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COMPUTER SIMULATION OF LIPID OXIDATION
IN DRY FOODS DURING STORAGE

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Thongchai Yantarasri

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of the requirements for

MASTER OF SCIENCE degree in Food Science and
Human Nutrition

Dennis R. Heldman
Major professor

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COMPUTER SIMULATION OF LIPID OXIDATION IN DRY FOODS DURING STORAGE

By

Thongchai Yantarasri

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

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1983

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ABSTRACT

COMPUTER SIMULATION OF LIPID OXIDATION IN DRY FOODS DURING STORAGE

By

Thongchai Yantarasri

The general purpose of this investigation was to develop a method to assist food engineers in prediction of shelf life for dry foods undergoing oxidative rancidity. The more specific objective of this study was to develop a mathematical model to describe the kinetics of oxidative rancidity (k) as a function of product water activity (a_w) and to develop a computer model to predict the hexanal formation as a function of moisture uptake in dry foods during storage.

The quality index for oxidative rancidity in this study was hexanal concentration. The reaction order of hexanal formation was found to be zero order and the oxidation rate was found to relate exponentially to product water activity. The predicted results were in agreement with experimental verification data at conditions of 11 C and 35%RH, 21 C and 57%RH, and 21 C and 34%RH and predictions overestimated hexanal concentration at 32 C and 44%RH. A decrease in experimented hexanal concentration was found at 21 C and 70%RH and 21 C and 78%RH after the product gained moisture content in equilibrium with water activity of 0.8.

My family

and

my christian friends

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

Rancid flavor resulting from the oxidation of lipids is a primary concern during the storage of most dried food products. It is important to establish the storage life of a food product before it reaches an unacceptable flavor due to rancidity. Normally, the establishment of shelf-life of a product involves experiments which are time consuming, costly and require expertise. Changing either the environment or the type of package require repetition of each shelf life test. Therefore a computer simulation of oxidative rancidity which is more rapid, less expensive and still effective would be an alternative approach to shelf life tests. The computer simulation is also helpful to the product manufacturer in the selection of an appropriate package to achieve economical stability.

The development of an effective computer simulation requires experimental kinetic data of oxidation rate as a function of water activity and temperature as input. In addition, moisture transfer coefficients for the packaging material and the physical characteristics of the package are required. As an index of lipid oxidation, and rancid flavor, hexanal concentration has been used as an indicator of oxidative rancidity and corresponds closely to sensory panel tests [Boggs et al (1964), Bengtsson (1967), and

Fritsch and Gale (1977)].

The overall objective of this investigation was to develop and verify a computer model to predict the development of oxidative rancidity in dried foods. The specific objectives include: (1) to determine the relationship between the rate of lipid oxidation and product water activity based on experimental kinetic data, (2) to develop a mathematical model to describe the relationship between oxidation rate and water activity, (3) to incorporate a mathematical model describing the rate of hexanal formation as a function of water activity into the computer model, allow it to predict hexanal concentration during storage and (4) to verify the prediction model using experimental shelf-life data.

II. REVIEW OF LITERATURE

2.1 Lipid Oxidation

It is generally recognized that lipid oxidation in food occurs almost exclusively with unsaturated fatty acids. A lipid often reacts with oxygen and this reaction leads to the formation of hydroperoxide, carbonyl compounds and free fatty acids.

In their discussion of lipid systems, Maloney et al (1966) and Labuza et al (1969) described lipid oxidation as hydroperoxide decomposition proceeding in two steps: monomolecular decomposition during the initial period of oxidation and bimolecular decomposition when substrate becomes limiting. Subsequently, Labuza (1971), and Karel and Yong (1981) indicated that when at least 1-2% of the substrate (molar basis) was oxidized, monomolecular decomposition, in which the rate was proportional to the square root of the oxidized substrate occurred. When the substrate was oxidized above 2%, bimolecular decomposition, in which the rate was proportional to the peroxide concentration, was the controlling rate.

In studies containing antioxidant or in the complex food systems, different orders of oxidation rate were reported by Labuza (1971 and 1982), Labuza and Bergquist (1983), and Fritsch and Gale (1977). In addition to the

half order reaction rates found in very pure lipid systems, first order rates with the addition of antioxidants and zero order rates in some complex food systems were also discussed by Labuza (1971 and 1982).

Similarly, Quast et al (1972) found that their model also provided good correlation coefficients using zero order rate in potato chips, as did Labuza and Bergquist (1983) using zero order rate as measured by peroxide value in the same product. Fritsch and Gale (1977) found that first order kinetics described the rate of hexanal formation in breakfast cereals. The small differences between half order, zero order and first order rates were explained as being due to a low oxidized substrate [Labuza and Bergquist (1983)].

2.2 The Influence of Water Activity

Lipid oxidation was shown to be related closely to physical effects of water activity [Martin (1958), Salwin (1959), Maloney et al (1966), Labuza et al (1969), and Heidelbaugh and Karel (1970)]. These properties of water in foods were reviewed by Labuza et al (1970). These investigators indicated that water content in foods can be divided into three levels, the first level up to 5-10% moisture content called monolayer water, secondly a multilayer level and finally as capillary condensation water (acts as a solvent for various solutes).

Lipid oxidation rate varies with the level of water content at moisture contents above monolayer coverage.

Martin (1958), Salwin (1959), Maloney et al (1966), and Martinez and Labuza (1968) found that for freeze dried model systems and dehydrated foods in a dry state, maximum protection against oxidation occurred. Martin (1958) found the cereal flake retained longer stability at a moisture content above 5% and stability decreased rapidly at moisture content below 5%. Salwin (1959) also observed similar results on various dried foods which were found to become very susceptible to oxidation at very dry states.

To explain the effect of water activity on oxidative rancidity in the dry state of food, Maloney et al (1966) theorized that two mechanisms may be involved: 1) water is hydrogen bonded with hydroperoxides so that the hydroperoxides do not continue to decompose through initiation of lipid oxidation and 2) water interacts with metal catalysts making the hydroperoxide less effective. In addition, Salwin (1959) proposed that the water could attach to sites on the food surface, thereby protecting lipids from oxygen.

All of these previous studies indicate that dried foods have maximum resistance to lipid oxidation at some optimum moisture content (optimum water activity), close to the monolayer of water content. Oxidation increases when water content falls below this level. On the other hand, when the moisture content of food was increased above this optimum moisture content, the oxidation rate was found to increase to a maximum in the intermediate water activity

range of 0.55 to 0.85 [Labuza et al. (1969), and Heidelbaugh and Karel (1970)]. Labuza et al (1969) examined the oxidation of methyl linoleate, trioleate, and linoleic acid in model systems in which oxidation was measured by oxygen absorption, peroxide value and hexanal-heptanal production. These investigators found the rate of oxidation increased significantly at the moisture contents in the level of capillary condensation at which mobility of reactants became enhanced.

Similar results on a model system containing methyl linoleate and ground pork were found by Heidelbaugh and Karel (1970) who proposed that the catalysts became more mobile when moisture increased above the monolayer of water content. In addition, Chou et al (1972) proposed that new catalysts might also be dissolved in the system to enhance the reaction and also that swelling of the polymeric matrix of the food should open up new capillaries making more catalyst sites available for reaction. However, Labuza (1974) indicated that at still higher water activities (0.75 to 0.85), dilution of catalysts might again retard the oxidation rate.

2.3 The Complex Food System

In complex food systems containing protein and lipid, protein was reported to react with peroxidizing lipid or with their break-down products. This reaction was found in solution or dispersion [Roubal and Tappel (1966), Montagomery and Day (1965)] and in dry systems [Labuza

(1969), Zirlin and Karel (1969) Roubal (1970)].

Labuza (1969) found this protein-lipid interaction had a modifying effect on the lipid oxidation mechanism. Roubal (1970) reported that radicals derived from oxidizing lipids were trapped and thus reduced the reactivity in a matrix of a lipid-protein system. In an investigation of the interaction of off-flavor components with protein, Montgomery and Day (1965) found the removal of carbonyls with simultaneous formation of unsaturated polymeric pigment in a system containing L-tyrosine ethyl ester and n-heptanal.

On the other hand, nonenzymatic browning which normally is found in the lipid-protein systems [Andrew et al (1965), Zirlin and Karel (1969) and Eichner (1974)] is capable of inhibiting the lipid oxidation through browning of intermediates [Eichner (1974)]. Heidelbaugh and Karel (1970) also reported that a water binding agent could affect the oxidation rate by decreasing the optimum water activity from near 0.40 to near zero, thus the oxidation rate decreased at a low water activity level. This study was done in a glycerol-pork system.

Studies on the physical structure of lipid-protein in freeze dried emulsified systems by To (1978) and Gejl-Hansen (1977) indicated the matrix of encapsulated lipid was resistant to oxidation in a dry state. Break-down of the protective matrix by addition of water however, made the encapsulated lipid available for oxidation.

2.4 The Influence of Solid Surface

The solid surface over which the lipid is dispersed in a dry state has been found to influence the oxidation rate significantly [Togashi et al (1961), Honn et al (1951), and Sinha (1977)]. Togashi et al (1961) studied the oxidation of lipid film on glass and on a gelation surface with varying amounts of lipid. They found the protein surface greatly reduced the rate of lipid oxidation compared to the glass surface. This reduction was attributed to hills and valleys in the protein film which reduced the surface area of the lipid and the orientation effect of protein on lipid thus reducing susceptibility to oxygen attack. Togashi et al (1961) also found an increase in the peroxide value with a greater ratio of surface area to volume of lipid.

Sinha (1977) found similar results on both protein and glass surface by measuring the amounts of oxygen absorbed. He found the oxidation rate decreased with an increase in lipid content in his model systems. However, he found an insignificant change in the oxidation rate when the amount of lipid was increased to 5 and 10% of the system. He attributed this decrease of lipid oxidation to the thickness of the fat layer which was inhibiting the flow of oxygen through the reaction matrix.

Honn et al (1951) reported the dependence of the rate of oxygen consumption upon the lipid/solid ratio. They found that the most rapid rate of oxygen uptake occurred at a lipid/solid ratio characteristic of the surface area of the

absorbant. The markedly slower rate occurred above and below that ratio.

2.5 The Influence of Temperature

Similar to other qualitative determinations, the Arrhenius equation has been used to describe kinetics of lipid oxidation by several researchers [Ragnarsson and Labuza (1977), Ragnarsson et al (1977), and Labuza and Bergquist (1983)]. These investigators found that in pure lipid systems comparing the high temperature condition to a lower temperature condition, the data were consistent with the Arrhenius equation.

In terms of activation energies (E) obtained from the Arrhenius equation for lipid oxidation, Labuza and Bagquist (1983) obtained 11-13 kcal/mole in food systems and 20-22 kcal/mole (with added antioxidants) and 20.8 kcal/mole in potato chips as measured by peroxide value. Fritsch and Gale (1977) found 14.5 and 19.5 kcal/mole for wheat and corn cereals, respectively as measured by hexanal concentrations. Finally, Labuza (1971) suggested that the typical activation energies for the food systems containing lipids ranged between 10-24 kcal/mole.

2.6 Hexanal-A Measure of Oxidative Rancidity

Hexanal has been implicated as a major break-down product (resulting in off-ordors) and as a good indicator of lipid oxidation in potato granules [Buttery and Teranishi (1963), and Boggs et al (1964)], in frozen pears Bengtsson

et al (1967) , and in breakfast cereals [Fritsch and Gale (1977)].

Buttery and Teranishi (1963) found that hexanal content increased with time of storage exhibiting the major component among all the break-down products of lipid oxidation. Hexanal formation could be used to compare susceptibility to oxidative rancidity using different levels of antioxidant. This study was done by sampling the vapor above reconstituted dehydrated potato and analyzing it by gas chromatography. Boggs et al (1964) experimented on the same model and found the hexanal concentration was closely associated with flavor deterioration, as tested by sensory panel.

Bengtsson et al (1967) found a good correlation between hexanal formation in pears and off-flavor development. However, he found a decrease in hexanal concentration after passing a maximum, which could be related to the transient properties of hexanal. Subsequently, hexanal was oxidised to form another component.

The best study of oxidative rancidity in breakfast cereal was conducted by Fritsch and Gale (1977) by measuring hexanal content as an index of rancidity. They found this method was simple, rapid and a very effective analytical tool, comparable to a sensory evaluation with a correlation coefficient (r^2) of 0.99.

2.7 The Influence of the Semipermeable Package on Moisture Transfer

A package film is a material which allows permeation of moisture, gases and organic vapor by activated diffusion, in the absence of cracks, macroscopic, microscopic pores or pinholes [Hilton and Nee (1978)].

The rate of moisture vapor transfer through various types of package film was found to be a polynomial relationship for moisture vapor transfer rate versus water activity [Karel et al (1971)]. These moisture and oxygen transfer effects were suggested by Quast and Karel (1973) to be responsible for the deterioration of the food product.

2.8 Computer Simulation of Quality Change in Food

To date, several researchers have developed computer simulations to predict the shelf life of food products but only a few have attempted to predict the stability of dried food undergoing oxidative rancidity.

Among these researchers,Simon et al (1971) developed a computer-aided method for predicting the storage stability of a product stored in semipermeable containers, undergoing lipid oxidation. This study was conducted on freeze dried shrimp bars in which organoleptic deterioration was correlated with oxygen uptake and with loss of carotenoid pigment.

Quast et al (1972a) developed a mathematical model for the oxidation of potato chips as a function of oxygen

uptake, equilibrium relative humidity and extent of oxidation. Subsequently, Quast and Karel (1972) presented a computer simulation to predict the storage behavior of potato chips undergoing deterioration by two interaction mechanisms: loss of crispness due to moisture adsorption and lipid deterioration due to oxygen adsorption.

Heldman (1974) proposed a basic computer simulation for storage conditions which influence vitamin stability. Lee (1976) established a computer model to predict ascorbic acid degradation in canned tomatoes. The program included the effect of pH, copper ion, and storage temperature. Purwadaria (1977) developed a computer simulation to predict the retention of ascorbic acid as a function of time, temperature and water activity in a dry food system inside wax paper packages. Riemer and Karel (1977) developed a similar computer model to predict the retention of ascorbic acid in dehydrated tomato juices.

Mizarahi et al (1970) developed a mathematical model to predict the extent of browning in dehydrated cabbage and Singh and Heldman (1976) developed a computer simulation to predict the deterioration of ascorbic acid in a liquid food.

III. THEORETICAL CONSIDERATION

3.1 The Kinetics of Oxidative Rancidity

The rate of hexanal formation throughout this study is assumed to be of zero order, compared to first order kinetics. The equations to describe the relationship between hexanal concentration and time can be illustrated below.

Zero Order:

$$\frac{dH}{dt} = k$$

$$\text{or } H = H_o + kt \qquad (3.1)$$

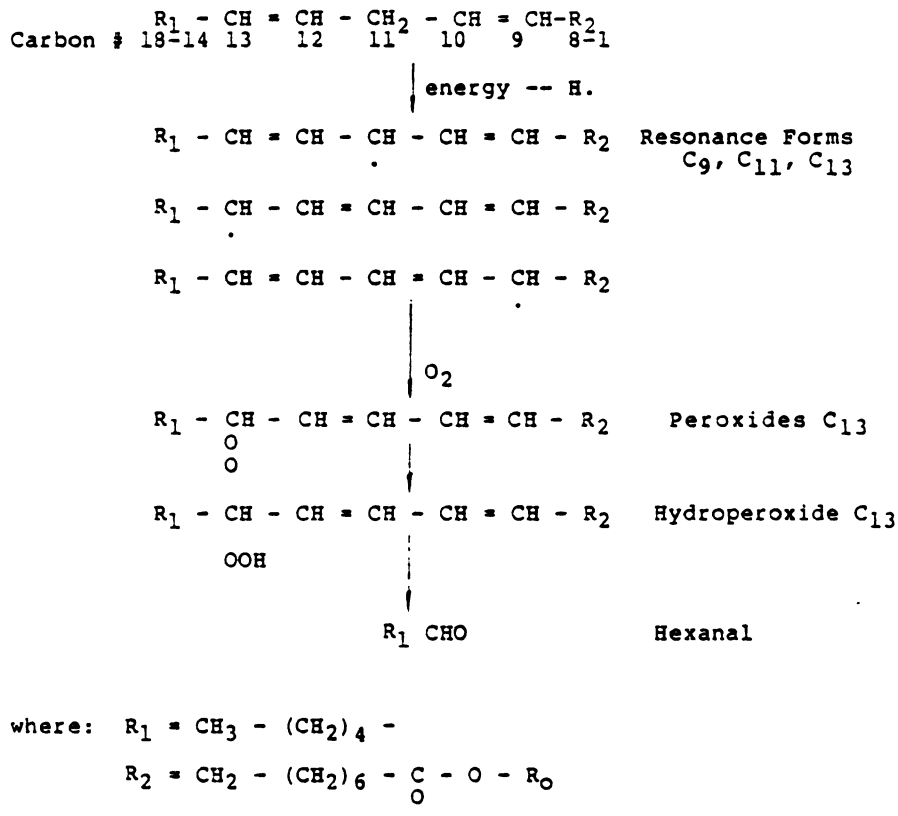
First Order:

$$\frac{dH}{dt} = kH$$

$$\text{or } H = H_o \exp(kt) \qquad (3.2)$$

As shown in Figure 3.1, hexanal is a break-down product from hydroperoxide decomposition of linoleic acid, which is the main unsaturated fatty acid in corn oil [de Man (1980)]. Since corn oil was the source of lipid in the food model system for this investigation, the rate of hexanal formation depends on the rate of hydroperoxide decomposition.

