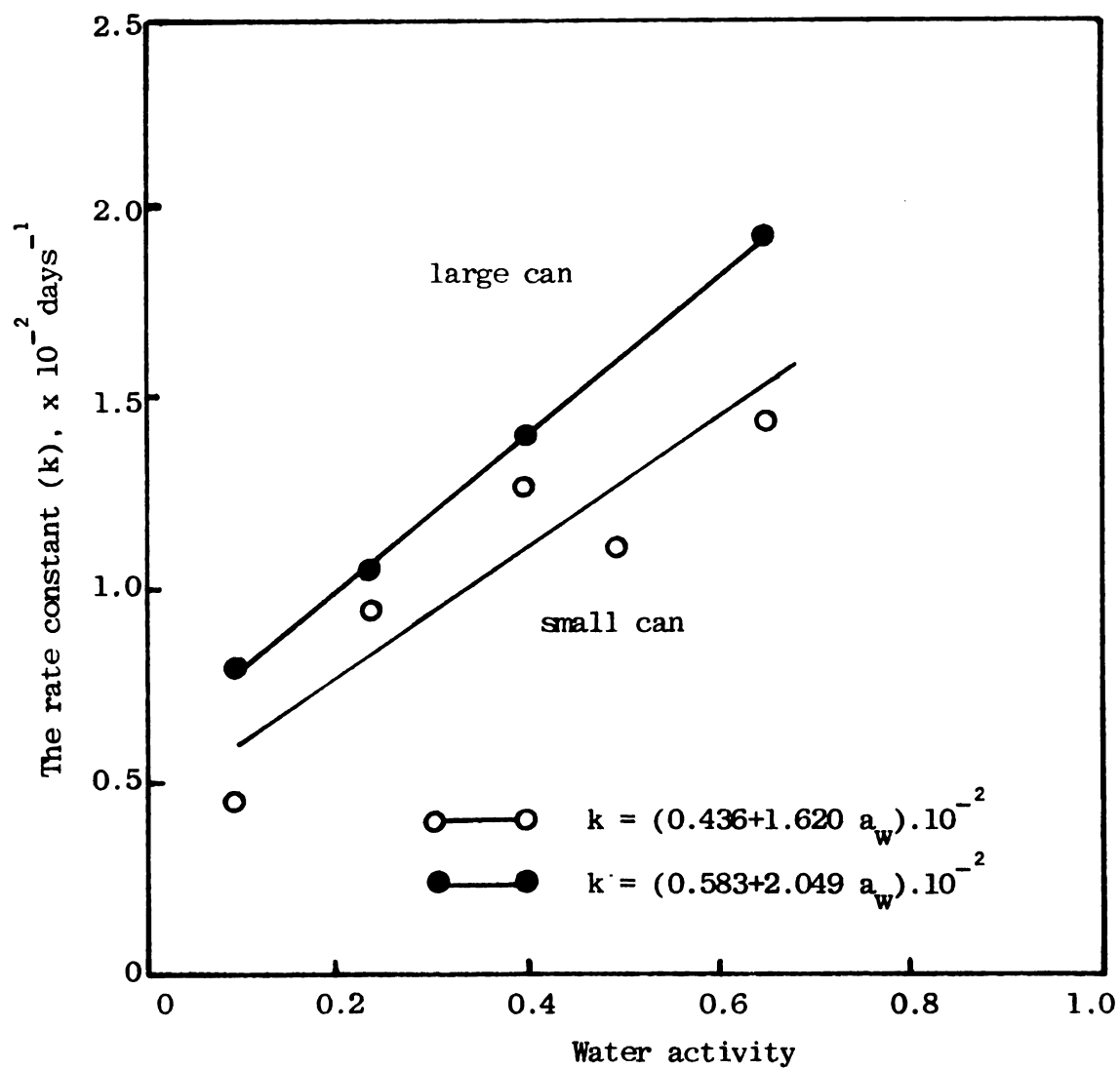


Figure 11. The rate constant of ascorbic acid degradation (k) as a function of a_w at 20°C.

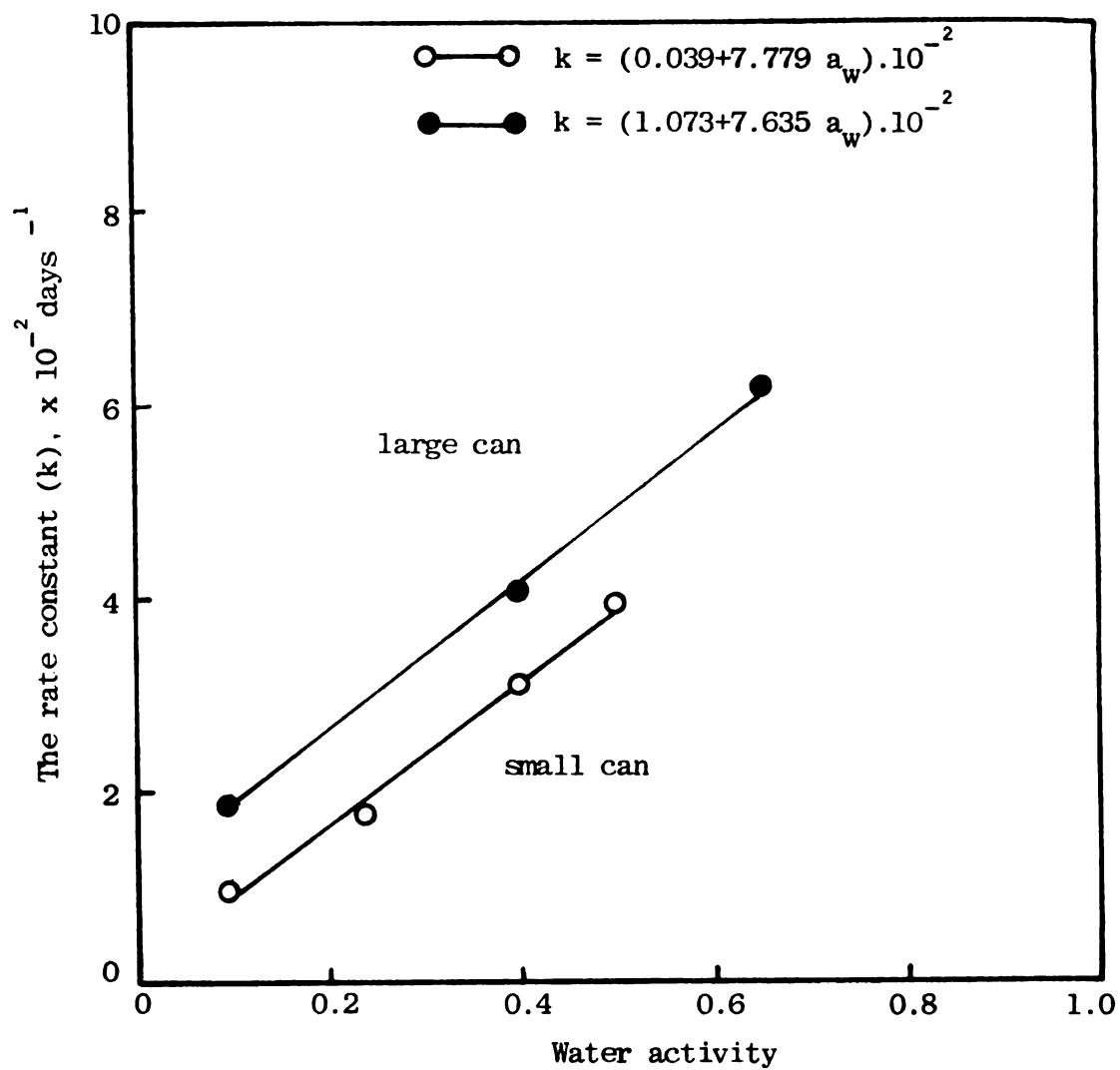


Figure 12. The rate constant of ascorbic acid degradation (k) as a function of a_w at 30°C.

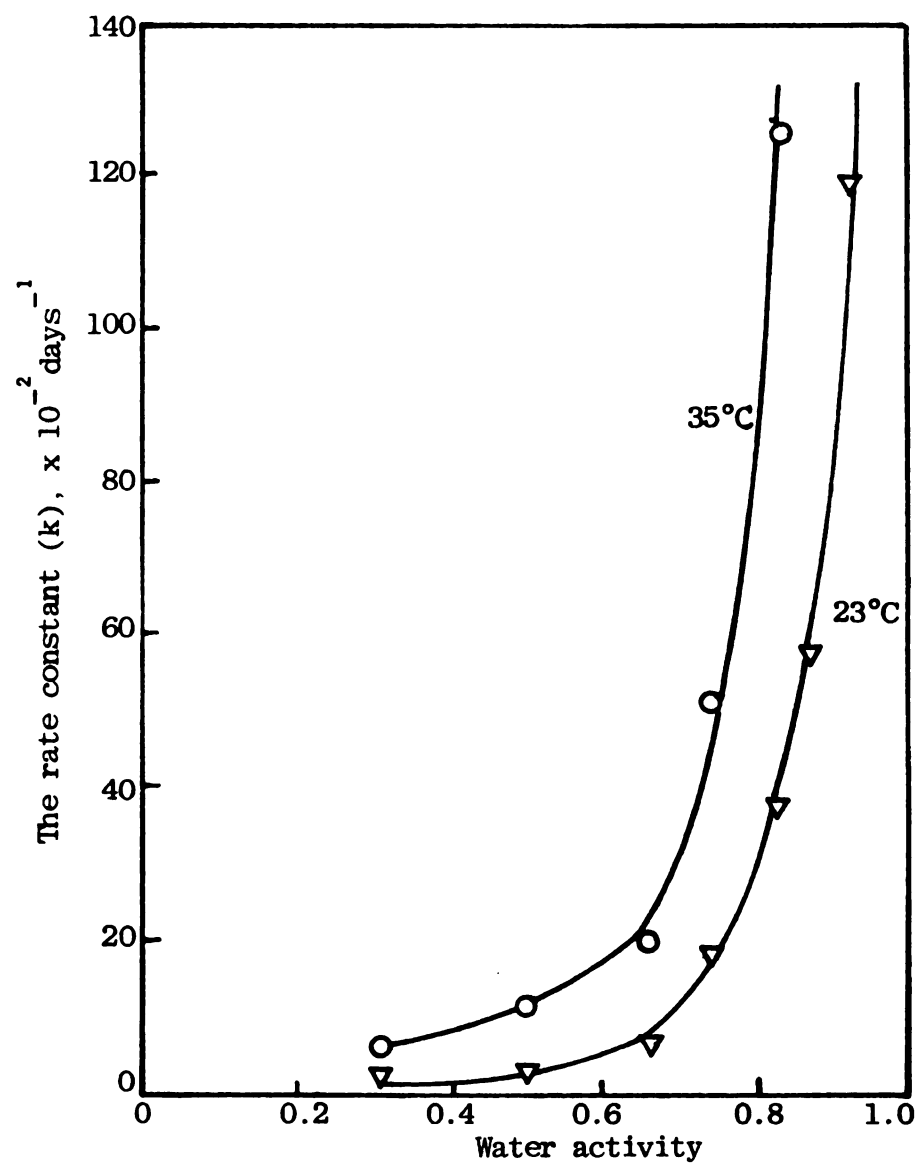


Figure 13. The rate constant of ascorbic acid degradation (k) as a function of a_w in Lee and Labuza's model food system.

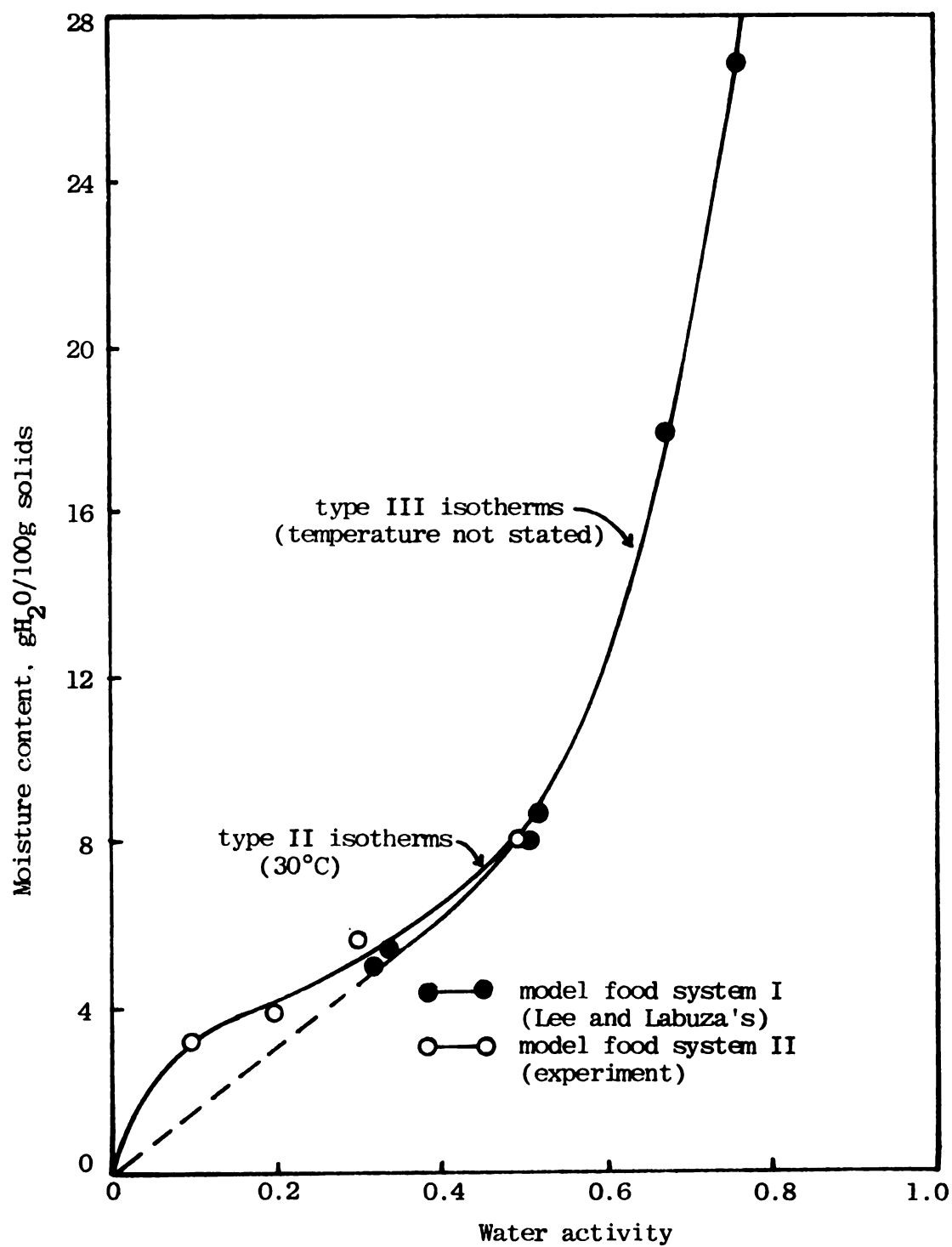


Figure 14. Sorption isotherms of model food system I and model food system II.

between the molecules of water are greater than the attractive forces between the water vapor as adsorbed gas and the model food system as adsorbent. On the contrary, a type II isotherm occurs when the attractive forces between the molecules of water are smaller than the attractive forces between the water vapor and model food system.

