COMPUTER SIMULATION OF LIQUID FOOD QUALITY DURING STORAGE

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ABSTRACT

COMPUTER SIMULATION OF LIQUID FOOD QUALITY DURING STORAGE

By

Rajinder Paul Singh

This dissertation is a discussion of a procedure that can help a food engineer in predicting the quality changes in a liquid food during storage. The procedure is based on kinetics of quality degradation and computer-aided prediction models. The specific objectives of this study were to develop mathematical models that describe (1) the kinetics of quality degradation and oxygen uptake in a liquid food; (2) the oxygen diffusion accompanied by a second-order chemical reaction in a liquid food during storage; and (3) the influence of light intensity on rates of quality degradation and oxygen uptake. A computer simulation of these models was developed to predict the quality history of a liquid food.

The quality index studied in this research was reduced ascorbic acid. Infant formula was selected as the model system. The overall reaction of ascorbic acid degradation and oxygen uptake was assumed and confirmed to be a second-order reaction under limited dissolved

oxygen concentration in the liquid. The second-order rate constants were calculated for ascorbic acid degradation and dissolved oxygen uptake in infant formula samples exposed to light in 1-cm deep exposure cells. These storage experiments were conducted at five light intensities (dark, 1071 lux, 2142 lux, 3213 lux, and 4284 lux) and three initial dissolved oxygen concentrations (1.0 ppm, 4.86 ppm, and 8.71 ppm). Actual shelf-life tests were conducted to compare with the computer predicted results.

The results showed that the vitamin loss occurred within a 0-2 cm layer along the container wall. The computer-aided results on vitamin degradation agreed with the results obtained from actual shelf-life tests. The standard deviations were within 1.43 to 5.10 percent of initial ascorbic acid concentrations. The results obtained in this study illustrate that the quality of a liquid food can be predicted if the information on the rates of quality degradation is available.

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COMPUTER SIMULATION OF LIQUID FOOD QUALITY DURING STORAGE

By

Rajinder Paul Singh

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LIST OF SYMBOLS

(A)	=	concentration of quality index, mg/liter
a	=	$(A)/(A)_o$, dimensionless
(B)	=	dissolved oxygen concentration, ppm
C	=	gas concentration in Equation 3-23, mg/liter
b	=	$(B)/(B)_o$, dimensionless
D_A	=	diffusion coefficient of quality index in liquid, cm^2/hr
D_B	=	diffusion coefficient of oxygen in liquid, cm^2/hr
D_c	=	diffusion coefficient of oxygen in container wall, cm^2/hr
F	=	net rate of transfer of moles of oxygen, mg/cm^2 hr
H	=	solubility, $moles/cm^3$ atm
k	=	second-order rate constant, liter/mg hr
$\bar{k}$	=	average second-order rate constant, liter/mg hr
k'	=	slope in Equation 3-28
L	=	light intensity, lux
M	=	the number of distance increments considered in finite difference equation
P	=	permeability coefficient, cc.mil/day m^2 atm
p	=	$(A)_o/(B)_o$, dimensionless; partial pressure of oxygen, atm, in Equation 3-26
S	=	surface area of container, cm^2

s = D_A/D_B, dimensionless

t = time, hr.

(X) = concentration of A reacted at time 't', mg/liter

x = distance into liquid phase, cm.

y = distance into container wall, cm.

z = $\sqrt{\frac{k(A)_o}{D_B}}\,(x)$, dimensionless

θ = $k(A)_o t$, dimensionless

$$\delta_z^2(a_{i,n}) = \frac{a_{i-1,n} - 2a_{i,n} + a_{i+1,n}}{(\Delta z)^2}$$

δ = thickness of container wall, cm

ε = extinction coefficient of light

Subscripts

o = initial time for concentrations and zero depth for light intensity 'L'

d = dark

I. INTRODUCTION

Liquid foods in storage may undergo spoilage due to several deteriorative mechanisms. These mechanisms affect the quality resulting in degradation of nutrients, development of off-flavors and change in the product color. The overall emphasis in storage of any food product is on keeping the deteriorative mechanisms at minimum rates. The deterioration of quality of liquid foods is influenced by several factors including temperature, light intensity and dissolved oxygen content.

In this dissertation, a numerical procedure for prediction of the quality index history in a liquid food during storage is developed. The overall objective in mind is the use of a computer-aided prediction model in selecting storage environments best suited for liquid foods. As will be discussed later, the prediction models require specific information on rates of degradation of the given quality index. This type of information is obtained through laboratory-scale pilot studies.

The major emphasis in this research has been to illustrate the procedures that are necessary to mathematically predict the quality history of a liquid food. The

research is designed to assist in evaluation of storage stability for new product package combinations. This type of information is helpful to the product manufacturer in selecting appropriate packaging material for new or existing products. A second use of the simulation is the capability to predict the nutrient concentration at any time during storage and the use of such information for labeling purposes.

For the purpose of this study, ascorbic acid (vitamin C) was selected as the quality index. The liquid food selected was an infant formula. Vitamin C is fairly sensitive to the storage conditions including temperature, light intensity, and presence of oxygen. The infant formula was selected to assure better control of the initial concentration of various nutrients and better control on microbial contamination. In addition, the product is virtually oxygen-free in the bottles. The storage temperature in this study was kept constant. The influence of light intensity and presence of dissolved oxygen on vitamin degradation was evaluated. The mathematical functions and constants obtained in this study are specifically for vitamin C in infant formula. The procedures for using this information should be applicable to other liquid foods, with minor modifications.

The specific objectives of this research were:

(i) to develop a theoretical mathematical model to describe oxygen uptake in an infant formula accompanied with a chemical reaction involving reduced ascorbic acid;

(ii) to incorporate the influence of initial dissolved oxygen, light intensity and oxygen permeability of a container wall into the mathematical model;

(iii) to develop a computer-aided mathematical prediction of reduced ascorbic acid concentration and dissolved oxygen concentration in infant formula during storage; and

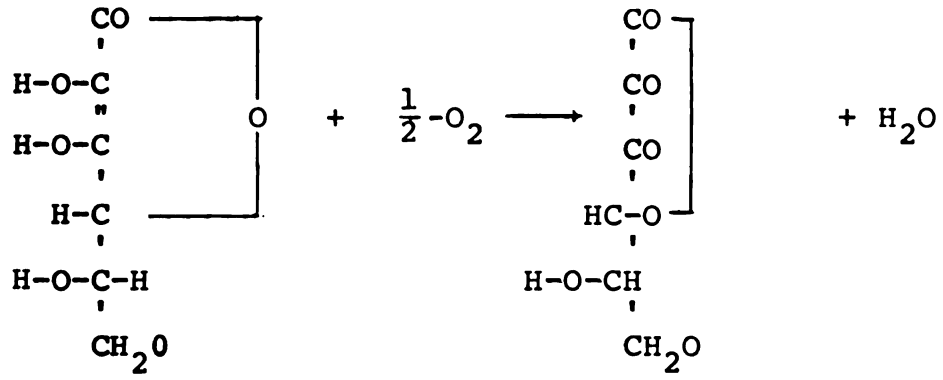
(iv) to verify the computer-aided predictions of reduced ascorbic acid and dissolved oxygen concentration histories in infant formula by comparisons to results obtained in the laboratory tests.

II. REVIEW OF LITERATURE

2.1 Ascorbic Acid Oxidation-- General Scheme

Pure ascorbic acid (Vitamin C. L-threo-2, 3, 4, 5, 6-pentahydroxy - 2 - hexenoic acid - 4 - lactone) occurs as white, odorless crystals or powder, melting at about 190°C (374°F). It is optically active and is soluble in water (1 gram in approximately 3 ml) (Hay et al., 1967). It is a very strong reducing agent. In structure, it resembles a simple sugar, but is modified to contain an enediol and acid lactose group. It is easily oxidized in air.

The most significant characteristic of ascorbic acid is its reversible oxidation to dehydroascorbic acid. The latter is reversibly reduced in the body to the physiologically active ascorbic acid. When dehydroascorbic acid is allowed to stand in solution, the lactone ring gradually opens; the irreversible oxidation product, 2,3-diketo-l-gulonic acid which is devoid of anti-scorbutic properties, is obtained (Mazur and Harrow, 1971). Thus, the first step of ascorbic acid oxidation is as follows:



l-ascorbic acid dehydroascorbic acid

The oxidation reaction is favored in the presence of air, hydrogen peroxide, quinones, irradiation, enzymes (ascorbic acid oxidase, peroxidase, cytochrome oxidase) or metals (Cu^{++} and Fe^{++}). The oxidative degradation is also enhanced by pH values greater than 5.0.

2.2 Influence of Light on Ascorbic Degradation in Milk

In a preliminary report, Hand et al. (1938) reported a possible relationship of ascorbic acid and riboflavin degradation to light intensity, oxygen concentration and light catalyzed off-flavors in milk. Krukovsky and Guthrie (1945) further concluded that the destruction of ascorbic acid in milk was involved in the development of lipid oxidized flavor resulting from light acting as a pro-oxidant.

In one of the earlier reports, Burgwald and Josephson (1947) found complete disappearance of ascorbic acid when milk was exposed for 1-2 hours to room daylight for four days. Several investigators have observed

complete loss of ascorbic acid activity in milk exposed in clear glass bottles for 10-30 minutes to sunlight (Buriana (1937), Herried et al. (1952), Holmes and Jones (1944), Josephson et al. (1946), Kon and Watson (1936). Containers made of colored glass (yellow, green, brown, ruby, etc.) provided some protection to the ascorbic acid oxidation (Houston et al. (1938), Fomicheva (1962), Stull (1953)).

The light transmission in milk was studied by Burgess and Herrington (1955a). They reported that sunlight is capable of destroying ascorbic acid in milk at depths approaching 26 mm. Their results indicate that at 546 nm an 18-mm layer of whole milk transmitted more than one percent of the incident light and at 365 nm a 4.5-mm layer transmitted 2 percent of the incident light. In another paper, Burgess and Herrington (1955b) reported the effective penetration depths of light into milk. The values of effective depth of light penetration in whole milk ranged from about 0.1 cm at 253 nm to 2 cm at 578 nm.

During the 1960s, several papers have been published on the influence of fluorescent lights on the ascorbic acid content in milk stored in glass, paper and polyethylene containers (Somogyi and Ott (1962), Hendrickx et al. (1964)). Radema (1962) reported a 35 percent loss of Vitamin C in milk after exposure at 8°C to 40-w lamps with color temperature of 6500 K and light intensity of 500 lux. The loss was at a lower rate when lamps with a color temperature of 3000 K were used.

Aurand et al. (1966) studied the effect of riboflavin, ascorbic acid and sunlight on the development of oxidized flavor in milk. They reported that riboflavin was the primary factor responsible for the development of light-induced oxidized flavor, whereas ascorbic acid was only a secondary factor and that riboflavin was unnecessary for initiation or continuation of ascorbic acid destruction.

Hendrickx (1963) investigated the influence of light on whole and skim milk. He observed greater loss of vitamin C in skim milk than in whole milk. He indicated that the serum of irradiated milk contributes most of the light-induced flavors. Friedrich and Waiblinger (1969) reported that milk, in clear polyethylene bottle, exposed to fluorescent light of 1500 lux intensity at 10°C resulted in a rapid breakdown of ascorbic acid from 14 to 4 mg/liter in 8 hours. After oxidation, the total content of ascorbic acid, dehydroascorbic acid and 2,3-diketo-gulonic acid decreased only slightly. The relationship between the ascorbic acid destruction and the light intensity in the range of 400-500 nanometers was reported to be statistically significant. Thus, spectral transmittance of polyethylene was found to be a controlling factor in ascorbic acid oxidation.

Hansen et al. (1972) published an abstract indicating that riboflavin and ascorbic acid breakdown in milk, packaged in plastic containers, initiated after only 2 hours of storage under fluorescent light. The deterioration

of these nutrients was directly proportional to the amount of off-flavor development. It was also reported that plastic containers containing a special pigment gave 100 percent protection to the nutrients and flavor of milk when exposed to fluorescent light.

Dimick (1973) reported that riboflavin destruction in milk held in plastic and glass containers was not significantly different and amounted to approximately 10-17 percent loss following 72 hours of exposure. He observed higher rates of ascorbic acid losses in milk held in glass and plastic containers when compared with fiberboard containers. Heldman and Kirk (1974) confirm these losses in milk. In a related study, Sattar and deMan (1973) reported significant losses of ascorbic acid and riboflavin in milk held in clear plastic pouches at 5°C and exposed to 100 and 200 foot-candles light intensity. These losses were minimal in opaque plastic pouches.

Recent research by Singh et al. (1974) has illustrated the use of kinetic analysis in describing the influence of light on riboflavin loss in milk during storage. These results indicate that first-order rate constants and activation energies are good parameters in evaluating the ability of a container to protect the product from light-induced loss of quality.

2.3 Influence of Dissolved Oxygen on Ascorbic Acid Oxidation

In aqueous solutions, ascorbic acid degrades more easily, especially in the presence of dissolved and headspace oxygen. Theoretically, 1 ml of oxygen reacts with 15.7 mg of ascorbic acid (based on one mole of ascorbic acid combining with one atom of oxygen) (Bayes, 1950). This is equivalent to a reaction of 3.3 mgm of ascorbic acid with 1 ml of air.

Bayes (1950) studied the influence of oxygen on ascorbic acid in aqueous standardized solutions stored for 6 weeks at 35°C (95°F). He obtained a fairly good agreement between the experimental and theoretical values of ascorbic acid, indicating that the destruction of ascorbic acid is directly proportional to the amount of available oxygen in the containers.

One of the earliest investigations on the influence of dissolved oxygen on ascorbic acid degradation was made by Guthrie et al. (1938). They observed that the destruction of ascorbic acid and the development of oxidized flavor were largely or completely prevented by removing the dissolved oxygen from the milk. Sharp et al. (1940) developed a continuous milk deaerating unit to prevent the oxidized flavor and ascorbic acid degradation. Guthrie (1946) reported an 8.27 percent loss of Vitamin C in deaerated milk stored for 7 days at 40°F compared with 57.1 percent loss in aerated milk. The flavor of the

aerated milk was significantly "poor" and that of deaerated milk was "good," after 7 days of storage.

The kinetics of auto-oxidation of ascorbic acid in sugar solutions in the presence of dissolved oxygen was studied by Joslyn and Miller (1949a). They concluded that the oxidation reaction was essentially first-order with respect to the ascorbic acid concentration. They further reported that under conditions of limited oxygen supply the sugar solutions showed reduced initial rates of oxidation (Joslyn and Miller, 1949b).

Khan and Martell (1967) worked on the influence of molecular oxygen on oxidation of ascorbic acid. The rate of the uncatalyzed oxidation of ascorbic acid was found to be proportional to oxygen concentration at 20 percent and higher concentrations of molecular oxygen.

Significant losses of several nutrients in milk in the presence of dissolved oxygen and exposure to sunlight during storage were reported by Ford (1967). He recommended the removal of dissolved oxygen from milk to stabilize ascorbic acid and prevent degradation of such vitamins as Vitamin B_{12} and folic acid. Burton et al. (1970) reported that the stability of Vitamin C and folic acid is wholly determined by the level of residual oxygen in sterilized milk.

2.4 Quality Degradation in Fruit Juices

Researchers in the past have reported quality deterioration, such as development of off-flavors, degradation in color, etc., in fruit juices held in storage. However, published literature in this area is not as exhaustive as for milk.

Tressler and Pederson (1936) reported no deterioration of pasteurized grape juice packed in high vacuum or in bottles containing negligible oxygen. However, they found rapid deterioration when the bottles were partially filled with the juice. They noted a change in color from bright purple-red to brown. In addition, there were detrimental changes in aroma and flavor. These authors also indicated that the presence of air in the headspace of bottled strawberry juice resulted in increased deterioration of color.

The degradation of ascorbic acid during storage was observed by Beattie et al. (1943). They noted that in several fruit juices the changes in color occurred concurrently with progressive losses of ascorbic acid during storage. Nebesky et al. (1949) reported that heat and oxygen content were the most specific accelerating agents responsible for deterioration of color during storage. Deaerated juices stored at 21.1 to 26.7°C retained their color and exhibited very little change during storage for six months. They also reported that anthocyanin pigments isolated from strawberries and

currants exhibited no deterioration when oxygen was excluded. They found detrimental changes in the solutions of pigments when the samples were exposed to light during storage.

Timberlake (1960) showed that oxidation of ascorbic acid in the presence of copper and iron was significant in black currant juice. He also discussed the effects of some metal chelating agents on the ascorbic acid oxidation.

2.5 Computer Simulations of Food Quality

Recently researchers at Massachusetts Institute of Technology have made attempts to mathematically predict the shelf-life of dehydrated foods. Their main objective has been to incorporate information (1) on laboratory tests on the properties of food, (2) on the kinetics of food deterioration reaction, and (3) on properties of packaging materials, in developing prediction models of packaging protection required for a given storage life (Karel, 1972).

Mizrahi et al. (1970a) studied the mathematical prediction of extent of browning of freeze-dried cabbage stored in packages made of materials with different water-vapor permeabilities. They developed a simulation that incorporated the kinetic data of browning reaction, moisture content inside the package and mass-transfer characteristics of packages. They reported a fairly good agreement between the experimental data and the predicted values. This prediction model was later used in accelerated tests of

browning in dehydrated cabbage (Mizrahi et al. 1970b). The accelerated tests reduced the time required to obtain browning rate data at low moisture contents from over a year to only 10 days. This work emphasizes one of the major advantages of computer simulation models. The accelerated tests, along with computer simulations, provide a rapid determination of the storage stability of a food component.

A computer-aided prediction of oxidative deterioration of a shrimp product was presented by Simon et al. (1971). They correlated the organoleptic degradation with absorption of oxygen and with loss of carotenoid pigment. They reported that the prediction of storage stability was comparable to actual storage tests based on the pigment loss.

Quast et al. (1972a) developed a mathematical model to describe the oxidation of potato chips as a function of oxygen pressure, extent of oxidation and equilibrium relative humidity. Quast and Karel (1972b) presented a simulation of storage life of potato chips undergoing simultaneous deterioration by two mechanisms, with interaction between the mechanisms. The two mechanisms involved in deterioration were oxidation due to atmospheric oxygen and textural changes due to moisture uptake. This simulation was later used in determining optimal permeabilities which allow simultaneous deterioration (Quast and Karel, 1973). They also studied the influence of several packaging conditions on these permeabilities.

Labuza et al. (1972) developed mathematical models of food stability and incorporated information on sorption isotherms in the simulations. They studied the moisture gain in tea and moisture gain with a chemical reaction (browning) in dry milk.

The computer-aided shelf-life simulation studies have been limited to dry and dehydrated foods. However, these studies demonstrate the capability of predicting the quality changes in a food product.

III. THEORY

There are various changes which might take place in a liquid food stored after packaging. Many of these changes are influenced by the storage conditions and the container material. As an illustration, a plastic container containing a liquid food is shown in Figure 3.1. The product has a certain initial vitamin concentration and dissolved oxygen concentration. The container wall, depending on its optical clarity, allows certain light transmission. In addition, the container material has a given permeability for oxygen from the atmosphere into the product. The outside odors may permeate through the container wall and influence the flavor of the product. The container wall also allows loss of product ingredients via absorption. In case of a carbonated beverage stored in highly permeable plastic containers, carbon dioxide might be lost via migration.

In this section, the following mathematical models are discussed:

(1) Kinetic reaction model of vitamin degradation and oxygen uptake in a liquid food.

(2) Oxygen diffusion accompanied by a chemical reaction in a liquid food during storage.

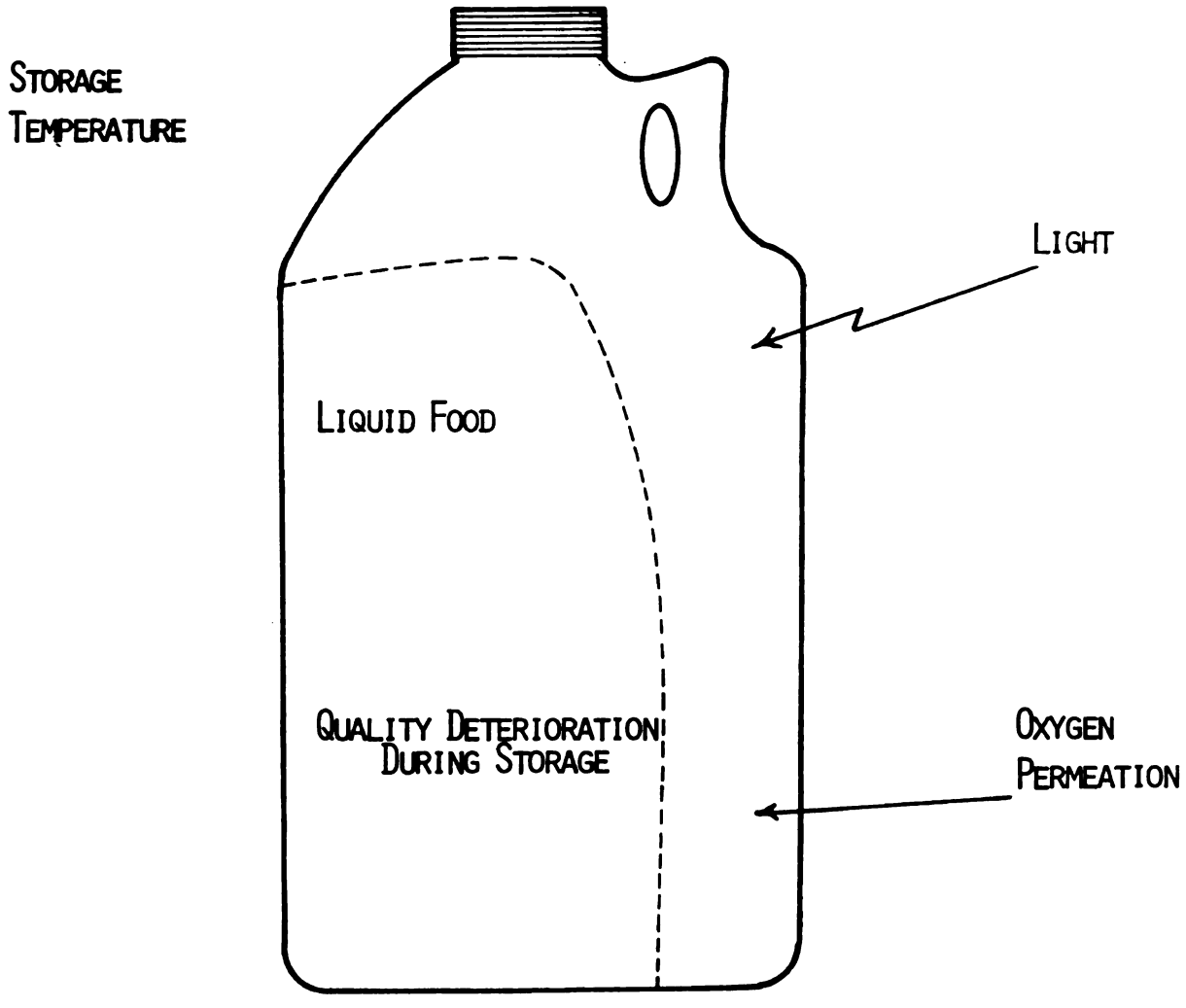


Figure 3.1.--Factors influencing quality deterioration in liquid foods during storage.