In pure lipid systems, Maloney et al (1966) and Labuza et al (1969), presented three steps of lipid oxidation (Figure 3.2) and indicated that the rate of reaction



where: $R_1 = CH_3 - (CH_2)_4 -$

$R_2 = CH_2 - (CH_2)_6 - \underset{O}{C} - O - R_o$

Figure 3.1 Hexanal formation in typical break-down pathway for oxidation of linoleic acid [adapted from Labuza (1971)].

Initiation:

$$ROOH \xrightarrow{(M)} RO\cdot + \cdot OH \qquad \text{Monomolecular}$$

$$\text{or } 2\ ROOH \xrightarrow{(M)} R\cdot + RO_2\cdot + H_2O \qquad \text{Bimolecular}$$

Propagation:

$$R\cdot + O_2 \xrightarrow{k_q} ROO\cdot$$

$$ROO\cdot + R'H \xrightarrow{k_p} ROOH + R\cdot$$

$$ROOH \longrightarrow \text{breakdown products such as hexanal}$$

Termination:

$$2\ ROO\cdot \xrightarrow{k_{t1}}$$

$$ROO\cdot + R\cdot \xrightarrow{k_{t2}}$$

$$R\cdot + R\cdot \xrightarrow{k_{t3}}$$

} non - radical end products

Figure 3.2 Three steps of lipid oxidation [adapted from Labuza et al (1969)]

occurred in two different orders of oxidation. First, the rate of monomolecular hydroperoxide decomposition k_m (half order) occurrs during the initial period of oxidation when oxygen concentration is not limited. The oxidation rate can be illustrated as follows.

$$-\frac{d(O_2)}{dt} = \frac{d(ROOH)}{dt} = \frac{k_p\, k^{\frac{1}{2}}\, (M)^{\frac{1}{2}} (R'H)\ (ROOH)^{\frac{1}{2}}}{(2k_t)^{\frac{1}{2}}}$$

$$= k_m\, y^{\frac{1}{2}}$$

As the amount of hydroperoxide increases, the decrease in substrate concentration becomes limiting and the rate of oxidation becomes bimolecular hydroperoxide decomposition k_b as follows:

$$\frac{d(O_2)}{dt} = \frac{d(ROOH)}{dt} = \frac{k_p\ \ k_{11}^{\frac{1}{2}}\, M^{\frac{1}{2}}\ (R'H)\ (ROOH)}{(2k_t)^{\frac{1}{2}}}$$

$$= k_b\ (1-y)y$$

Labuza (1971 and 1982) indicated that lipid oxidation kinetics followed half order for very pure lipid in model systems and first order when antioxidants were added. In the complex systems where protein is present, as in this study, the protein might interact with the lipid oxidation pathway as show in Figure 3.3. This interaction between the lipid and protein might modify the rate of lipid oxidation [Labuza et al (1969)], as well as the rate of hexanal

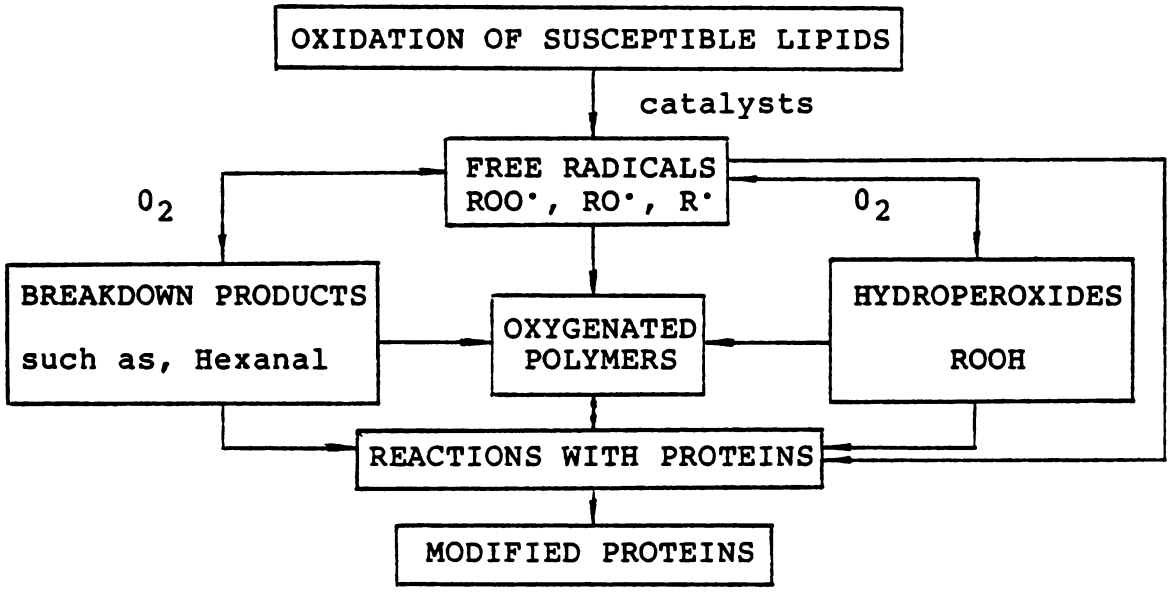


Figure 3.3 Possible interactions between proteins and peroxidizing lipids[adapted from Karel and Yong (1981)].

formation.

According to Quast et al (1972a) and Labuza (1983) in complex systems, the lipid oxidation kinetics followed a zero order model in potato chips; while Fritsch and Gale (1977) found that the first order relationship described hexanal formation in breakfast cereals. Labuza (1982) concluded that the data was best described by zero order kinetics in complex foods.

Since the model system in this study is a complex system as those Quast et al (1972), Labuza (1983) and Fritsch and Gale (1977) and, zero order and first order are justified to be applicable for hexanal formation in this study.

3.2 The Influence of Water Activity

The relationship between the rate of oxidative rancidity and water activity can be developed from the simple mathematical equation for vitamin stability as suggested by Heldman (1974). Due two of the factors that influence the quality deterioration rate at a constant temperature are oxygen and moisture. Assuming oxygen is in excess, then the equation is as follows:

$$k = f\ (a_w) \qquad (3.3)$$

The entire picture of how water activity influences lipid oxidation compared to other models of deterioration was reviewed by Labuza (1971) as illustrated in Figure 3.4.

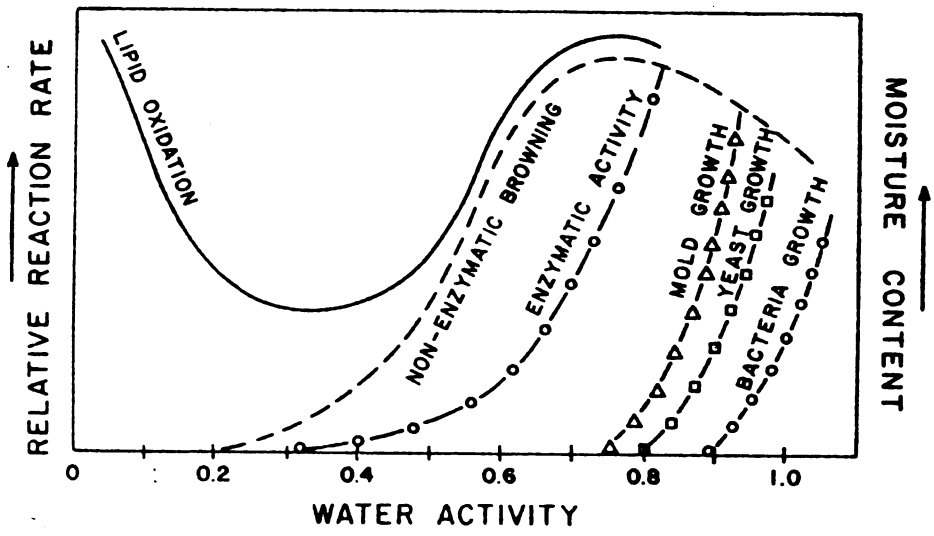


Figure 3.4 Stability of foods as a function of water activity [Labuza (1971)]

The minimum oxidation rate is expected to occur above monolayer coverage of water activity or intermediate water activity range[Martin (1958), Salwin (1959), Maloney et al (1966), and Martinez and Labuza (1968)].

To date, only Quast et al (1972) and Quast and Karel (1972) have developed a mathematical relationship between the rate constant and water activity for the deterioration of potato chips undergoing lipid oxidation. However, this relation is a polynomial equation containing several parameters which are difficult to obtain.

Since the simple mathematical equation suggested for vitamin retention by Heldman (1974) can be applied to any quality deterioration, it will be utilized in this investigation.

3.3 Sorption Isotherm

The BET equation [Brunauer et al (1938)] will be utilized to describe the relationship between moisture content and water activity of the model food system in this study. The equation can be illustrated as follows:

$$\frac{a_w}{M(1-a_w)} = \frac{1}{w_m c} + \frac{(c-1)\ a_w}{a_w c} \qquad (3.4)$$

This isotherm equation has been applied to several types of foods. It has been applied to proteins by Shaw (1944), Bull (1944), Dunford and Morrison (1945), to wheat by Becker and Sallans (1956) and to dry food model systems

by Purwadaria (1977). Boquet et al (1979) concluded that the BET equation could be used to describe the moisture content water activity relationship for milk products and starchy foods in the range of 0.10-0.80 water activity.

Since the model system in this study is similar to the system used by Purwadaria (1977) in which the isotherm data fit the BET equation, this equation is considered to be applicable.

The application of the BET isotherm equation to a food system will be acceptable when the BET assumptions are met. The assumptions in derivation of the BET equation are: 1) there is more than one layer of water molecules on the surface of a solid, 2) the energy of adsorption for water molecules is equal to the heat of vaporization of water in all layers except the monolayer, 3) the energy of absorption for the monolayer is the same for all molecules that exist in that layer [Labuza (1968)]. Since the assumptions of this model are not entirely true for food materials, the BET equation is usually good between a range of a_w from 0.1 to 0.5 [Labuza (1968)].

3.4 The Influence of Package Film

As previously reviewed in Section 2.2, the oxidation rate is influenced by the rate of moisture transport through the package film. Assuming the water activity inside the package is always in equilibrium, the product absorbs the moisture by rapid transfer through the package wall. The

rate of moisture penetration through the package material which was proposed by Heldman (1974) can be expressed by the following:

$$\frac{dM}{dt} = KAP_S (a_w^o - a_w)/xw_S \qquad (3.5)$$

3.5 The Arrhenius Equation

In order to investigate rates of oxidative rancidity at different temperatures, the Arrhenius equation can be utilized. The equation is as follows:

$$k = k_o \exp (-E/RT_A) \qquad (3.6)$$

The relationship between oxidation rate and temperature has been described by the Arrhenius equation recently by Ragnarsson and Labuza (1977), Ragnarsson et al (1977), Labuza and Bergquist (1983). The typical mathematical models which have been used to describe the relationship between temperature and the oxidation rate of oxidative rancidity are the extrapolation model or Q_{10} and the Arrhenius equation as discussed by Ragnarsson and Labuza (1977).

The extrapolation of the rate constant (k) to a temperature change of 10 C (Q_{10}) can be expressed as:

$$Q_{10} = \frac{k \text{ at } T+10}{k \text{ at } T}$$

This Q_{10} value can be related to the activation energy (k) through the following equation.

$$\text{Log } Q_{10} = \frac{(2.189\ E)}{(T+10)T}$$

Ragnarsson and Labuza (1977) stated that while activation energy is approximately constant, Q_{10} is not; but increases with decreaseing temperature. Therefore, the prediction of the rate constant (k) based on accelerated shelf life test is higher than it would actually occur. Furthermore these investigators also indicated that the Q_{10} strongly depends on temperature, thus it is a poor prediction for the temperature sensitive qualities.

Since Q_{10} value is not constant and the deviation will be inverse with the temperature change, the Arrhenius equation with constant activation energy (E) is more applicable in this study.

3.6 The Computer Simulation

There are only a few computer models that are able to predict the rate of quality deterioration as a function of water activity taking into account the effect of moisture penetration through the storage package. Among these models, Quast and Karel (1972) first developed a computer to predict the storage life of potato chips undergoing deterioration by two mechanisms, loss of crispness and lipid oxidation.

The next computer model is presented by Purwadaria

(1977), utilizing a basic computer simulation which was proposed by Heldman (1974), Purwadaria developed a mathematical model to predict stability of ascorbic acid in the dried food model system. When the oxygen is assumed to be in excess, the rate constant is a function of water activity as follows:

$$k = f\ (a_w)$$

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

$$\frac{dM}{dt} = KAP_s\ (a_w^{\circ} - a_w)/xw_s \qquad (3.5)$$

The water activity inside the package can be calculated by the BET equation. At the same time, Riemer and Karel (1978) developed a similar computer model which successfully predicts ascorbic acid retention in dehydrated tomato juice. This relation is a function of time, temperature and water activity inside the package.

Comparing computer simulations by Quast and Karel (1972), Purwadaria (1977), and Riemer and Karel (1978), the model of Purwadaria (1977) is more simple, contains less parameters, is very similar to the model food system in this study and it has already provided an accurate prediction of the degradation of vitamin C. Therefore, the Purwadaria model (1977) system in considered to be applicable in this study.

The computer model in this study is illustrated in

Figure 3.4. The main difference between this computer model and Purwadaria (1977) is that the latter computer model predicted ascorbic acid degradation while the model in this study predicted oxidative rancidity. Another difference was that the mathematical model used by Purwadaria was a linear relationship describing the oxidation rate as a function of water activity.

This computer program (Figure 3.5) is capable of predicting the change in moisture content and hexanal formation in the model system product during storage in a typical package by using equations (3.1) to (3.5). In the initial prediction steps, the computer uses the input characteristics of the sample (m_o, w_s, w_m, and c) and of the package (K, A and x), the condition of the storage environment (a_w^o and P_s) and the desired time increment (dt). The program calculates the water activity of the sample (a_w) from equation (3.4) and the initial moisture content (M_o). The moisture gain (dM) is calculated from equation (3.5) followed by the summation of moisture content of the sample (M_{t+dt}). The loop starts over again at equation (3.4) and repeats the calculations until the desired storage time is reached.

Addition of the kinetic data for oxidative rancidity H_o and f (a_w) as input to the program alongs with equations (3.1), (3.2), (3.3) and (3.5) allow the program to calculate the hexanal concentration as a function of time (H_{t+dt}) as well.

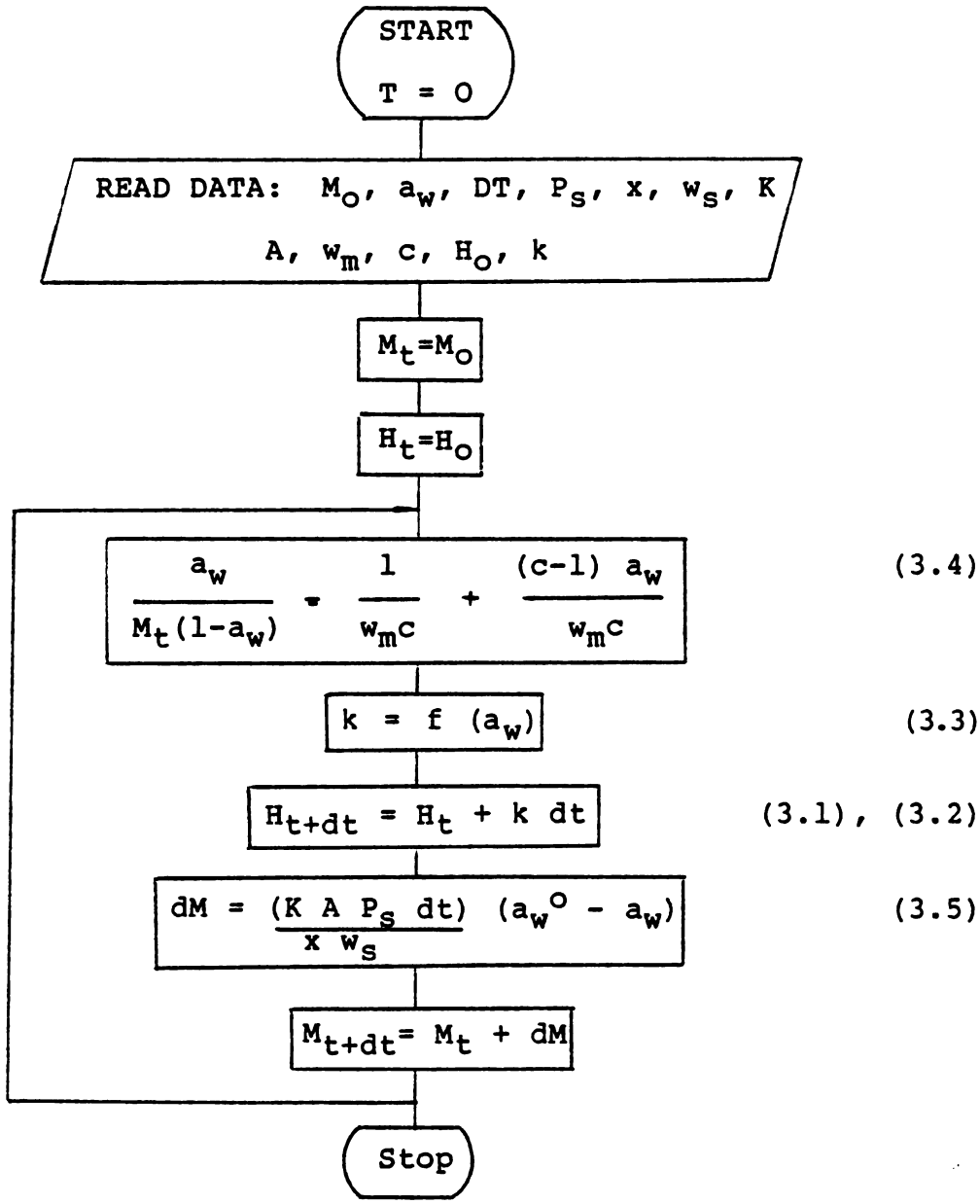


Figure 3.5 The computer simulation flow chart to predict the hexanal concentration and moisture gain during storage at any temperature

IV. EXPERIMENTAL

4.1 Model System and Preparation

A dehydrated model food system was used throughout this investigation. The composition of the model system was similar to a breakfast cereal with supplemental fat added to assure detectable levels of oxidative rancidity. The exact composition of the model system was formulated as illustrated in Table 4.1. The preparation method was similar to Kirk et al. (1976).