Verification of computer prediction of vitamin retention during storage

Computer simulation, as illustrated in Figure 1 (flow chart in Appendix 3), was developed using the mathematical model of k as a function of a_w . The computer-predicted ascorbic acid retention in the model food system (Figure 15-17) gives good agreement with the experimental data. The standard deviation of comparison between the computer-predicted results and experimental data are 5.84, 4.15, and 6.58% at 10, 40, and 85% RH, respectively.

The computer result is slightly slower in ascorbic acid degradation than the experimental data for 10% RH. This may be due to the diffusion effect of water which can occur at the monomolecular region. Duckworth et al. (1963) showed that the water soluble compounds have substantial mobility and may be diffused out of the specific sites in cells and react with each other in this low water activity. If this is true, the ascorbic acid as a water soluble compound may also diffuse out of the specific sites and be exposed to oxygen. Hence, it might accelerate the ascorbic acid degradation.

Some scattering in the experimental data might be due to lack of uniformity of the surface area of the waxed paper bag because folding and heat sealing were done manually.

At 85% RH, the computer prediction results indicated higher ascorbic acid retention compared to the experimental data. This might be due to several factors. First, the mathematical model of k as a function of a_w was developed only for the range of 0.1 to 0.65 water activities. Thus, k for 0.85 a_w is obtained by extrapolating the mathematical model which probably results in some error.

Secondly, the BET equation is not satisfactory to predict water adsorption in the capillary region as discussed previously. It predicted lower moisture contents than the experimental data, hence, the predicted vitamin degradation was also lower.

Lee and Labuza (1975) postulated the effect of decreasing viscosity at higher water activities which may cause the exponential rate of ascorbic acid degradation in their model food system. The decreasing viscosity will increase mobilization of the reaction species in the aqueous phase so that the ascorbic acid and metals were more easily mobilized.

Influence of temperature

The influence of temperature on the rate constant of ascorbic acid degradation is expressed in the Arrhenius equation at various water activities as illustrated in Figure 18 for 303 x 406 cans. The activation energy (E), calculated from the function, is 15.1, 16.4, and 19.6 kcal/mole for a_w of 0.10, 0.40, and 0.65, respectively.

The objective of developing the Arrhenius curves is to determine a mathematical relationship among k , a_w , and temperature. Using the Arrhenius equations, k for various a_w at any temperature can be

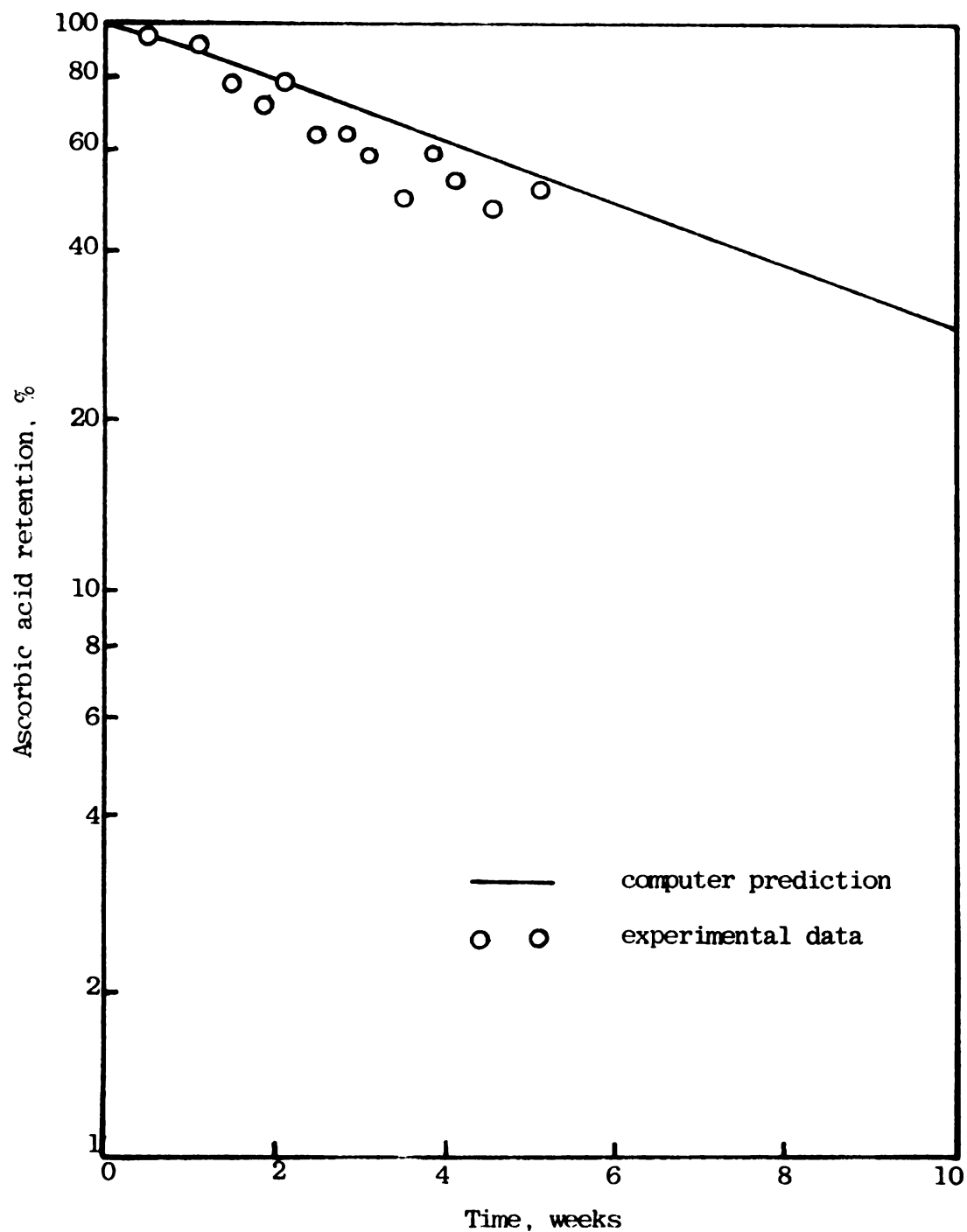


Figure 15. Computer prediction and experimental data for ascorbic acid retention in the model food system during storage at 10% RH.

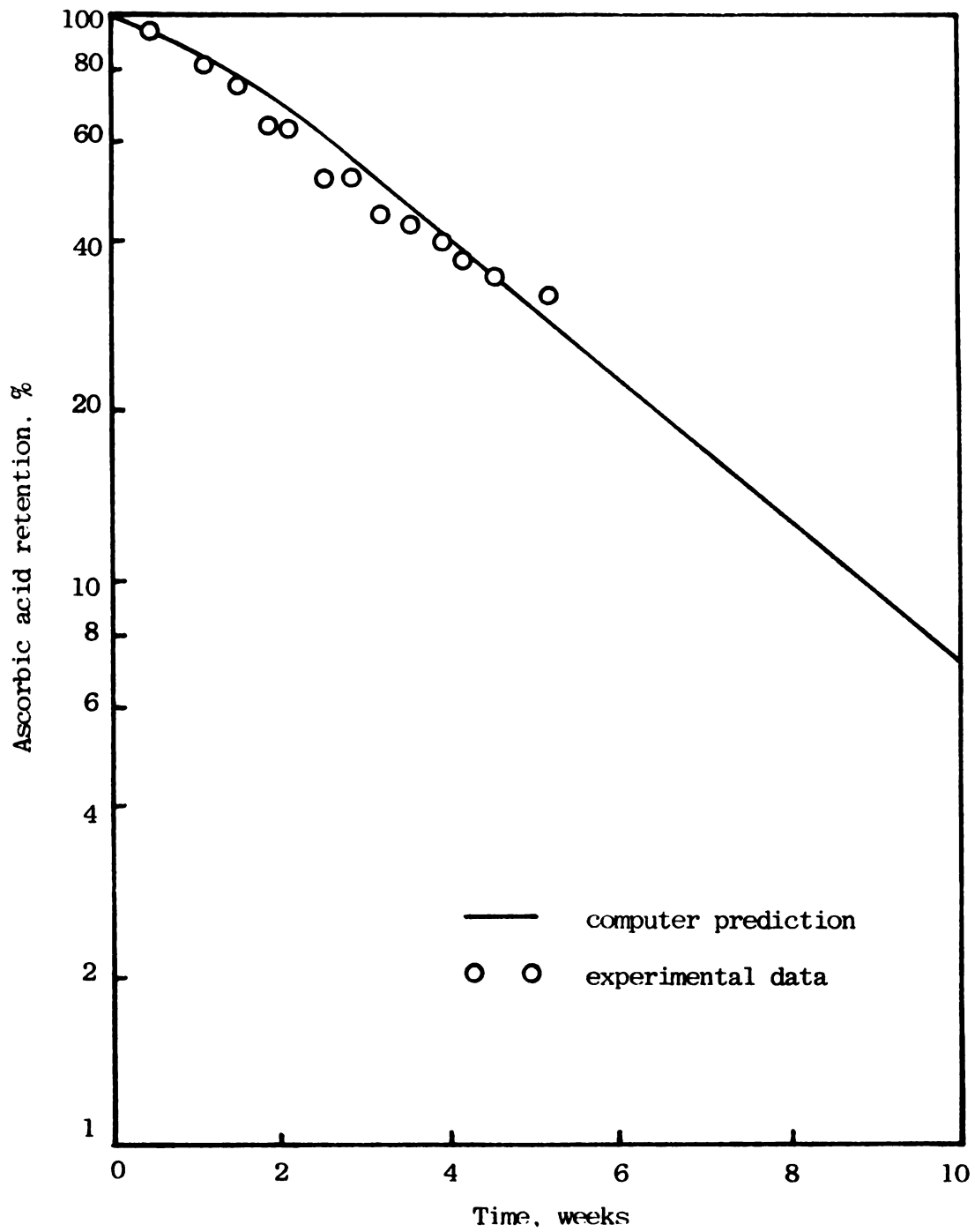


Figure 16. Computer prediction and experimental data for ascorbic acid retention in the model food system during storage at 40% RH.