(3) Influence of light intensity on vitamin degradation and oxygen uptake.

These models are incorporated in a computer simulation to predict the vitamin concentration history in a liquid food.

3.1 Kinetic Model of Vitamin Degradation and Oxygen Uptake

In this study, the oxidative degradation of reduced ascorbic acid in an infant formula is being investigated. The kinetic reaction model is therefore developed for reduced ascorbic acid oxidation. In the presence of dissolved oxygen, the reaction scheme is as follows:

$$\underset{\text{(reduced ascorbic acid)}}{A} + \underset{\text{(oxygen)}}{B} \xrightarrow{k} \underset{\text{(dehydroascorbic acid and } H_2O)}{\text{Products}} \qquad (3\text{-}1)$$

where k is the rate constant.

If the dissolved oxygen, B, undergoes a second-order reaction of finite speed with a dissolved reactant, A, the rate of reaction can be expressed as:

$$\frac{-d(A)}{dt} = k(A)(B) \qquad (3\text{-}2)$$

Initially $(A) = (A)_o$ and $(B) = (B)_o$; let (X), expressed as concentration, be the amount of A that has reacted at time 't'. Then at any time,

$$(A) = (A)_o - (X) \tag{3-3}$$

$$(B) = (B)_o - (X) \tag{3-4}$$

The concentration units of (A), (B) and (X) are moles/liter. The most commonly used units of vitamin concentration and dissolved oxygen concentration are mg/liter and parts per million, respectively. Therefore in the rest of this dissertation the units of vitamin concentration (A) and dissolved oxygen concentration (B) will be mg/liter and parts per million respectively, unless otherwise stated.

From Equation (3-3),

$$\frac{-d(A)}{dt} = \frac{d(X)}{dt} \tag{3-5}$$

Substituting Equations (3-3) to (3-5) in Equation (3-2) gives:

$$\frac{-d(A)}{dt} = \frac{d(X)}{dt} = k\,((A)_o - (X))((B)_o - (X)) \tag{3-6}$$

Integration from t=0 gives the concentration of X, or A and B at any time:

$$\ln\left[\frac{(A)_o-(X)}{(B)_o-(X)}\right] = \ln\left[\frac{(A)}{(B)}\right] = ((A)_o-(B)_o)kt + \ln\left[\frac{(A)_o}{(B)_o}\right] \tag{3-7}$$

A computer program, KINFIT, was used to fit the experimental data in Equation (3-7) (Dye and Nicely, 1971). The program is useful in plotting the data to the best

fit and calculating standard deviations on the calculated parameters. The input of variables (e.g., dissolved oxygen concentrations, vitamin concentrations, time) is accompanied with their respective variances. This approach assists in accounting for the internal errors of vitamin assays and small variations in storage durations. The program is specifically written for chemical reactions and for evaluating kinetic parameters of these reactions.

The rate constants 'k' calculated from experimental data are used in the computer simulation of the nutrient history in a liquid food. The mathematical model used in this scale-up is discussed in the following section.

3.2 Oxygen Diffusion Accompanied by a Second-Order Chemical Reaction in a Liquid Food

In this section, the diffusion of oxygen accompanied by second-order chemical reaction with ascorbic acid in a liquid food is discussed. The theory is developed with the following assumptions:

(1) The thermal convective diffusion in the liquid is assumed negligible. This assumption neglects internal diffusion of vitamin or dissolved oxygen due to any temperature differentials within the container. The assumption is valid if the storage temperature is maintained constant.

(2) The diffusion coefficients of oxygen and ascorbic acid are assumed constant. The assumption is valid at constant storage temperatures.

(3) The second-order rate constant 'k' varies with depth inside the liquid. This assumption is discussed further in section 3.3.

The equations which describe the variations of the ascorbic acid concentration (A) and dissolved oxygen concentration (B) in time and space within the liquid in the presence of a second-order reaction (Equation 3-1) are the following (Danckwerts, 1970):

$$D_A \frac{\partial^2(A)}{\partial x^2} = \frac{\partial(A)}{\partial t} + k(A)(B) \qquad (3\text{-}8)$$

$$D_B \frac{\partial^2(B)}{\partial x^2} = \frac{\partial(B)}{\partial t} + k(A)(B) \qquad (3\text{-}9)$$

with the initial condition

$$(B) = (B)_o \;,\; (A) = (A)_o \quad x \geq 0,\; t=0 \qquad (3\text{-}10)$$

When the liquid food is stored in a glass bottle, the boundary conditions on the dissolved oxygen and vitamin concentration are allowed to vary with time. In a situation when the liquid food is stored in a plastic container permeable to oxygen, the dissolved oxygen concentration at the wall is expressed as a function of the oxygen permeation through the wall. The way in which these boundary conditions are handled for these specific cases is discussed in Section 3.4.1.

An analytical solution encompassing these parameters in functional form is impossible (Brian et al, 1961).

Therefore, the differential equations (3-8, 3-9) were approximated by the implicit finite difference techniques. It can be seen that the number of separate solutions necessary in this method for each variation of the parameters becomes excessive. To resolve these problems, the equations were put into dimensionless form through the following substitutions:

$$a = \frac{(A)}{(A)_o}$$

$$b = \frac{(B)}{(B)_o}$$

$$p = \frac{(A)_o}{(B)_o}$$

$$s = \frac{D_A}{D_B}$$

$$z = \sqrt{\frac{k(A)_o}{D_B}}\,(x)$$

$$\theta = k(A)_o t$$

The dimensionless form of Equations (3-8) and (3-9) is:

$$sp\frac{\partial^2 a}{\partial z^2} - s\,\frac{\partial a}{\partial \theta} = ab \qquad (3\text{-}11)$$

$$\frac{\partial^2 b}{\partial z^2} - \frac{\partial b}{\partial \theta} = ab \qquad (3\text{-}12)$$

with the initial conditions

$$a = 1,\ b = 1 \text{ at } \theta = 0,\ z \geq 0 \tag{3-13}$$

Equations (3-11) and (3-12) can be solved along with information on the rate constant, diffusion coefficient for oxygen and ascorbic acid and initial concentrations of ascorbic acid and dissolved oxygen. The numerical method used in this study is presented in section 3.4. The rate constant 'k' is evaluated for a given light intensity. The influence of light intensity on rate constant 'k' is discussed in section 3.3.

3.3 Influence of Light Intensity on Vitamin Degradation and Oxygen Uptake

The second-order rate constant describing vitamin degradation and oxygen uptake can be expressed as a function of the light intensity. Thus

$$k = f(L) \tag{3-14}$$

The light intensity is a function of depth inside the liquid. Assuming an exponential extinction of light inside the liquid medium gives

$$L = L_o\, e^{-\varepsilon x} \tag{3-15}$$

Thus, the second-order rate constant can be expressed as a function of incident light intensity and depth inside the liquid medium, as follows

$$k = f(L_o\, e^{-\varepsilon x}) \qquad (3\text{-}16)$$

where the function can be evaluated from experimental data.

As discussed in Chapter II, the light extinction in a liquid food, e.g., milk, is in a thin layer along the walls of the container (Burgess and Herrington, 1955b). The light penetration inside a liquid food depends upon the incident light intensity and the extinction coefficient, ε. Specially designed experimental trials, such as the ones that will be discussed in this dissertation are helpful in investigating the effective depth of light penetration for the given liquid food.

The experimentally determined function of Equation (3-16) is used in solving Equations (3-11) and (3-12) numerically. The mathematical procedure is presented in section 3.4.

3.4 Computer-Aided Prediction Model of Vitamin Destruction in a Liquid Food

Equations (3-11) and (3-12) can be solved numerically provided the following information is available:

(a) Rate constant 'k' as a function of light intensity and depth obtained from experimental data (Equation 3-16).

(b) Light and oxygen transmission through container walls.

(c) Diffusion coefficients of ascorbic acid and oxygen in the liquid.

Equations (3-11) and (3-12) are solved by the following time-centered, implicit finite-difference equations according to the Crank and Nicolson formulation for the geometry shown in Figure 3.2:

$$sp\left[\frac{1}{2}\delta_z^2 a_{i,n+1} + \frac{1}{2}\delta_z^2 a_{i,n}\right] - p\left[\frac{a_{i,n+1} - a_{i,n}}{\Delta\theta}\right] = \left[\frac{a_{i,n+1} - a_{i,n}}{2}\right] \left(b_{i,n+\frac{1}{2}}\right) \tag{3-17}$$

$$\left[\frac{1}{2}\delta_z^2 b_{i,n+1} + \frac{1}{2}\delta_z^2 b_{i,n}\right] - \left[\frac{b_{i,n+1} - b_{i,n}}{\Delta\theta}\right] = \left[\frac{b_{i,n+1} + b_{i,n}}{2}\right] \left(a_{i,n+\frac{1}{2}}\right) \tag{3-18}$$

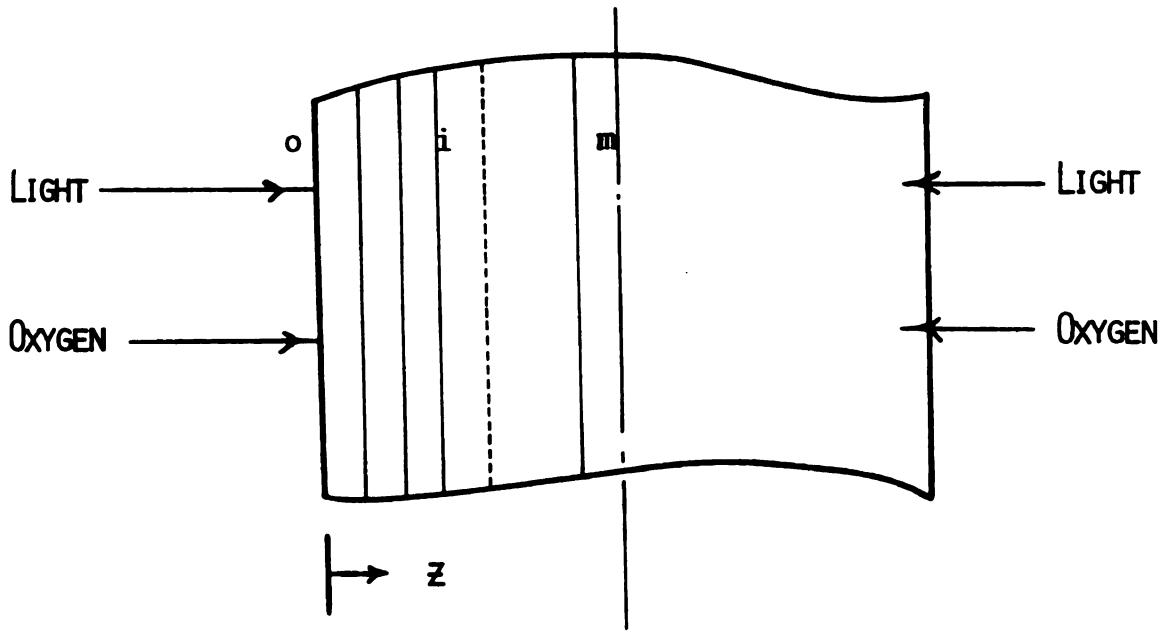
The implicit equations have been solved by a method similar to the method presented by Brian et al. (1961). The method of solution is as follows:

1. Assume that the values $a_{i,n}$ and $b_{i,n}$ are known at some time-step n for i = 0,1,2,. . . M.

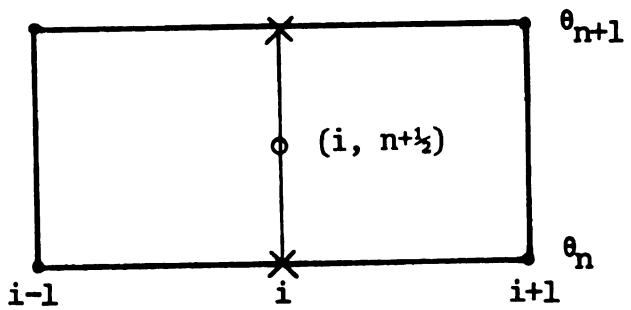
2. The values $a_{i,n+\frac{1}{2}}$ (i = 1,2,. . . M) were calculated by using the explicit finite-difference equation

$$sp\left(\delta_z^2 a_{i,n}\right) - p\left(\frac{a_{i,n+\frac{1}{2}} - a_{i,n}}{\Delta\theta/2}\right) = a_{i,n}\, b_{i,n} \tag{3-19}$$

3. Inserting these values of $a_{i,n+\frac{1}{2}}$ into Equation (3-18), a system of M simultaneous linear equations is



(a) liquid in container exposed to light and oxygen



(b) Crank-Nicolson Method

Figure 3.2.--A portion of a finite-difference grid of liquid in a container exposed to light and oxygen.

obtained which, together with the boundary conditions to be discussed later, was solved for the values $b_{i,n+1}$ ($i = 1,2,3 \ldots M$). The tridiagonal method of solving equations was used to solve these simultaneous equations (Carnahan et al., 1969).

4. The calculated values of $b_{i,n+1}$ were used to calculate $b_{i,n+\frac{1}{2}}$ as

$$b_{i,n+\frac{1}{2}} = \frac{b_{i,n+1} + b_{i,n}}{2} \quad (i = 1, 2 \ldots M) \qquad (3\text{-}20)$$

5. These values of $b_{i,n+\frac{1}{2}}$ were inserted into Equation (3-17) to obtain a system of M simultaneous linear equations. These equations, along with the boundary conditions, were again solved by the tridiagonal method to yield values $a_{i,n+1}$ ($i = 0, 1, 2, \ldots M$). Thus, the complete set of future-time concentration $a_{i,n+1}$ and $b_{i,n+1}$ was obtained.

This procedure was repeated as the calculation proceeded from one time-step to another.

The above implicit finite-difference method was chosen in order to avoid severe stability limitations encountered when an explicit method is used (Perry and Pigford, 1953).

The forward and backward difference forms used in finite differences lead to discretization errors of $O(\Delta t + \Delta x^2)$. The central difference form of Crank-Nicolson method used in this study reduces the dependency

on the time increment from $O(\Delta t)$ to $O[(\Delta t)^2]$ (Carnahan, 1969). This method converges with discretization error $O[(\Delta t)^2 + (\Delta x)^2]$.

Brian et al. (1961) used a similar method for infinitely rapid chemical reaction and reported that the results deviate from true solutions to the differential equations by less than 2 percent. In this dissertation, the predicted values are compared with the actual experimentally measured values to confirm the validity of this method.

The boundary conditions for these difference equations are discussed in section 3.4.1.

3.4.1 Initial and Boundary Conditions

The initial and boundary conditions for the difference equations were handled as follows:

(a) Initial condition:

at time t=0,

$$\left.\begin{aligned} a_{i,o} &= 1 \\ b_{i,o} &= 1 \end{aligned}\right\} \quad (i=0,1,2,3 \ldots M) \qquad (3\text{-}21)$$

(b) The boundary conditions for a container with no oxygen permeation through the walls, such as glass, are:

(i) at the wall:

The vitamin and dissolved oxygen are consumed at a finite rate as determined from Equation 3-7. The equation is solved at each time step to

calculate new concentration values for vitamin and oxygen at the boundary node.

(ii) at the center:

$$a_{m,n} = a_{m-1,\ n-1}$$
$$b_{m,n} = b_{m-1,\ n-1} \qquad (3\text{-}22)$$

(c) The boundary conditions on oxygen concentration at the wall for a container permeable to oxygen are developed for a one-dimensional case.

Assuming a concentration gradient $\frac{\partial C}{\partial X}$ exists across the two sides of the film, the net rate of transfer of moles of oxygen across a unit area of a plane perpendicular to x-axis at a given moment is given by Fick's first law of diffusion:

$$F = D_c \frac{\partial C}{\partial X} \qquad (3\text{-}23)$$

This equation can be integrated between

$C = C_1$ (gas concentration in the surrounding atmosphere)

and $C = C_2$ (gas concentration in the liquid) at $x = 0$ and $x = \delta$ respectively, as follows:

$$F = \frac{D_c}{\delta} (C_1 - C_2) \qquad (3\text{-}24)$$

The flux can be expressed as number of diffused molecules per unit time. Thus for a given area of the film, S:

$$F = \frac{D_c S}{\delta} (C_1 - C_2) \tag{3-25}$$

Assuming Henry's law is valid, the concentration, C, of oxygen on the surface of the container wall is a function of the partial pressure of oxygen:

$$C = H\ p \tag{3-26}$$

Combining Equations (3-25) and (3-26)

$$F = D_c H\ S\ \frac{(p_1 - p_2)}{\delta} \tag{3-27}$$

The outside partial pressure of oxygen, p_1, is 0.21 atmosphere. The quantity ($D_c H$) is commonly known as the permeability coefficient. This coefficient can be defined in terms of the following quantities:

$$D_c H = \frac{(\text{amount of gas})(\text{thickness})}{(\text{area})(\text{time})(\text{pressure difference})}$$

Several types of units have been used in the past to express this coefficient. In this study, the following units were used:

$$\frac{\text{cc}\quad\text{mil}}{\text{day}\ \text{m}^2\ \text{atm}}$$

Equation (3-27) is used in the computer program to calculate the amount of oxygen transferred at the boundary into the container during small steps of time. The computer program is discussed in section 4.3.

IV. EXPERIMENTAL MATERIAL AND PROCEDURES

Experiments were conducted primarily to generate data in order to calculate the rate constant 'k' described in section 3.1. This required obtaining:

(i) Mass average vitamin concentration data as a function of storage time,

(ii) Mass average dissolved oxygen concentration data as a function of storage time.

The storage temperature was held constant (at 7.2°C) in these experiments. Light intensity and initial dissolved oxygen concentration were varied.

In addition, experiments were conducted to observe the influence of high initial dissolved oxygen concentration (above saturation with atmospheric oxygen) on vitamin degradation. Scale-up experiments with larger-size containers were also conducted.

4.1 Experimental Materials

4.1.1 Exposure Cells

In order to maintain better control on experimental variables, special plexiglass cells were fabricated for

light exposure studies. The cells are 1 cm in depth with an exposed surface area of 31.67 cm^2 (Figure 4.1). The top surface of these cells is made out of clear plexiglass. The bottom and sides of the cells are made of opaque plexiglass. These cells have two small openings (1 mm diameter), on the sides, for filling and removal of samples. The light transmission curve for clear plexiglass and polyethylene (used in plastic bottles), obtained from a spectrophotometer, is shown in Figure 4.2.

4.1.2 Liquid Food

The liquid food system selected for this study was an infant formula. The infant formula was selected for the following reasons:

(a) The infant formula from the same batch has uniform initial concentration of various nutrients, as well as overall composition.

(b) Infant formula in bottles provides a better control on the initial microbiological contamination.

(c) The product is deaerated before bottling. This results in low initial dissolved oxygen concentration.

The infant formula, Similac, was obtained directly from the Ross Laboratories, Columbus, Ohio. The product was contained in 4-oz. ready-to-serve glass bottles. The nutritional composition of this infant formula is presented in Table 4.1.

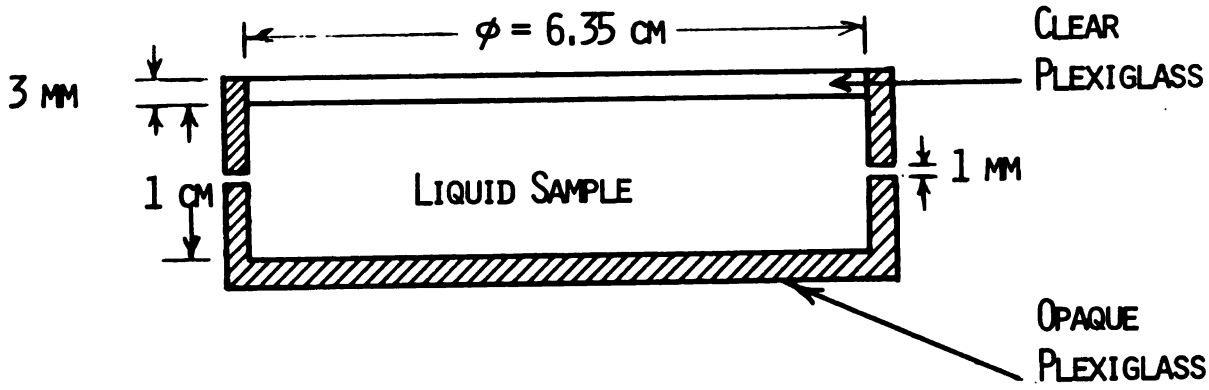


Figure 4.1.--An exposure cell.

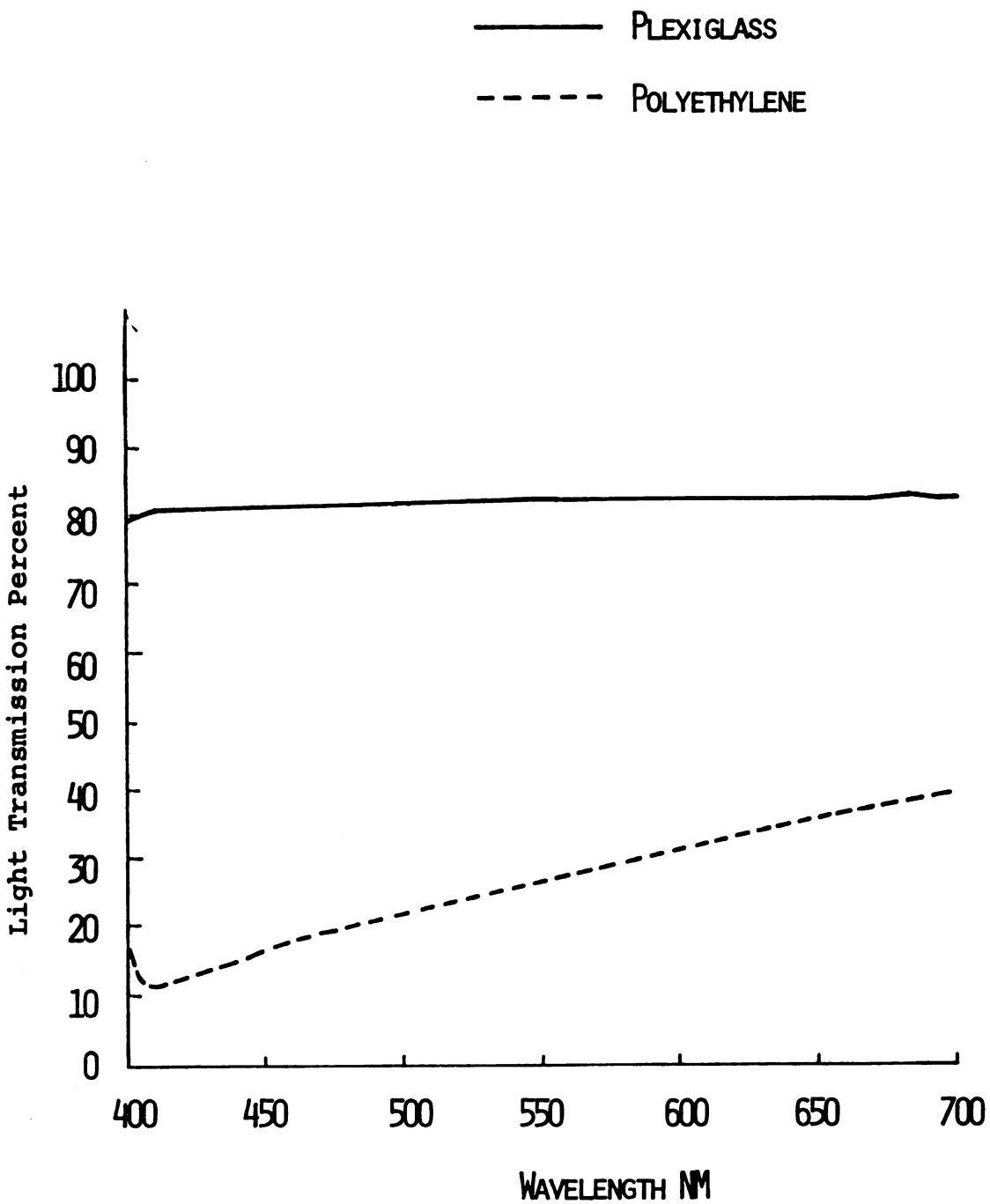


Figure 4.2.--Light transmission through plexiglass and high density polyethylene.