The model system was prepared by adding water to the blended, dry ingredient to make a slurry with 55% total solids. The slurry was heated to 60 C before corn oil was added followed by homogenization at 1500 psig in first stage and 500 psig in second stage.

The model system was placed in aluminum trays 1 cm thick and frozen in a -40 C environment for at least one half hour. The aluminum trays containing the frozen model system were placed on the plates in a F.J. Stokes Model 200, 3F-2 Freeze Dryer and drying was accomplished with a platen temperature of 43 C and absolute pressure of 6.667×10^{-7} kPa.

The dried model system (moisture content less than 2g H_2O / 100g solid) was ground and sieved through a screen (mesh number 17) in order to get uniform particle size. The dry product was mixed again for 2 minutes to achieve uniform

Table 4.1 Composition of model food system.

Component	Percent (by weight)
Soy protein[a]	9.36
Corn oil[b]	10.00
Corn starch	69.44
Fructose	4.68
Sucrose	4.68
Salt	1.84

a = Isolated soy protein (87%).
b = no antioxidant added.

distribution of fat.

4.2 Equilibration

After being prepared, the dried sample was equilibrated at different controlled temperatures and relative humidities by two different methods:

4.2.1 Dynamic Equilibration Method

The dynamic equilibration system is illustrated in the schematic diagram in Figure 4.1. The samples were equilibrated in the chamber which was maintained at constant relative humidity (20 to 75% RH) and temperature (21 to 43 C) using an air conditioning unit (Amico Aire Cat. No. 4-5460). The desired temperature and relative humidity were established by controlling water temperature in a bath and monitoring dry bulb temperature.

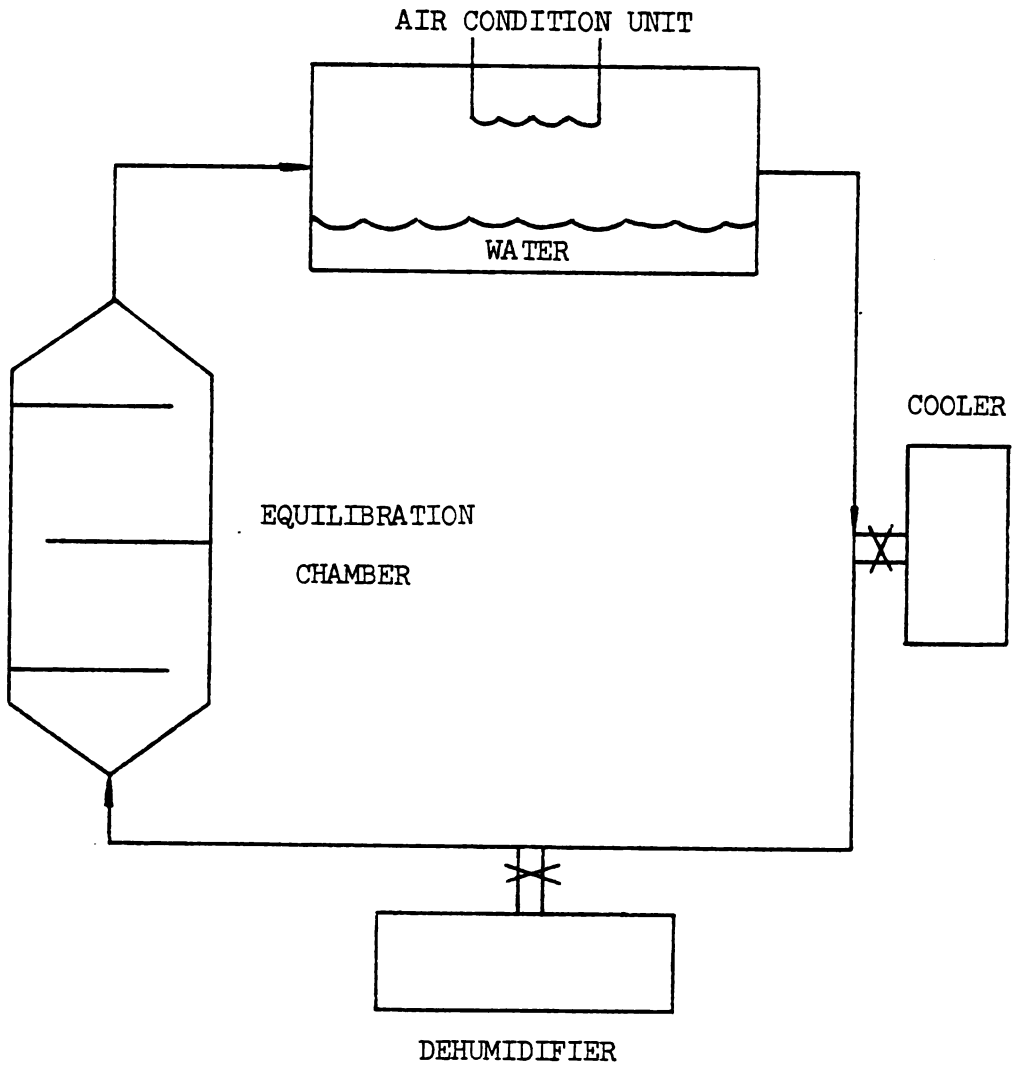


Figure 4.1 Schematic diagram of equilibration system

In order to measure temperature and relative humidity inside the chamber during equilibration, both wet bulb and dry bulb temperature were periodically measured using copper-constantan thermocouples which connected to a Hewlet-Packard 3497 Data Acquisition system and Hewlet Packard 85A minicomputer. A cooler using dry ice was connected to the system to obtain a constant low temperature (10 C) and a dehumidifier was connected to the system to obtain a constant low relative humidity (20% RH). The equilibration time normally required at 6 to 24 hours for adsorption and desorption.

4.2.2 Static Equilibration Method

Very low relative humidity conditions (30%) were achieved with static equilibration. The samples were equilibrated for about 5 days in a closed container containing a saturated $MgCl_2$ solution maintained at relative humidity of 30% RH at 10 C. The container was stored in the room with a controlled constant temperature (10C). The cover of container was plugged with an electric hygrometer sensor (Hygrodynamics Model 15-3001) to measure relative humidity inside the container throughout the equilibration period.

4.3 Measurement of Oxidative Rancidity

Hexanal concentration was used as an indicator of oxidative rancidity in the dry model system. The total hexanal content was determined by head space analysis using

gas chromatography (Hewlett Packard 5840A) as described by Fritsch and Gale (1977) : 10 ft x 1/8 inch glass column with 10% silicone OV-101 on acid washed 60-80 meshs chromosorb W, a column temperature of 100 C, an injection port temperature of 200 C. The procedure was modified by changing the detector block temperature to 350 C, the helium flow rate to 30 ml/min, the detector air flow to 300 ml/min and the hydrogen flow to 30 ml/min.

Fifteen grams of a well mixed sample was placed in a 250 ml flask and then 2 ml of 4 heptanone (25 ppm solution) was added as the internal standard. Twenty five ml of cold distilled water was added to make the well mixed slurry and boiled distilled water was added up to the 150 ml mark. The flask was immediately capped with four layers of aluminum foil. The slurry was swirled for about 45 sec and 5 ml of head space gas was injected into the gas chromatograph.

The hexanal content in the sample was expressed as the peak area ratio of hexanal to the internal standard heptanone from gas chromatographic response. The response was converted to hexanal content as ppm Hexanal on a dry basis (µg Hexanal/g dry sample) by using the calibration curve.

The calibration curve was determined by plotting a curve showing the relationship between the peak area ratio of a known amount of hexanal versus the internal standard heptanone.

4.4 Moisture Content Determination

The moisture content was determined by modified vacuum oven method as described by AACC Method 44-40 (1961). Two grams of sample were placed in an aluminum dish and covered with perforated aluminum foil to allow moisture to escape. The sample was weighed, dried at 98 to 100 C for about 5 hours in partial vacuum having a pressure equivalent to 3.33 kPa or less. After cooling in a desiccator, the sample was weighed soon after adjusting to room temperature.

The moisture contents of the sample during storage time were obtained by measuring the weight change of the sample compared to the initial weight of the sample. By knowing the moisture content at the initial weight of the sample (using AACC Method 44-40 as previously discussed in this section), the moisture contents during storage time could be calculated. The weight change of the sample was measured by using an electric over head weighing machine (Mettler P1920).

4.5 Measurement of the Lipid Oxidation Rate as a Function of Water Activity and Temperature

The model system was dried to a moisture content less than 2% in a vacuum oven at a temperature of 30 C with vacuum pressure maintained equivalent to 3.73 kPa or less for at least one hour. This approach provided assurance that sufficiently low water activity was established in the model system. The model food system was placed in aluminum trays and equilibrated in a chamber (Section 4.2.1) at

different relative humidities (23,30,45,60 and 75% RH) at 32 C, and at different temperatures (10,21,32 and 43 C) at a relative humidity of 30% RH.

The equilibrated sample at a relative humidity of 30% RH and 10 C was achieved by equilibrating the sample over a salt solution (Section 4.2.2). When the sample reached a constant weight, sixty grams of the sample were placed into 303 x 406 cans and the cans were immediately sealed. The cans containing the equilibrated samples with water activities of 0.23, 0.30, 0.45, 0.60 and 0.75 were stored in a room with a controlled temperature of 32 C. The cans containing the equilibrated sample with water activity of 0.3 were stored in rooms with controlled constant temperatures of 10, 21, 32 and 43 C.

One can from each room was sampled and the oxidative rancidity was analyzed as hexanal concentration at each specific period of time until the experiment was completed.

The rate constant for hexanal formation was obtained by plotting hexanal content versus time at each condition. The relationship between the rate constant and temperature was obtained by plotting the rate constant versus inverse absolute temperature with the water activity of storage held constant. The relationship between the rate constant and water activity was obtained by plotting the rate constant versus water activity with the temperature of storage held constant.

4.6 Measurement of Sorption Isotherm

Two gram of a well mixed model system was placed in a covered aluminum dish and was dried in vacuum oven having a pressure equivalent to 3.33 kPa or less for one hour at a temperature of 30 C to ensure that adsorption would occur during equilibration. The sample in the covered dish was weighed, and equilibrated to relative humidities of 10, 20, 30, 40, 60 and 75% RH at a temperature of 32 C. After 6 to 24 hours, the sample reached a constant weight and the total weight was recorded and moisture content on a dry weight basis was determined.

The adsorption isotherm was obtained by plotting moisture content of the model system versus relative humidity or water activity at 32 C. In the same manner, the desorption isotherm was achieved but instead of predrying the sample in a vacuum oven, a two gram sample in an aluminum dish was put in a room at 90% RH for about one hour before it was weighed and equilibrated in the equilibration chamber for about 6 to 24 hrs. This was done in order to ensure moisture desorption during equilibration.

The monomolecular layer moisture content (w_m) and the energy constant (c) of the BET equation for either sorption and desorption isotherm was determined by plotting $a_w/M(1-a_w)$ vs a_w. Similarly, the adsorption and desorption isotherm and BET constants were determined at a temperature of 21 C.

4.7 Measurement of the Moisture Transfer Coefficient

The rate of water vapor transmission through the package film was determined by the standard method for water vapor transmission of materials in sheet form (ASTM, E 96 1966). Thirty grams of activated anhydrous calcium sulfate were placed in polystyrene film square pouches (total surface area 0.0966 m^2 and thickness 0.0000559 m) to maintain 0% RH inside package. The packages were stored and weighed daily for seven days in the rooms controlled at 30% RH and temperatures of 10, 21, 32 and 43 C. The water vapor transmission was determined from the weight changes of the packages at each temperature.

4.8 Model Verification Experiments

Polystyrene film with thickness 0.0000559 m with 0.21 m width and 0.23 m length was used as a package material. Sixty grams of the model food system with moisture content about 8% were placed into the tared packages, which were sealed immediately in order to prevent moisture migration between the model and the atmosphere. Each of the nine packages containing the sample were stored in rooms at different temperatures (10, 21, 32 and 43 C) at 30% RH, and at different relative humidities (30, 45, 75 and 90% RH) at 20 C.

One of the packages from each room was sampled every two weeks during the first two months and once each month for the following 4 months. Total weight and moisture

content were recorded and the oxidative rancidity in terms of hexanal content was analysed and recorded.

V. RESULTS AND DISCUSSION

5.1 Measurement of Moisture Transfer Coefficient

The moisture transfer coefficient (K) for the experimental package film was measured at a constant relative humidity of 30% and at temperatures of 10, 21, 32 and 43C. The results are presented in Table 5.1. These results indicate that temperature does not have a significant influence on the moisture transfer coefficient (K) of the packaging film. The average of all K values presented in Table 5.1 is 7.825×10^{-15} kg m/m^2 s Pa with the standard deviation of 0.897×10^{-15}. The K values are close to the coefficient (15.6×10^{-15} kg m/m^2 s Pa) presented by Karel (1975) for the same kind of packaging material (polystyrene). The difference in K values might be attributed to a different density and/or orientation of polymer chain of materials which allow the different rate of moisture transfer.

5.2 Sorption Isotherms

The sorption isotherms obtained by measuring the moisture content at various water activities at two temperatures (21 and 32C) are illustrated in Figure 5.1. In Figure 5.2, the adsorption isotherm of this study is compared to the whole corn flour [Kurmar (1924)], and Purwadaria (1977)

Table 5.1 Moisture transfer coefficient (K) for polystyrene package film at constant relative humidity 36%.

Temperature (C)	$Kx10^{15}$ (k_g H_2O . $m/m^2.s.Pa$)
11	8.788
21	6.781
33	8.309
41	7.423

model system isotherms. The isotherms obtained in this investigation and those obtained by Purwadaria's (1977) are for model systems of similar composition; except for fat content. The sorption isotherms obtained in this investigation were more similar to Purwadaria's isotherms than whole corn flour. The small differences between the isotherms measured in this investigation as compared to those measured by Purwadaria (1977) could be attributed to the different temperatures of these studies and the types of components used for these model systems.