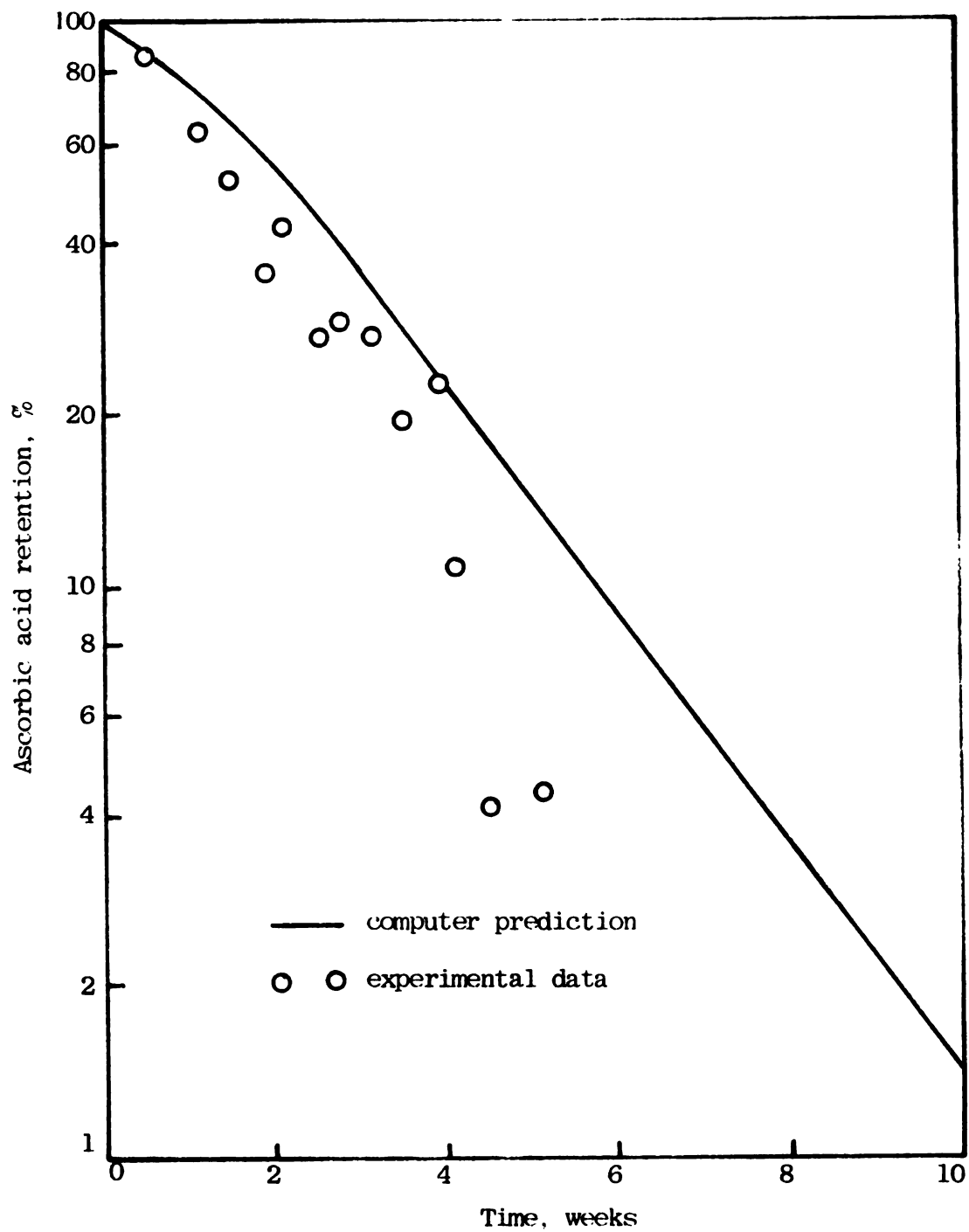


Figure 17. Computer prediction and experimental data for ascorbic acid retention in the model food system during storage at 85% RH.

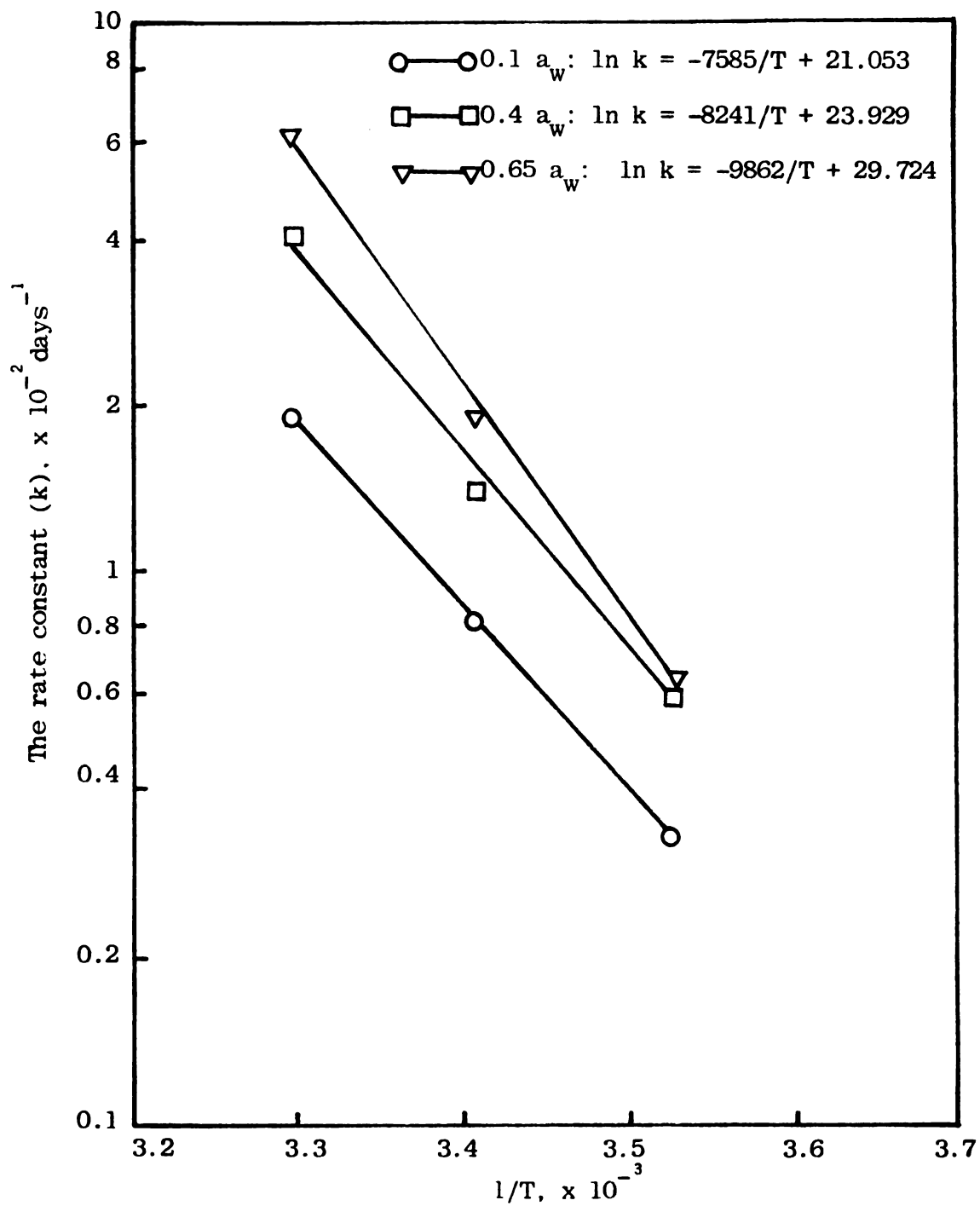


Figure 18. The Arrhenius curves for ascorbic acid degradation in the model food system packed in large cans.

obtained and later a mathematical model can be established to express the relationship between k and a_w by utilizing the least square fitting method.

Computer Simulation of Vitamin Degradation

Influence of various input parameters

The computer simulation developed in this study is based on (1) the first order kinetic reaction between ascorbic acid and oxygen, and (2) the assumption that oxygen is not a limiting factor. Thus, the simulation can be used to predict the vitamin degradation in dry foods during storage when those assumptions are met.

The output from the computer simulation is in the form of product moisture content and vitamin retention in the food product as a function of time. The simulation can be used to evaluate the effect of packaging film materials, the characteristics of food products, and the storage environments. The parameters involved as input data and an example of each quantity and unit are listed in Table 6. An illustration of some of the computer predictions with various input parameters indicates the value of the simulation approach.

The influence of varying RH (Figure 19) with all the other input conditions held constant at the values given in Table 6, shows that the vitamin degrades more rapidly as RH increases.

Figure 20 illustrates the influence of temperature with all other parameters held constant. As temperature decreases, the vitamin retention in the food product will increase.

Table 6. Various input parameters for the computer simulation.

Parameter	Quantity and Unit
Storage temperature affects:	At 30°C:
1. energy constant (c)	1. $c = 25$
2. monomolecular moisture content (w_m)	2. $w_m = 4.1$
3. k as a function of a_w	3. $k = (1.073 + 7.765a_w) \cdot 10^{-2}$
4. absolute pressure	4. $p_s = 33.26 \text{ mmHg}$
Storage relative humidity (RH)	40%
Initial moisture content (M_o)	1%
Product mass per unit of packaging surface area (w_s/A)	0.088 g/cm ²
Packaging film thickness (x)	0.009 cm
Moisture transfer coefficient (K)	$7.25 \times 10^{-5} \text{ gH}_2\text{O-cm/m}^2\text{-hr-mmHg}$

An increase in the initial moisture content (Figure 21) provides more rapid vitamin degradation if the other parameters are held constant.

Figure 22 illustrates the influence of moisture transfer coefficient (K). The destruction of vitamin occurs more rapidly at higher K values.

A larger packaging film thickness (Figure 23) will give higher vitamin retention, but at a certain point increasing packaging film thickness will not give an effective increase of vitamin retention. The influence of product mass per unit packaging surface area (Figure 24) is quite similar to packaging film thickness.

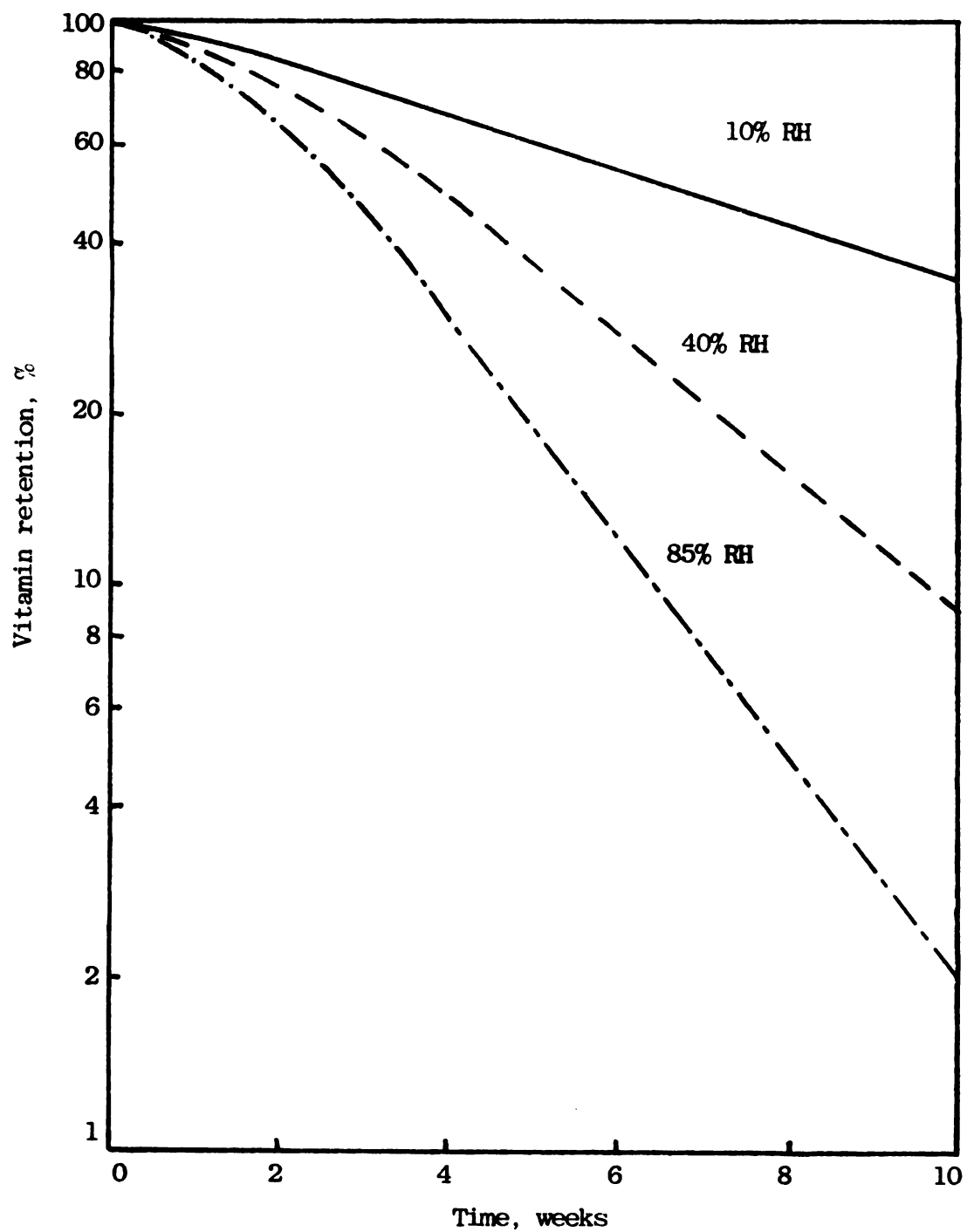


Figure 19. Computer prediction of vitamin retention in a food product during storage at various relative humidities (see Table 6).