TABLE 4.1.--Nutritional Composition of Similac, Ready to Feed Infant Formula.

Nutrients	Per Liter	Vitamins	Per Liter
Fat	36 gm	Vitamin A	2500 USP unit
Carbohydrate	71 gm	Vitamin D	400 USP unit
Protein	15.5 gm	Vitamin E	9 Int. unit
Minerals	3.7 gm	Vitamin C	55 mg
Calcium	0.6 gm	Vitamin B_1	0.65 mg
Phosphorus	0.44 gm	Vitamin B_2	1 mg
Magnesium	0.04 gm	Niacin	7 mg
Iron	trace	Vitamin B_6	0.4 mg
Copper	0.4 mg	Folic Acid	0.05 mg
Iodine	0.04 mg	Pantothenic Acid	3 mg
Water	901.8 gm	Vitamin B_{12}	1.5 mcg

4.1.3 Light and Temperature Control

General Electric lamps (40W, Coolwhite) were used in these studies. The spectral distribution of these fluorescent lamps is presented in Figure 4.3. It should be noted that the radiation intensity is very high in the area of 450 nanometers. As indicated earlier, this is the critical area with respect to light-induced and oxidized flavors. A reflector-holder with two fluorescent lamps was hung from the ceiling. The height of the lamps above the cells was adjusted to achieve the desired light intensity measured on the top surface of the cells. A constant-temperature water bath (American Instruments Model 4-8600) was used to control temperature around the cells. A

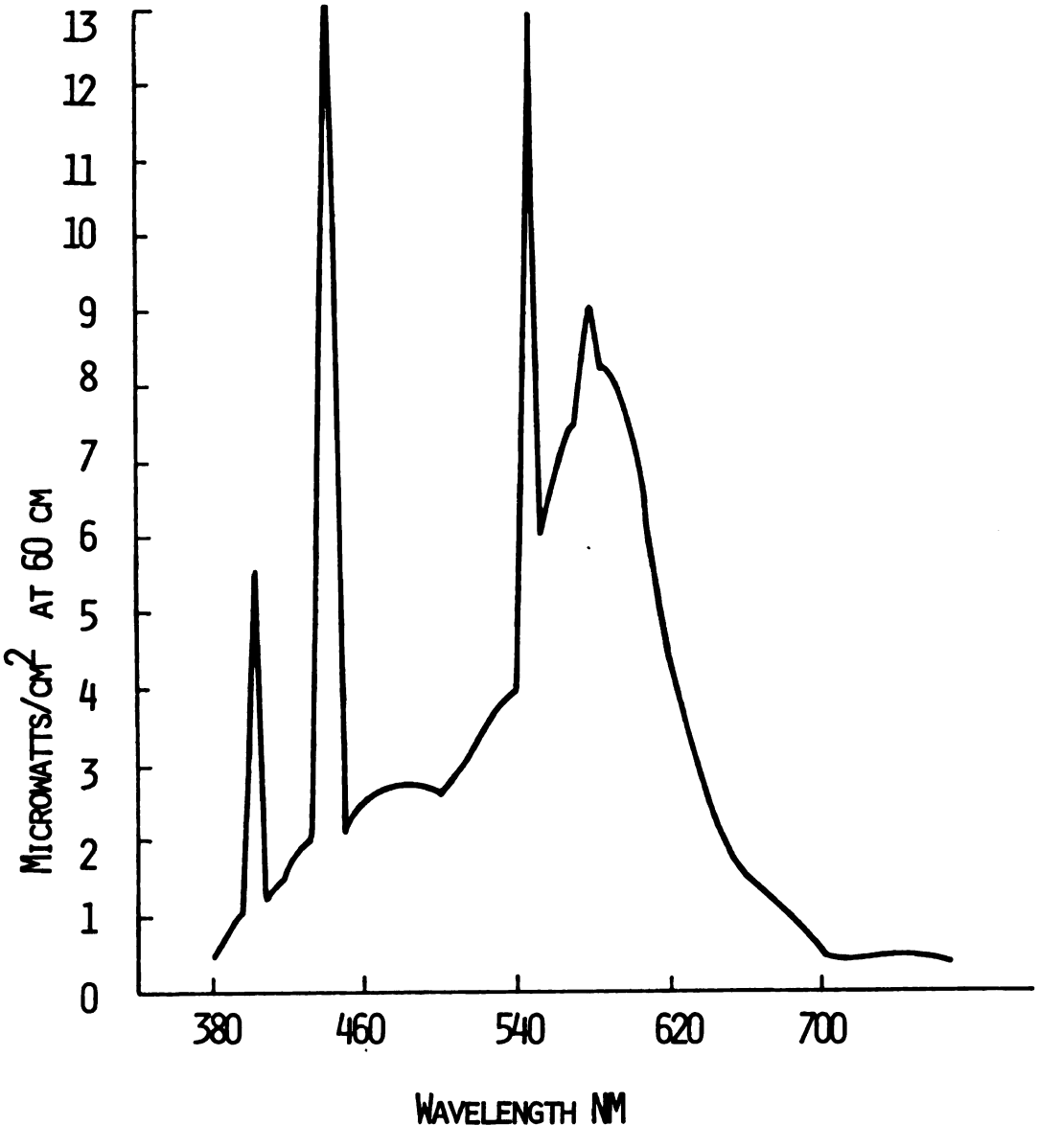


Figure 4.3.--Spectral distribution of F-40 cool white fluorescent lamp. "A Practical Guide to Westinghouse Fluorescent Lamps," Westinghouse Electric Corporation, Bloomfield, N. J.

Tektronix J16 digital photometer was used to measure light intensities.

4.2 Experimental Procedures

4.2.1 Light Exposure

The infant formula was transferred from the bottles into the cells using a 50 cc hypodermic syringe with a 17-gauge needle. Random checks on dissolved oxygen content showed no increase in dissolved oxygen when this transfer was done carefully with the hypodermic syringe. The openings in the cells were closed using surgical tape.

The cells were arranged on a platform in the constant-temperature water bath with their sides submerged in water. The top surface of the cells was kept above water, as shown in Figure 4.4.

After completion of the desired time exposure, the liquid sample was removed from the cell using a hypodermic syringe. The sample was then either assayed for ascorbic acid or analyzed for dissolved oxygen concentration.

4.2.2 Dissolved Oxygen Measurements

The dissolved oxygen measurements were conducted using a Beckman Laboratory Oxygen Analyzer Model 777. The instrument consists of a polarographic electrode that is used to determine the oxygen content in gaseous samples or dissolved oxygen in aqueous or non-aqueous solutions. The operation of the sensor is as follows: The sensor is

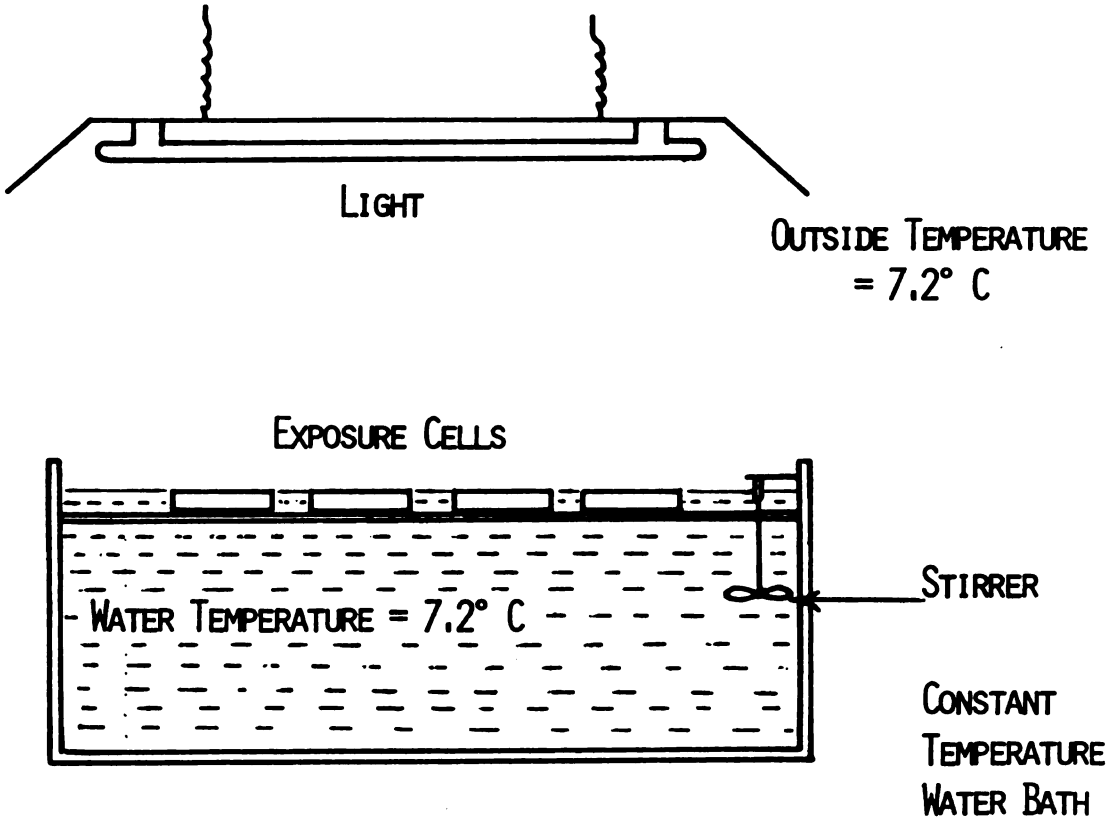


Figure 4.4.--Experimental cells exposed to light.

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placed in the sample and a potential of approximately 0.8 V is applied between the gold cathode and the silver anode. The oxygen diffuses through the Teflon membrane and is reduced at the cathode. The reduction of oxygen causes a current flow. The current produced is then amplified and the oxygen content is indicated on the dial in units of "percent oxygen." The instrument was calibrated to obtain the values in "parts per million, oxygen." The calibration procedure is described by Mack (1974).

4.2.3 Storage Conditions

The following storage experiments were conducted:

(a) Three trials with initial dissolved oxygen concentration of 1.0 ppm, 4.86 ppm and 8.71 ppm; respectively were conducted. The dissolved oxygen concentration in the infant formula (measured immediately after opening the bottle) was 1.0 ppm. Using a laboratory gas diffuser, the liquid samples were saturated with atmospheric air to obtain a dissolved oxygen content of 8.71 ppm (at 7.2°C). The 4.86 ppm dissolved oxygen samples were obtained by mixing infant formula from bottles and the samples saturated with atmospheric oxygen in equal ratios by volume.

All storage experiments were conducted at 7.2°C (45°F) and five light intensities: 1071 lux (100 ft-c), 2142 lux (200 ft-c), 3213 lux (300 ft-c), 4284 lux (400 ft-c) and dark.

The vitamin assay and dissolved oxygen measurements were conducted on duplicate samples at 0, 4, 8, 15 and 24 hour storage durations.

4.2.4 Vitamin Assay Procedure

The vitamin assay procedure is described in detail by Kirk and Ting (1974). A summary of procedures is as follows: A 25-ml sample was pipetted into a 50-ml volumetric flask. Then 6 percent metaphosphoric acid was added to make the solution to the 50-ml mark. The contents of the flask were well shaken and the solution was filtered using Whatman filter paper No. 41. The filtrate was then analyzed in the Technicon Autoanalyzer for ascorbic acid as follows.

The reagents used in the autoanalyzer were:

1. 2,6-dichloro-indophenol: 2% in water then filtered
2. Thiourea: 5% in 50% ethanol
3. Metaphosphoric acid: 6%
4. Sodium acetate: 50% of NaOAc. 3 H_2O
5. Boric acid: 3 g in 100 ml of 50% sodium acetate 5% H
6. O-phenylene diamine hydrochloride: 0.1%

The autoanalyzer was allowed at least 20-30 minutes warm-up time. Reagents were then pumped until the system stabilized (10-15 minutes). The baseline on the recorder-chart was adjusted to 5 percent transmission. The sample

probe was placed in a high standard (dehydroascorbic acid 100 mg/ml). On achieving steady state, the full-scale record was adjusted to give a 95 percent transmission reading. The full range of standards was then sampled at a rate of 50 samples/hour with a sample wash time ratio of 2:1. Blanks were run with boric acid-sodium acetate.

The standard curve for vitamin concentration against percent transmission was obtained using a stock solution of ascorbic acid prepared by adding 500 mg/ml of ascorbic acid in 6 percent metaphosphoric acid to make the final concentrations of standard ascorbic acid to 20 mg/ml, 40 mg/ml, 60 mg/ml, 80 mg/ml and 100 mg/ml.

An aliquot of the stock solution was transferred into a 100-ml volumetric flask, along with approximately 50 ml of metaphosphoric acid. 2,6-Dichloroindophenol solution was added to make the solution pink. A few drops of thiourea were added until the solution was colorless. The solution was then made to the 100-ml mark with metaphosphoric acid (6 percent). The final concentration was 100 mg/ml of dehydroascorbic acid. This was then used to obtain the 95 percent transmission on the recorder.

4.2.5 Storage Trial with High Initial Dissolved Oxygen Concentration

A trial was conducted to observe the influence of very high initial dissolved oxygen concentration. The purpose of this trial was to determine the order of nutrient degradation reaction when the dissolved oxygen

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is in abundant supply. The infant formula was purged with pure oxygen to obtain a dissolved oxygen concentration of "60 percent oxygen" on the Beckman oxygen analyzer (note that 100 percent saturation with air is equivalent to "21 percent oxygen"). The samples of infant formula with high initial dissolved oxygen were transferred into 1-cm. cells. These cells were exposed to 1071 lux and 4284 lux light intensities. Both ascorbic acid and dissolved oxygen were monitored at 0, 2, 4, 8 and 15 hour time intervals.

4.2.6 Storage Trials with 3-cm.-Deep Cells

Storage trials were conducted in 3-cm-deep cells with and without partitions, as shown in Figure 4.5. The purpose of these trials was to determine the effective depth of light penetration in infant formula. These trials were conducted under 4284 lux light intensity. The liquid formula had an initial dissolved oxygen concentration of 8.71 ppm.

4.2.7 Storage Trials with Regular-Size Glass and Plastic Bottles

Several storage trials were conducted to verify the computer-predicted results for vitamin loss in infant formula stored in larger-size containers. The glass bottle used in this trial was 6 cm in diameter and 6 cm in height. The plastic container measured 6 cm diameter by 10 cm

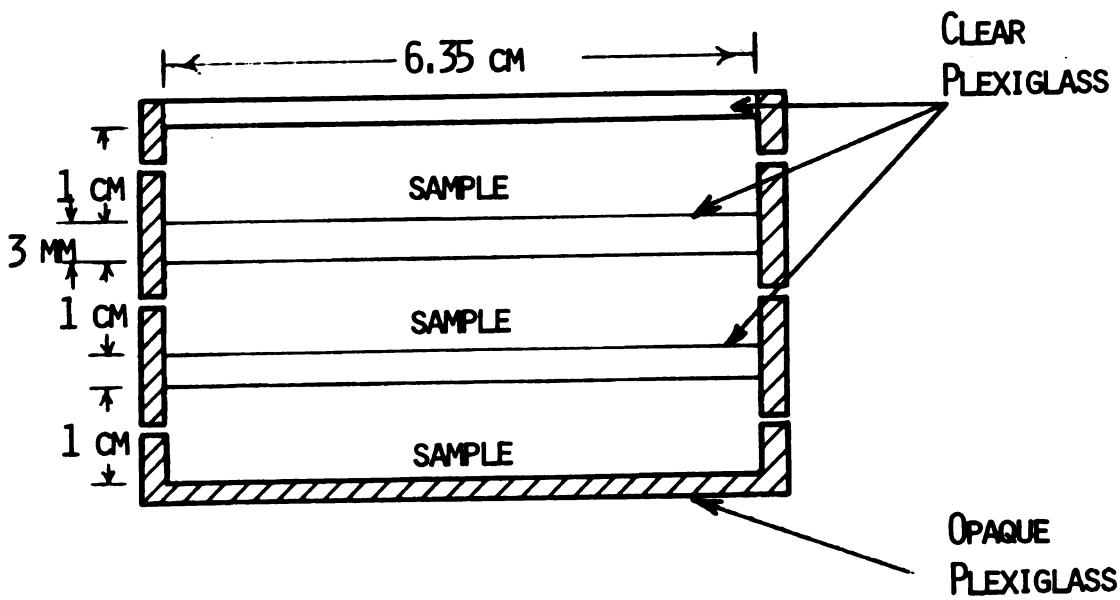

Figure 4.5.--A 3-cm deep exposure cell.

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height. These trials were conducted at three light intensities, 535 lux (50 ft-c), 1071 lux (100 ft-c) and 4284 lux (400 ft-c). The two initial dissolved oxygen concentrations observed were 8.71 ppm and 4.86 ppm.

4.3 Description of Computer Program

The various components of the computer program developed in this study are discussed in this section.

(1) PROGRAM MAIN: This program reads the input parameters, it sets the initial conditions, calls subroutine QUALITY to obtain new time concentration values. It then modifies the boundary nodes for the next time increment. The concentrations of oxygen and vitamin are printed at specified time intervals. This procedure is repeated for the next time interval.

(2) SUBROUTINE QUALITY: This subroutine calls subroutine RATE to obtain rate constant values. It calls subroutine DIMEN to obtain non-dimensional parameters, subroutine OXYGEN to obtain new time oxygen concentrations and subroutine VITAMIN to obtain new time vitamin concentrations.

(3) SUBROUTINE RATE: This subroutine calculates the rate constants for the given dissolved oxygen concentrations and light intensity. This subroutine includes the experimentally determined functions from Equation 3-28.

(4) SUBROUTINE DIMEN: This subroutine calculates the non-dimensional parameters discussed in section 3.2.

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(5) SUBROUTINE VITAMIN AND SUBROUTINE OXYGEN: These subroutines use the time-centered finite difference approach to calculate the new time oxygen and vitamin concentration values from old time values. Both of these subroutines call subroutine TRIDAG to solve the simultaneous equations.

(6) SUBROUTINE TRIDAG: This subroutine solves the simultaneous equations. The subroutine is obtained from Carrahan (1969).

A fortran listing of the computer program appears in Appendix B.

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V. RESULTS AND DISCUSSION

The primary objective of this study was to develop a computer-aided prediction model to describe the history of a quality index in a liquid food. The first section is a presentation of experimental results necessary to determine specific input requirements for the computer program. The computer-aided predictions and experimental results from storage studies are also compared in this section. The second section in this chapter involves the illustration of the computer program output with a set of chosen input conditions.

5.1 Ascorbic Acid Degradation and Oxygen Uptake in Model System

One of the important input variables for the computer-aided mathematical model is the second-order rate constant. The rate constant is obtained from laboratory storage trials on degradation of a quality index in the given liquid food. For the purpose of this study, the rate constants were obtained for ascorbic acid degradation in an infant formula. The experimental procedures were described in Chapter IV. The results from laboratory experiments are discussed in this section.

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5.1.1 Order of the Reaction

The liquid foods prior to storage may be exposed to atmospheric oxygen. During canning or bottling operations, they may be deaerated. Thus, during storage, the dissolved oxygen in the liquid food is present in concentrations at or below that of saturation with atmospheric oxygen. Khan and Martell (1967) and Joslyn and Miller (1949b) have reported that the kinetics of ascorbic acid oxidation in a liquid is first-order when oxygen is present in concentrations above that of saturation with atmospheric oxygen. Under conditions of limited oxygen supply they indicate a nonlinear dependence of the initial rate of oxidation on oxygen concentration. In this study, the overall kinetics of this reaction under limited oxygen supply was assumed to follow second-order mechanism. The discussion of results in this section justifies this assumption.

From Equation (3-7), a plot of $\log_n$ [(A)/(B)] versus storage time should be a straight line if the second-order reaction (Equation 3-2) is followed. The plot of $\log_n$ [(A)/(B)] versus storage time for samples exposed in 1 cm cells to 4284 lux (initial dissolved oxygen = 4.86 ppm) is shown in Figure 5.1. (The data on vitamin and dissolved oxygen concentrations is tabulated in Appendix A.) The second-order rate constants were calculated from the slope of the straight line using Equation (3-7). The computer program KINFIT was used to obtain these rate constants for the various storage conditions.