The sorption isotherm data measured in this study were analyzed using the BET equation as a model. The BET parameters were evaluated based on least-squares analysis as provided by STANDARD PAC Software on a HP85 minicomputer. For instance the adsorption isotherm data at 32 C was described by a regression line (Figure 5.3) between water activity of 0.5, with BET constants (w_m and c) of 5.26 and

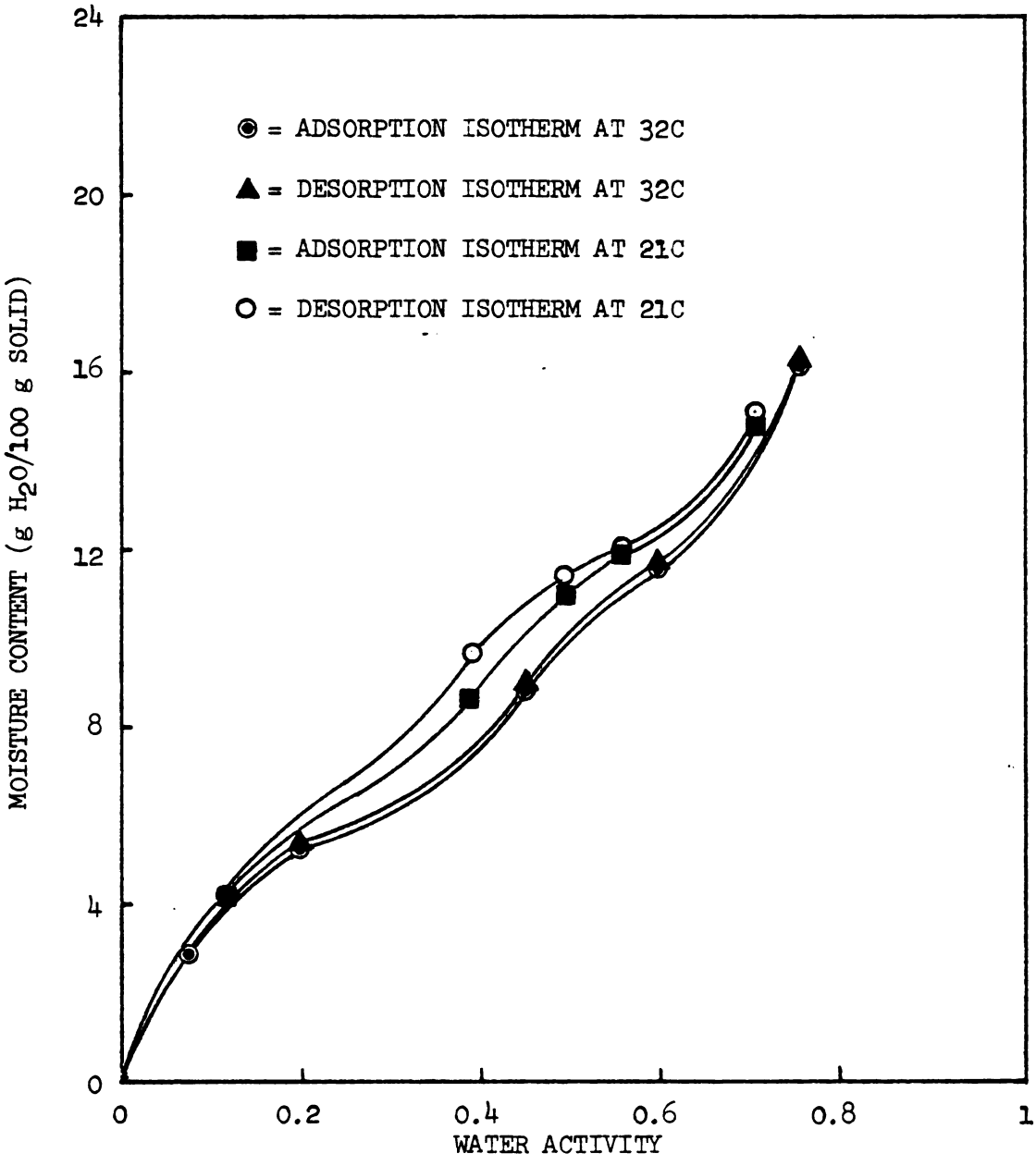


Figure 5.1 Sorption isotherm for the model system at 21 C and 32 C with moisture content based on total solid.

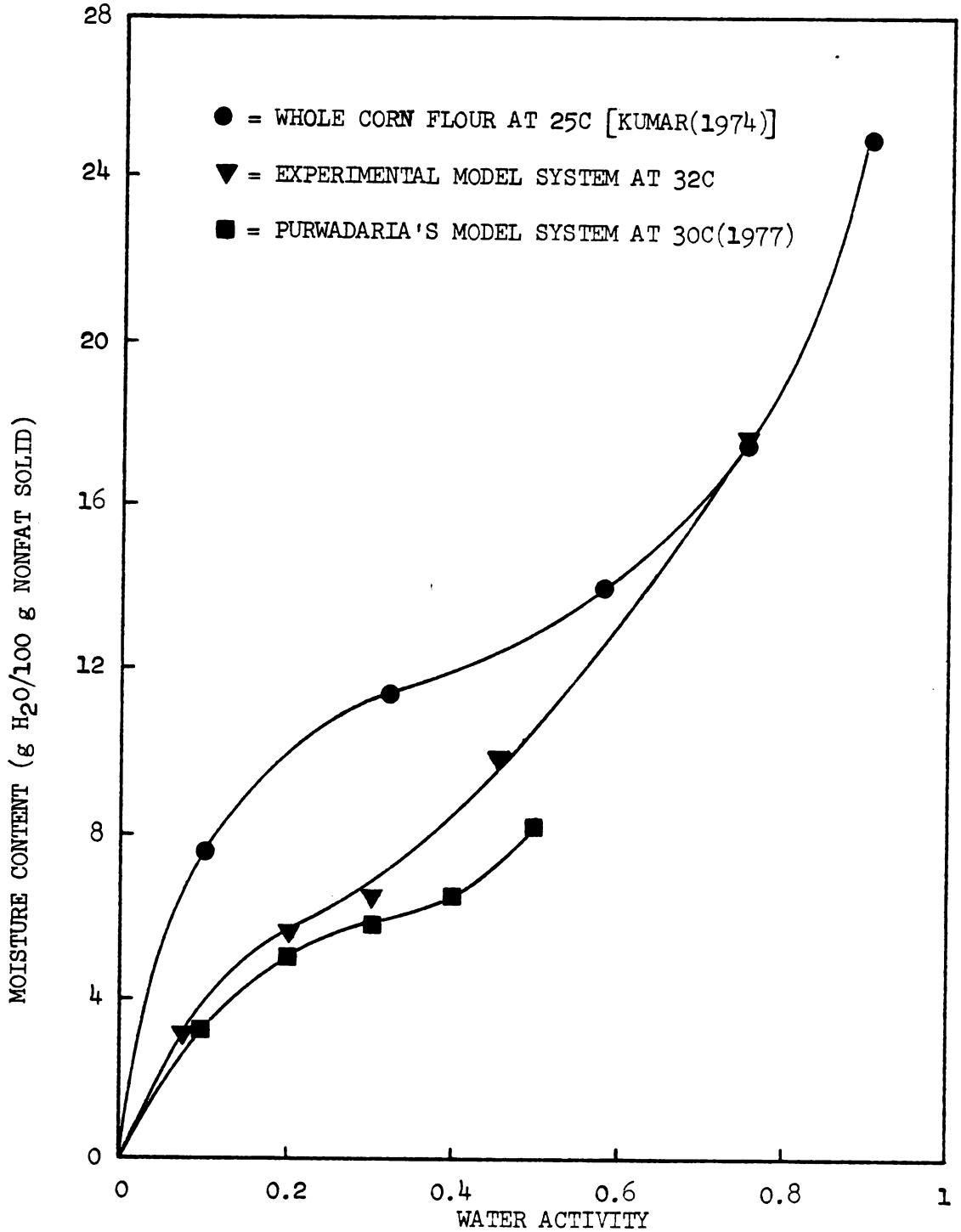


Figure 5.2 Sorption isotherm of the model system compared to other systems.

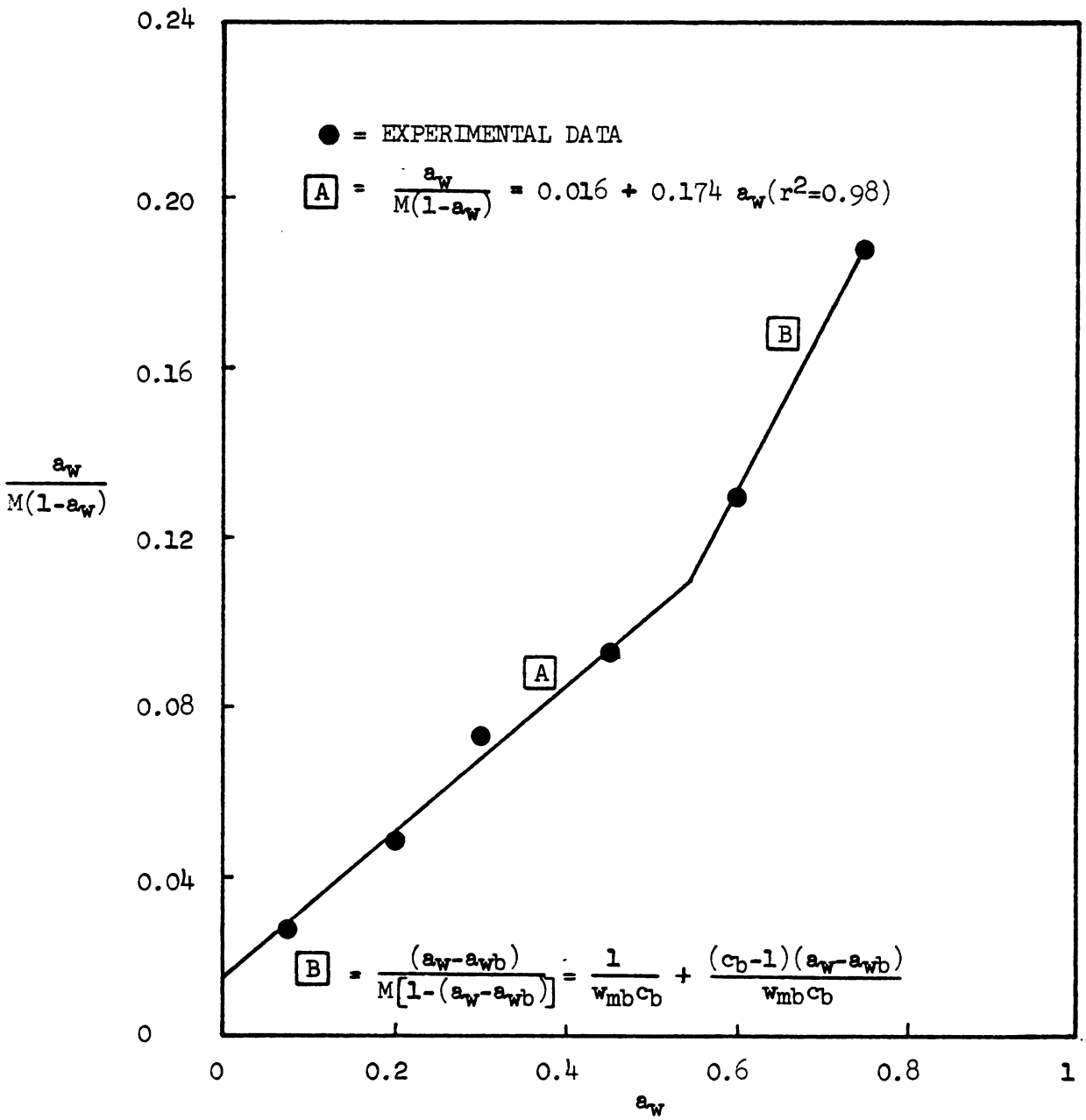


Figure 5.3 BET model and modified sorption model for adsorption isotherm data at 32C

11.88, respectively.

All the results of BET constants for all adsorption and desorption isotherms at 21 and 32C are shown in Table 5.2. These BET constants are similar to those obtained by Purwadaria (1977) and Salwin (1959). The BET energy constant (c) was found to range from 8.90 to 17.90 (21 to 32C) in this study, while Purwadaria (1977) found a range from 12.5 to 17.5 (20 to 30C). The BET monomolecular layer constant (w_m) was found to range from 5.62 to 5.26 (21 to 32C). Purwadaria (1977) found that the constant ranged from 4.9 to 4.2 (20 to 30C). Salwin (1959) found w_m values of 5.87 in instant macraroni, 5.68 in instant starch, 5.46 in potato disc and 6.14 in ground beef.

In order to predict moisture content at water activities over 0.5, a modified mathematical sorption model, similar to the BET model was established. This modified sorption equation can be described as follows:

$$\frac{(a_w - a_{wb})}{M[1-(a_w-a_{wb})]} = \frac{1}{w_{mb}c_b} + \frac{(c_b - 1)\ (a_w-a_{wb})}{w_{mb}c_b} \qquad (5.1)$$

The sorption isotherm data above water activities of 0.5 were used to evaluate the modified parameters by the same method as BET parameter determination. All the modified sorption parameters are shown also in Table 5.2. The results illustrated in Table 5.2 show an intersection between the BET equation and the modified sorption equation) in the water activity range between 0.49 to 0.55 (for all

Table 5.2 BET constants (w_m and c) and intersection water activity (a_{wb}) for adsorption and desorption at 21C and 32C.

	Temperature			
	21C		32C	
	Adsorption	Desorption	Adsorption	Desorption
a_{wb}	0.486	0.523	0.551	0.546
when $a_w \leq a_{wb}$	c = 17.90 w_m = 5.59 (r^2 = 0.95)	c = 12.62 w_m = 6.10 (r^2 = 0.96)	c = 11.88 w_m = 5.26 (r^2 = 0.98)	c = 8.90 w_m = 5.62 (r^2 = 0.93)
when $a_w > a_{wb}$	c_b = 4.33 w_{mb} = 2.51	c_b = 5.03 w_m = 2.16	c_b = 4.40 w_{mb} = 2.04	c_b = 4.64 w_{mb} = 2.03

adsorption and desorption isotherms at both 21 and 32C). This limit of the BET model at water activities below 0.5 agrees with results discussed by Labuza (1968) as previously presented in Section 3.5.

5.3 The Order of Rate Constant

All the kinetic data and rates of oxidation obtained from different constant environments are shown in Tables A.1 to A.9 The experimental data indicate that hexanal concentration in the sample increases with the storage time and the rate of hexanal formation varies depending on the temperature and relative humidity of the sample during storage

as will be described later. Kinetic data from different constant environments using zero order and first order relationships, indicates that the zero order relationship provides the best description based on the magnitude of the correlation coefficient (r^2). This is shown in Figure 5.4 where both the zero order and first order regression line were plotted for samples stored at 32 C with a water activity of 0.60. The correlation coefficient r^2 of the zero order was 0.96 for the sample stored at 32 C and water activity of 0.60 is better than r^2 at 0.791 for first order relationship. Consequently, a zero order relationship was chosen to be applicable for the analysis of results in this study.

The zero order relationship between hexanal concentration and time found in this study supports the results by Quast et al (1972), and Labuza and Bergquist (1983) who used zero order to describe the formation of peroxide in potato chips. On the other hand, the composition of the model system in this study is similar to breakfast cereals as used by Fritsch and Gale (1977) and first order kinetics were utilized. This difference might be attributed to the higher fat content used in this investigation (10%) and the potential of containing different unsaturated fatty acids in the model system as compared to breakfast cereal [Labuza (1971)].

The results of kinetic analysis at 10 C and water activity of 0.32 do not indicate any significant changes in

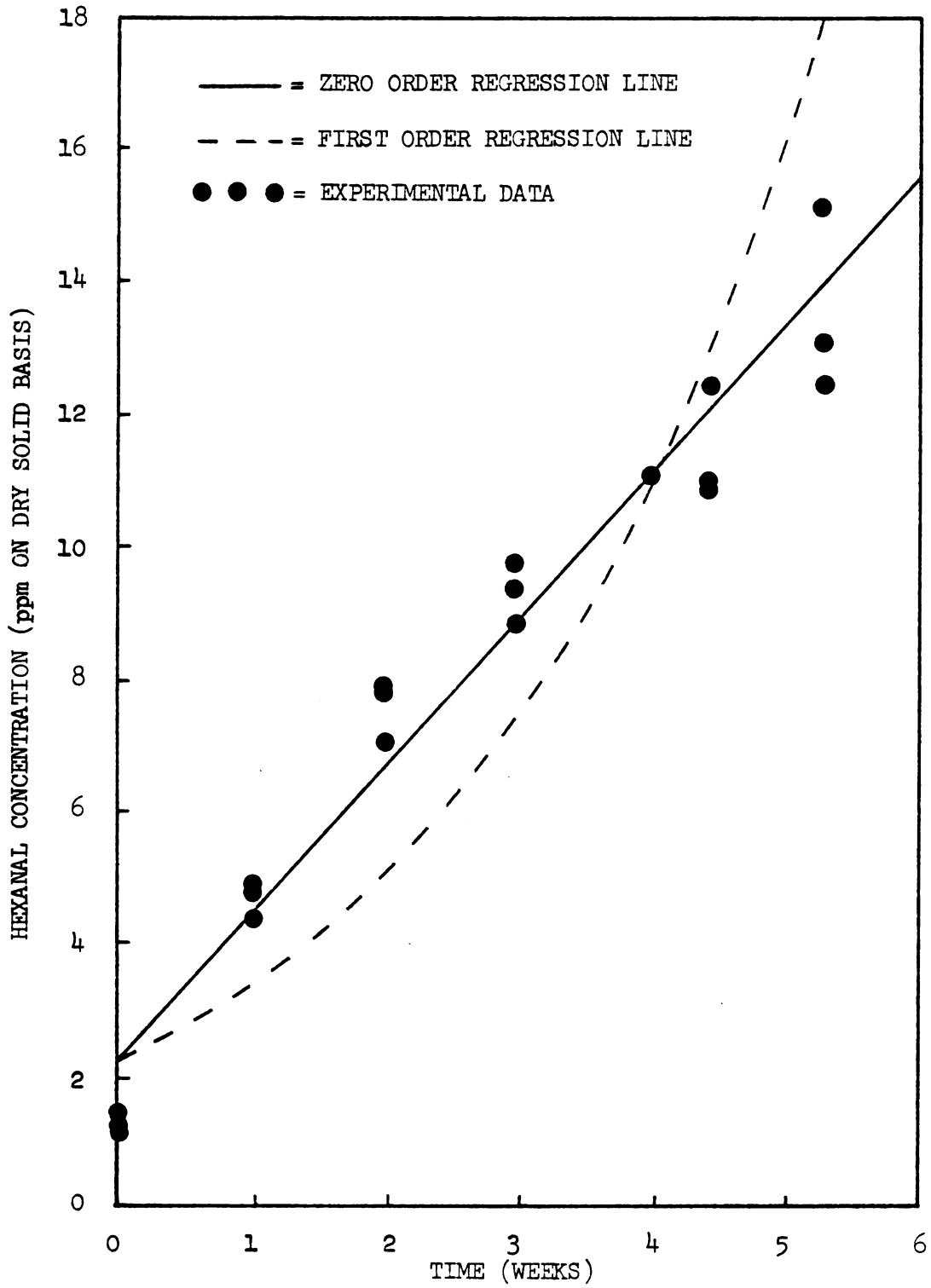


Figure 5.4 Regression lines of zero order and first order expressions to describe experimental data for the samples stored at 32 C and water activity of 0.6.

hexanal concentration. It seems that the hexanal formation under these conditions is too low to be detected accurately.