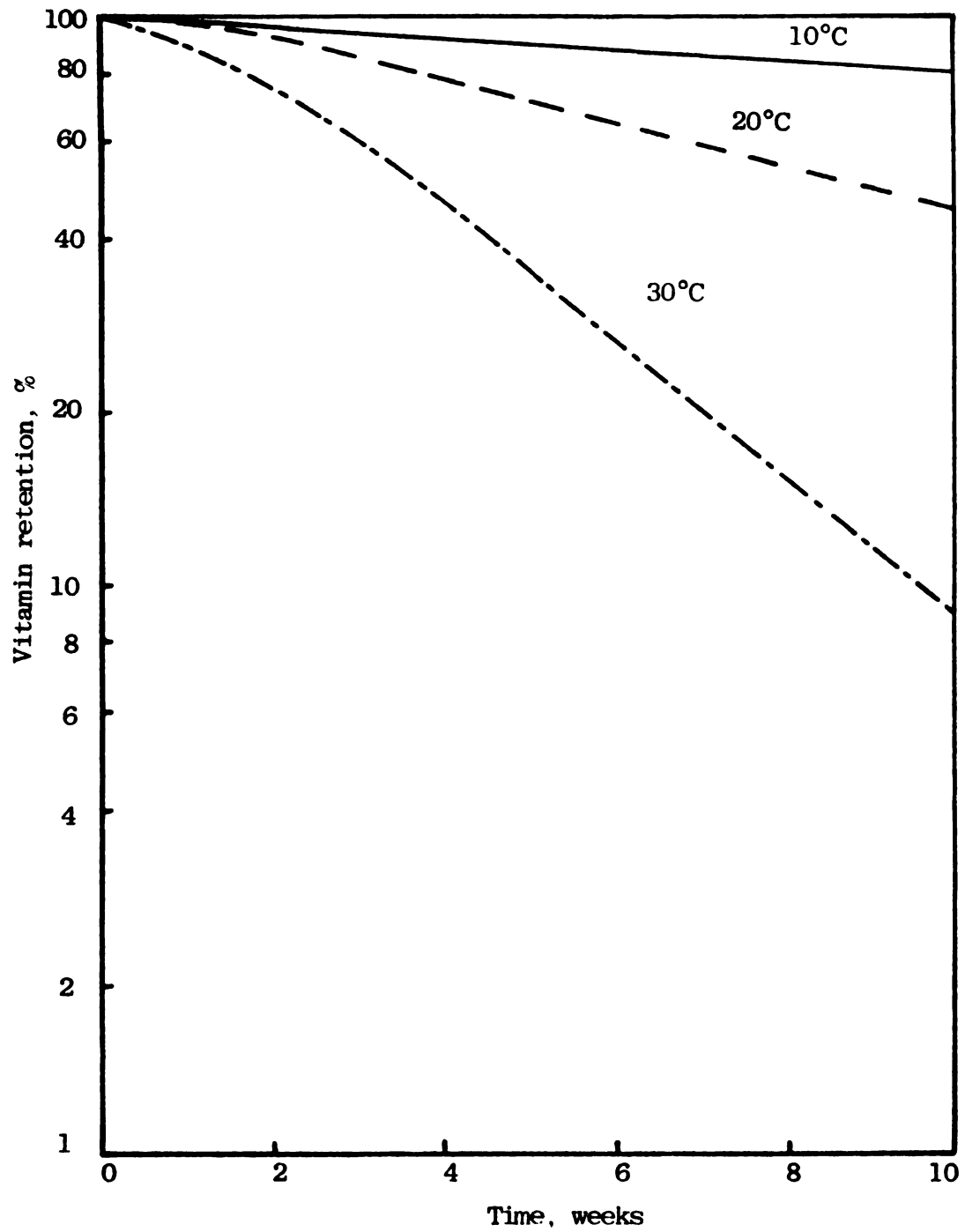


Figure 20. Computer prediction of vitamin retention in a food product during storage at various temperatures (see Table 6).

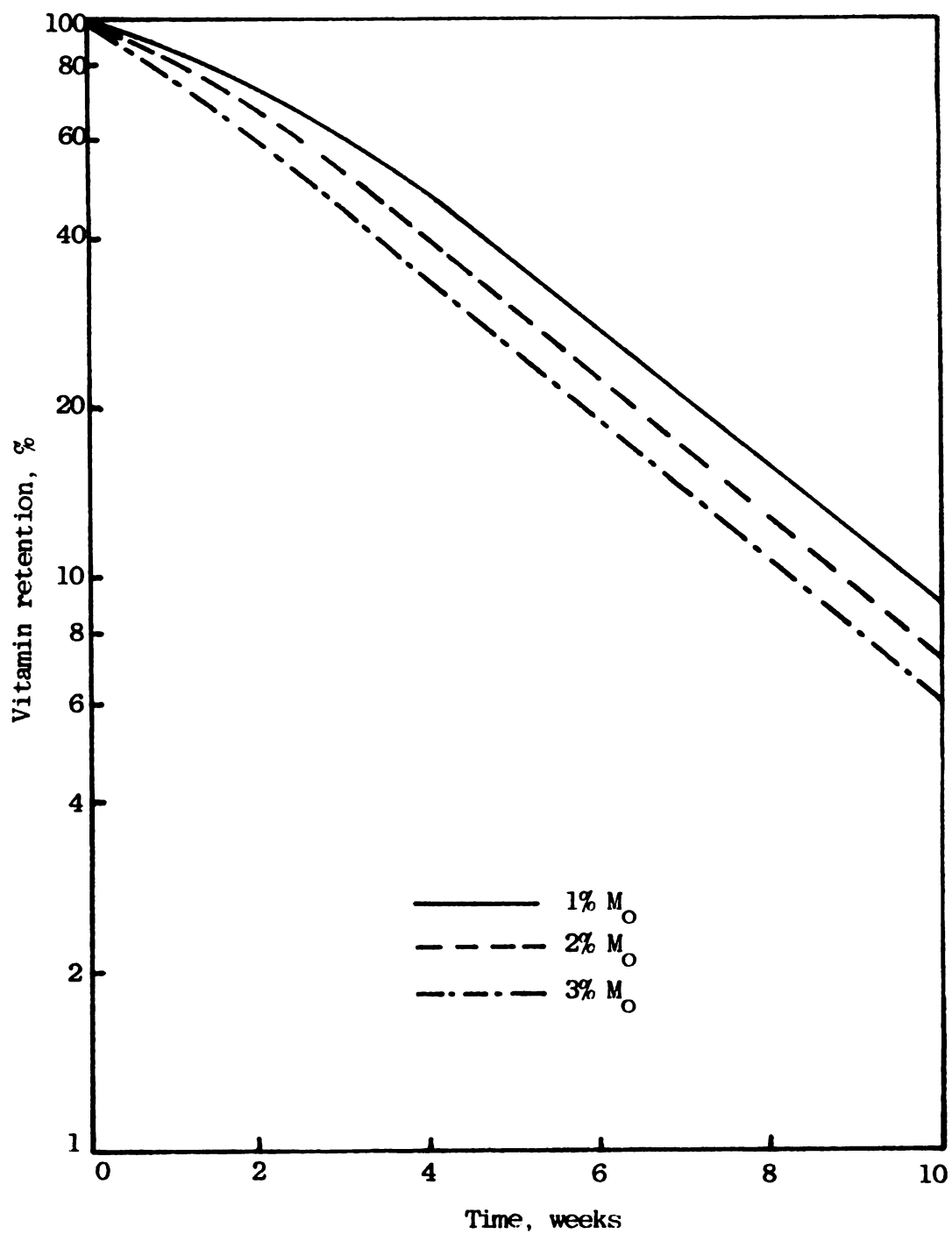


Figure 21. Computer prediction of vitamin retention in a food product during storage at various initial moisture contents (see Table 6).

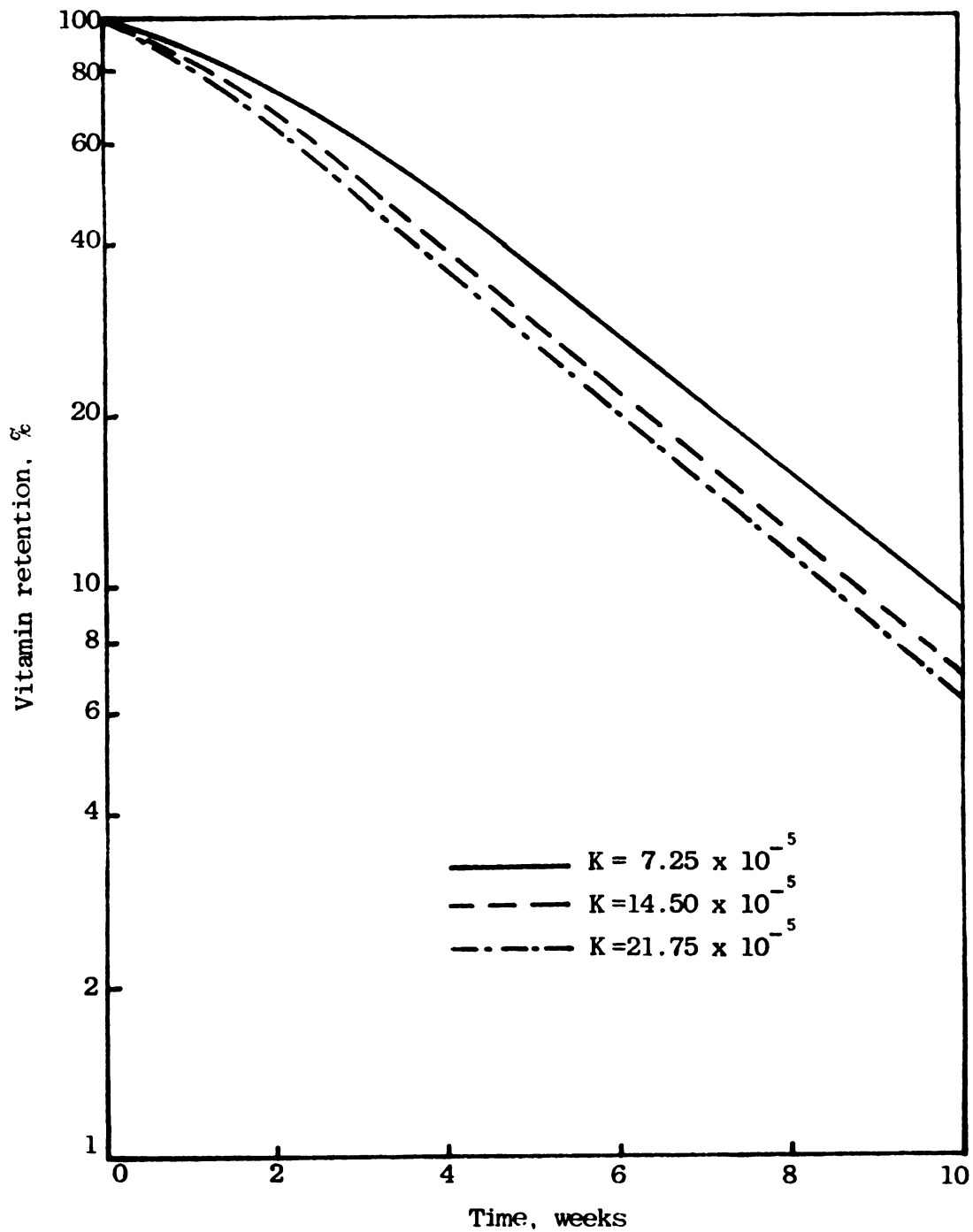


Figure 22. Computer prediction of vitamin retention in a food product during storage at various moisture transfer coefficients (see Table 6).

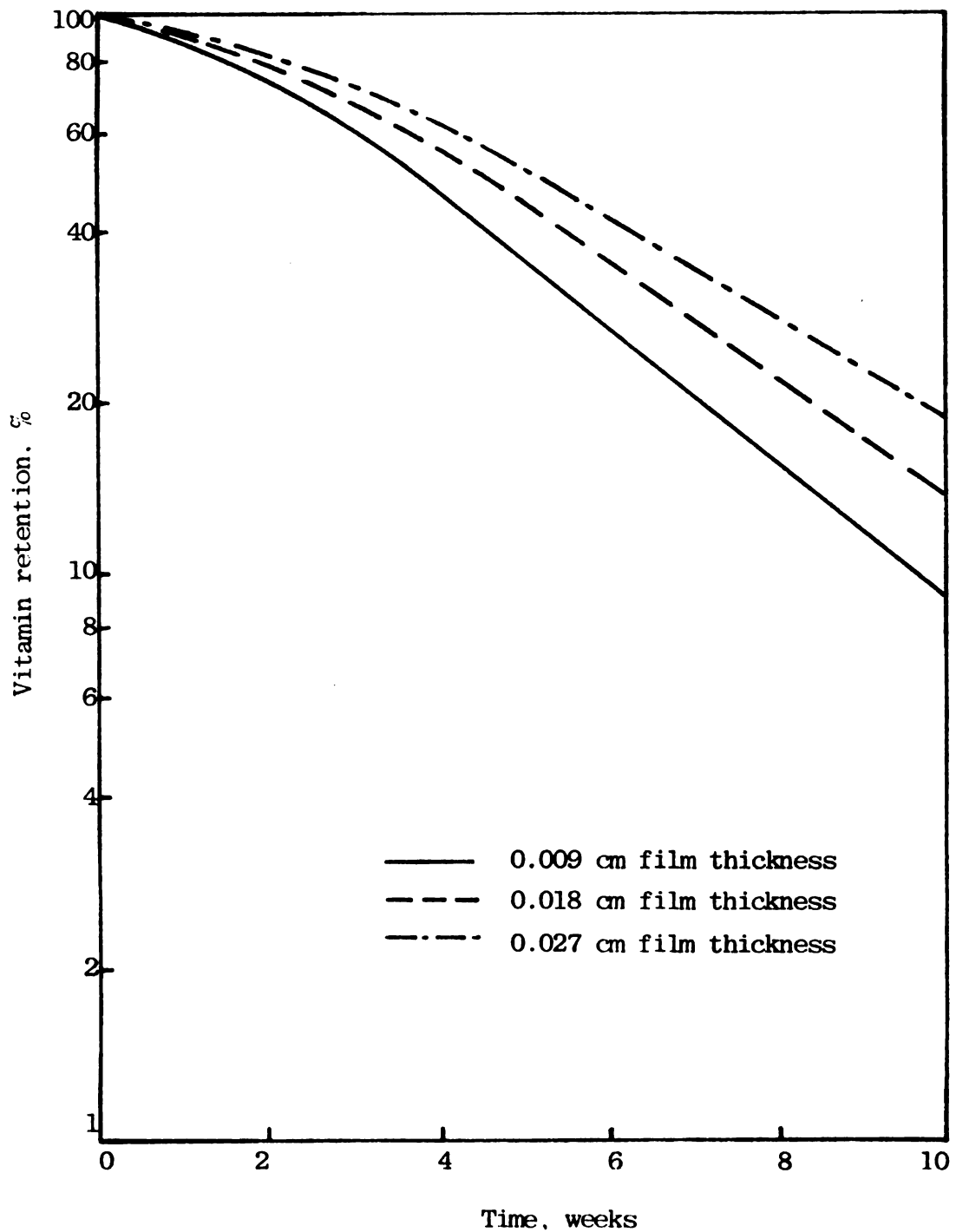


Figure 23. Computer prediction of vitamin retention in a food product during storage at various packaging film thicknesses (see Table 6).