Figure 5

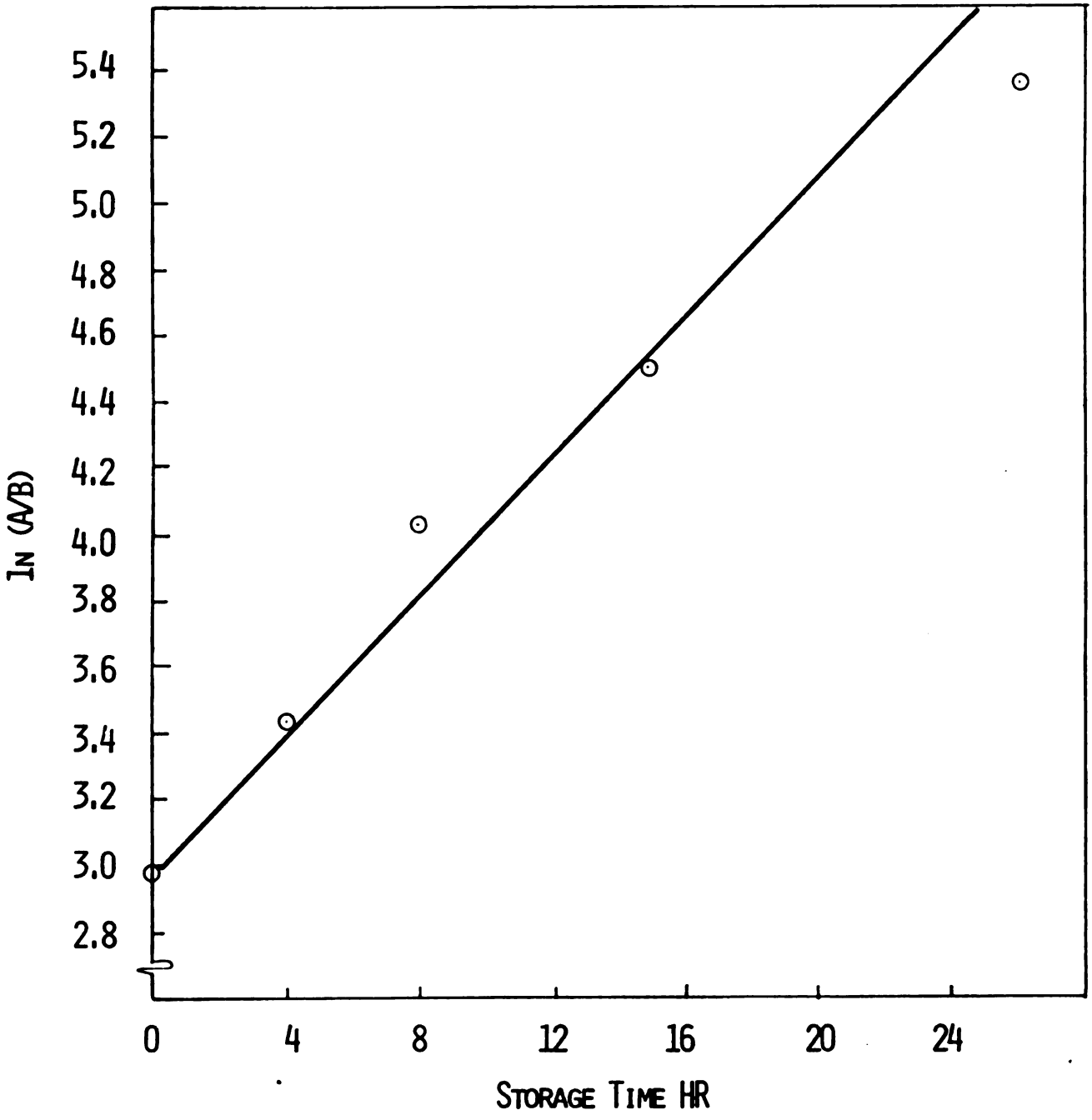

Figure 5.1.--A second-order reaction model of vitamin degradation and oxygen uptake for samples exposed to 4284 lux light intensity (initial dissolved oxygen = 4.86 ppm).

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The calculated second-order rate constants for three initial dissolved oxygen concentrations and five light intensities are presented in Table 5.1. The rate constants are based on the average of duplicate trials with five measurements during each storage trial. The low standard deviations obtained for these rate constants confirm that the reaction follows second-order kinetics. The rate constants were also calculated using concentrations with units in moles/liter, the results were similar to those reported in Table 5.1.

The increase of dissolved oxygen concentration from 4.86 ppm to 8.71 ppm in samples exposed to light results in increased rate constants. There is no significant difference in rate constants (based on one standard deviation on each rate constant) for samples with initial dissolved oxygen concentrations between 1.00 and 4.86 ppm. The rate constants show an increase when samples held in dark are compared with samples under 1071 lux light intensity.

The rate constants calculated for the trial when the initial dissolved oxygen content was 8.71 ppm (or saturation with atmospheric oxygen) is plotted as a function of transmitted light intensity in Figure 5.2. The plexiglass used in this study allowed 82 percent light transmission. The light intensity values were adjusted accordingly.

TABLE 5.1.--Second-order Rate Constants of Ascorbic Acid Degradation and Oxygen Uptake in Infant Formula Exposed to 0, 1071, 2142, 3213 and 4284 lux Light Intensities.

Incident Light Intensity	I.D.O. = 1.00 ppm		I.D.O. = 4.86 ppm		I.D.O. = 8.71 ppm	
	Rate Constant $k \times 10^4$	Std. Dev. $\times 10^4$	Rate Constant $k \times 10^4$	Std. Dev. $\times 10^4$	Rate Constant $k \times 10^4$	Std. Dev. $\times 10^4$
lux	liter/mg hr		liter/mg hr		liter/mg hr	
Dark	1.273	0.552	1.267	0.883	1.168	0.41
1071	8.654	2.170	4.782	0.522	12.759	1.32
2142	13.124	4.260	10.178	2.220	18.162	1.98
3213	5.941	2.240	9.112	1.200	16.560	3.19
4284	9.643	3.780	13.251	1.240	15.925	3.63

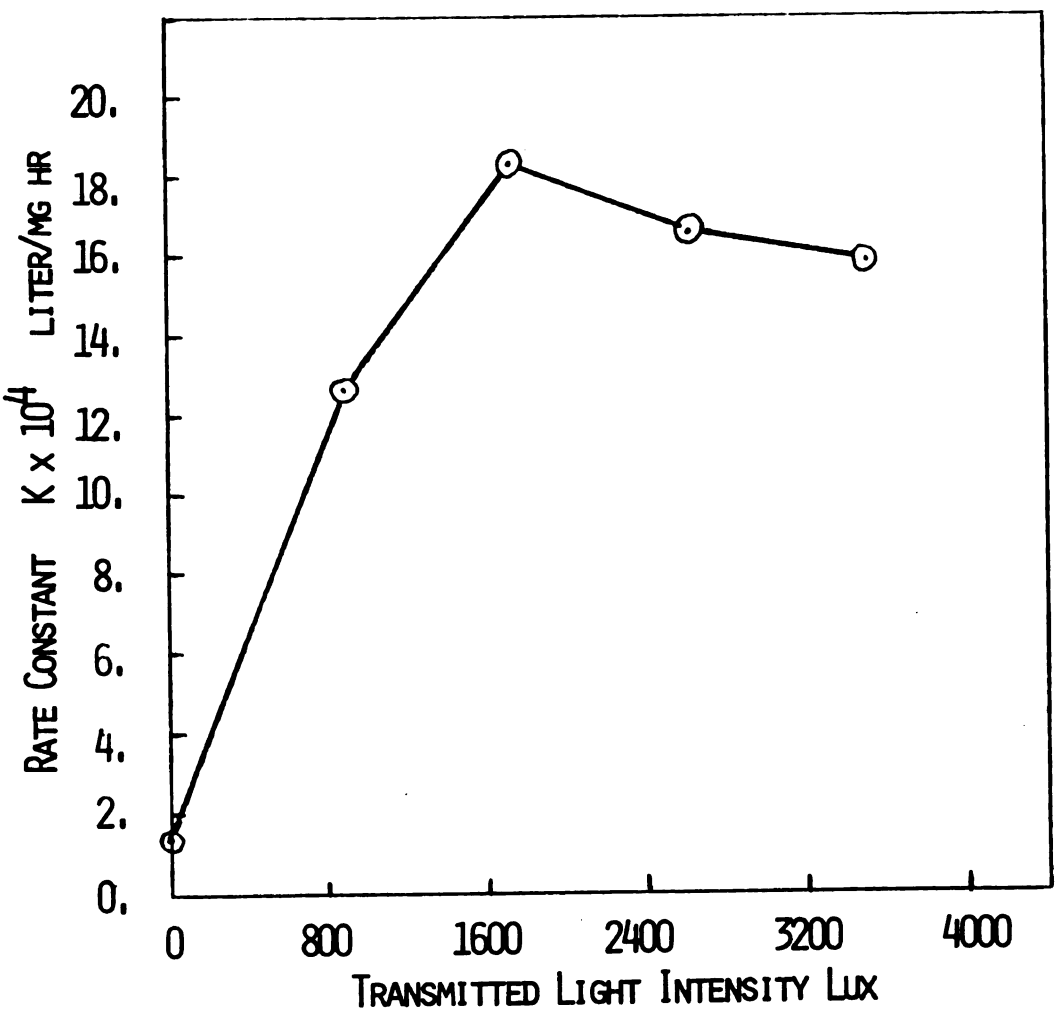

Figure 5.2.--Influence of transmitted light intensity on second-order rate constants (initial dissolved oxygen = 8.71 ppm).

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The rate constants increase linearly as a function of light intensity with a peak value at 1756 lux (transmitted) light intensity. From Figure 5.2 it appears that the rate constant decreases with increasing light intensity above 1756 lux. However, based on one standard deviation scatter, the rate constants above 1756 lux do not change significantly. Similar observations with rate constants obtained at initial dissolved oxygen concentrations of 1.00 and 4.86 ppm indicate that above 1756 lux (or 2142 lux incident light intensity) there is no significant difference in the rate constants.

Thus Equation 3-16 can be modified for the linear function as follows:

$$k = k_d + k' L_o e^{-\varepsilon x} \tag{3-28}$$

The rate constants, $\bar{k}$, obtained from 1-cm deep cells are average rate constant values, or

$$\bar{k} = \frac{\int k dx}{\int dx} \tag{3-29}$$

Substituting Equation (3-28) in (3-29) gives

$$\bar{k} = \frac{\int (k_d + k' L_o \bar{e}^{\varepsilon x}) dx}{\int dx} \tag{3-30}$$

Integrating from 0 to 1 (for 1 cm cell)

$$\bar{k} = kd - k' \frac{L_o}{\varepsilon} (\bar{e}^{\varepsilon} - 1) \tag{3-31}$$

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Equation (3-31) is solved for k'. The extinction coefficient is calculated by assuming 99 percent light extinction in the 1-cm layer. This assumption is valid for milk and similar opaque liquid foods. Further discussion on this assumption is presented in section 5.1.2.

With the knowledge of k', k_d, ϵ and incident light intensity, Equation 3-28 is used to calculate rate constant at any depth inside a liquid medium.

The information obtained in the experimental measurements of rate constants is incorporated in the subroutine RATE of the computer program.

5.1.2 Influence of Depth with Respect to Light Source on Rate of Vitamin Degradation

In section 5.1.1, it was assumed that there is 99 percent light extinction in the 1-cm layer of infant formula along the walls of the container. This assumption is justified from the results obtained from storage experiments when 3-cm deep, divided cells were used. The results are presented in Figure 5.3. Maximum loss of vitamin occurred in the top 1 cm layer. The losses in the middle and bottom layers are comparable to those of dark storage. The dissolved oxygen concentration history is shown in Figure 5.4. The second-order rate constants obtained from the data of middle and bottom layer did not show any significant difference.

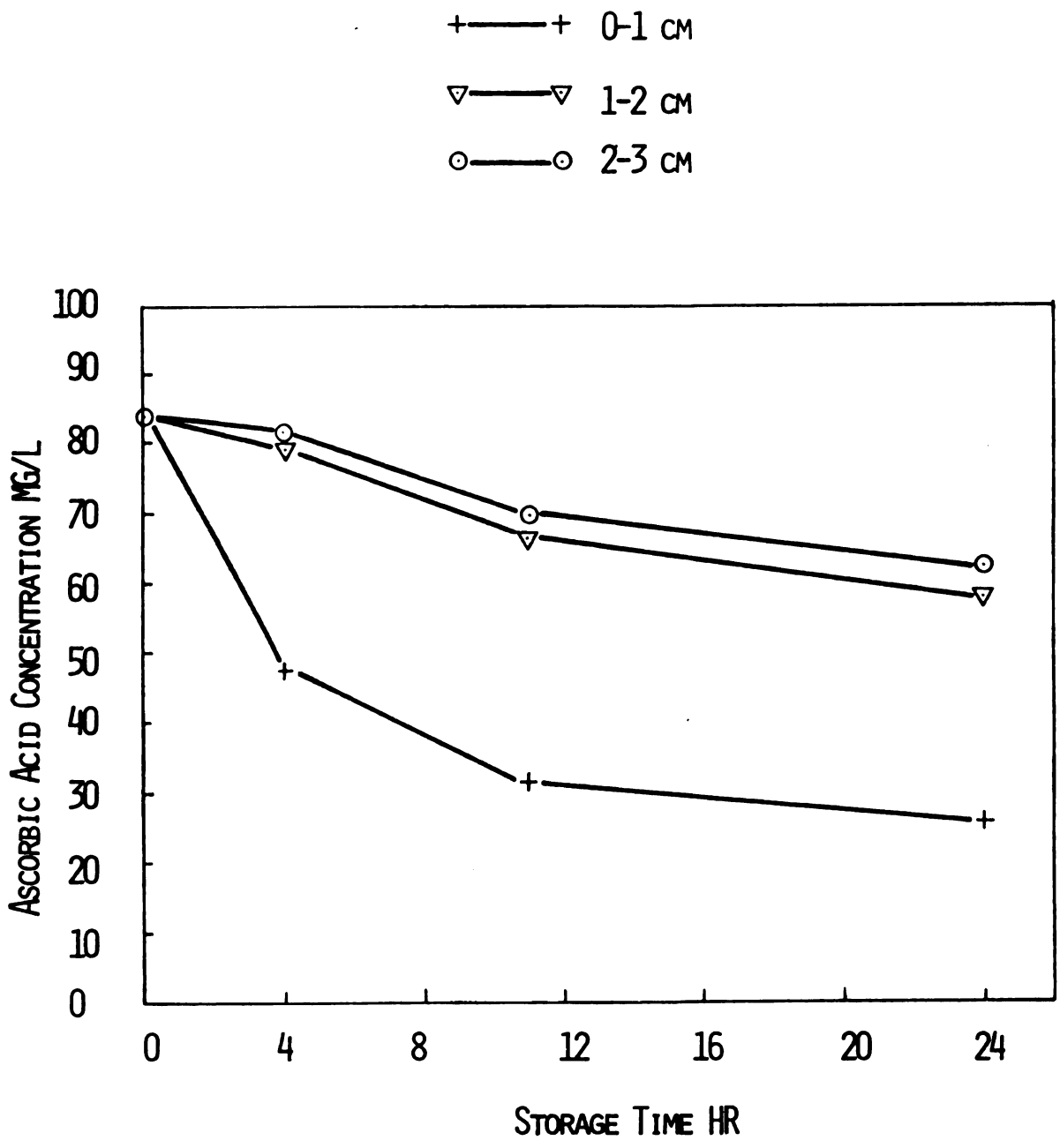

Figure 5.3.--Ascorbic acid degradation in infant formula exposed to 4284 lux light intensity in a 3-cm divided cell.

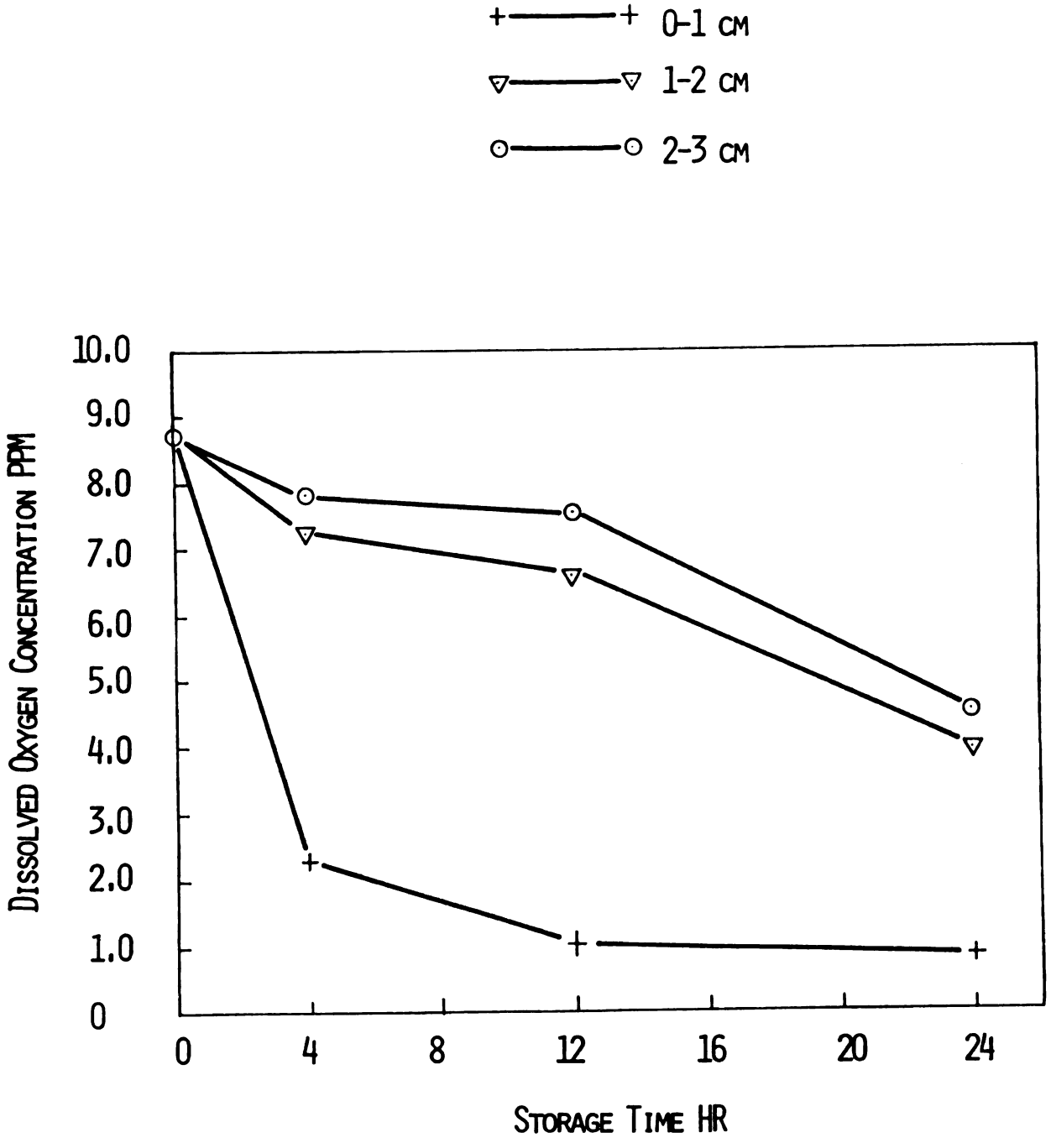

Figure 5.4.--Dissolved oxygen uptake in infant formula exposed to 4284 lux light intensity in a 3-cm divided cell.

In another trial, 3-cm deep divided and undivided cells were used. The ascorbic acid concentration data plotted as a function of time is presented in Figure 5.5. The calculated mass average of the concentrations in three layers is comparable with the concentration values for the undivided cell. It is acknowledged that there is 82 percent light transmission through plexiglass. Therefore, in a divided cell, there is less light intensity reaching the middle layer than in an undivided cell. These results indicate that the outside layer (approximately 1 cm) experiences vitamin loss influenced by light. These results on light extinction in infant formula are comparable with the studies of Burgess and Herrington (1955b).

The above results indicate that the vitamin degradation in liquid foods exposed to light occurs mainly in a thin layer along the walls of the container. The thickness of this layer depends on the incident light intensity. The contents in the central region of the container do not experience any losses due to light. There is, however, degradation of the vitamin in the central region due to the dissolved oxygen concentration. The vitamin losses in the central region would be comparable to losses under dark conditions.

5.1.3 Influence of Light Intensity on the Rate of Vitamin Degradation

The reduced ascorbic acid concentration history in infant formula exposed to light in experimental cells is

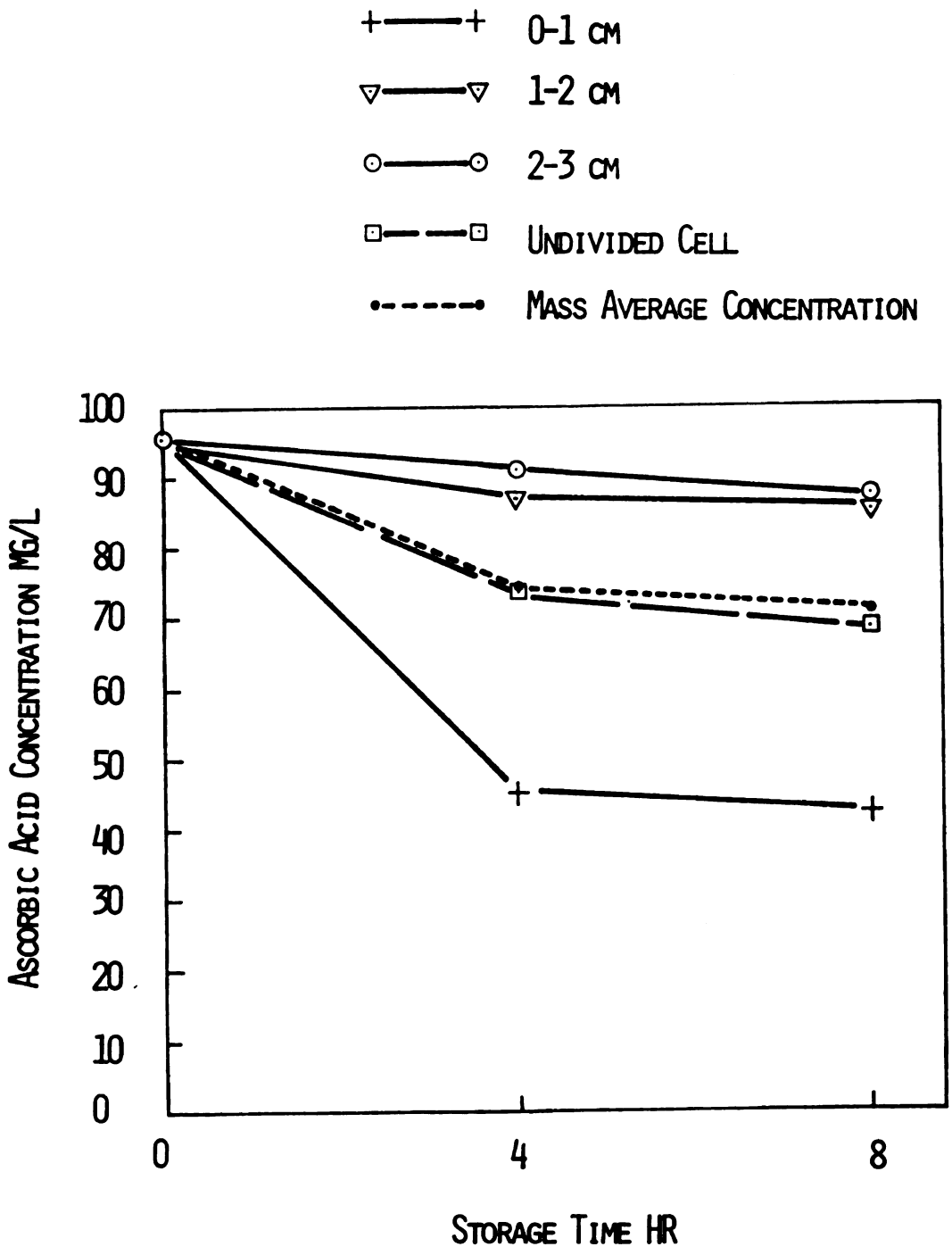

Figure 5.5.--Ascorbic acid degradation in infant formula exposed to 4284 lux light intensity in 3-cm divided and undivided cells.

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presented in Figure 5.6. In this trial, the initial dissolved oxygen concentration in the infant formula samples was 8.71 ppm. The rate of vitamin degradation in samples held in dark storage is small compared to the samples exposed to light during storage. These results indicate that increase in light intensity increases the rate of vitamin degradation.