The results in table 5.3 contain all oxidation rate constants at different environments. The zero order rate constants and the kinetic data at different constant environmental conditions are shown in Tables A.1 to A.9. The results in Table 5.3 were used to analyse the influence of water activity and temperature on the rate constants in Section 5.4 and 5.5.

The rate constants for lipid oxidation were determined by analysis of hexanal concentration in the model system by using a least-square analysis with an HP85 and its STANDARD PAC Software. These kinetic data were obtained from the samples stored at different constant water activities and temperatures which are shown in Tables A.1 to A.9.

5.4 Effect of Water Activity on the Oxidation Rate

The influence of water activity (a_w) on the rate constant (k) for lipid oxidation is illustrated in Figure 5.5. These results show that the rate constants increase exponentially with water activity. The data were described by an exponential relationship using a least-squares analysis from a minicomputer HP85 and a statistical STANDARD PAC. The following relationships were obtained:

$k = 0.165 \exp (4.229\ a_w)$ at 32C, $r^2 = 0.98$

$k = 0.031 \exp (4.228\ a_w)$ at 21C, $r^2 = 0.98$

$k = 0.06 \exp (4.233\ a_w)$ at 10C, $r^2 = 0.98$

Table 5.3 Zero rate constant at various constant temperature and water activity

Temperature (C)	Water Activity	Rate Constant (1/week)	Correlation Coefficient
10	0.32	0.0004	0
21	0.32	0.214	0.880
32	0.32	0.682	0.798
43	0.32	3.301	0.882
32	0.07	0.185	0.977
32	0.20	0.443	0.899
32	0.32	0.682	0.798
32	0.45	0.796	0.811
32	0.60	2.221	0.961
32	0.75	4.275	0.810

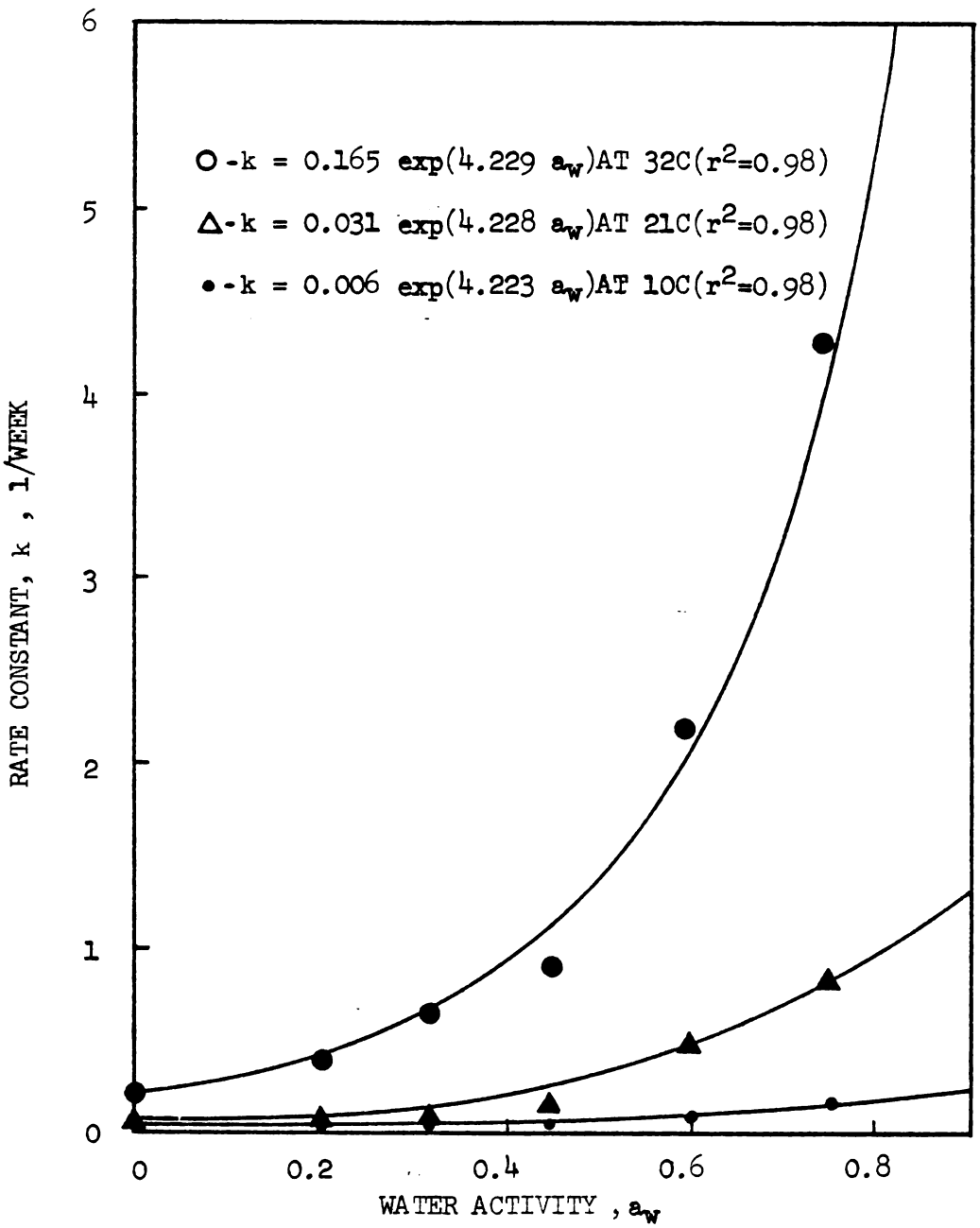


Figure 5.5 Influence of water activity on rate constants at 10, 21 and 32 C.

The results indicate that the rate constants increase for the entire range of water activity from 0 to 0.75. The results depicting the lowest rate constant at the lowest water activity is different from the results of Martin (1958), Salwin (1959), Maloney (1966), and Labuza et al (1969). However, the results of the current investigation are in agreement with results by To (1978), Gejl-Hansen (1977), Heidelbaugh and Karel (1970) and Sinha (1977) in dry model systems and dry food systems.

The observed relationship of oxidation rate at low water activity may be explained by one or more of the following:

1. The sample in this study contains protein which can be considered as a emulsifying agent. This emulsifier forms a matrix of lipid and protein in which the matrix entraps oxidizing lipids and resists oxidation [To (1978), Gejl-Hansen (1977)]. This matrix was found to be stable in the dry state, thus oxidation rate is low in dry state.

2. The proteins and reducing sugars in the model system of this study may be water binding agents. Water binding agents decrease the optimum water activity at which the oxidation rate is minimum from above or at the monolayer of water activity to near zero [Heidelbaugh and Karel (1970)]. Hence, the oxidation rate would decrease at low water activities.

3. The model system in this study contains soy protein and 10% corn oil, the same components as in the system by

Sinha (1977). This investigator found the lowest oxidation rate at this level of oil content when compared to different levels of oil content used. Sinha (1977) and other investigators [Honn et al (1951), and Togashi (1961)], found that an increase of lipid content decreased the rate of lipid oxidation due to a lower ratio of surface area to volume of lipid. Sinha (1977) attributed the high lipid content effect to viscous drag on neighboring lipid molecules and reduction of the flow of oxygen through the molecules, thus decreasing the oxidation rate.

All of the phenomena discussed can result in decreased rate of lipid oxidation in the studied model system. The effect of high lipid content [Sinha (1977)] seems to be potentially the most important effect on the rate of oxidation because of the similar components and similar amounts of lipid in the system used as compared to this investigation. This effect of high lipid content can be investigated by conducting a similar experiment using different amounts of lipids in the model food system under various constant water activities during storage. The model system should contain no protein in order to eliminate the interference of lipid-protein interaction.

At higher water activity, the results show increasing oxidation rate. This increase might be attributed to the enhancement of the mobilizing water which several researches found in various dry foods and model systems [Labuza et al (1969), and Heidelbaugh and Karel (1970)]. This

enhancement of water effect is due to the swelling of the polymeric matrix making more catalytic sites available for reaction [Chou et al (1972)] and the increased mobilization of reactant and catalyst [Heidelbaugh and Karel (1970)].

In addition, the stable matrix of lipid-protein in emulsion in the dry state was found to break-down with increasing water activity and cause release of oxidizing lipid exposing it to oxygen [To (1978) and Gejl-Hansen (1977)]. Consequently, the oxidation rate increased as well.

5.5 Effect of Temperature on the Oxidation Rate

Based on the data presented in Table 5.3, the relationship between rate constants and temperature was described by the Arrhenius equation as shown in Figure 5.6. The Arrhenius constant or reference rate constants (k_o) and activation energy (E) are as follows:

$$k_o = 1.211 \times 10^{19} \text{ /week}$$

$$E = 112.32 \text{ kJ/mole}$$

The activation energy obtained to describe the influence of temperature on hexanal formation is in agreement to those reported by Labuza (1971), Fritsch and Gale (1977) and Labuza and Bergquist (1983). The activation energy of 112.32 kJ/mole in this study is higher than the 60.86 and 81.84 reported by Fritsch and Gale (1977) for wheat and corn cereal flakes, respectively (based on hexanal formation). Labuza and Bergquist (1983) reported values of 84 to 92

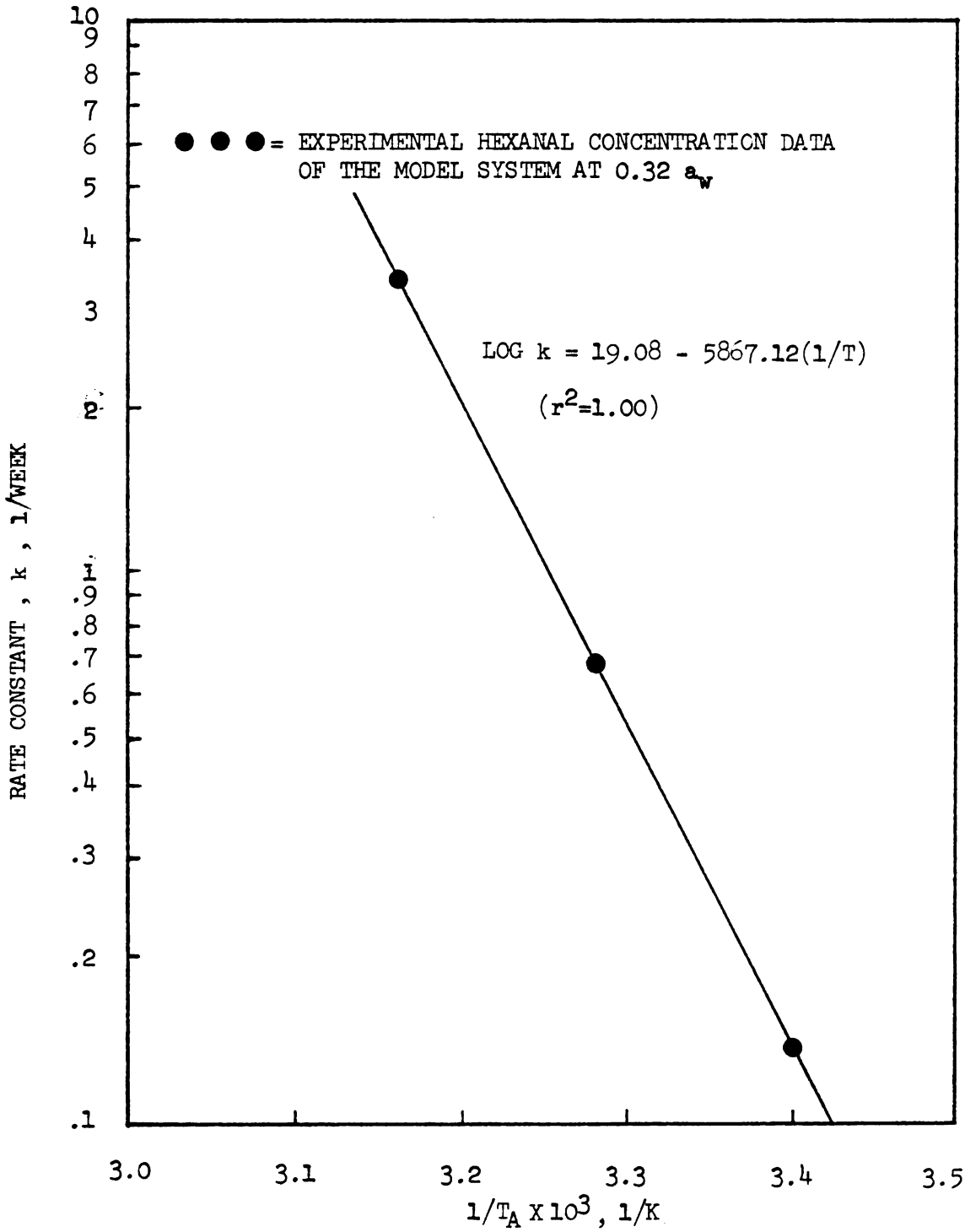


Figure 5.6 Arrhenius equation of zero order reaction describing the influence of temperature on the rate constant of hexanal formation.

kJ/mole for food systems with added antioxidants and 87.3 kJ/mole in potato chips (based on peroxide value) while Labuza (1971) suggested activation energy constants of 42 to 101 kJ/mole for lipid oxidation of food systems, in general.

Based on the same index of oxidative rancidity (hexanal formation), the activation energy constant obtained in this investigation is about double the value reported by Fritsch and Gale (1977). This difference of the activation energy constant is probably attributed to the higher lipid content in the model systems for this investigation.