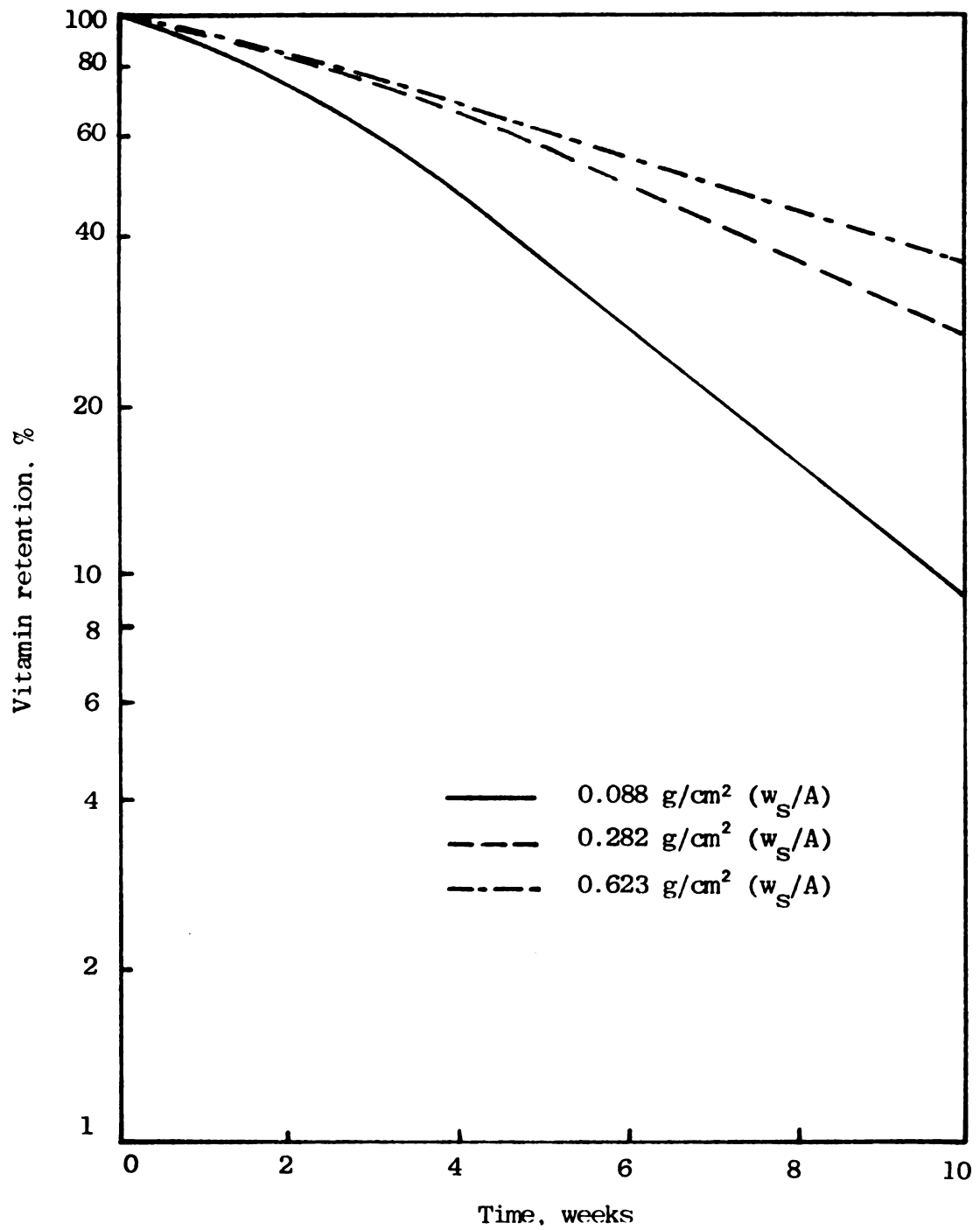


Figure 24. Computer prediction of vitamin retention in a food product during storage at various product mass per unit packaging surface area (see Table 6).

Influence of independent variables

The computer simulation developed so far uses the time increment as the independent variable (Appendix 3). Another possibility is to use the inside water activity increment as the independent variable (see flow sheet in Appendix 4). Figure 25 exhibits both of the computer prediction results at 40% RH.

The advantage of using the water activity increment as the independent variable is the possibility of applying the trapezoidal rule, as illustrated in Appendix 4, which theoretically gives better predictions. On the other hand, the accuracy in the computer simulation using the time increment as the independent variable could be increased if a smaller time increment is used. The simulation using the water activity increment as the independent variable has a disadvantage. As the vapor pressure differential between outside and inside water activity decreases and approaches zero, dt (Appendix 4) approaches infinity. This limits the prediction of the vitamin degradation after food product achieves the moisture equilibrium where the vapor pressure differential is zero.

Influence of storage temperature and relative humidity fluctuation

In the real environment, food products will be subject to the fluctuation of storage temperature and relative humidity which are influenced by weather.

Lee (1976) successfully simulated the temperature fluctuation by the Fourier series. Based on this method, a computer simulation was

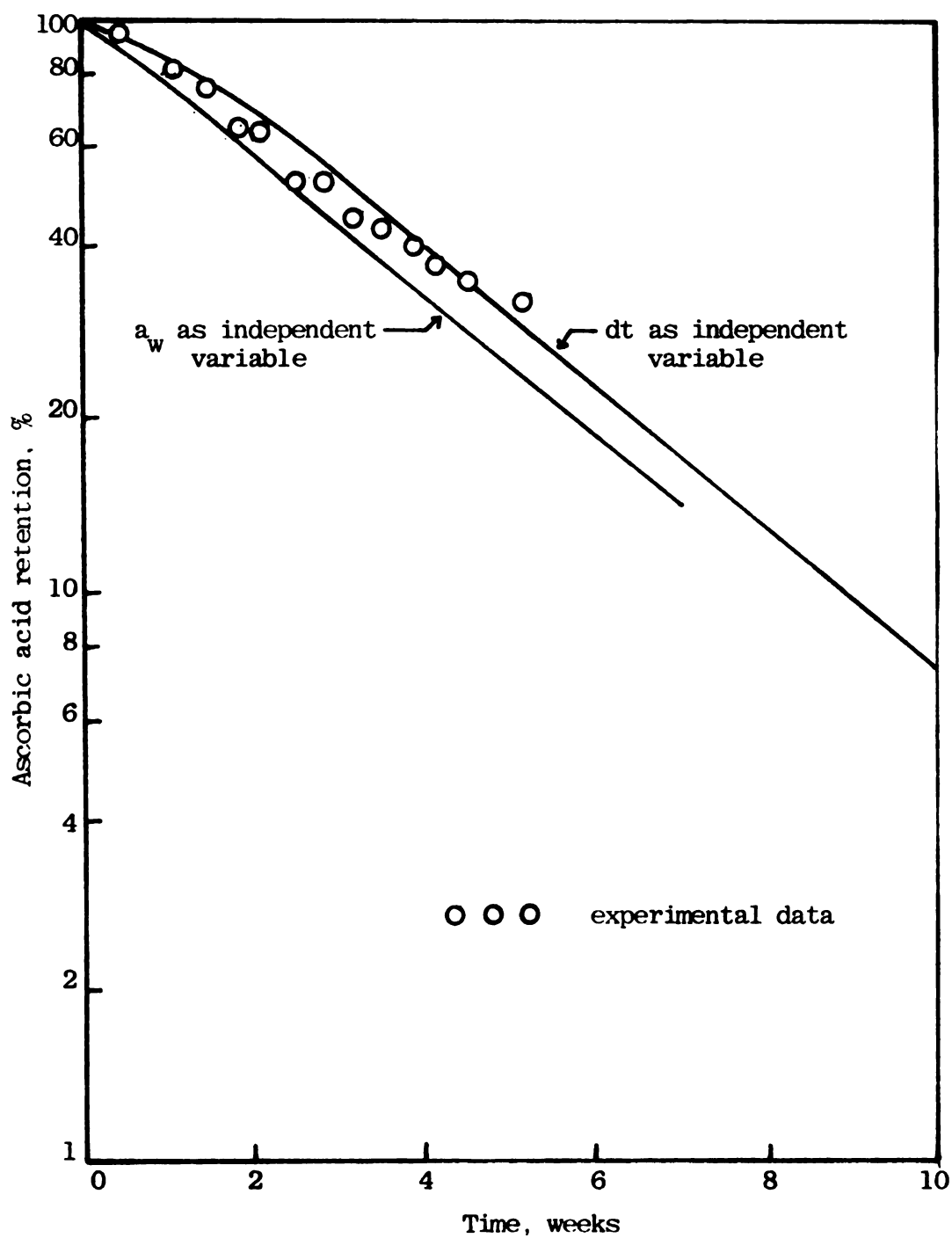


Figure 25. Computer prediction using dt and a_w as independent variables compared to experimental data for ascorbic acid retention in a food product during storage at 40% RH and 30°C.

developed to predict the relative humidity for a one-year period (Appendix 5) and the result is presented in Appendix 6. The computer-predicted relative humidities are in excellent agreement with the weather data. Ten-day averages of the daily average dry bulb and dew point temperatures as reported by the National Weather Service for Lansing, Michigan for 1975 were used to compute the relative humidity data. Usually, storage temperature is maintained above a minimum temperature in the warehouse. Taking 10°C as the minimum temperature and using the weather data for inlet air temperature and relative humidity, computer prediction results are exhibited in Figure 26.

A computer simulation (Appendix 7) was developed incorporating the Fourier series to predict the warehouse temperature and relative humidity fluctuation, the Arrhenius equation to determine the rate constant (k) at any temperature, and the least square fitting to establish the relationship of k and a_w . The results of computer prediction for ascorbic acid degradation and moisture uptake in the model food system during a one-year storage are illustrated in Figures 26 and 27 along with the predicted temperature and relative humidity.

Fifty percent of the ascorbic acid degrades in about 5 months, 3 months, 1.5 months, and 4 months after the food product stored in the beginning of January, April, July and October, respectively.

In January to April, food product is kept under low temperature and relative humidity in the warehouse so that the vitamin degrades slowly. As the temperature and relative humidity begin to increase in May, the vitamin retention decreases rapidly.

The food product stored in May follows the same pattern as the food product stored in January but at a much higher rate of vitamin degradation.

Since the temperature and relative humidity are high in July, the food product stored during this period starts to lose the vitamin content quickly and then destruction becomes gradually slower when the temperature drops in September.

The October storage period illustrates a rate of vitamin degradation which is slower than the food product stored in April or July but more rapidly than in January because of the high relative humidity and low temperature.

Figure 27 illustrates that the food product stored in the warehouse adsorbs moisture until 15-20g H_2O /100g solids because of the high relative humidity and temperature during spring and summer, and then the moisture content begins to decrease in October as a result of decreasing storage relative humidity and temperature.

If this phenomenon occurs in the real warehouse system, the food product will lose its crispiness. However, the moisture transfer into the package is also influenced by the bulk of food product stored in the warehouse and the stacking system. Small volume of air compared to large volume of food product stored in the warehouse might yield a microenvironment different from what indicated by the weather data. The stacking system, for example, the secondary container wherein the boxes are placed, may act as a barrier against moisture transfer into the product.