Trials conducted at 535 lux (50 ft-c) showed more vitamin loss than the trials under dark conditions (Figure 5.7). This indicates that even a low light intensity has a detrimental effect on the vitamin. The trends of vitamin loss and oxygen uptake between 0 to 4 hour intervals are shown in Figure 5.7. The two-hour concentration values fall in line with 0 to 4 hour values. This trend confirms the validity of measuring vitamin concentration at four-hour intervals.

The experimental data of ascorbic acid concentration and dissolved oxygen concentration at five light intensities (dark, 1071 lux, 2142 lux, 3213 lux and 4284 lux) and three initial dissolved oxygen concentrations (1.00 ppm. 4.86 ppm and 8.71 ppm) are presented in Tables A.1, A.2, A.3, A.4, A.5, and A.6 (Appendix A).

5.1.4 Influence of Dissolved Oxygen on Rate of Vitamin Degradation

An important observation from Figure 5.6 is the gradual decrease in the rate of vitamin degradation as the storage time increases in samples exposed to light. This

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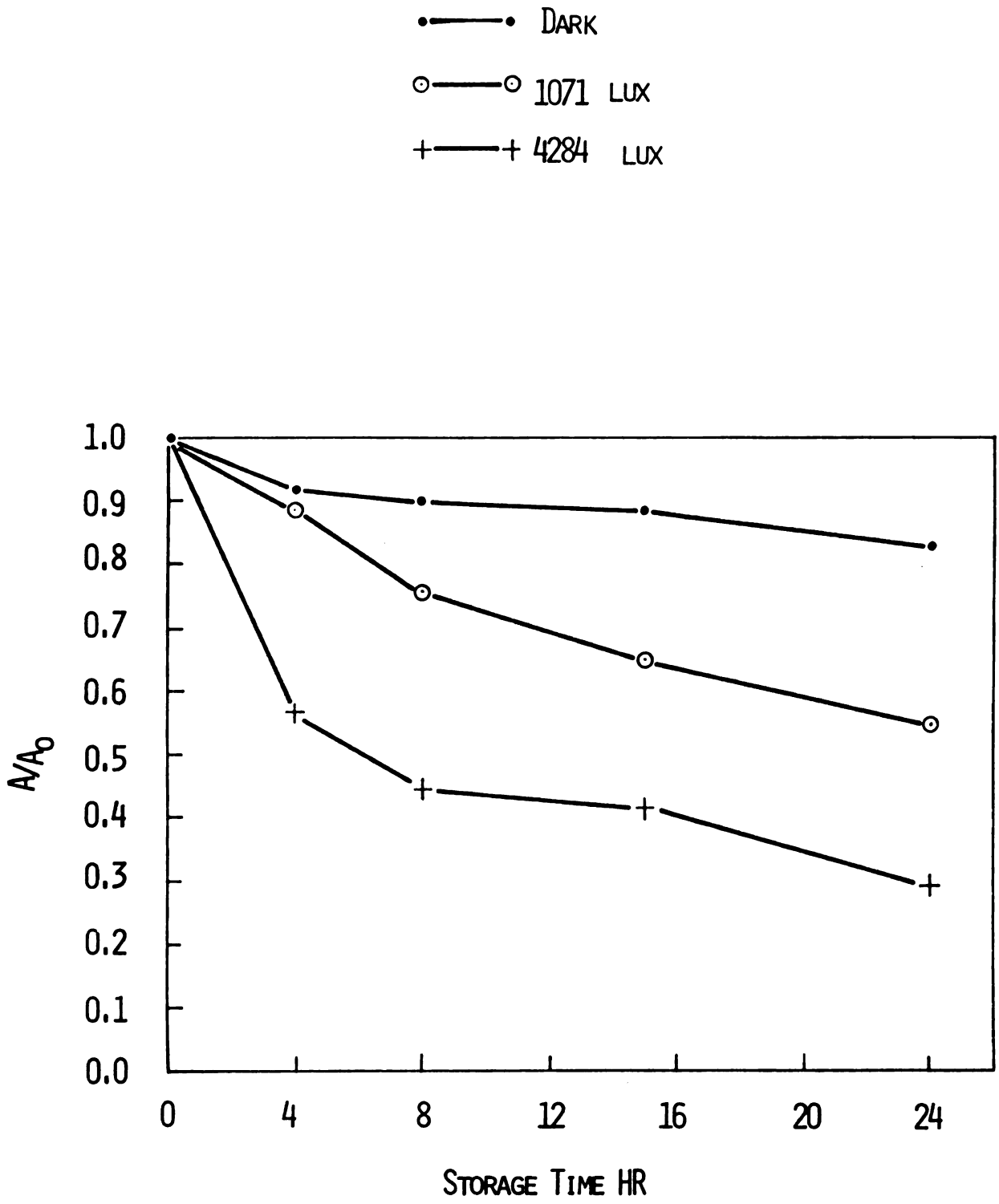

Figure 5.6.--Ascorbic acid degradation in infant formula exposed to 0, 1071 and 4284 lux light intensities in 1-cm cells (initial dissolved oxygen = 8.71 ppm).

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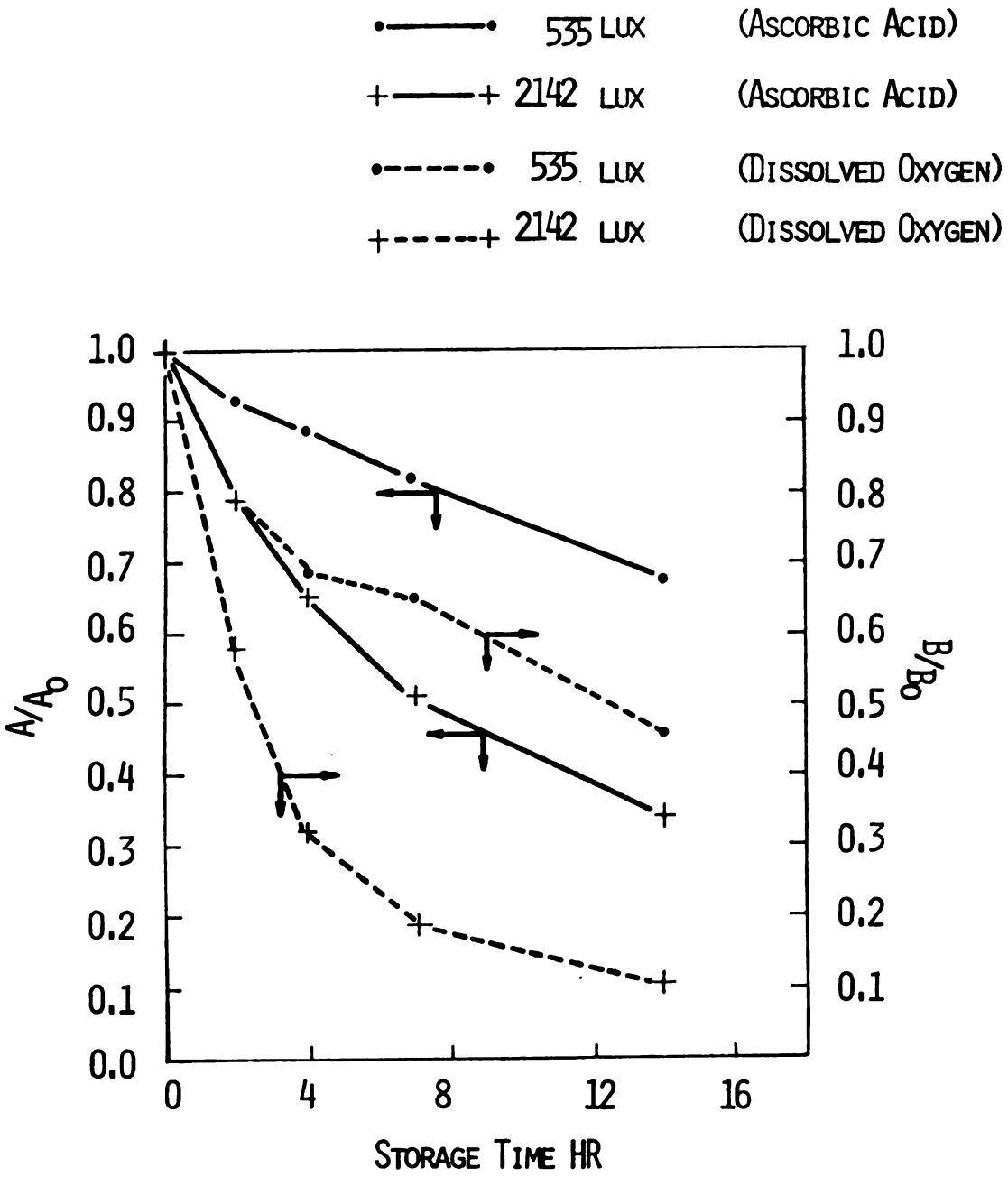

Figure 5.7.--Ascorbic acid degradation and dissolved oxygen uptake in infant formula exposed to 535 lux and 2142 lux light intensity in 1-cm cells.

indicates that the reaction rate is initially high, and reduces with time. The dissolved oxygen concentration history in different cells, exposed to same conditions as in Figure 5.6, is shown in Figure 5.8. This figure confirms that dissolved oxygen is consumed very rapidly and is in limited supply. The limited presence of oxygen results in the observed reduction of the rate of vitamin degradation at longer storage times.

An attempt was made to observe the vitamin degradation when dissolved oxygen is present in abundant supply. Joslyn and Miller (1949b) earlier reported that the ascorbic acid oxidation in a liquid medium is first-order when oxygen is present in concentrations above saturation with atmospheric oxygen.

The ascorbic acid history in infant formula with dissolved oxygen concentrations above atmospheric saturation is presented in Figure 5.9. The straight line relationship obtained on semi-log coordinate paper indicates that the vitamin degradation is first-order. The dissolved oxygen concentration during the experiment was above 0.21 atmosphere (or above saturation with atmospheric oxygen). The dissolved oxygen concentration data is presented in Table A.7 (Appendix A). The experiment confirms that the vitamin loss is first-order when oxygen is present in abundant supply. Under realistic conditions, however, liquid foods are exposed to oxygen concentrations at or below saturation with atmospheric oxygen, as a result

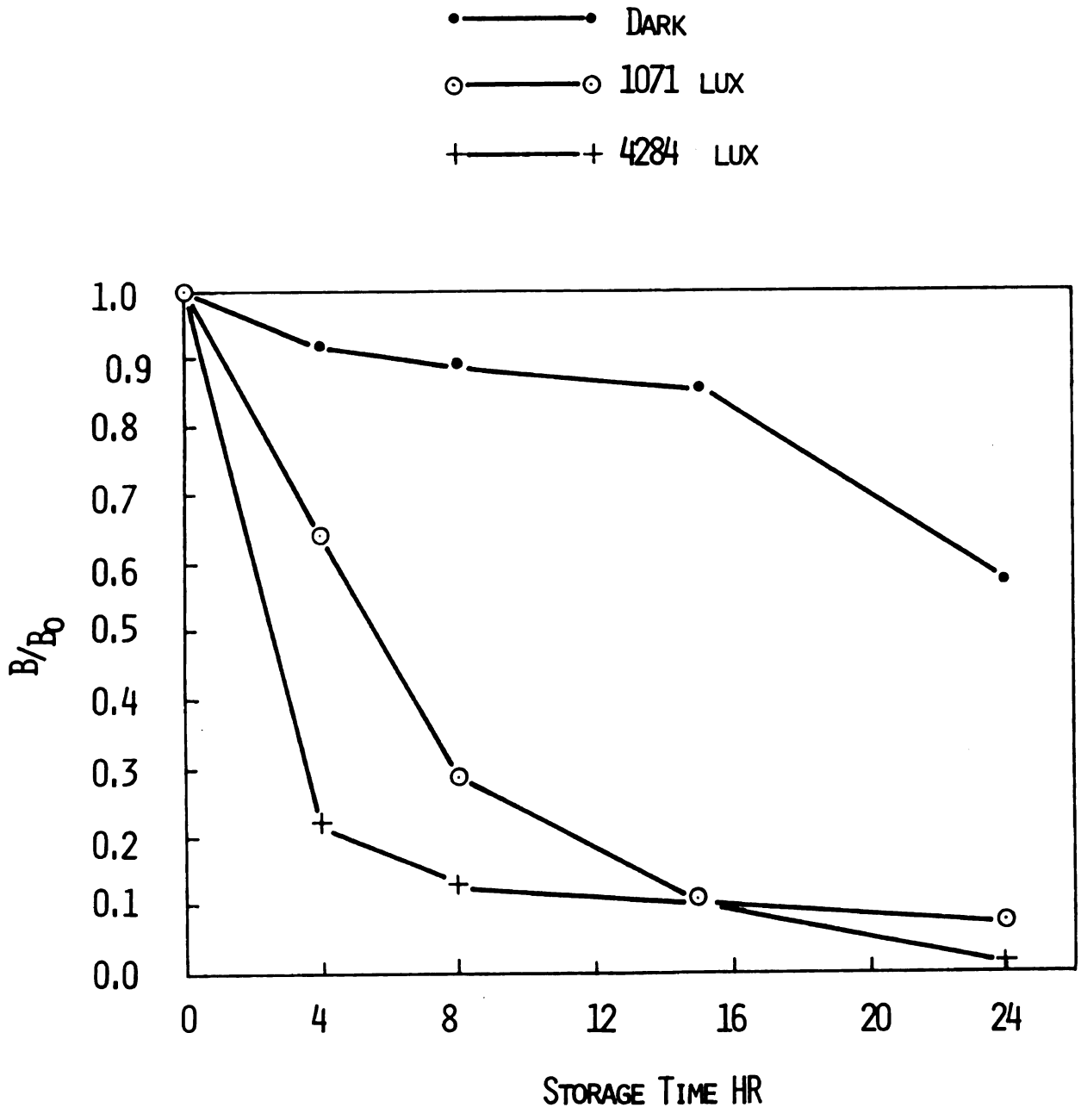

Figure 5.8.--Dissolved oxygen uptake in infant formula exposed to 0, 1071 and 4284 lux light intensities in 1-cm cells.

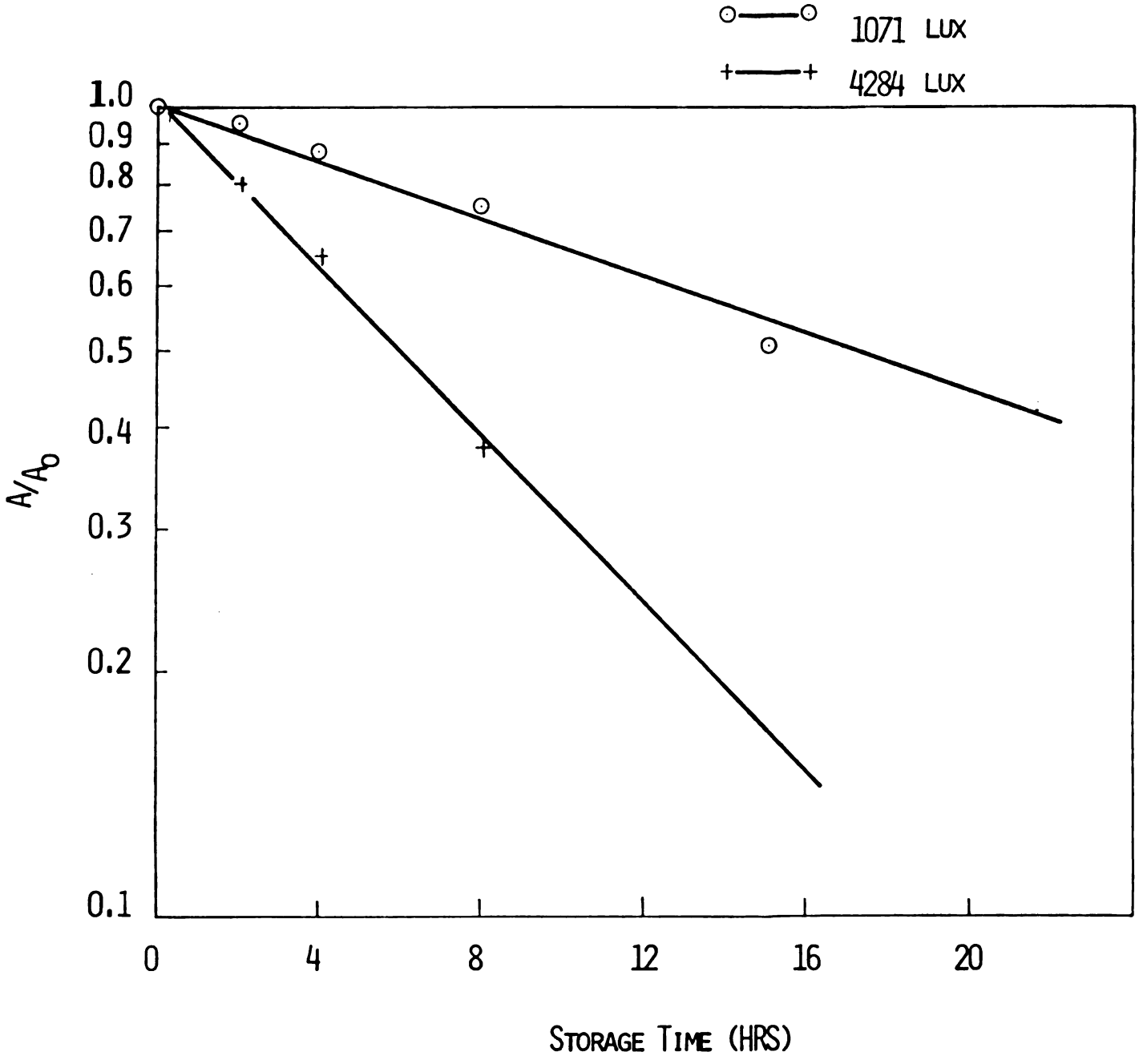

Figure 5.9.--Ascorbic acid degradation in the presence of dissolved oxygen concentrations above saturation with atmospheric oxygen.

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oxygen is present in limited supply. Under these conditions, the ascorbic acid oxidation can be best described by a second-order reaction as discussed in section 5.1.1.

5.1.5 Comparison of Results from Computer Model and Storage Trials

In this section, results from five storage trials on ascorbic acid degradation in glass and plastic bottles are compared with computer-predicted results. As indicated earlier, the computer model was developed for rectangular geometry. The storage trials were, however, conducted in cylindrical shaped bottles of 6 cm diameter commonly used for marketing infant formula. These bottles were exposed to the desired light intensity on two sides. The results from storage trials are presented in Tables A.8 and A.9 (Appendix A).

The computer program was provided with the initial concentration values of ascorbic acid and dissolved oxygen. The diffusion coefficients of ascorbic acid (assumed to be same for glucose molecule) and oxygen were obtained from Weast (1971) and Danckwerts (1970), respectively. These coefficients are 1.36×10^{-5} cm^2/sec (for oxygen) and 0.673×10^{-5} cm^2/sec (for vitamin). A space increment of 0.0625 cm and a time increment of 0.125 hr was selected. Decreasing these increments to still smaller values did not change the mass average concentrations significantly.

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Trial 1.--Infant formula was exposed to 4284 lux light intensity in a glass bottle. The initial dissolved oxygen concentration was 8.71 ppm. The experimentally measured concentrations along with the computer predicted time history are shown in Figure 5.10. The standard deviations are 5.10 percent of initial ascorbic acid concentration and 2.86 percent of initial dissolved oxygen concentration.

Trial 2.--Infant formula with initial dissolved oxygen concentration of 4.86 ppm in a glass bottle was exposed to 535 lux light intensity. The experimental results and computer-predicted concentrations are illustrated in Figure 5.11. The standard deviations are 1.43 percent of initial ascorbic acid concentration and 5.71 percent of initial dissolved oxygen concentration.

Trial 3.--Infant formula with initial dissolved oxygen concentration of 4.86 ppm in a glass bottle was exposed to 4284 lux light intensity. The experimental results and computer-predicted concentrations are illustrated in Figure 5.12. The standard deviations are 2.53 percent of initial ascorbic concentration and 5.65 percent of initial dissolved oxygen concentration.

Trial 4.--Infant formula was exposed to 1071 lux light intensity in a plastic bottle. The initial dissolved oxygen concentration was 8.71 ppm. The results are illustrated in Figure 5.13. The standard deviations

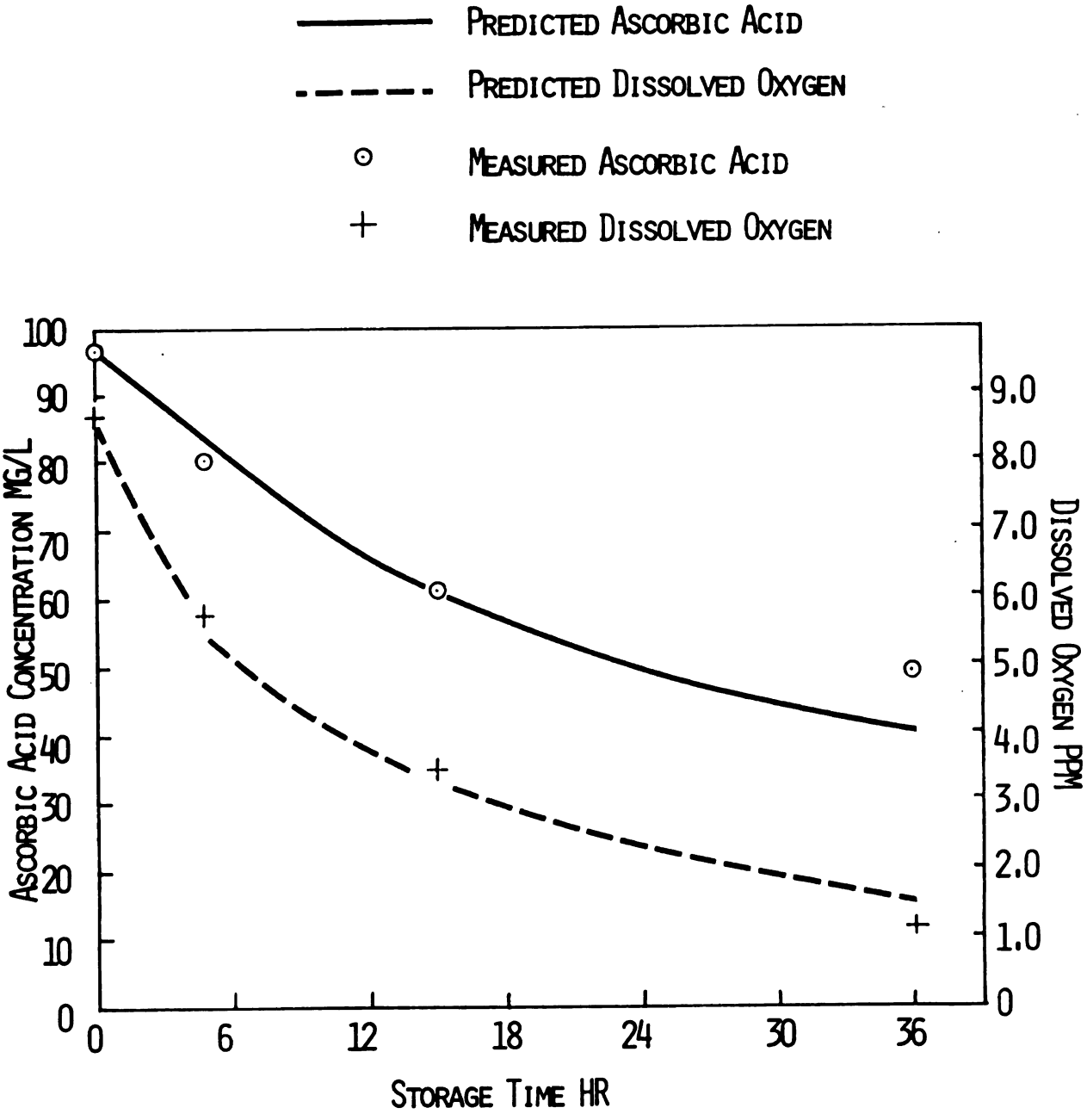

Figure 5.10.--Computer-predicted and experimentally determined reduced ascorbic acid and dissolved oxygen concentration history in infant formula in glass bottles under 4284 lux light intensity.