5.6 The Verification of Computer Prediction for Moisture Content.

The results from the computer prediction, based on the computer flow chart shown in Figure A.1, and the experimental data for the moisture change in the sample during storage can be discussed in two parts, adsorption and desorption with results shown in Figure 5.7 and 5.8, respectively. At conditions of 21 C and 57%RH, 21 C and 76%RH and 21 C and 78%RH, the predicted adsorption of moisture in the model food system occurs because the initial water activities of the samples (0.46; 0.34 and 0.63) are lower than the storage water activities (0.57, 0.76, and 0.78, respectively). On the other hand, at 21 C and 34%RH, and 32 C and 44%RH, the predicted desorption of moisture in the sample occurs because the initial water activity of the samples (0.36 and 0.45) are higher than the storage water

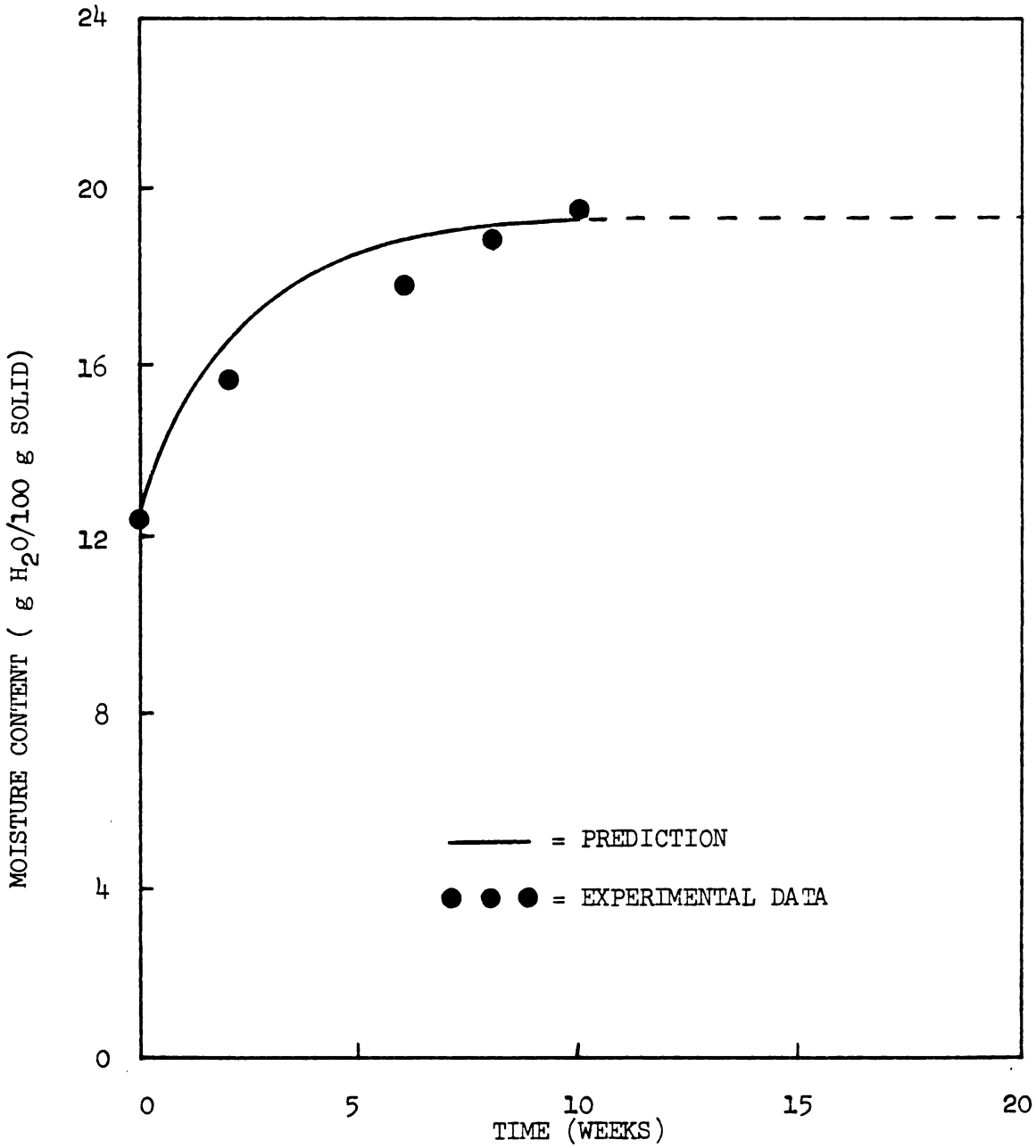


Figure 5.7 Comparison of computer prediction and experimental data for product moisture content during storage at 21 C and 78%RH.

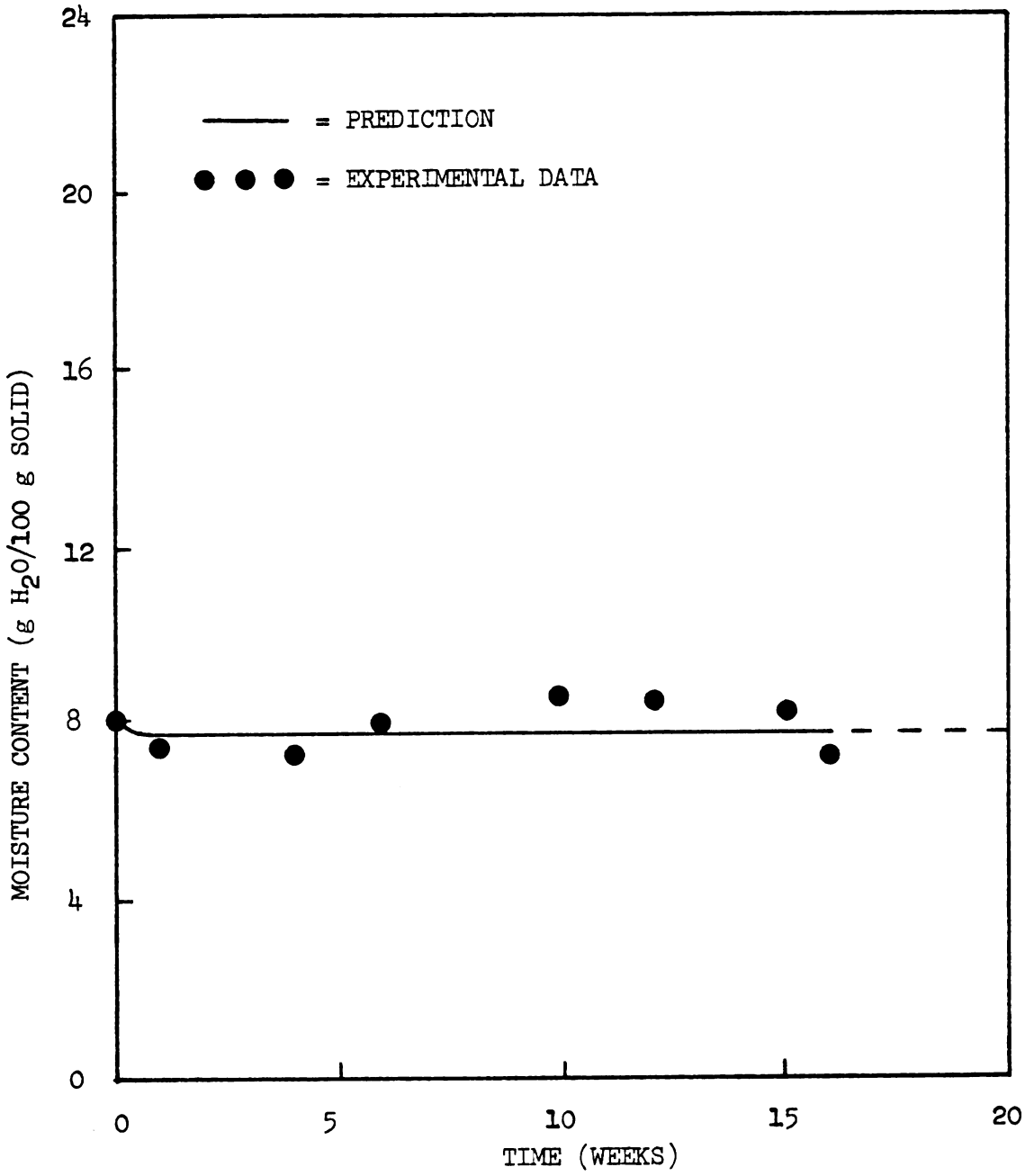


Figure 5.8 Comparison of computer prediction and experimental data for product moisture content during storage at 32 C and 44%RH.

activity (0.34 and 0.44, respectively).

The computer predictions for the sample moisture content are in reasonable agreement with experimental data in all storage conditions with standard deviations between the predicted moisture content and experimental data (s_1) of 0.359, 0.213, 0.808, 0.590, 0.396 and 0.306 at 11 C and 35%RH, 21 C and 34%RH, 21 C and 57%RH, 21 C and 75%RH, 21 C and 48%RH, 32 C and 49%RH, respectively.

The deviations between the predicted and experimental data might be attributed to the variation of moisture content as shown by the data. The variation of the experimental moisture content in the samples may be due to the air circulation in the experimental room which affected the reading of weight change of the samples while using the over head scales, as described previously in Section 4.4.

5.7 Verification of Computer Prediction for Hexanal Concentration

The computer prediction as shown in Figure A.1 for hexanal concentration of the sample was obtained by using the kinetic data of hexanal formation in the samples held at constant temperature and relative humidity during storage. The experimental hexanal concentration was obtained from the hexanal formation in the sample stored inside the packaging material at different temperatures and relative humidities.

The predicted hexanal concentrations are compared to the experimental hexanal concentrations in different storage

environments (11 C and 35%RH, 21 C and 34%RH, 21 C and 57%RH, 32 C and 44%RH, 21 C and 76%RH and 21 C and 78%RH). Experimental results and computer prediction are plotted in Figure 5.9 for the storage condition of 11 C and 35%RH. Agreement between experimental results and computer prediction is the same for the three storage conditions (11 C and 35%RH, 21 C and 34%RH and 21 C and 57%RH) with unbiased estimate of standard deviation between prediction and experiment of 0.065, 0.176 and 0.427, respectively. The variation in experimental hexanal concentration in these storage conditions could be attributed to the variations in relative humidity of the storage environment and to the technique for hexanal analysis. Based on the standard deviations of relative humidities obtained from different temperature as shown in Table A.10, the standard deviation between predicted and experimental hexanal concentration was found to increase with increasing standard deviations of relative humidity in the storage room with a correlation coefficient of 0.76 as shown in Figure 5.11

At a storage condition of 32 C and 44%RH, as shown in Figure 5.10 the predicted values were higher than the experimental data over the entire range of storages time with a standard deviation between prediction and experiment of 2.72.

In addition, the over estimation of hexanal concentration at 32 C and 44%RH might be attributed to the hexanal loss through the film at high concentrations of hexanal

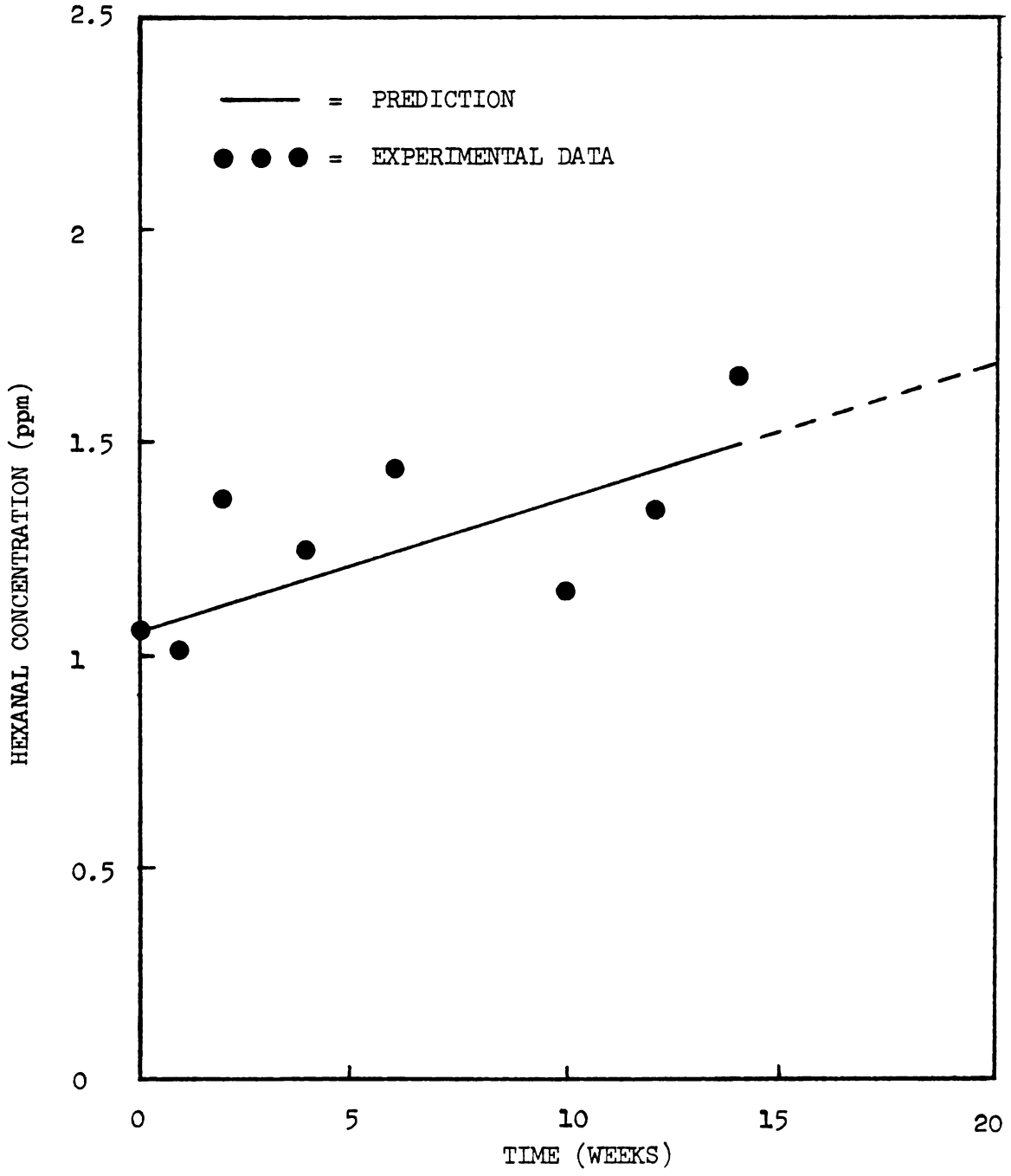


Figure 5.9 Comparison of computer prediction and experimental data for hexanal concentration in the model system during storage at 11 C and 35%RH.

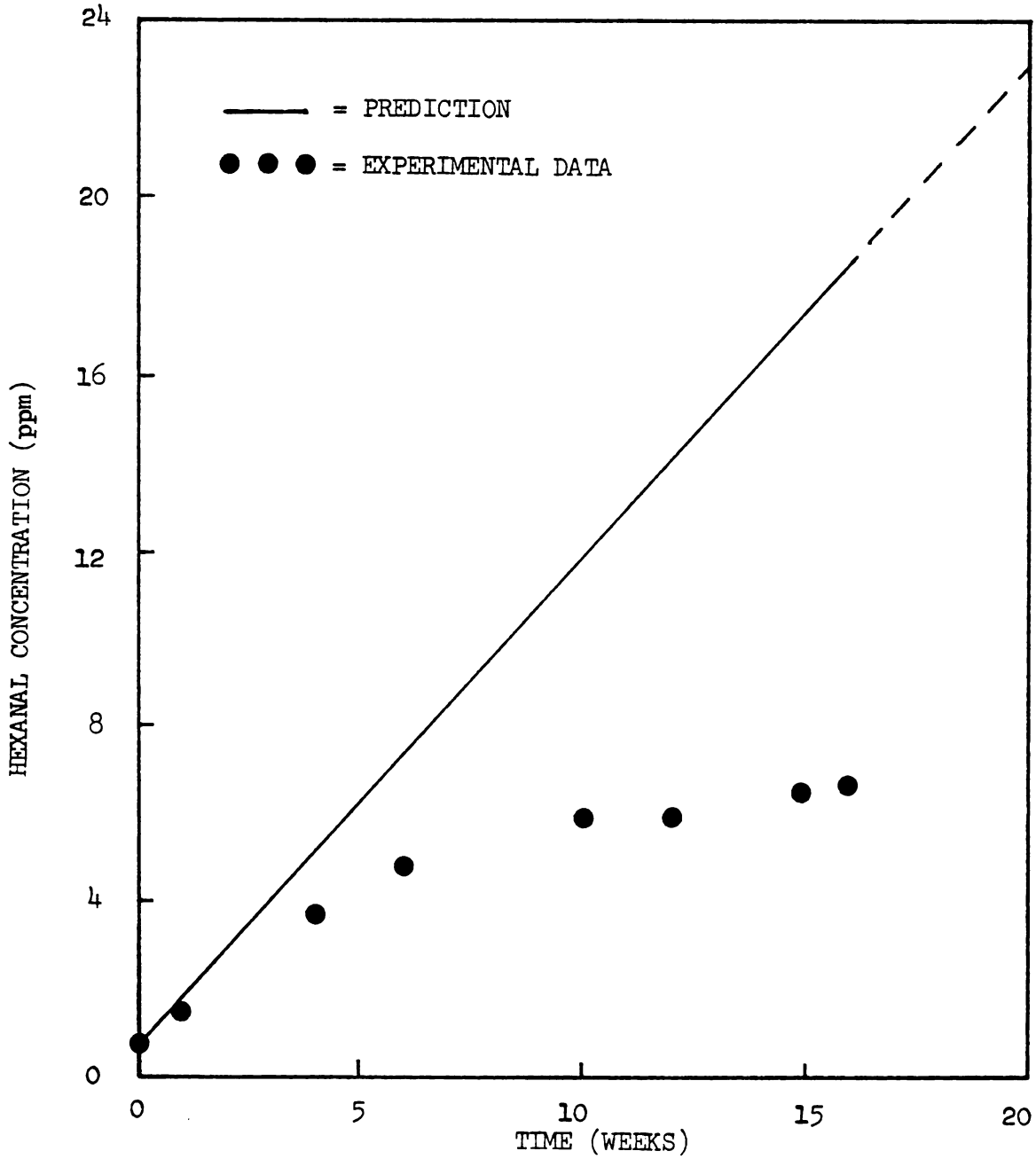


Figure 5.10 Comparison of computer prediction and experimental data for hexanal concentration in the model system during storage at 32 C and 44%RH.