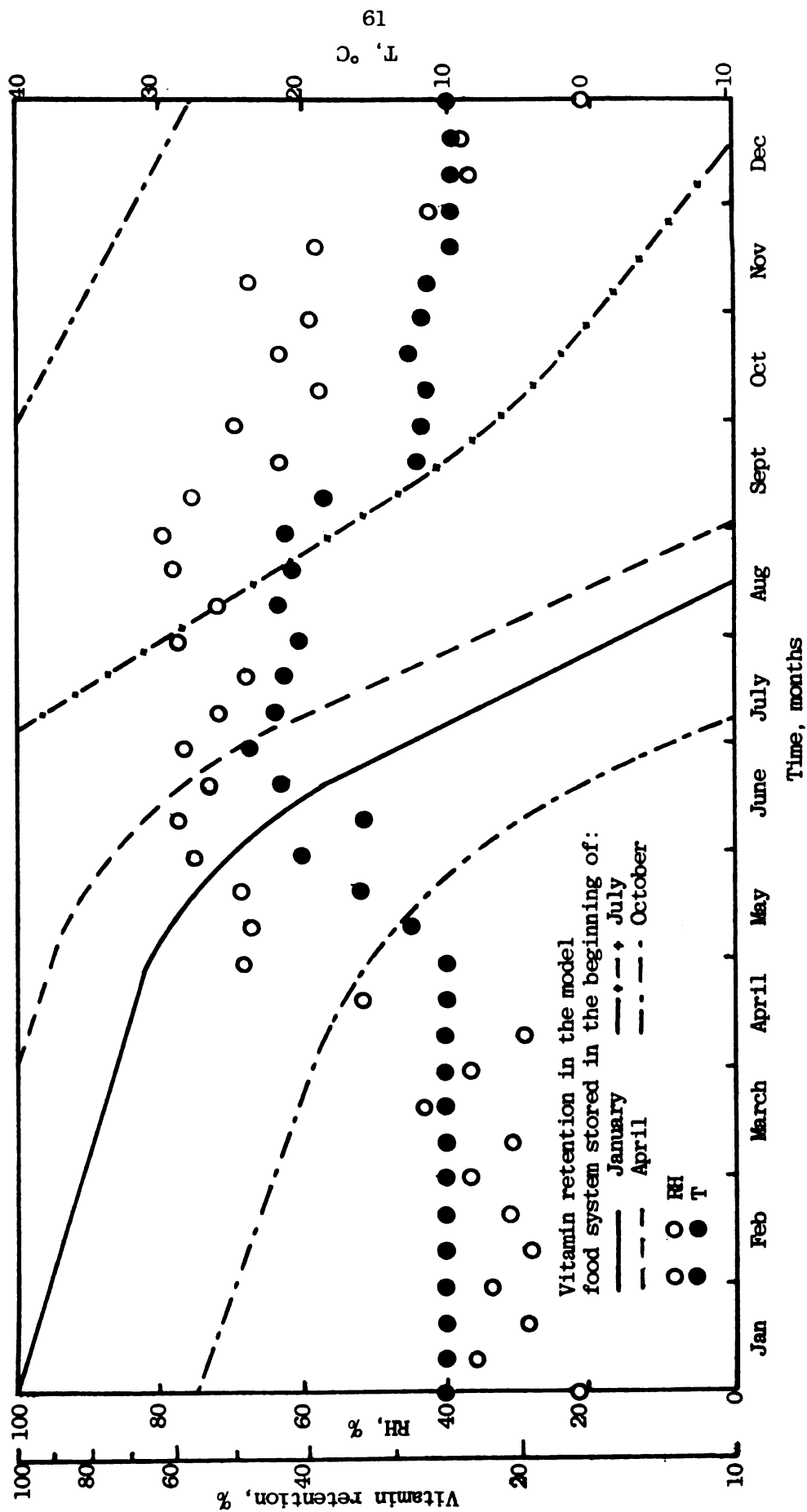


Figure 28. Computer prediction of vitamin retention, ware-house temperature and relative humidity during 1975 in Lansing, Michigan.

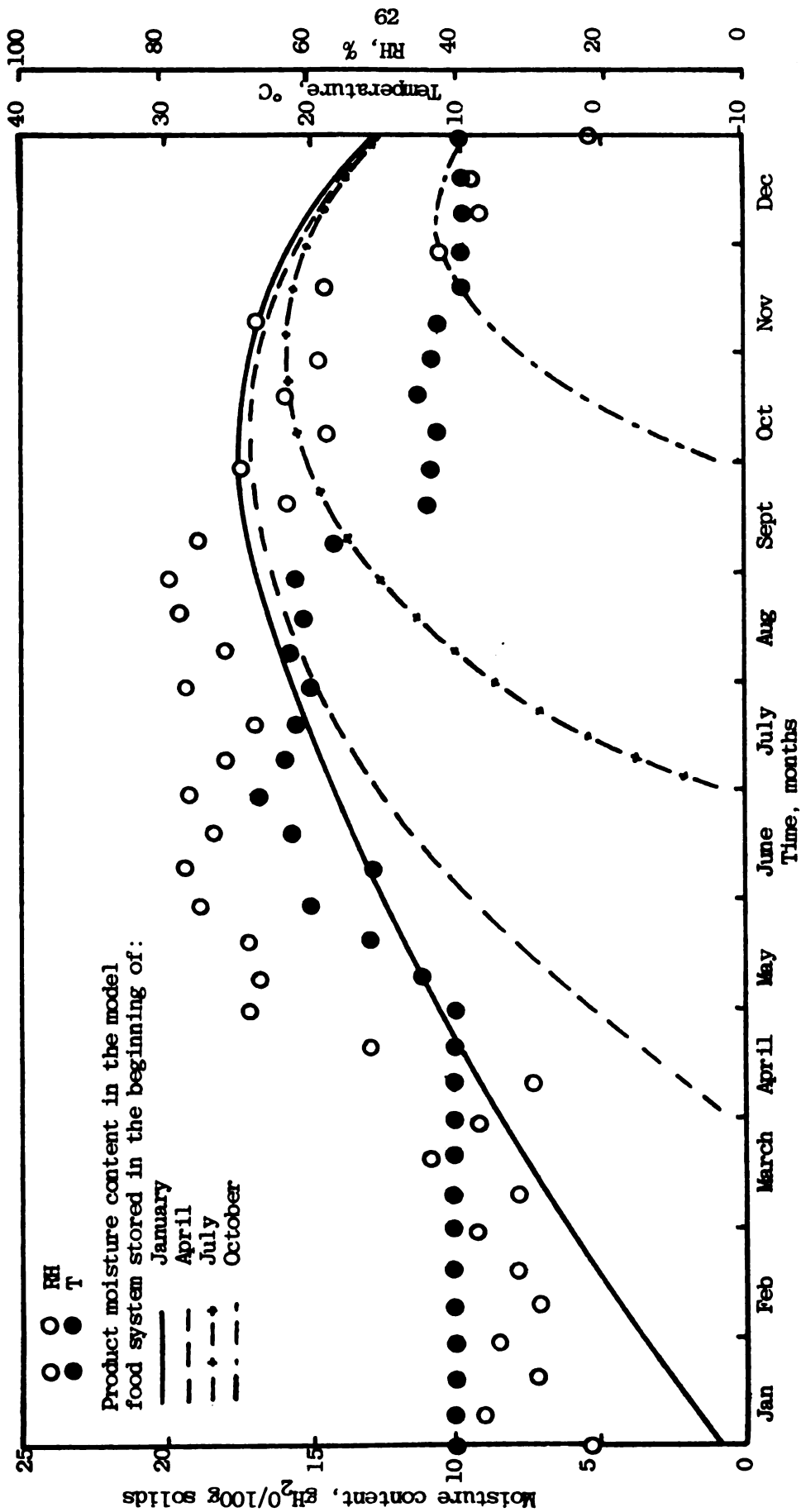


Figure 27. Computer prediction of product moisture content, and ware-house temperature and relative humidity during 1975 in Lansing, Michigan.

CONCLUSIONS

1. The mathematical model of the relationship between the rate constant of ascorbic acid degradation (k) and water activity (a_w) is found to be a linear function of temperature at 10, 20, and 30°C.

2. The computer simulation successfully predicts the ascorbic acid retention and the moisture uptake in the model food system compared to experimental data.

3. The computer simulation accounts for the influence of storage temperature and relative humidity as well as various product and packaging film characteristics.

4. The simulation is applicable for prediction of the vitamin degradation in dry foods based on the following conditions:

(a) the reaction between the vitamin and oxygen follows first order kinetics,

(b) the mathematical model of the relationship between k and a_w , and the sorption isotherms of the food products are known,

(c) oxygen is not a limiting factor, and all the moisture transferred through the packaging film is assumed to be adsorbed by the food product.

5. The computer simulation using subroutines including the Fourier series to predict the storage relative humidity and temperature fluctuation, the Arrhenius equation to determine the rate constant of vitamin degradation (k) at any temperature, and least square fitting to establish the linear relationship of k and a_w , provides an excellent prediction of vitamin retention in food products during a one-year period.

SUGGESTIONS FOR FURTHER STUDY

The author suggests that further work is required:

1. To experimentally verify the computer simulation in predicting vitamin degradation and product moisture content at lower storage temperatures.
2. To experimentally verify the computer simulation in predicting the ascorbic acid degradation and product moisture content in a commercial breakfast cereal stored at a commercial warehouse.
3. To utilize sorption isotherm equations other than the BET equation for higher water activities in the computer simulation.
4. To establish mathematical models describing the relationship between the rate of vitamin degradation and product water activity for other vitamins and to develop computer simulation based on these models.
5. To develop computer simulation to optimize the product composition, packaging material characteristics, and storage environment to get maximum vitamin retention.

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REFERENCES

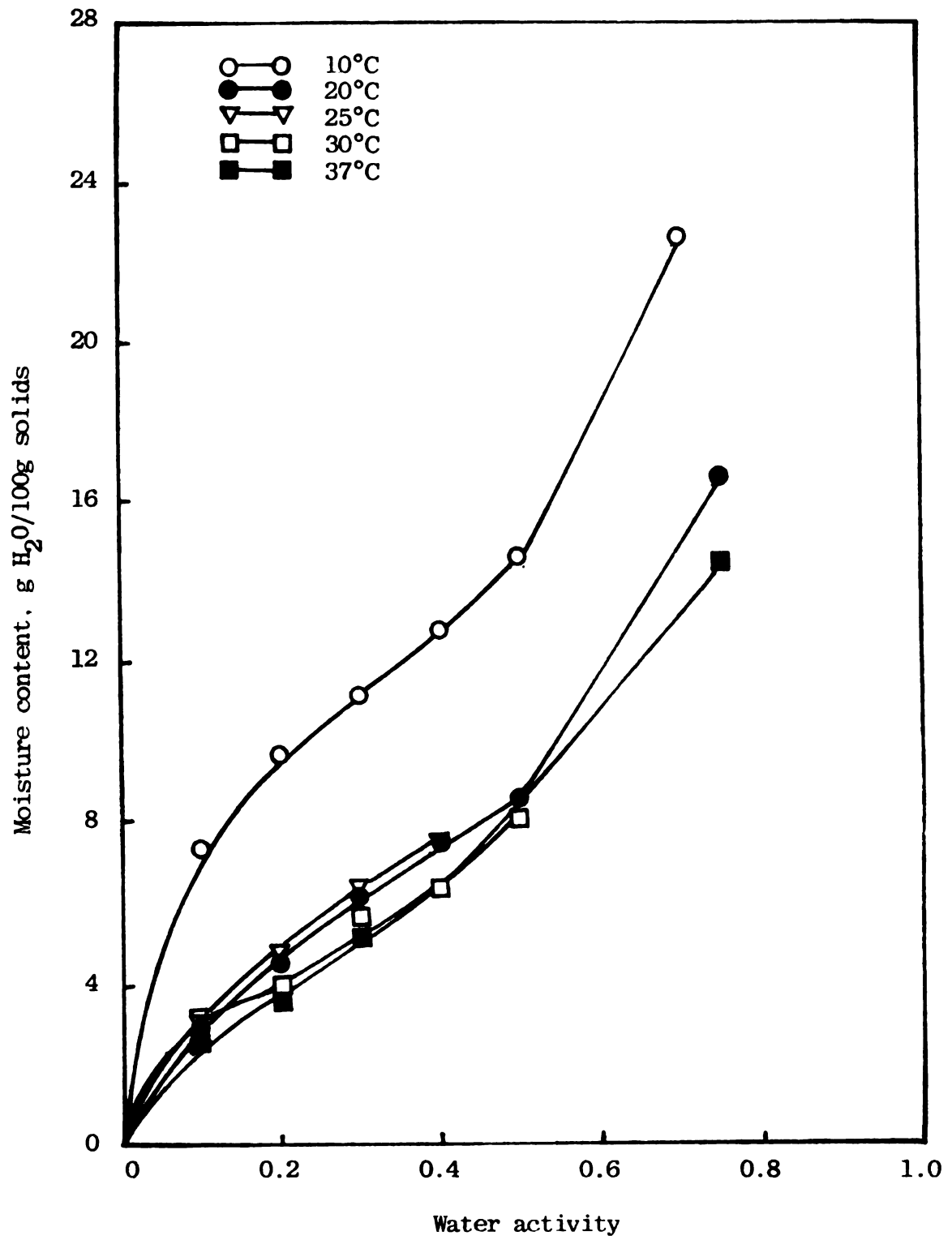
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APPENDIX

Appendix 1. Sorption isotherm curves for the model food system.



Appendix 2. Calculation of energy constant (c) and monomolecular moisture content (w_m) of the model food system.