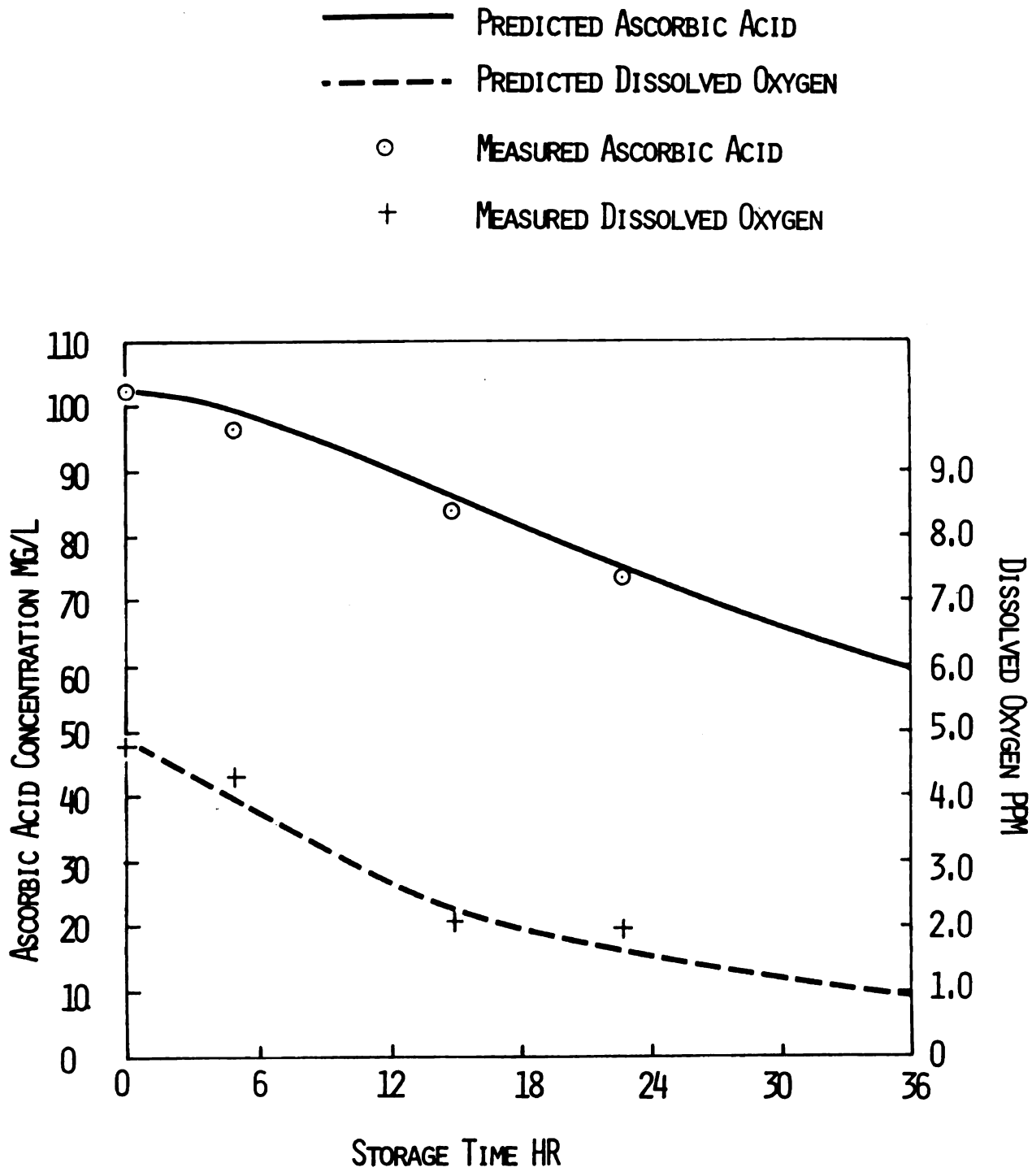

Figure 5.11.--Computer-predicted and experimentally determined reduced ascorbic acid and dissolved oxygen concentration history in infant formula in glass bottles under 535 lux light intensity.

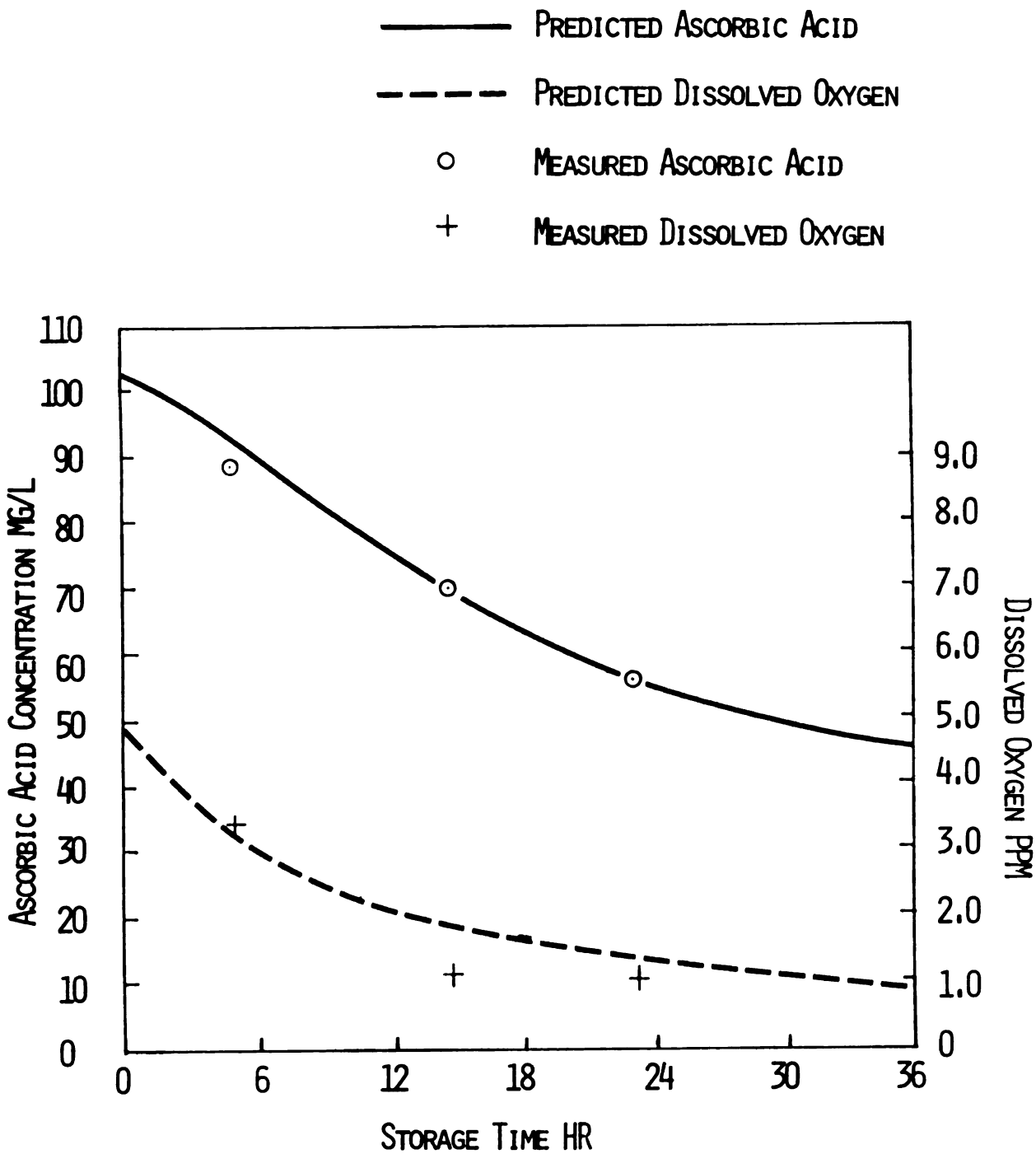

Figure 5.12.--Computer-predicted and experimentally determined reduced ascorbic acid and dissolved oxygen concentration history in infant formula in glass bottles under 4284 lux light intensity.

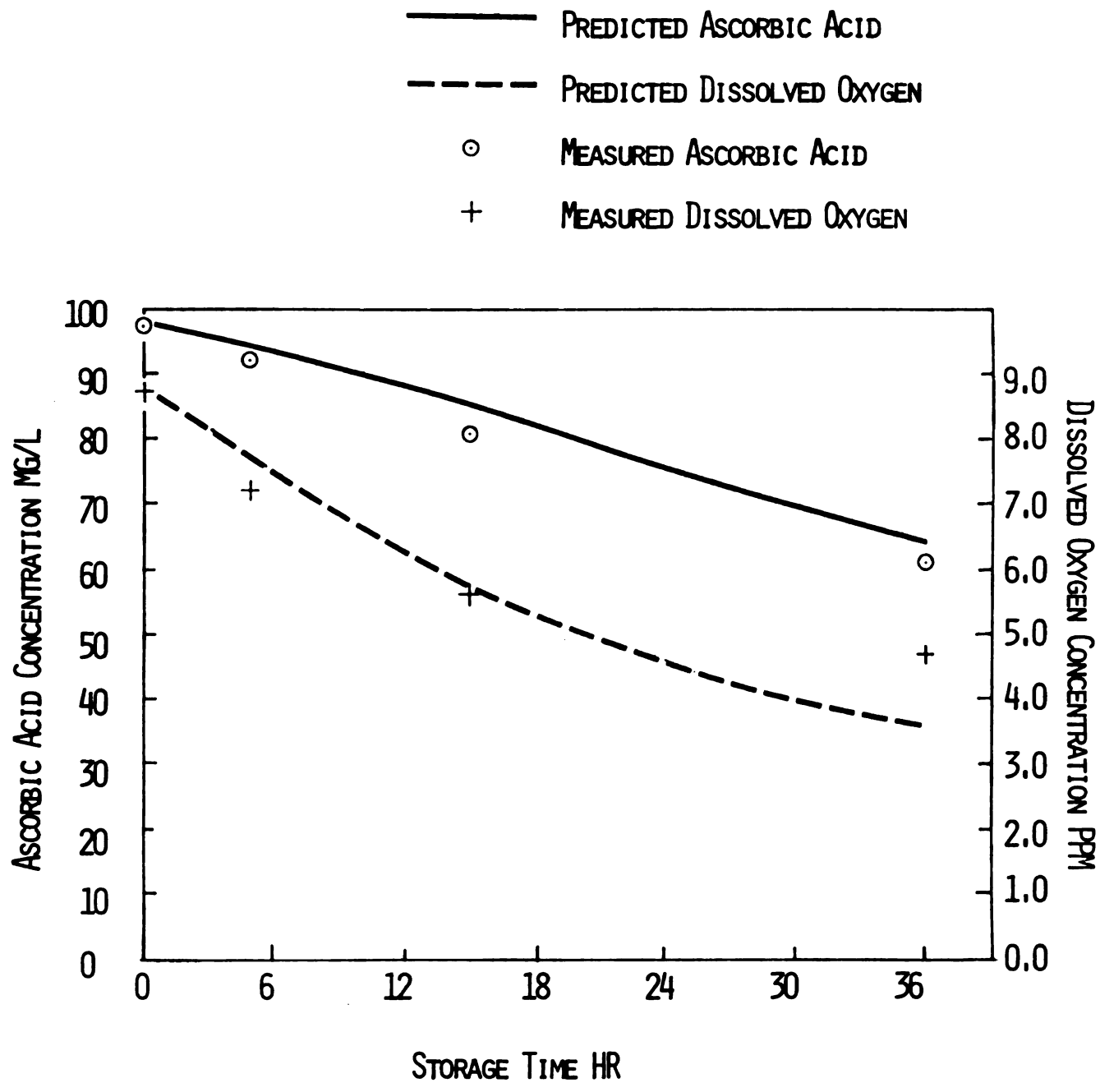

Figure 5.13.--Computer predicted and experimentally determined reduced ascorbic acid and dissolved oxygen concentration history in infant formula in plastic bottles under 1071 lux light intensity.

are 2.74 percent of initial ascorbic acid concentration and 7.01 percent of initial dissolved oxygen concentration.

Trial 5.--Infant formula with 4.86 ppm initial dissolved oxygen concentration in plastic bottle was exposed to 535 lux light intensity. The results obtained from storage trial and those predicted are shown in Figure 5.14. The standard deviations are 3.68 percent of initial ascorbic acid concentration and 3.78 percent of initial dissolved oxygen concentration.

The small deviations between the predicted and the experimentally measured concentrations are due to one or more of the following reasons: (1) the assumed permeability constant for the plastic container, (2) the inherent errors in experimental measurements, and (3) the assumed rectangular geometry for the cylindrical shaped containers.

In the following section, a general discussion on the various capabilities of the computer program developed in this study are discussed.

5.2 Computer-Aided Prediction of Quality Deterioration in Liquid Foods

The mathematical model developed in this study is based on a second-order reaction between the quality index and oxygen. Thus, a quality degradation reaction in a liquid food which follows a second-order rate kinetics can be predicted by this computer program. The computer output includes information on the quality index and dissolved

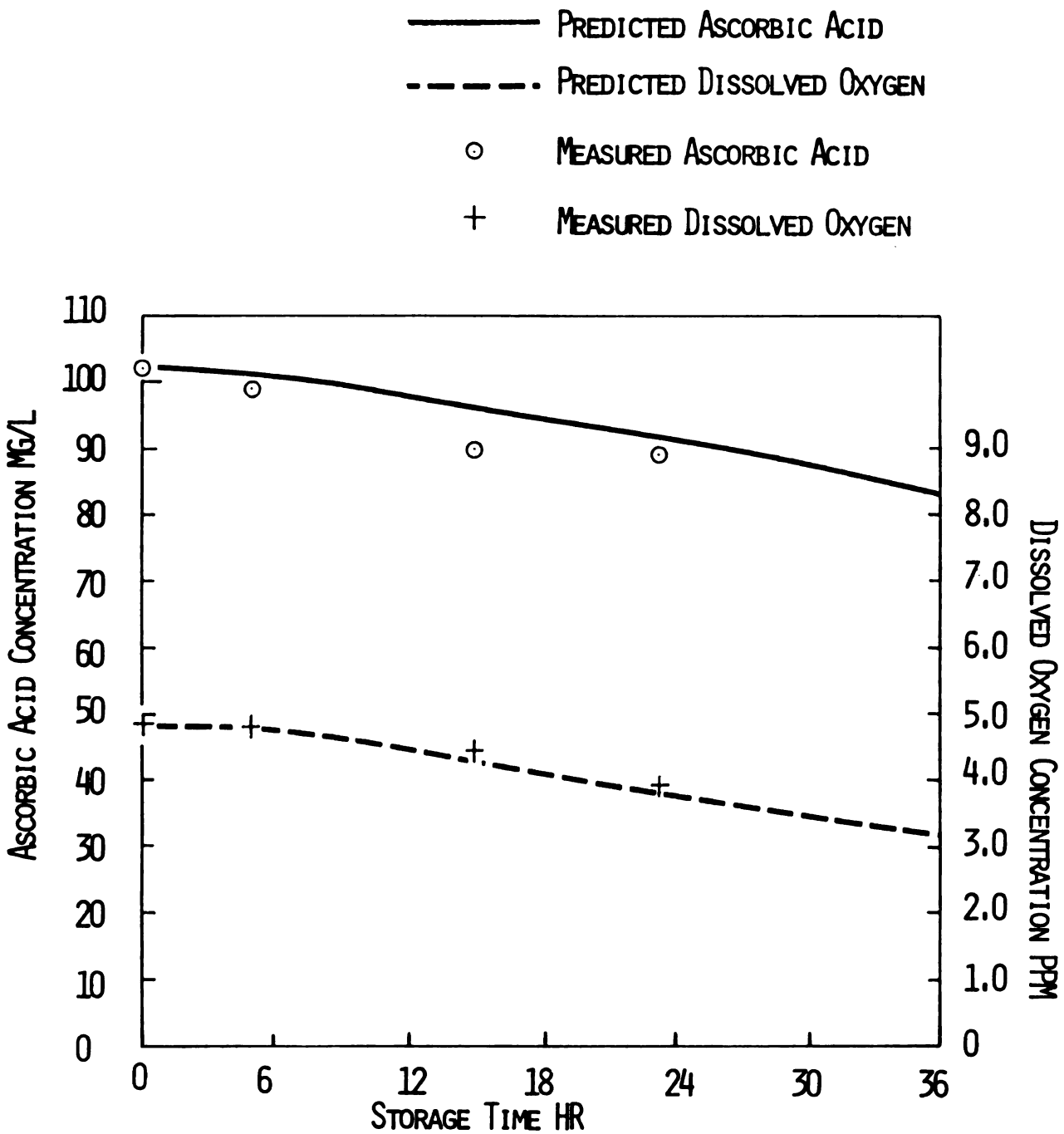

Figure 5.14.--Computer predicted and experimentally determined reduced ascorbic acid and dissolved oxygen concentration history in infant formula in plastic bottles under 535 lux light intensity.

oxygen concentration as a function of time at various locations inside the container. In addition, the program predicts the mass average concentrations of the quality index and dissolved oxygen as a function of time.

As an illustration, the following information was provided as input conditions to the computer. The quality index used in this illustration is vitamin concentration.

Type of container = Glass

Initial vitamin concentration = 100 mg/liter

Initial dissolved oxygen content = 8.71 ppm

Incident light intensity = 2142 lux

Cross-sectional width of the container = 6.0 cm

Sides exposed to light = 2 (opposite)

Diffusion coefficient of oxygen = 1.36×10^{-5} cm^2/sec

Diffusion coefficient of vitamin = 0.673×10^{-5} cm^2/sec

Space increment = .0625 cm

Time increment = 0.125 hr

Total time of storage = 36 hr.

For the above input, the vitamin concentration history along the container wall and at the center are plotted in Figure 5.15. As expected, the vitamin degradation along the wall is very rapid. The decrease in vitamin concentration occurs at a much slower rate in the central core of the container. Figure 5.15 illustrates the mass average concentration of the vitamin, also. The

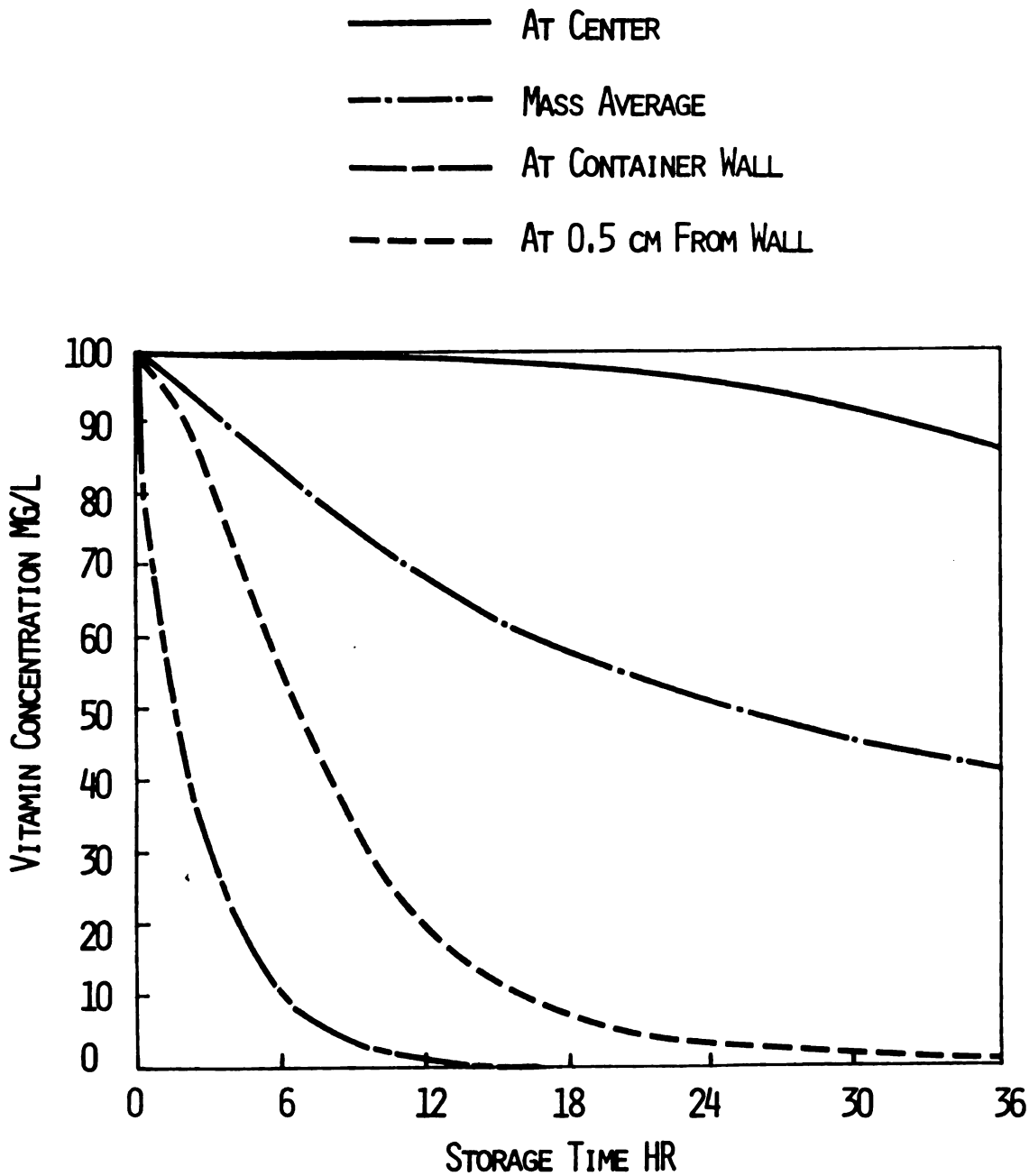

Figure 5.15.--Computer prediction of vitamin concentration history in a glass container (for conditions see page 71).

time history of dissolved oxygen concentration at these locations is plotted in Figure 5.16. The decrease is very rapid initially, indicating a rapid uptake of oxygen by contents due to oxidation reactions within the container.

The vitamin concentration at various locations and times inside a container is presented in Figure 5.17. The significant decrease in the vitamin concentration occurs in the 1 cm layer along the wall of the container. The vitamin destruction rate in the 1 to 2 cm layer increases due to diffusion as the storage time increases.