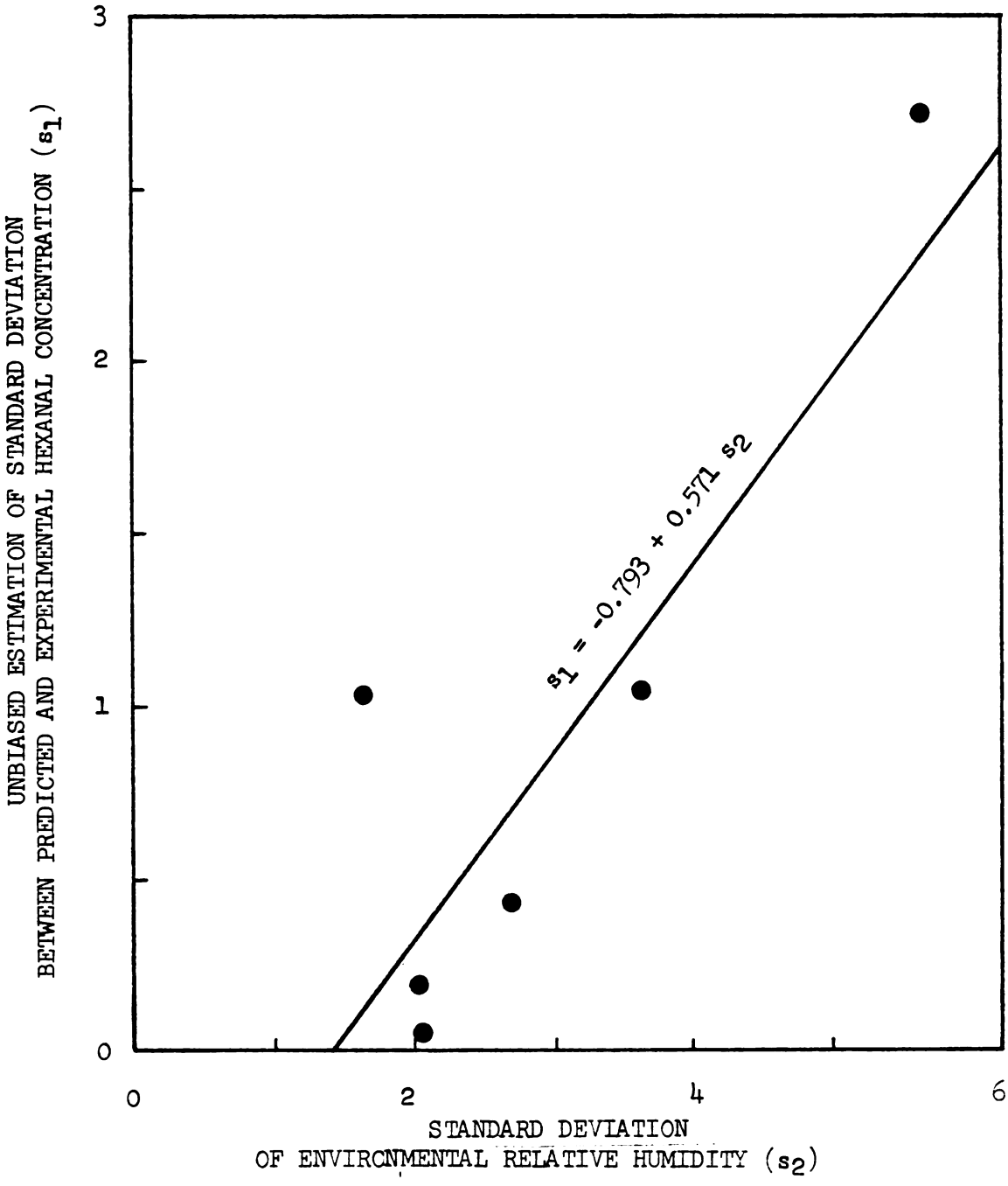


Figure 5.11 Correlation between unbiased estimation of standard deviation between prediction of hexanal concentration and experimental data (s_1) and standard deviation of relative humidity environmental storage (s_2).

inside the package. To date, the rate of hexanal penetration through polystyrene film such as those utilized in this study has not been measured. The hexanal concentration measured in this study (using hot water to liberate hexanal from the sample) is not true hexanal concentration in the headspace within the package. If the correlation between the concentration of hexanal in the headspace within the package (at normal conditions) and the hexanal concentration measured by analytical technique in this study is known, and the rate of hexanal diffusion though the film is known, the computer model can be modified to predict accurate hexanal concentration in the sample during storage.

At high relative humidity storage (21 C and 76%RH and 21 C and 78%RH) (Figure 5.12), the prediction of hexanal concentration concurred with the experimental results during the first 10 weeks at 21 C and 76%RH and during the first 6 weeks in 21 C and 78%RH with standard deviations of 1.026 and 1.031, respectively. After these storage periods, the hexanal concentration dropped rapidly with the decrease apparently related to the increase in moisture content of the sample up to about 18% or a water activity of 0.8. At a water activity level of 0.8, moisture is in the capillary condensation range within the product and accelerates several modes of reactions (Figure 3.4).

The decrease in hexanal concentration might be attributed to the interaction between protein and oxidizing lipids contained in this model system as previously

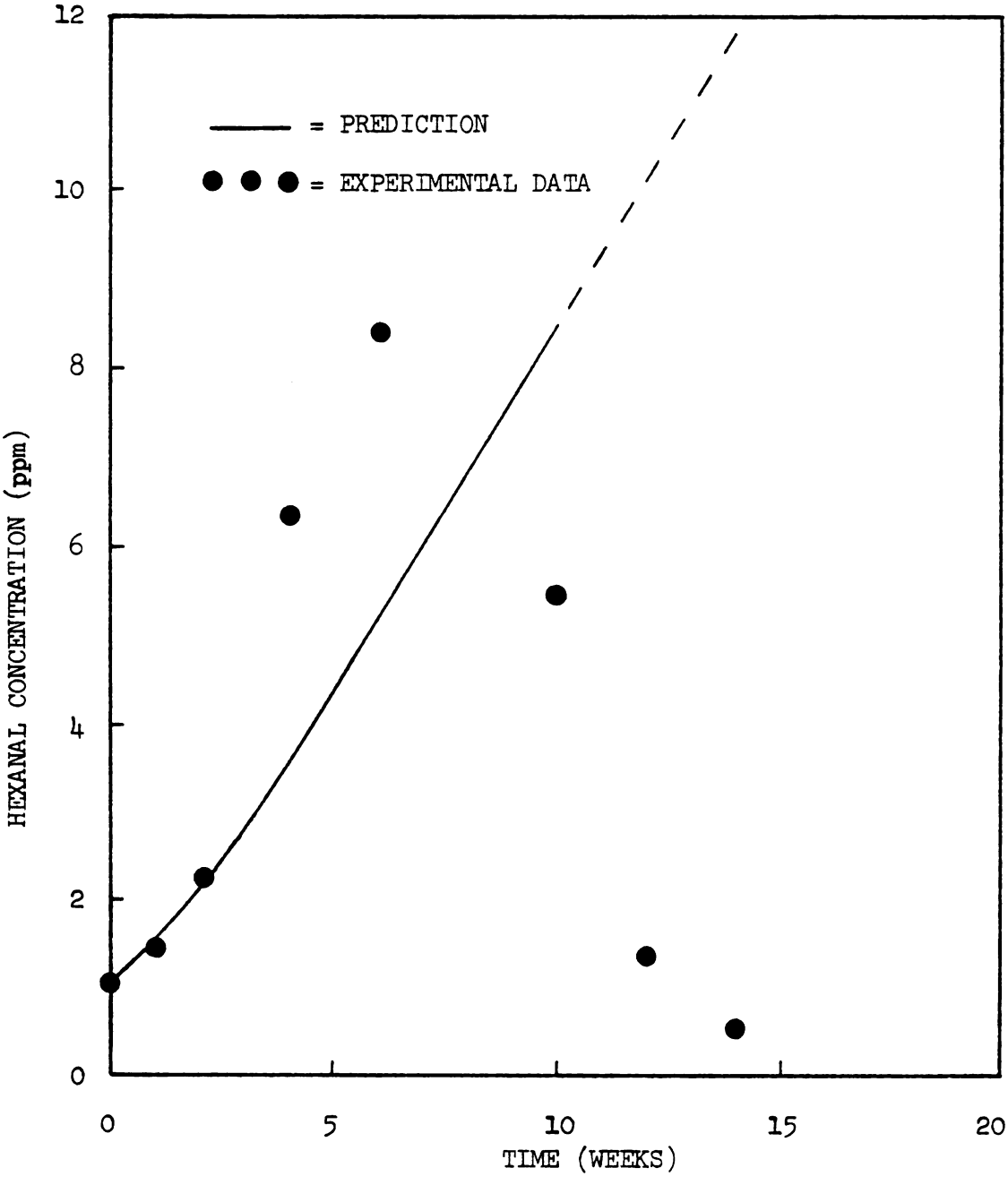


Figure 5.12 Comparison of computer prediction and experimental data for hexanal concentration in the model system during storage at 21 C and 76%RH.

discussed in Section 2.3. As described in Figure 3.3, protein can reduce the rate of lipid oxidation by interacting with free radicals, hydroperoxides and break-down products including hexanal. One of the most common interactions that occurs is non-enzymatic browning which generally has the maximum rate at water activities of about 0.6 to 0.8 [Karel and Yong (1981)] which is close to the point that hexanal concentration start to decrease.

On the other hand, non-enzymatic intermediates which occur are capable of inhibiting lipid oxidation [Eichner (1974)]. The reaction similar to aldehyde - amine condensation, which Montgomery and Day (1965) found to reduce the carbonyl content in heptanal - L - tyrosine ethyl ester solution, might also occur and decrease the hexanal concentration in the sample. This decrease in hexanal concentration might also involve a dilution effect. Labuza (1973) observed a decrease in the oxidation rate with increasing water activity from 0.68 to 0.85 in intermediate moisture foods containing 30% meat and 10% raisins. Finally, hexanal, a carbonyl compound may be oxidized to form free fatty acids. Bengtsson et al (1967) found hexanal decreased after passing a maximum of hexanal concentration in pears.

Non-enzymatic browning, which is related to lipid oxidation in most common dried foods is also a function of water activity. A mathematical model to describe the relationship between non-enzymatic browning and water activity in a food system can be established. Once the

mathematical model for non-enzymatic browning is incorporated in this computer model, the computer simulation can predict two mechanisms of food deterioration; lipid oxidation and non-enzymatic browning.

To use the proposed computer prediction model to verify the oxidative rancidity in a commerical product, for example, breakfast cereal, a new mathematical relationship [$k = f(a_w)$] is required. The lipid oxidation in breakfast cereal would be expected to be high at very low water activity as described by Martin (1958). The oxidation rate can not be described by an exponential equation as illustrated in this investigation.

The commercial packaging material for breakfast cereal is usually wax paper or a laminated aluminum package film which is a better barrier to moisture transfer. Therefore, the moisture content of the product would be expected to be lower for a longer storage period and the storage life would be expected to be short due to the high oxidation rate at very low water activity.

VI. CONCLUSION

1. The experimental results at constant temperature and water activity indicate that the lipid oxidation based on hexanal concentration in a dry food model system can be described by zero order kinetics.

2. The rate constant for hexanal formation in a dry model food system as a function of water activity can be described by an exponential relationship.

3. The rate constant for hexanal formation in a dry model food system as a function of temperature can be described by the Arrhenuis relationship.

4. The computer prediction of moisture content in a dry model food system is in agreement with the experimental moisture content data for all conditions at relative humidities in the storage rooms in the range from 34 to 78%RH.

5. The computer predictions of hexanal concentration in a dry model food system are in agreement with the experimental hexanal concentration data for most conditions at low relative humidities of the storage room in the range from 34 to 57%RH. A portion of the variation may be attributed to the variations in the storage environments.

6. Based on hexanal concentration in the dry model food system, hexanal concentration was found to decrease at

storage conditions of 75 and 78%RH after the model system moisture content increased to a water activity of approximately 0.8. This decrease in hexanal concentration could be attributed to the several modes of lipid - protein interaction which occur and enhance the hexanal reaction.

7. The computer model in this study could be utilized to predict the hexanal concentration in any kind of food product accurately if the composition of the food products are similar to the model system in this study. Temperature and relative humidity in storage should not be greater than 21 C and 57%RH respectively and the package material should have a hexanal permeability equal to or less than the package material used in this study.

6.1 Suggestions For Future Work

1. To experimentally investigate the influence of different amounts of lipid content on the oxidation at various water activity levels during storage in a sample model system containing no protein.

2. To experimentally examine the rate of hexanal loss from the storage package and the correlation between the hexanal content inside a package and the hexanal content obtained from the technique in this study and then to incorporate these parameters into the computer model to improve the accuracy of the hexanal content prediction in the sample.

3. To establish a mathematical model to describe the rate of nonenzymatic browning as a function of water

activity and incorporate that model into the computer model in this study to make it capable of predicting the deterioration due to two mechanisms, browning and rancidity.

4. To verify experimentally the computer simulation to predict the rancidity in commercial dry foods.

NOMENCLATURE

NOMENCLATURE

A = Surface area of the package; m^2

a_w = Water activity of the sample

a_{wb} = Water activity at the intersection between BET equation and modified sorption isotherm equation (5.1)

a_w^o = Outside water activity (RH/100)

B_1, B_2 = Constants in equation (3.3)

c = BET energy constant

c_b = Modified sorption isotherm constant

D = Storage time; hr

dM = Moisture change in a food product; kg

dt = Time differential; hr

dM/dt = Rate of moisture transfer through the package film; kg H_2o/kg solid.s

E = Activation energy, kJ/kg-mole

F_1 = $(-(M*c-2*w_m*c) + SQRT ((M*c-2*M-w_m*c)^2 -4*M^2*(1-c)))/(2*M*(1-c))$

F_2 = $((-M(c_b+a_{wb}c_b-2a_{wb}-2)) - SQRT ((M (c_b+2a_{wb}c_b-2a_{wb}-2) -w_m c_b)^2 - 4(M(1-c_b) (M(1-a_{wb}c_b + 2a_{wb} - 2 a_{wb}^2 c_b + a_{wb}^2) + a_{wb} w_{mb} c_b))))/(2M(1-c_b))$

H = Hexanal concentration of the sample; ppm on dry basis

H_o = Initial hexanal concentration of the sample; ppm on dry basis

H_2O = Water

k = Rate constant of oxidative rancidity; 1/week

k_1 = Monomolecular initiation rate constant

k_{11} = Bimolecular initiation rate constant

k_q, k_p = Propagation rate constants

k_t, k_{t1}, k_{t2}, k_{t3} = Termination rate constant

k_m = Over all monomolecular rate constant

k_b = Over all bimolecular rate constant

k_o = Reference rate constant of Arrhenius equation

K = Moisture transfer coefficient of the package; kgH_2O m/m^2 hr Pa

M = Moisture content of the sample; $gH_2O/100$ g solid

M_o = Initial moisture content of the sample; $gH_2O/100$ g solid

(m) = Substrate concentration

N = Number of calculation loop

O_2 = Oxygen present as free oxygen

P_s = Saturated vapor pressure of water; Pa

Q_{10} = Extrapolation of the rate constant (k) to a temperature change of 10 C

$R^{\cdot}$, $RO^{\cdot}$, $ROO^{\cdot}$ = Free radical intermediates

RH = Relative humidity; %

R'H = Substrate concentration

ROOH = Hydroperoxide concentration

r^2 = Correlation coefficient

s_1 = Standard deviation on the predicted value and experimental data

s_2 = Standard deviation on the mean value

T = Temperature; C

t = Time

T_A = Absolute temperature; Kelvin (K)

w_m = BET constant

w_{mb} = Modified sorption isotherm constant

w_s = Solid weight of the sample; kg

x = Thickness of the package film; m

y = (ROOH) = (O_2)

Subscripts

A = Absolute temperature

b = Modified sorption isotherm

o = Initial reference

s = Solid or saturated vapor

t = time or termination

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APPENDICES

APPENDIX A

Table A.1 Hexanal concentration history and order of reaction held at temperature 32 C and water activity of 0.6.

Time (weeks)	Hexanal concentration (ppm)	Mean (ppm)	Standard deviation
0	1.360, 1.289, 1.151	1.267	0.106
1	4.405, 4.958, 4.888	4.750	0.301
2	7.869, 7.805, 7.050	7.575	0.456
3	8.788, 9.793, 9.443	9.341	0.510
4	11.060	11.060	-
4.44	11.461, 11.495, 12.447	11.801	0.560
5.29	13.046, 15.206, 12.462	13.571	1.445

Method All the data were fit with a least square analysis using minicomputer HP85 to obtain the kinetics of hexanal formation.

Zero Order ($r^2 = 0.961$)

$H = 2.224 + 2.221t$

$K = 2.221$ 1/week

Table A.2 Hexanal concentration history and order of reaction held at temperature 10 C and water activity of 0.32 a_w.

Time (weeks)	Hexanal concentration (ppm)	Mean (ppm)	Standard deviation
0	2.664, 2.147, 1.743	2.185	0.462
1	1.826, 1.785, 1.942	1.851	0.081
2	3.033, 2.362, 3.428	2.941	0.539
3	2.096, 2.157, 2.381	2.211	0.150
4	3.744, 2.808, 3.701	3.418	0.528
6	2.172, 2.064, 2.357	2.198	0.148
8	2.067, 2.058, 2.140	2.088	0.045

Zero Order ($r^2 = 0$)

$H = 2.412 + 0.0004t$

$k = 0.0004$ 1/week

Table A.3 Hexanal concentration history and order of reaction held at temperature 21 C and water activity of 0.32 a_w.