BET equation:

$$a_w/M(1-a_w) = 1/w_m + (c-1)a_w/w_m$$

a_w : water activity

M: moisture content, gH₂O/100g solids

c: energy constant

w_m : monomolecular moisture content

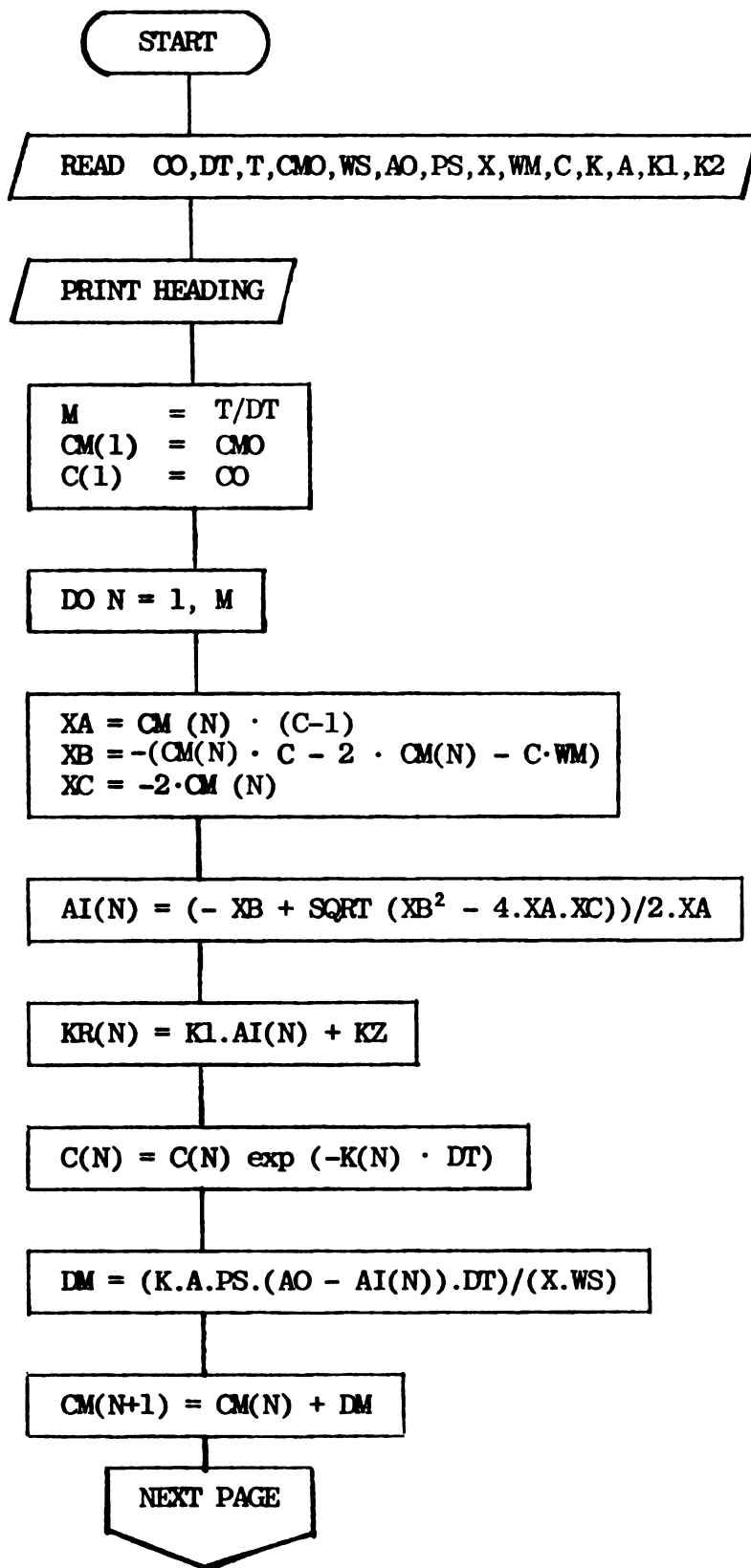
Least square fitting of BET equation, c, and w_m for each temperature are as follows:

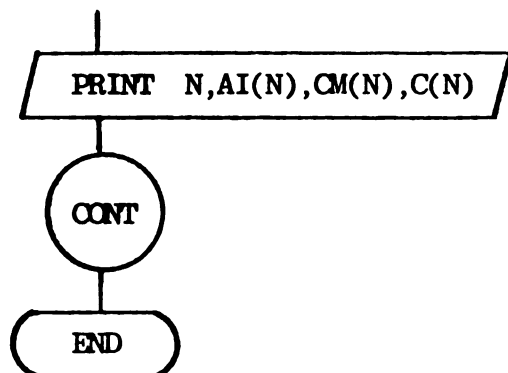
Range of a_w	T, °C	BET monolayer equation	c	w_m
0.1 - 0.4	10	$y = .1236x + .0018$	69.7	7.97
0.1 - 0.5	20	$y = .1898x + .0163$	12.6	4.85
0.1 - 0.5	25	$y = .1939x + .0136$	15.2	4.82
0.1 - 0.5	30	$y = .2236x + .0132$	17.9	4.22
0.1 - 0.4	37	$y = .2507x + .0129$	20.4	3.79

where: $y = a_w/M(1-a_w)$

$x = a_w$

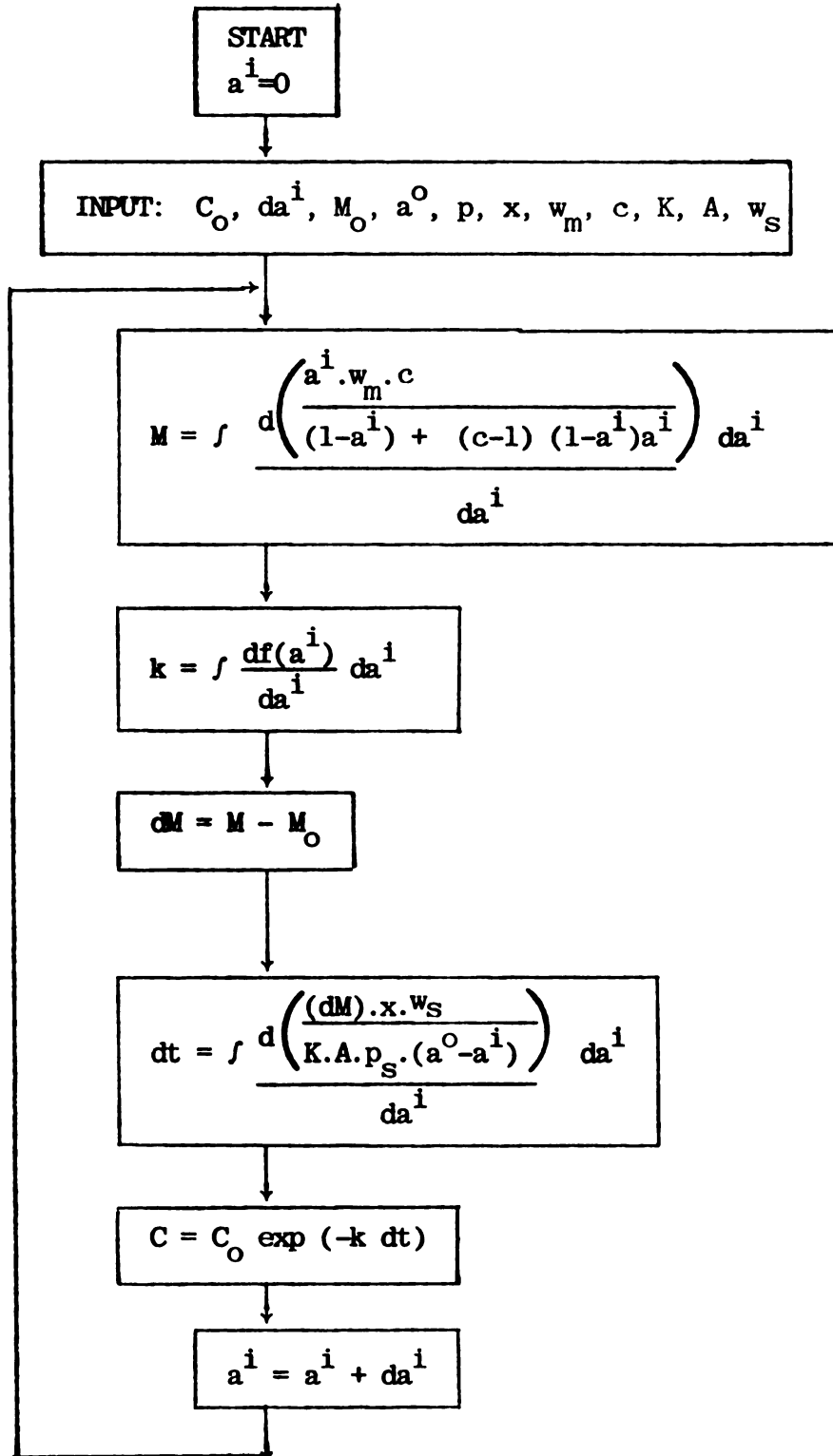
Appendix 3. Computer flowchart to predict the moisture content and ascorbic acid degradation in the model food system during storage at a given storage temperature and relative humidity.



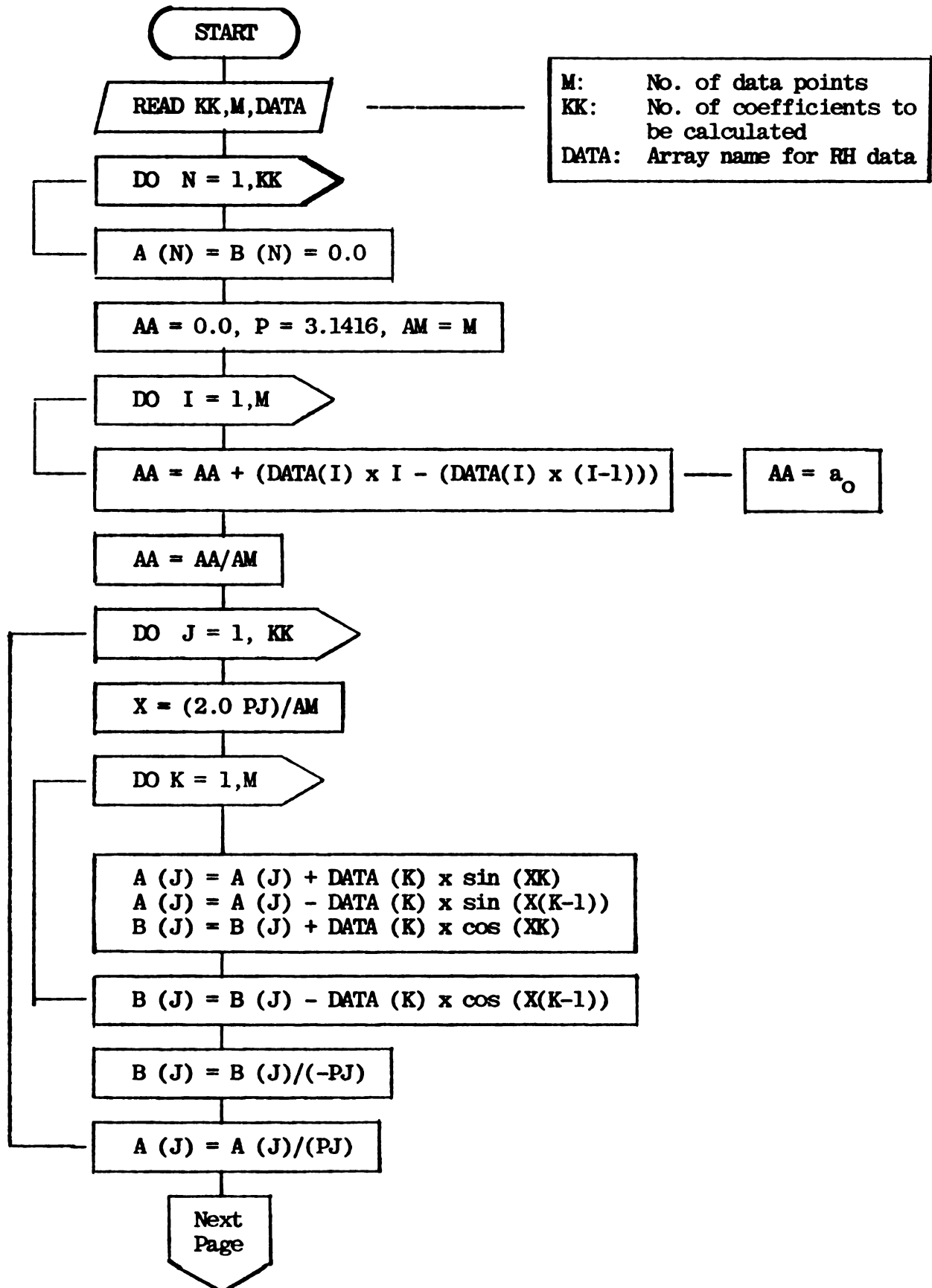


- KR: The rate constant of ascorbic acid degradation
 CO: Initial ascorbic acid concentration, %
 DT: Time differential, day
 T: Storage time, days
 CMO: Initial moisture content, gH₂O/100g solids
 WS: Product mass, g
 C: Energy constant of the model food system
 WM: Monomolecular moisture content of the model food system
 AO: Outside water activity, RH/100%
 AI: Inside water activity
 PS: Saturated vapor pressure, mmHg
 X: Packaging film thickness, cm
 K: Moisture transfer coefficient, $\frac{\text{gH}_2\text{O} - \text{cm}}{\text{m}^2 - \text{hr} - \text{mmHg}}$
 A: Packaging surface area, m²
 K1, K2: Constants from the mathematical model describing the relationship of KR as a function of AI

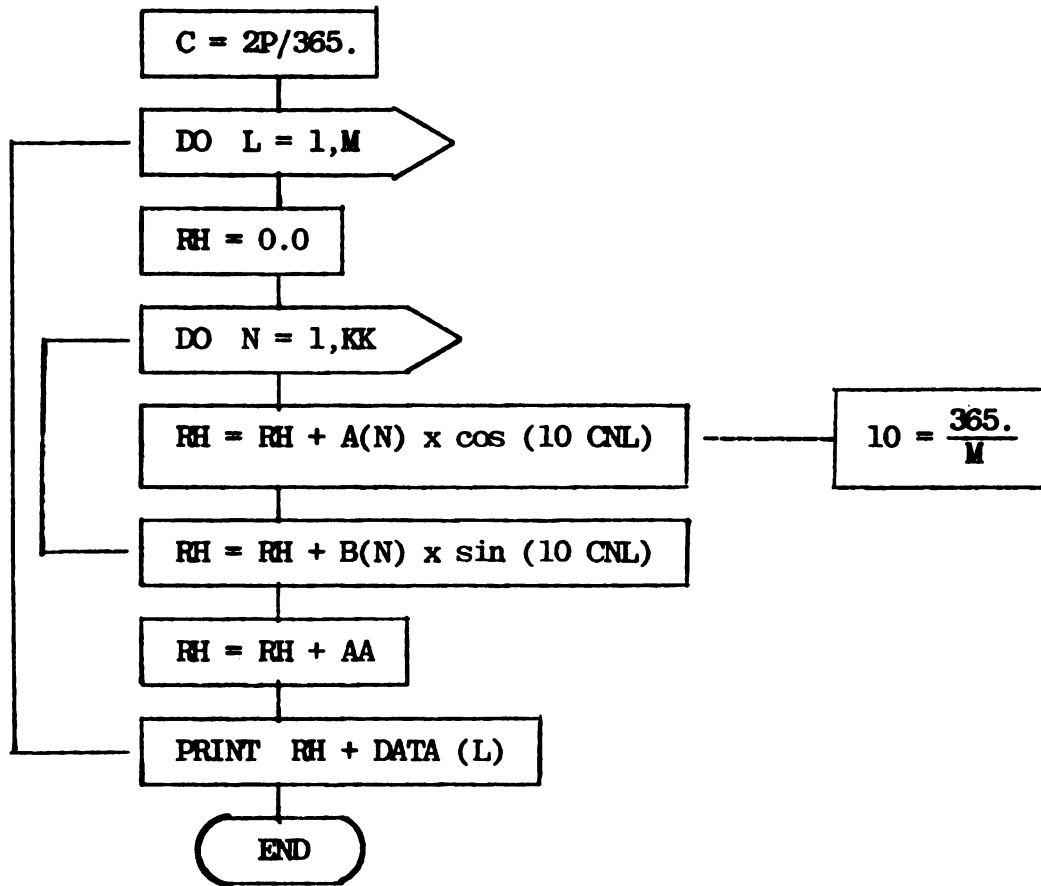
Appendix 4. The computer simulation flow sheet using water activity increment as independent variable.