The influence of different light intensities on the rate of vitamin destruction is shown in Figure 5.18. The input parameters are the same as in Figure 5.15, except for the light intensity value. As expected, the mass average vitamin degradation is greater at higher light intensities.

The influence of the container size on rate of mass average vitamin loss is presented in Figure 5.19. The input variables were held constant except for the cross-sectional width of the container. The vitamin loss is increased as the size of container is decreased. This indicates that light intensity is more detrimental to the nutrient when the liquid food is stored in smaller size (or smaller cross-sectional width) containers.

The initial dissolved oxygen content is another important variable which determines the rate of vitamin degradation in a liquid food. The influence of this factor is illustrated in Figure 5.20. The high initial dissolved oxygen concentration results in accelerated loss of vitamin.

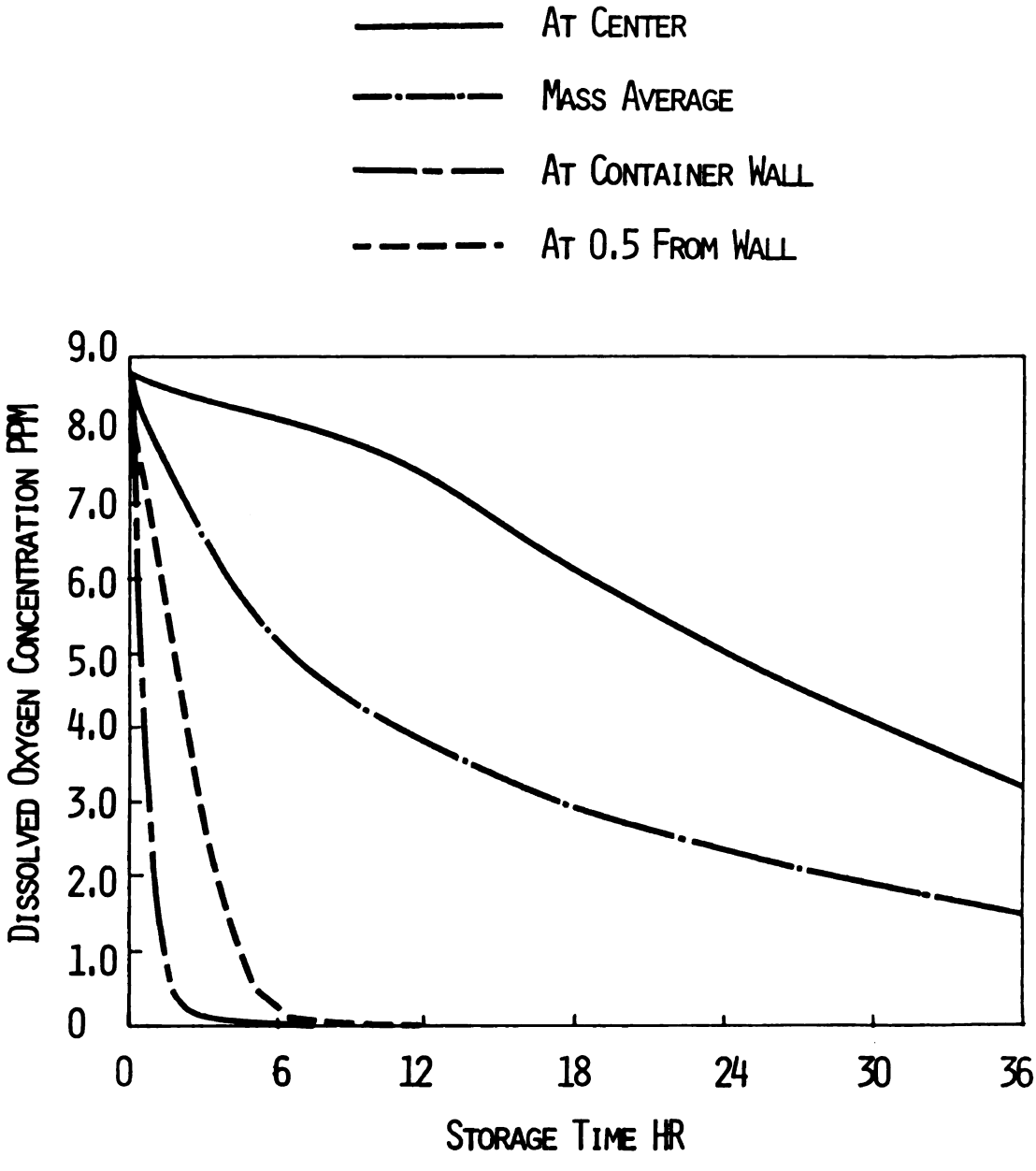

Figure 5.16.--Computer prediction of dissolved oxygen concentration history in a glass container (for conditions see page 71).

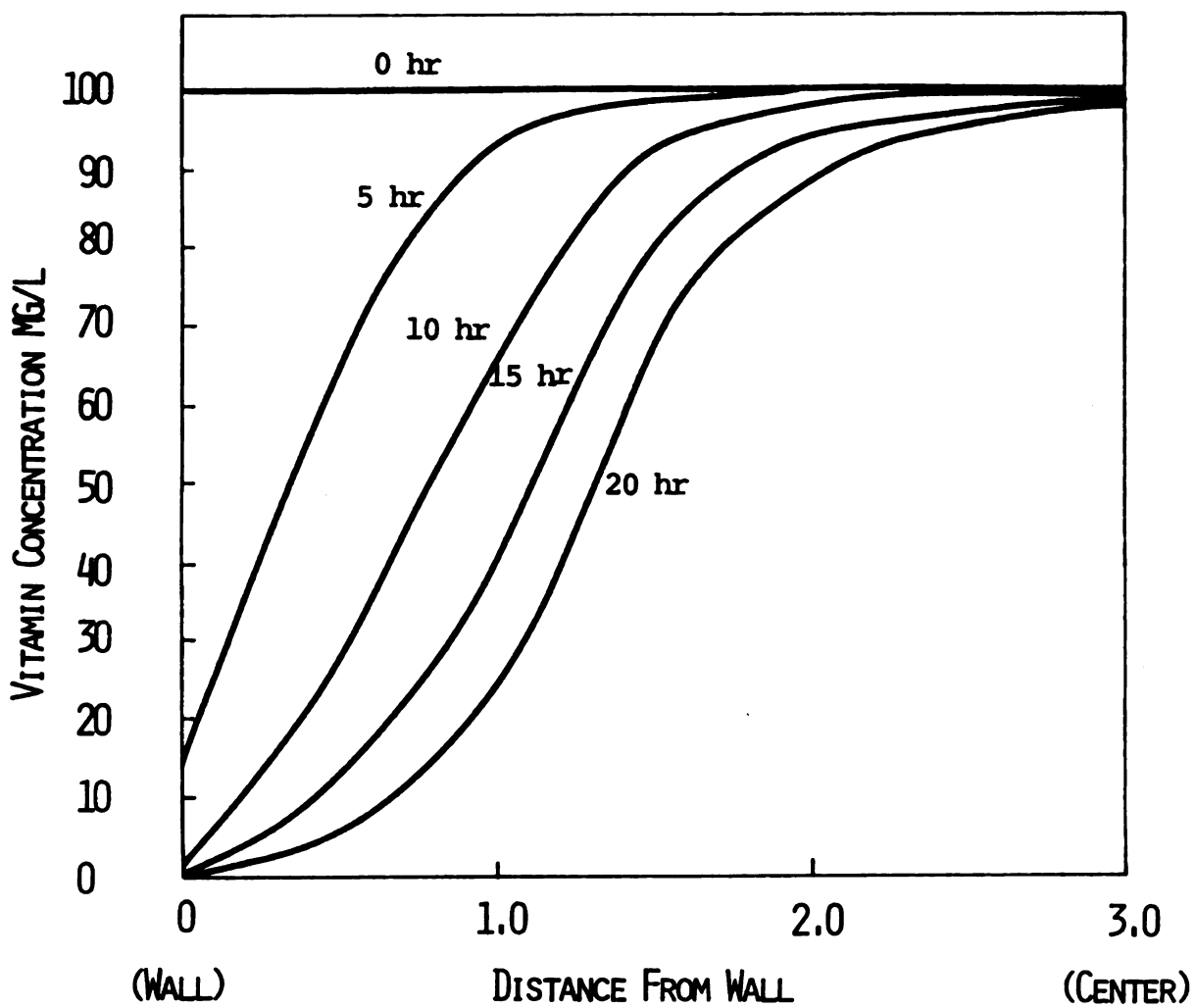

Figure 5.17.--Computer prediction of vitamin degradation as a function of location inside a glass container.

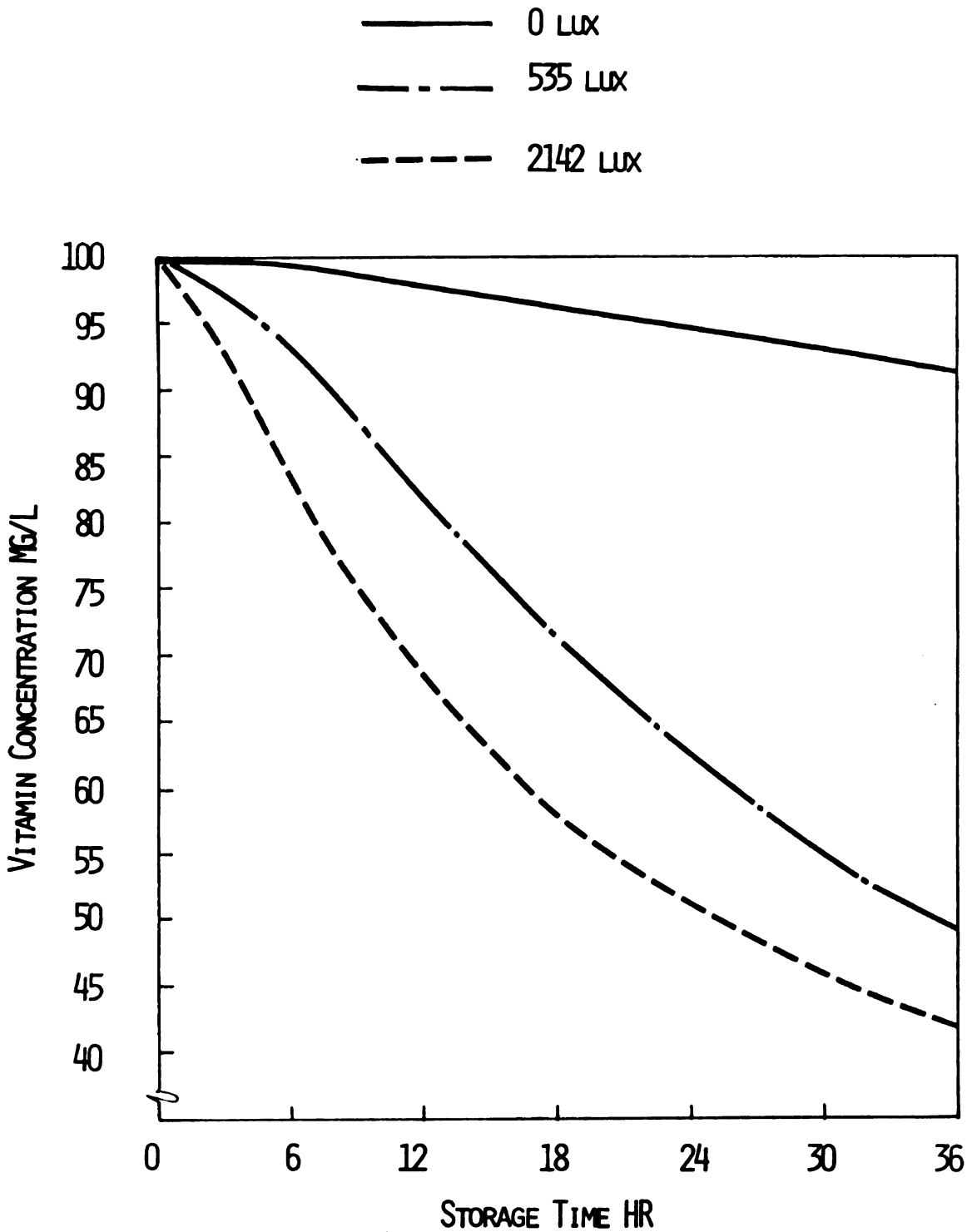

Figure 5.18.--Influence of light intensity on predicted mass average vitamin concentration history in a glass container.

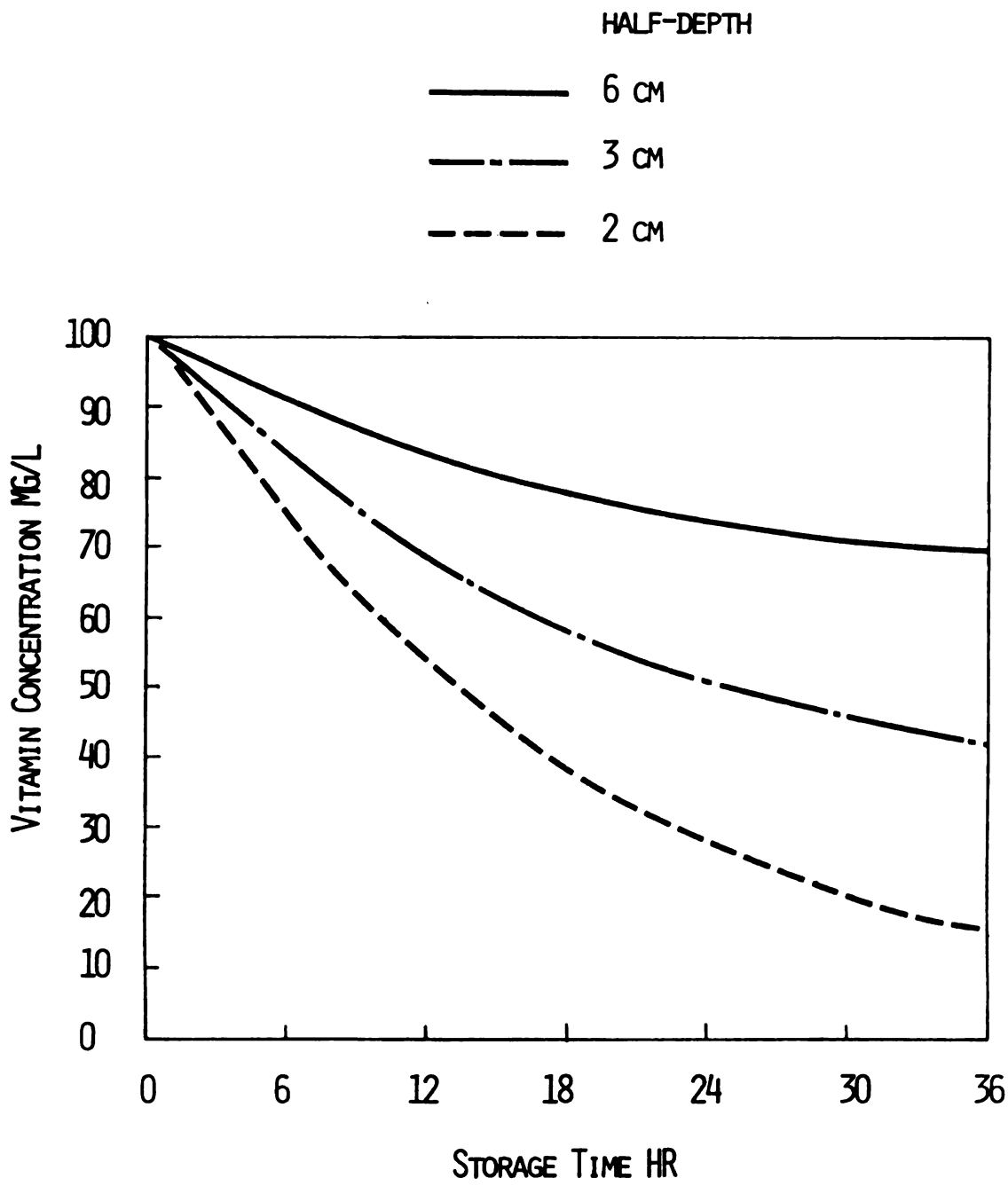

Figure 5.19.--Influence of container size on vitamin concentration history.

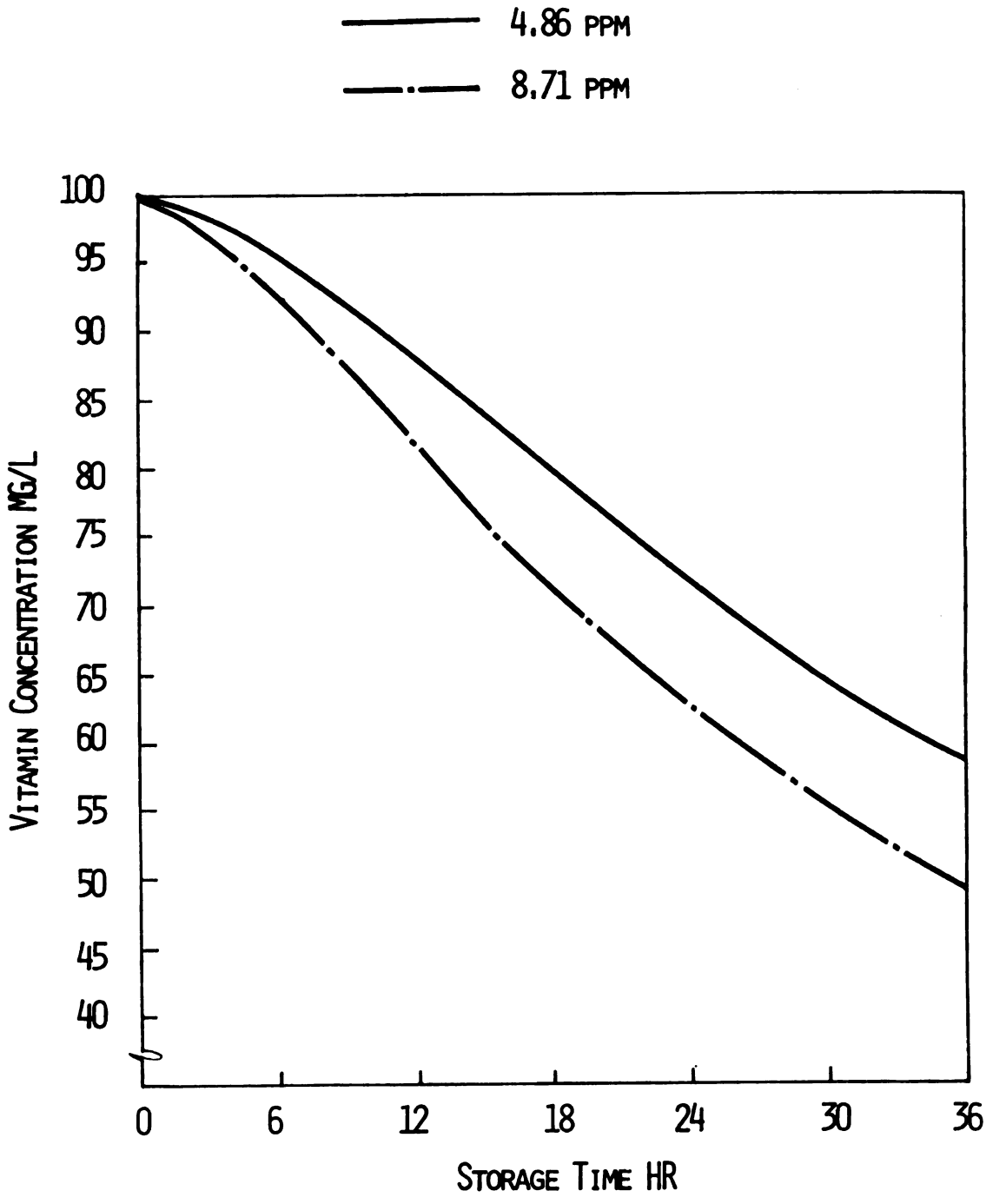

Figure 5.20.--Influence of initial dissolved oxygen concentration on predicted mass average vitamin concentration history (light intensity = 535 lux).

An attempt was made to compare the rate of vitamin degradation in a plastic bottle (permeable to oxygen) with rate in a glass bottle. The oxygen permeability coefficient for plastic is 3000 cc mil/day m^2 atm (Karel, 1974). The results are plotted in Figure 5.21. These results show the significance of light transmission through the container wall. The rate of vitamin degradation in a glass bottle is more accelerated than the rate in a plastic container with 20 percent light transmission (through the wall). During the storage time the dissolved oxygen concentration in the plastic container is maintained at a higher level than in glass container. It is apparent that light transmission through the container wall plays a major role in the light-induced destruction of vitamin..

The preceding results illustrate the capabilities of this computer-aided prediction model. As indicated earlier, the program requires specific values for rate constants describing vitamin degradation and oxygen uptake. These rate constants are obtained from experimental studies as discussed in the Experimental section.

An attempt was made to observe the influence of smaller time increments on the predicted results. It was found that with a time increment of .0625 hr the mass average concentration value changed by less than 0.25 percent. Similarly decreasing the depth increment from .0625 cm to .03125 cm did not significantly change the predicted results. The computer time used for the time

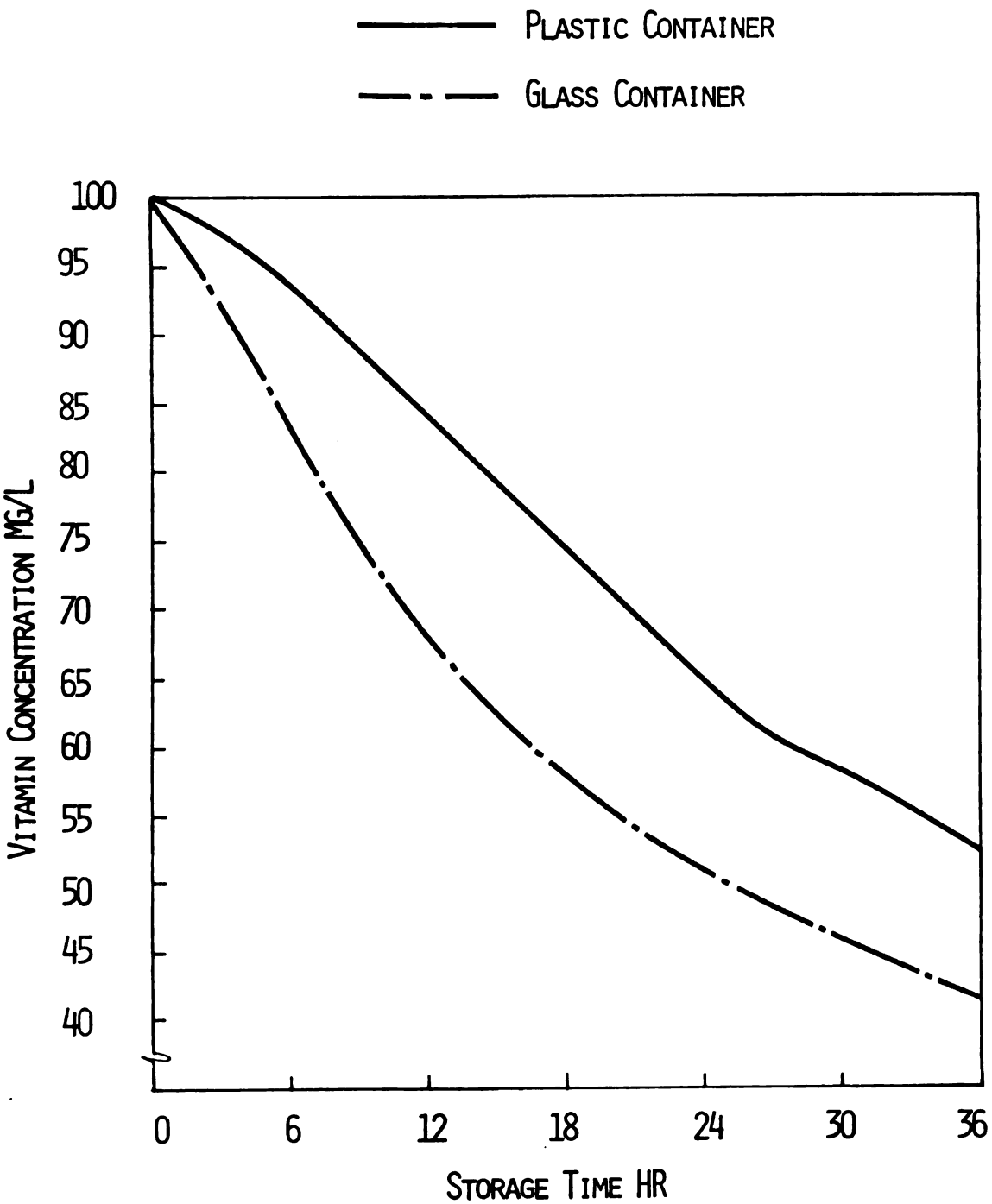

Figure 5.21.--Influence of the type of container on predicted mass average vitamin concentration history.

increment of 0.13 hr for total storage time of 36 hours was 10 seconds.