Time (weeks)	Hexanal concentration (ppm)	Mean (ppm)	Standard deviation
0	1.022, 0.721, 0.877	0.873	0.151
1	1.160, 1.227, 1.161	1.183	0.038
2	1.232, 1.339, 1.612	1.394	0.196
6	1.869	1.869	-
8	1.930, 1.733, 1.715	1.793	0.119
10	2.733, 2.064, 2.769	2.522	0.397

Zero Order ($r^2 = 0.833$)

$H = 0.988 + 0.136t$

$k = 0.136$ 1/week

Table A.4 Hexanal concentration history and order of reaction held at temperature 32 C and water activity of 0.072 a_w.

Time (weeks)	Hexanal concentration (ppm)	Mean (ppm)	Standard deviation
0	0.966, 1.134, 1.316	1.139	0.175
2	1.614, 1.510, 1.593	1.572	0.055
4	1.885, 2.026	1.956	0.100
6	2.401, 2.479, 2.173	2.351	0.159
8	2.649, 2.489, 2.687	2.608	0.105
10	3.179, 3.116, 3.520	3.272	0.217
12	4.340, 3.772, 3.810	3.974	0.318
14	3.882, 5.199, 3.067	4.049	1.076

Zero Order ($r^2 = 0.880$)

$H = 1.091 + 0.218t$

$k = 0.218$ 1/week

Table A.5 Hexanal concentration history and order of reaction held at temperature 32 C and water activity of 0.20 a_w.

Time (weeks)	Hexanal concentration (ppm)	Mean (ppm)	Standard deviation
0	0.972	0.972	-
1	1.405, 1.656	1.531	0.177
2	2.280, 2.365, 2.808	2.484	0.284
3	2.606, 2.641, 2.257	2.501	0.212
4	3.137, 2.905, 2.841	2.961	0.156
5	3.584, 3.517, 3.546	3.549	0.034
6	3.802, 3.991, 3.766	3.853	0.121
7	3.587, 3.790, 4.433	3.937	0.442
8	4.270, 4.663, 4.654	4.529	0.224
9	5.431, 6.613, 4.888	5.644	0.882

Zero Order ($r^2 = 0.899$)

$H = 1.223 + 0.443t$

$k = 0.443$ 1/week

Table A.6 Hexanal concentration history and order of reaction held at temperature 32 C and water activity of 0.32 a_w.

Time (weeks)	Hexanal concentration (ppm)	Mean (ppm)	Standard deviation
0	1.719	1.719	-
2	2.331, 2.627, 2	2.319	0.314
3	3.412, 3.398, 3.345	3.385	0.035
4	4.179, 3.982, 4.077	4.079	0.099
5	4.350, 3.652, 6.234	4.745	1.336
6	3.484, 6.537	5.011	2.159
8	7.191, 7.731, 6.189	7.037	0.782

Zero Order ($r^2 = 0.798$)

$H = 1.348 + 0.682t$

$k = 0.682$ 1/week

Table A.7 Hexanal concentration history and order of reaction held at temperature 32 C and water activity of 0.45 a_w.

Time (weeks)	Hexanal concentration (ppm)	Mean (ppm)	Standard deviation
0	0.894, 0.832	0.863	0.044
1	2.124, 2.215, 2.190	2.176	0.047
2	2.854, 2.905, 2.774	2.844	0.066
3	4.332, 5.620, 5.607	5.186	0.740
4	4.653, 4.472	4.563	0.128
5	4.070, 5.543, 4.905	4.839	0.739
6	6.522, 6.655, 5.205	6.127	0.802

Zero Order (r^2 = 0.811)

H = 1.444 + 0.796t

k = 0.796 1/week

Table A.8 Hexanal concentration history and order of reaction held at temperature 32 C and water activity of 0.75 a_w.

Time (weeks)	Hexanal concentration (ppm)	Mean (ppm)	Standard deviation
0	1.282, 1.239	1.261	0.030
1	5.404, 5.008, 5.432	5.281	0.237
3	15.747, 16.523, 14.745	15.672	0.891
3.43	11.123, 8.565, 8.711	9.466	1.437
4.14	16.974, 20.620	18.797	2.578
4.57	25.108, 19.777, 23.910	22.932	2.797

Zero Order ($r^2 = 0.810$)

$H = 0.655 + 4.275t$

$k = 4.275$ 1/week

Table A.9 Hexanal concentration history and order of reaction held at temperature 43.3 C and water activity of 0.32 a_w.

Time (weeks)	Hexanal concentration (ppm)	Mean (ppm)	Standard deviation
0	1.123, 0.838, 0.855	0.939	0.160
1	4.264, 3.794, 4.091	4.050	0.238
2	6.923, 5.038, 5.777	5.913	0.950
2.57	7.352	7.352	-
3	8.032, 6.980, 7.935	7.649	0.581
3.71	13.995, 16.110, 15.459	15.188	1.083
4.14	15.625	15.625	-

Zero Order (r^2 = 0.882)

H = 0.249 + 3.301t

k = 3.301 1/week

Table A.10 The environmental condition of the different storage rooms.

Temperature (C)		Relative humidity (%RH)		Time periods
Mean	standard deviation	Mean	standard deviation	(weeks)
10.84	0.82	34.68	2.06	14
20.51	0.56	34.11	2.10	11
21.45	0.75	57.46	2.72	9
20.87	0.85	75.71	1.66	14
21.42	0.45	77.81	3.66	10
32.51	1.06	44.18	5.66	16

Table A.11 The experimental data for moisture content and hexanal concentration of the model system inside the storage package at storage condition 11 C, 35%RH.

Time (weeks)	Moisture content (gH_2O/100 g solid)	Hexanal concentration (ppm)	
		mean	Standard deviation
0	8.82	1.06	0.26
1	9.04	1.01	0.06
2	8.81	1.37	0.03
4	7.56	1.25	0.09
6	8.40	1.44	0.62
10	9.40	1.22	0.10
12	9.57	1.45	0.05
14	9.30	1.78	0.32

Table A.12 The experimental data for moisture content and hexanal concentration of the model system inside the storage package at storage condition 21 C, 34%RH.

Time (weeks)	Moisture content (gH_2O/100 g solid)	Hexanal concentration (ppm)	
		mean	Standard deviation
0	8.83	1.27	0.19
1	8.83	1.64	0.22
3	7.77	1.67	0.19
5	7.43	1.85	0.15
9	8.48	1.82	0.05
11	8.73	2.06	0.22

Table A.13 The experimental data for moisture content and hexanal concentration of the model system inside the storage package at storage condition 21 C, 57%RH.

Time (weeks)	Moisture content (gH_2O/100 g solid)	Hexanal concentration (ppm)	
		mean	Standard deviation
0	10.23	3.06	-
1	10.70	2.32	0.07
3	10.11	3.90	-
5	10.47	5.82	0.59
9	14.15	7.85	0.15

Table A.14 The experimental data for moisture content and hexanal concentration of the model system inside the storage package at storage condition 21 C, 76%RH.

Time (weeks)	Moisture content (gH_2O/100 g solid)	Hexanal concentration (ppm)	
		mean	Standard deviation
0	8.82	1.06	0.26
1	12.29	1.44	0.05
2	13.21	2.28	0.14
4	14.23	6.31	0.79
6	16.01	8.35	0.77
10	17.20	5.45	0.22
12	17.81	1.38	0.49
14	16.72	0.51	0.02
16*			

* visible mold growth

Table A.15 The experimental data for moisture content and hexanal concentration of the model system inside the storage package at storage condition 21 C, 78%RH.

Time (weeks)	Moisture content (gH_2O/100 g solid)	Hexanal concentration (ppm)	
		mean	Standard deviation
0	12.55	4.44	1.02
2	15.62	7.97	1.16
6	17.81	9.31	0.52
8	18.79	0.82	0.16
10	19.49	0.37	0.07
12*			

*visible mold growth

Table A.16 The experimental data for moisture content and hexanal concentration of the model system inside the storage package at storage condition 32 C, 44%RH.

Time (weeks)	Moisture content (gH_2O/100 g solid)	Hexanal concentration (ppm)	
		mean	Standard deviation
0	8.21	0.84	-
1	7.56	1.45	0.07
4	7.33	3.73	0.24
6	8.01	4.80	0.10
10	8.76	5.95	0.50
12	8.64	5.85	0.35
15	8.29	6.52	1.16
16	7.38	6.71	0.26

Table A.17 Example of input parameters for the computer simulation at storage condition 21 C, 57%RH

Parameter	Quantity
Storage temperature influences:	21.45 C
c, w_m	17.9, 5.59
a_{wb}, c_b, w_{mb}	0.486, 4.33, 2.51
P_s	2.56 kPa
B_1, B_2	0.031, 4.228
Storage relative humidity, RH	57.46 %RH
Initial moisture content, M_o	10.23 gH_2O/100g solid
Computer integration	
dt	6 hrs
Package influences	
x	0.0000559 m
A	0.0966 m^2
K	2.817 x 10^{-8} $gH_2O.m/m^2$. hr.Pa
Sample	
w_s	56.79 g
H_o	3.06 ppm

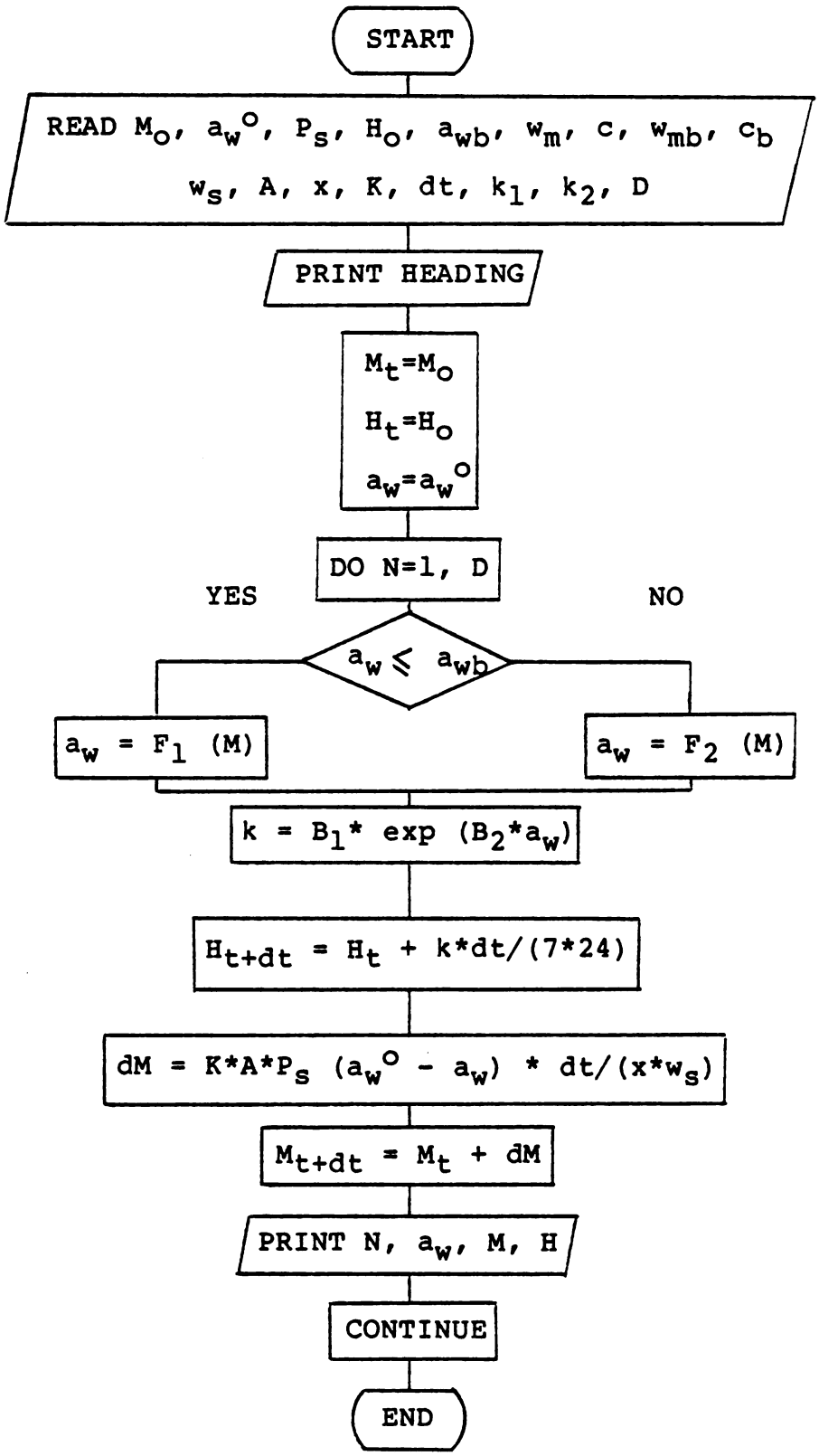

Figure A.1 Computer flow chart to predict the moisture content and hexanal concentration in the model food system.

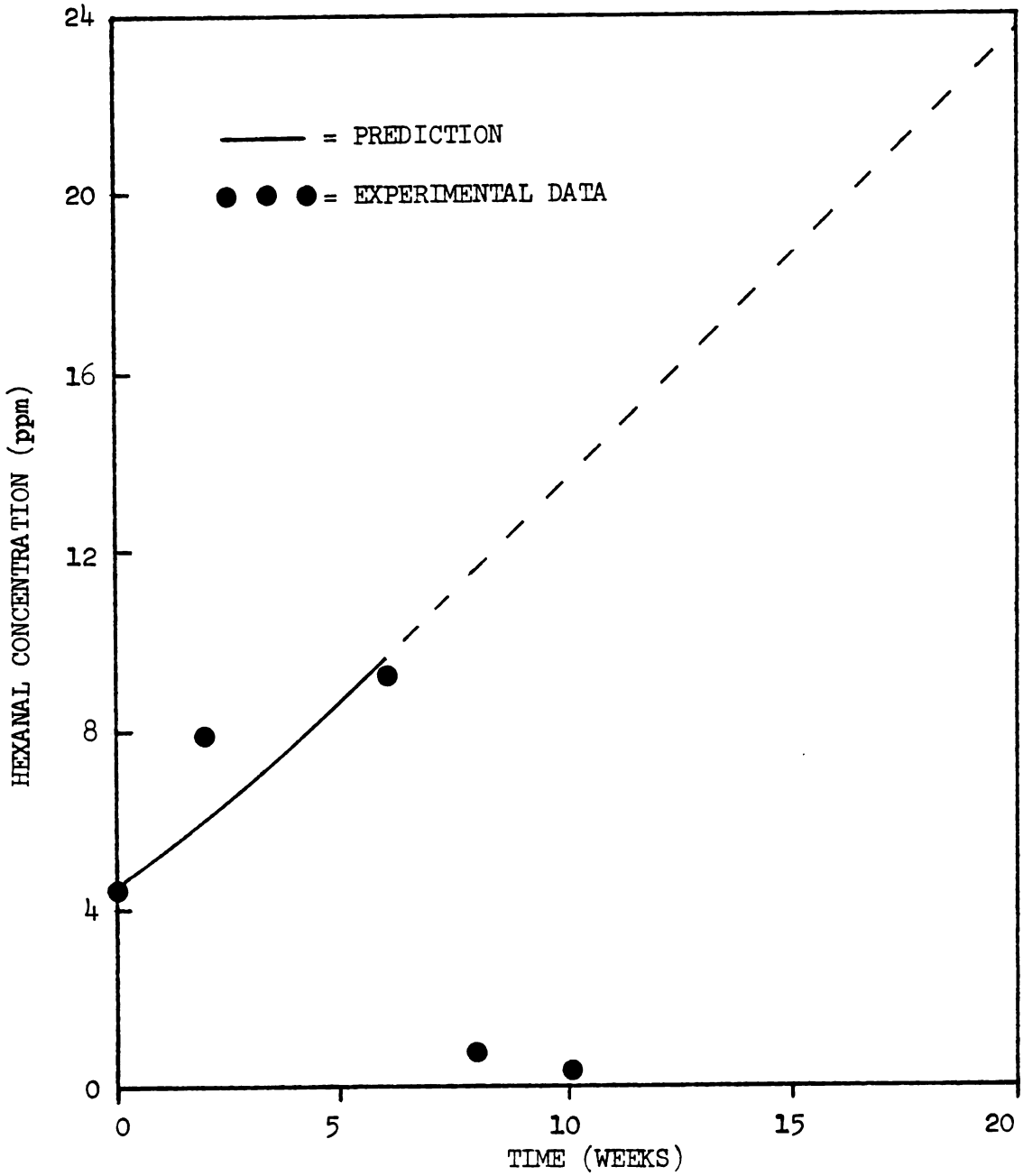

Figure A.3 Comparison of computer prediction and experimental data for hexanal concentration in the model system during storage at 21 C and 78%RH.

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