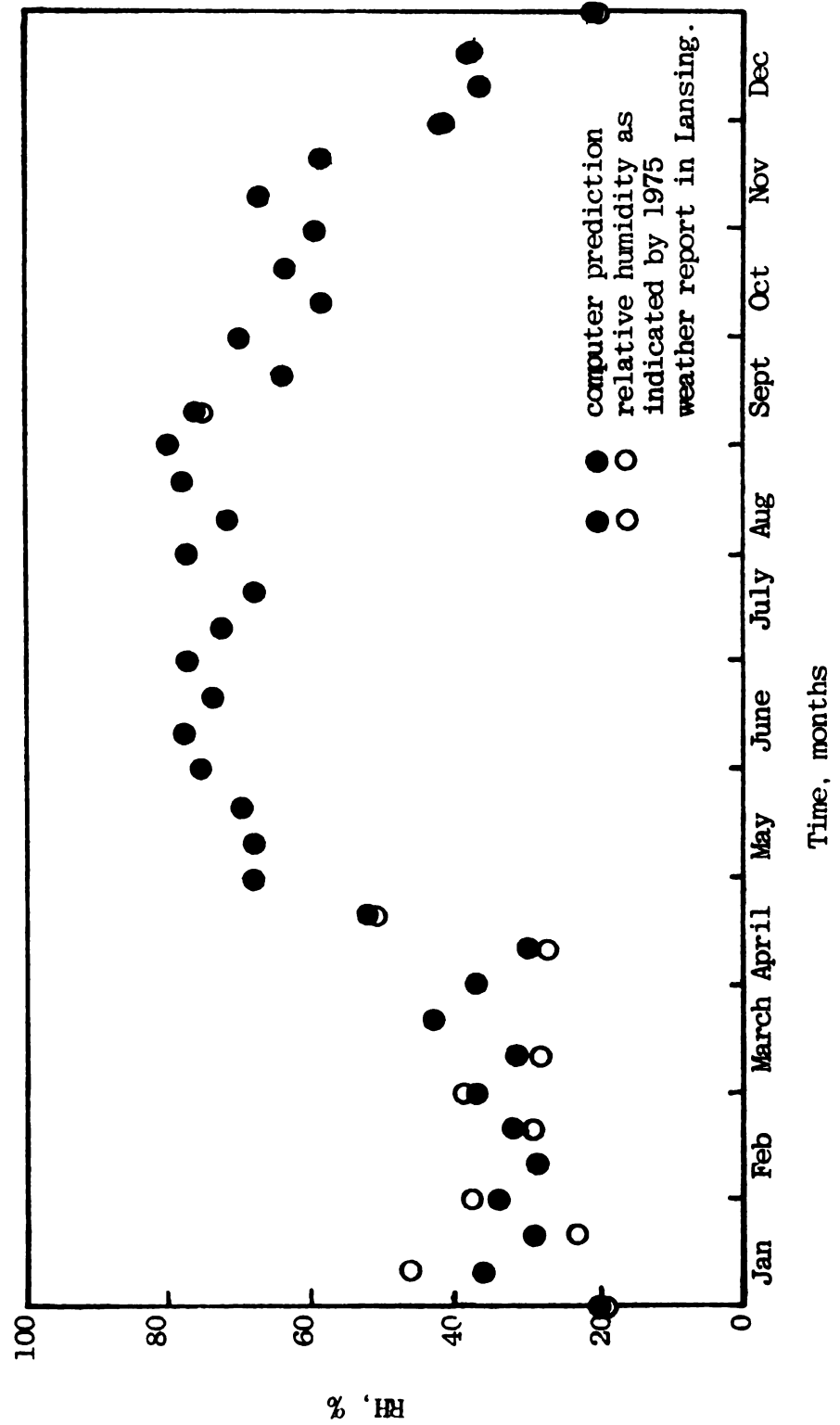
Appendix 5. Flow chart of computer simulation to predict RH based on the Fourier series.



Appendix 5. (continued)

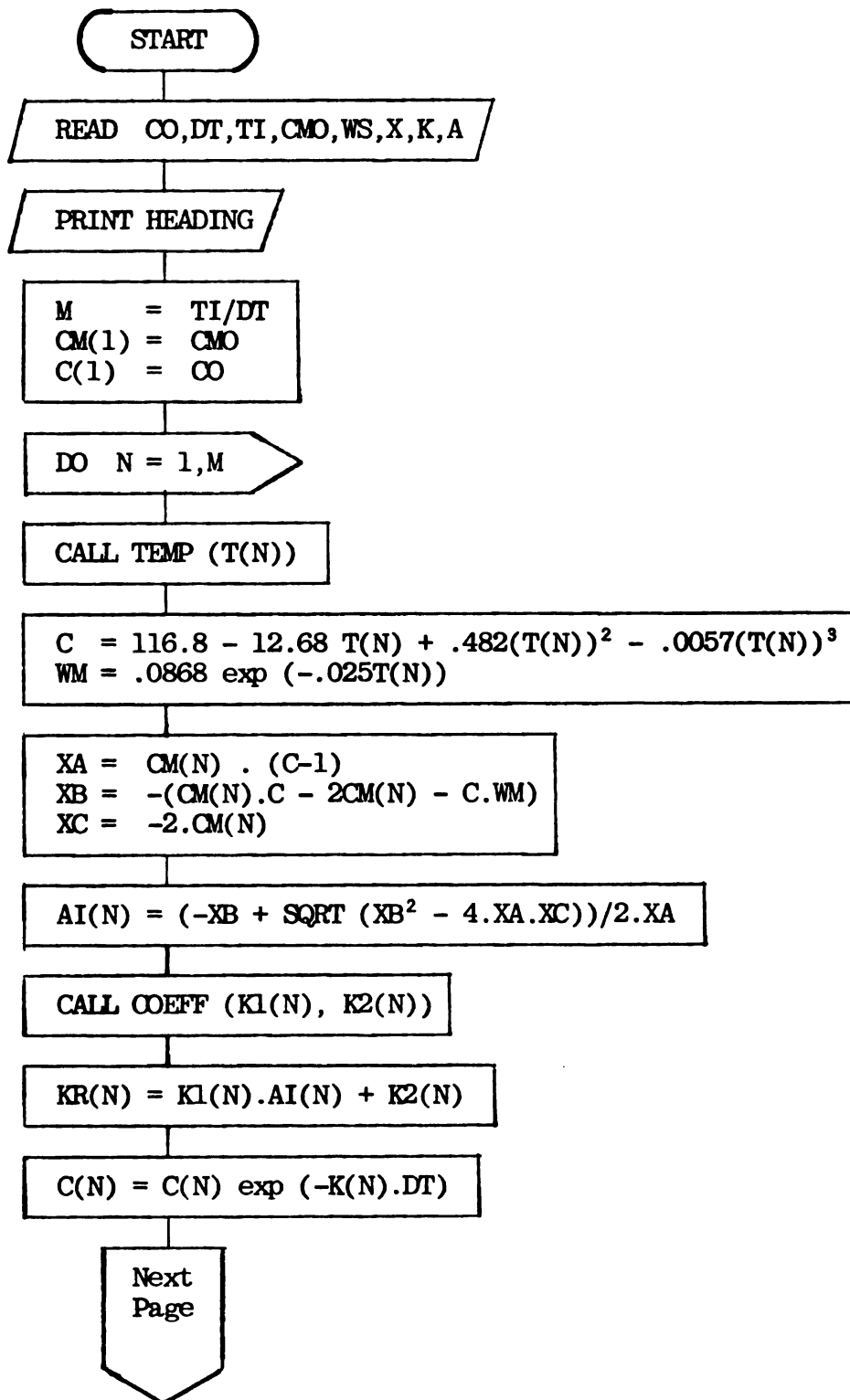


Appendix 6. Computer prediction results for relative humidity based on the Fourier series.

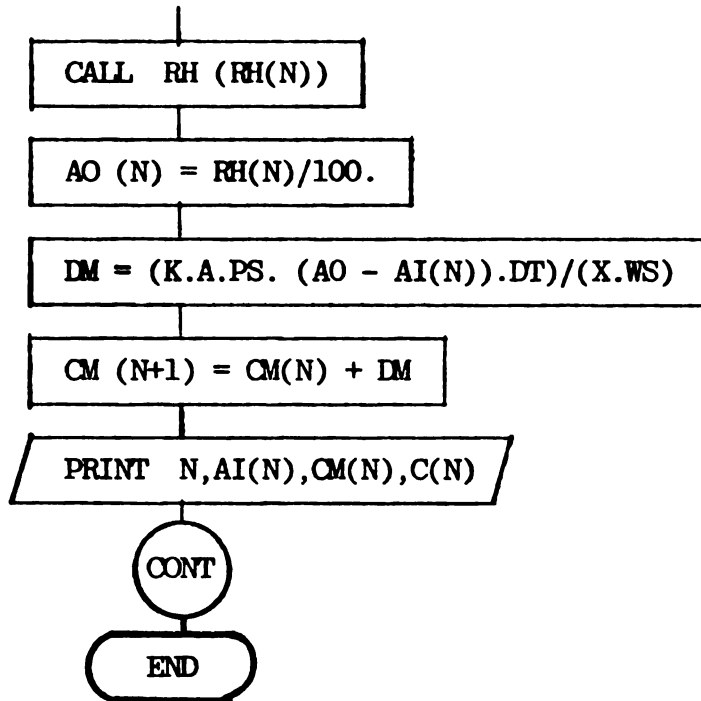


Appendix 7. Computer flow chart to predict the moisture content and ascorbic acid degradation in the model food system during a one-year period.

MAIN PROGRAM



Appendix 7. (continued)



Appendix 7. (continued)

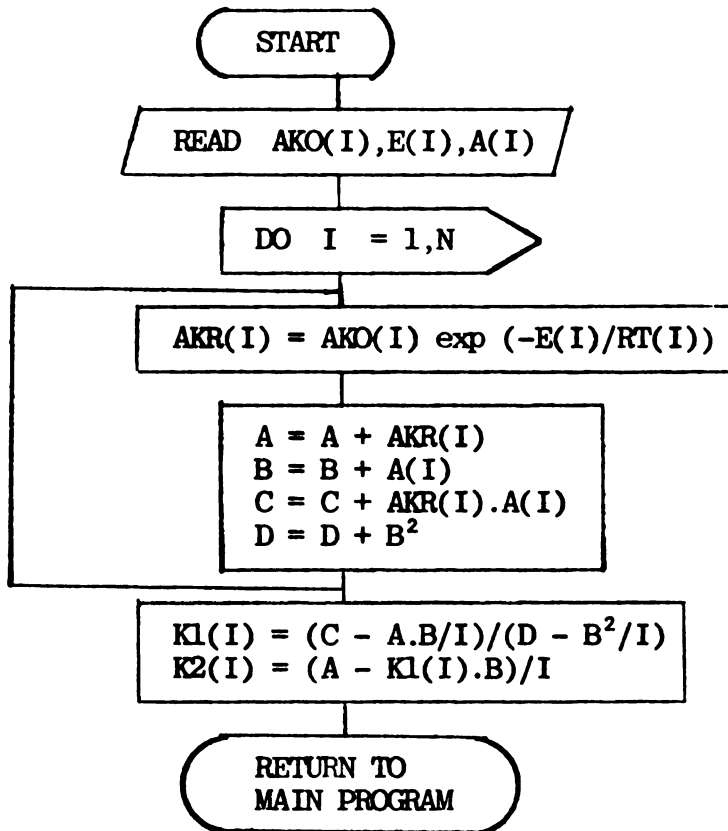
SUBROUTINE TEMP

The flowchart of subroutine TEMP is similar to flowchart in Appendix 5 if all parameter RH is changed to T.

SUBROUTINE RH

See flow chart in Appendix 5.

SUBROUTINE COEFF



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