In developing the theory in section 3.2 it was assumed that the thermal convective diffusion in the liquid is negligible. In a real situation if there is a large temperature differential present inside the container, it may result in convective currents in the liquid. The convective currents in this situation would result in increased light-induced loss of vitamin than predicted from the simulation developed in this study. Similarly, the diffusion coefficients will vary depending on the temperature and may influence the total light-induced vitamin loss. The predicted results, as indicated in the assumptions, are valid for a situation where the storage temperature is maintained constant.

The results obtained in section 5.1.5 indicate that the computer model developed in this dissertation can be successfully used in predicting ascorbic acid degradation in infant formula stored at constant temperature. The method can be used for describing concentration history of other quality factors in liquid foods. This information can help the food processor in predicting in advance the quality of an existing or new liquid food product, and in designing the package containers.

VI. CONCLUSIONS

1. The experimental results indicate that the ascorbic acid degradation and oxygen uptake in a liquid food under limited oxygen presence can be described by second-order rate kinetics.

2. The computer-predicted and experimental studies confirmed that the rate of vitamin degradation in liquid foods during storage is more accelerated in the presence of light than under dark conditions.

3. Infant formula with an initial dissolved oxygen concentration at saturation with atmospheric oxygen, in a typical glass bottle (6 cm diameter) showed approximately 50 percent ascorbic acid loss after 36 hours of storage. This loss occurred under 4284 lux light intensity at 7.2°C storage temperature.

4. The computer-predicted and experimental results confirmed that the rate of ascorbic acid degradation increases as initial dissolved oxygen concentration is increased.

5. The computer-predicted results showed that the influence of light on rate of ascorbic acid degradation increases as container size (cross-sectional width) is decreased.

6. A typical polyethylene container provides more protection to ascorbic acid than a glass container. The protection was obtained even with high dissolved oxygen levels present at all times compared with levels in glass containers.

7. The computer predictions and experimental results illustrate that the major portion of light-induced ascorbic acid degradation occurred within 0-2 cm layer along the container wall.

8. The computer-predicted results on vitamin degradation provided agreement with results obtained from actual shelf-life tests. The standard deviations were within 1.43 to 5.10 percent of initial ascorbic acid concentrations. A similar agreement was obtained for results on dissolved oxygen concentrations. The standard deviations were within 2.85 to 7.01 percent of initial dissolved oxygen concentrations.

6.1 Suggestions for Future Work

The author concludes that further work is needed:

(1) to determine rate constants and computer prediction of ascorbic acid degradation in fruit juices;

(2) to determine rate constants and computer simulation of color deterioration in liquid foods; and

(3) to incorporate the influence of thermal convective diffusion in the computer model.

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APPENDIX

TABLE A.1.--Ascorbic Acid Degradation in Infant Formula in 1 cm Cells Exposed to 0, 1071, 2142, 3213 and 4284 lux Light Intensities (initial dissolved oxygen = 1.00 ppm).

Exposure Time hr	Reduced Ascorbic Acid Concentration								
	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l
	Light = 0 lux			Light = 1071 lux			Light = 2142 lux		
0	96.14	96.14	96.14	96.14	96.14	96.14	96.14	96.14	96.14
4	92.54	96.14	94.34	93.02	91.10	92.06	88.70	91.34	90.02
8	96.51	96.61	96.56	85.35	88.94	87.15	93.02	93.50	93.26
15	94.94	94.94	94.94	86.55	85.83	86.19	89.18	84.87	87.03
24	93.50	94.94	94.22	80.55	80.55	80.55	81.27	79.35	80.31
	Light = 3213 lux			Light = 4284 lux					
0	88.93	89.16	89.05	88.93	89.16	89.05			
4	84.29	84.75	84.52	90.09	83.13	86.61			
8	81.27	79.87	80.57	81.73	88.47	85.10			
15	79.87	78.95	79.41	80.57	78.71	79.64			
24	81.27	81.50	81.38	74.30	74.30	74.30			

TABLE A.2.--Dissolved Oxygen Uptake in Infant Formula in 1 cm Cells Exposed to Storage Conditions of Table A.1.

Exposure time-hr	Dissolved Oxygen Concentration								
	Repl. 1 ppm	Repl. 2 ppm	Average ppm	Repl. 1 ppm	Repl. 2 ppm	Average ppm	Repl. 1 ppm	Repl. 2 ppm	Average ppm
	Light = 0 lux			Light = 1071 lux			Light = 2142 lux		
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
4	1.11	1.11	1.11	0.34	0.45	0.40	0.23	0.23	0.23
8	1.00	1.00	1.00	0.45	0.34	0.40	0.23	0.12	0.18
15	0.78	0.89	0.84	0.45	0.23	0.34	0.23	0.01	0.12
24	0.67	0.56	0.62	0.23	0.12	0.18	0.23	0.12	0.18
	Light = 3213 lux			Light = 4284 lux					
0	1.00	1.00	1.00	1.00	1.00	1.00			
4	0.45	0.34	0.40	0.45	0.45	0.45			
8	0.45	0.45	0.45	0.12	0.23	0.18			
15	0.56	0.56	0.56	0.45	0.34	0.40			
24	0.34	0.12	0.23	0.01	0.01	0.01			

TABLE A.3.--Ascorbic Acid Degradation in Infant Formula in 1 cm Cells Exposed to 0, 1071, 2142, 3213 and 4284 lux Light Intensities (initial dissolved oxygen = 4.86 ppm).

	Reduced Ascorbic Acid Concentration								
Exposure time-hr	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l
	Light = 0 lux			Light = 1071 lux			Light = 2142 lux		
0	80.89	87.69	84.29	80.89	87.69	84.29	80.89	87.69	84.29
4	86.05	83.23	84.64	70.57	72.45	71.51	66.59	68.23	67.41
8	84.88		84.88	64.48	64.49	64.49	55.57	54.64	54.61
15	80.19	78.08	79.14	50.65	54.87	52.76	52.53	52.06	52.30
24	77.61	77.51	77.56	48.66	49.24	48.95	41.03	41.00	41.02
	Light = 3213 lux			Light = 4284 lux					
0	96.28	95.60	95.94	96.28	95.60	95.94			
4	67.12	69.08	68.10	60.51	61.24	60.88			
8	57.57	61.24	59.41	49.15	53.63	51.39			
15	50.22	49.24	49.73	50.95	51.22	51.09			
24	49.48	50.95	50.22	50.72	50.11	50.42			

TABLE A.4.--Dissolved Oxygen Uptake in Infant Formula in 1 cm Cells Exposed to Storage Conditions of Table A.3.

Exposure time-hr	Dissolved Oxygen Concentration								
	Repl. 1 ppm	Repl. 2 ppm	Average ppm	Repl. 1 ppm	Repl. 2 ppm	Average ppm	Repl. 1 ppm	Repl. 2 ppm	Average ppm
	Light = 0 lux			Light = 1071 lux			Light = 2142 lux		
0	4.86	4.86	4.86	4.86	4.86	4.86	4.86	4.86	4.86
4	4.75	4.75	4.75	3.21	3.32	3.27	2.21	2.21	2.21
8	4.75	4.53	4.64	2.54	2.77	2.66	1.11	1.11	1.11
15	3.10	3.32	3.21	1.66	2.10	1.88	1.00	1.11	1.06
24	1.88	1.44	1.66	1.22	1.33	1.28	0.78	0.78	0.78
	Light = 3213 lux			Light = 4284 lux					
0	4.86	4.86	4.86	4.86	4.86	4.86			
4	2.43	2.10	2.27	1.88	1.88	1.88			
8	1.11	1.22	1.17	0.56	0.89	0.73			
15	0.89	0.89	0.89	0.67	0.45	0.56			
24	0.56	0.56	0.56	0.23	0.23	0.23			

TABLE A.5.--Ascorbic Acid Degradation in Infant Formula in 1 cm Cells Exposed to 0, 1071, 2142, 3213 and 4284 lux Light Intensities (initial dissolved oxygen = 8.71 ppm).

Exposure time-hr	Reduced Ascorbic Acid Concentration								
	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l
	Light = 0 lux			Light = 1071 lux			Light = 2142 lux		
0	90.67	94.11	92.39	94.68	95.13	94.91	94.68	95.13	94.91
4	83.57	86.32	84.95	84.15	83.26	83.71	82.82	83.70	83.26
8	83.35	82.89	83.12	78.33	76.99	77.66	71.16	72.51	71.84
15	81.51	82.20	81.86	68.92	69.37	69.15	61.53	61.53	61.53
24	76.25	77.16	76.70	55.93	56.38	56.16	50.78	53.69	52.24
	Light = 3213 lux			Light = 4284 lux					
0	90.67	94.11	92.39	90.67	94.11	92.39			
4	53.12	47.40	50.26	50.14	55.87	53.01			
8	43.73	43.05	43.39	44.65	39.15	41.90			
15	23.81	32.51	28.16	36.41	40.76	38.58			
24	21.29	34.12	27.71	24.73	28.39	26.56			

TABLE A.6.--Dissolved Oxygen Uptake in Infant Formula in 1 cm Cells Exposed to Storage Conditions of Table A.5.

Exposure time-hr	Dissolved Oxygen Concentration								
	Repl. 1 ppm	Repl. 2 ppm	Average ppm	Repl. 1 ppm	Repl. 2 ppm	Average ppm	Repl. 1 ppm	Repl. 2 ppm	Average ppm
	Light = 0 lux			Light = 1071 lux			Light = 2142 lux		
0	8.71	8.71	8.71	8.71	8.71	8.71	8.71	8.71	8.71
4	7.83	8.16	8.00	5.52	5.63	5.58	3.54	3.54	3.54
8	7.61	7.83	7.72	2.43	2.54	2.49		1.44	1.44
15	7.39	7.61	7.50	1.11	0.78	0.95	0.78	1.00	0.89
24	4.97	4.97	4.97	0.78	0.56	0.67	0.56	0.45	0.51
	Light = 3213 lux			Light = 4284 lux					
0	8.71	8.71	8.71	8.71	8.71	8.71			
4	1.88	1.88	1.88	1.66	2.10	1.88			
8	1.33	1.22	1.28	1.22	1.11	1.17			
15	1.00	0.67	0.84	0.89	1.00	0.95			
24	0.12	0.12	0.12	0.23	0.12	0.18			

TABLE A.7.--Dissolved Oxygen Uptake in Infant Formula in 1 cm Cells Exposed to 1071 and 4284 lux Light Intensities (initial dissolved oxygen = 60 percent oxygen).

Exposure time-hr	Dissolved Oxygen Concentrations--Percent Oxygen					
	Repl. 1	Repl. 2	Average	Repl. 1	Repl. 2	Average
	Light = 1071 lux			Light = 4284 lux		
0	60	60	60	60	60	60
2	51	54	53	50	47	49
4	54	53	54	50	51	51
8	52	53	53	38	36	37
15	34	36	35	25	24	25

TABLE A.8.--Experimentally Measured Ascorbic Acid Concentration History in Glass and Plastic Containers from Five Storage Trials.

	Ascorbic Acid Concentrations								
Exposure time-hr	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l	Repl. 1 mg/l	Repl. 2 mg/l	Average mg/l
	Trial = 1 Container = Glass Light = 4284 lux			Trial = 2 Container = Glass Light = 535 lux			Trial = 3 Container = Glass Light = 4284 lux		
0	96.69	97.35	97.02	103.48	102.32	102.90	103.48	102.32	102.90
5	80.98	79.67	80.33	97.44	96.28	96.86	89.07	86.51	87.79
15	61.33		61.33	84.42	83.72	84.07	69.30	70.00	69.65
23				73.25	74.88	74.07	59.76	54.65	57.21
36	49.59	50.24	49.92						
	Trial = 4 Container = Plastic Light = 1071 lux			Trial = 5 Container = Plastic Light = 535 lux					
0	96.69	97.35	97.02	103.48	102.32	102.90			
5	92.51	92.55	92.53	100.46	98.14	99.30			
15	80.45		80.45	90.93	89.07	90.00			
23				90.96	87.42	89.19			
36	61.15		61.15						

TABLE A.9.--Experimentally Measured Dissolved Oxygen Concentration History in Glass and Plastic Containers from Five Storage Trials.

Exposure Time-hr	Dissolved Oxygen Concentrations		
	Average ppm	Average ppm	Average ppm
	Trial = 1 Container = Glass Light = 4284 lux	Trial = 2 Container = Glass Light = 535 lux	Trial = 3 Container = Glass Light = 4284 lux
0	8.71	4.86	4.86
5	5.85	4.31	3.43
15	3.43	2.10	1.00
23		2.00	1.00
36	1.11		
	Trial = 4 Container = Plastic Light = 1071 lux	Trial = 5 Container = Plastic Light = 535 lux	
0	8.71	4.86	
5	7.28	4.86	
15	5.63	4.53	
23		3.98	
36	4.75		

```
      PROGRAM MAIN(INPUT,OUTPUT)
      DIMENSION AOLD(100),BOLD(100),ANEW(100),BNEW(100)
C***************
C        THIS PROGRAM SOLVES THE DIFFUSION EQUATIONS TO PREDICT MASS AVERAGE
C        CONCENTRATION HISTORY OF ASCORBIC ACID AND DISSOLVED OXYGEN IN
C        INFANT FORMULA.   THE FOLLOWING PROGRAM SYMBOLS ARE USED
C     AA     =  MATRIX, VITAMIN CONCENTRATION AT THE END OF TIME STEP MG/LITER
C     ALIGHT=  TRANSMITTED LIGHT INTENSITY
C     ANEW   =  MATRIX,DIMENSIONLESS VITAMIN CONCENTRATION AT THE END
C              OF THE TIME STEP
C     AOLD   =  MATRIX, DIMENSIONLESS VITAMIN CONCENTRATION AT THE START OF
C              TIME STEP
C     AVCON =MASS AVERAGE VITAMIN CONCENTRATION , MG/LIT
C     A0     =  INTITIAL VITAMIN CONCENTRATION , MG/LITER
C     BB     =  MATRIX, OXYGEN CONCENTRATION AT THE END OF TIME STEP,MG/LITER
C     BNEW   =  MATRIX,DIMENSIONLESS OXYGEN CONCENTRATION HISTORY AT THE END OF
C              THE TIME STEP
C     BOLD   =  MATRIX, DIMENSIONLESS OXYGEN CONCENTRATION AT THE START OF THE
C              TIME STEP
C     BVCON =  MASS AVERAGE OXYGEN CONCENTRATION , PPM
C     B0     =  INITIAL DISSOLVED OXYGEN CONCNETRAION , PPM
C     DA     =  DIFFUSION COEFFICIENT OF VITAMIN,CM**2/SEC
C     DB     =  DIFFUSION COEFFICIENT OF OXYGEN, CM**2/SEC
C     DTT    =  TIME INCREMENT, SEC
C     DX     =  SPACE INCREMENT, CM
C     HDEPTH=  HALF-DEPTH OF CONTAINER, CM
C     ICONTYP IS 0 FOR GLASS AND 1 FOR PLASTIC CONTAINER
C     IFREQ  =  FREQUENCY OF PRINT OUT OF RESULTS, HR
C     NODES  =  NUMBER OF NODES IN ONE LAYER
C     NT     =  TOTAL NUMBER OF NODES
C     M      =  NUMBER OF LAYERS IN ONE CM DEPTH ALONG THE WALL
C     RK     =  RATE CONSTANT,LITER/MG HR
C     TOTALT=  TOTAL TIME OF STORAGE , HR
C***************
      DIMENSION AA(100),BB(100)
      DIMENSION RK(10)
      COMMON/A/ A0,B0,DA,DB,ALIGHT
      COMMON/B/ M,NODES
      COMMON/D/ DX,DTT
      COMMON/E/ N
      COMMON/F/ RK,NT
C
```

```
C         READ AND CHECK INPUT PARAMETERS
C
45          READ 1,A0,B0,ALIGHT,TOTALT,DTT,HDEPTH
          1 FORMAT(6F10.5)
            READ 11,M,NODES,ICONTYP,IFREQ
         11 FORMAT(4I10)
            PRINT 10,A0,B0,ALIGHT,TOTALT,DTT,HDEPTH
50       10 FORMAT(*0*,* INITIAL VITAMIN CONCENTRATION =*,F10.2,* MG/LITER*/
           1     *0*,* INITIAL DISSOLVED OXYGEN CONCENTRATION =*,F10.2,*  PPM*/
           2     *0*,* TRANSMITTED LIGHT INTENSITY =*,F10.2,* LUX*/
           3     *0*,* TOTAL STORAGE TIME =*,F10.2,* HR*/
           4     *0*,* TIME INCREMENT =*,F10.2,* SEC*/
55         5     *0*,* HALF DEPTH OF CONTAINER =*,F10.2,* CM*)
            PRINT 12,M,NODES,ICONTYP,IFREQ
         12 FORMAT(*0*,* NUMBER OF LAYERS IN ONE CM =*,I10/
           1     *0*,* NUMBER OF NODES PER LAYER =*,I10/
           2     *0*,* TYPE OF CONTAINER=*,I10,*(PLASTIC=1,GLASS=0)*/
60         3     *0*,* FREQUENCY OF PRINT-OUT =*,I5,*   HR*)
C
C         DIFFUSION COEFFICIENTS FOR OXYGEN AND VITAMIN
C
            DA=.00000678
65          DB=.00000136
C
C         SET INITIAL CONDITIONS
C
            TT=0.
70          NT=M*NODES*HDEPTH+1.
            DO 2 I=1,NT
            AOLD(I)=1.
            BOLD(I)=1.
          2 CONTINUE
75          TTT=0.
C
C         CALL SUBROUTINE QUALITY TO COMPUTE CONCENTRATIONS
C
            NN=(TOTALT*3600.)/DTT
80          DO 3 N=1,NN
            TT=TT+DTT
            CALL QUALITY(AOLD,BOLD,ANEW,BNEW)
            TT1=TT/3600.
            DTT1=DTT/3600.
```

```
C
C        SET BOUNDARY CONDITIONS FOR NEXT TIME STEP
C
      B=B0*BOLD(1)
      A=A0*AOLD(1)
      B=A*(B0/A0)*EXP(-RK(1)*TT1*(A0-B0)*3600.)
      A=B*(A0/B0)*EXP(RK(1)*TTT*(A0-B0)*3600.)
      TTT=TT1+.5*DTT1
      BNEW(1)=B/B0
      ANEW(1)=A/A0
      ANEW(NT)=ANEW(NT-1)
      BNEW(NT)=BNEW(NT-1)
      DO 4 I=1,NT
      AA(I)=A0*ANEW(I)
      BB(I)=B0*BNEW(I)
    4 CONTINUE
C
C        DISSOLVED OXYGEN INCREASE AT THE WALL OF A PLASTIC CONTAINER
C        DH=(3000*DTT)/(3600.*24*MIL THICKNESS)
C        S=SURFACE AREA=.0199 (DIAMETER=6CM,HEIGHT=10CM)
C        ST=CONVERSION FACTOR (32000/(22400*VOLUME IN .1 CM LAYER))
C
      IF(ICONTYP.EQ.0) GO TO 9
      DH=(3000.*DTT)/(3600.*24.*2.)
      ST=32000./(22400.*.0188)
      BBB=DH*ST*.0199*(.21-(.21*BB(1))/8.71)
      BNEW(1)=BNEW(1)+BBB/B0
      BB(1)=BNEW(1)*B0
    9 CONTINUE
C        COMPUTE MASS AVERAGE CONCENTRATIONS
C
C
      AM=0.
      DO 5 I=1,NT
      AM=AM+AA(I)
    5 CONTINUE
      AVCON=AM/FLOAT(NT)
      BM=0.
      DO 6 I=1,NT
      BM=BM+BB(I)
    6 CONTINUE
      BVCON=BM/FLOAT(NT)
```

```
      TIME=TT/3600.
      IFR=IFREQ*(3600./DTT)
C
C        PRINT CONCENTRATION HISTORY
C
      IF(IFR*(N/IFR).NE.N) GO TO 13
      PRINT 8,TIME,(AA(I),I=1,NT,2)
    8 FORMAT(* *,F6.3,*  HOURS */*   VITAMIN*,11F10.2/10X,11F10.2/10X,11
     1F10.2/10X,11F10.2)
      PRINT 14,AVCON
   14 FORMAT(* *,*  MASS AVERAGE VITAMIN CONCENTRATION  *, F10.2)
      PRINT 15,(BB(I),I=1,NT,2)
   15 FORMAT(* *,10X/*  OXYGEN */10X,11F10.2/10X,11F10.2/10X,11F10.2/10X
     1,11F10.2)
      PRINT 16,BVCON
   16 FORMAT(* *,*  MASS AVERAGE OXYGEN CONCENTRATION  *,F10.2)
   13 CONTINUE
C
C        SET INITIAL CONDITIONS FOR NEXT TIME STEP
      DO 7 I=1,NT
      BOLD(I)=BNEW(I)
      AOLD(I)=ANEW(I)
    7 CONTINUE
    3 CONTINUE
      STOP
      END
```

```
      SUBROUTINE QUALITY(AOLD,BOLD,ANEW,BNEW)
C***************
C       THIS SUBROUTINE CALLS SUBROUTINES RATE,DIMEN,OXYGEN,VITAMIN  TO
C       COMPUTE CONCENTRATIONS OF VITAMIN AND OXYGEN
C***************
      DIMENSION AOLD(100),BOLD(100),ANEW(100),BNEW(100)
      DIMENSION ANEWM(100),BNEWM(100)
      DIMENSION RK(10)
      COMMON/A/ AO,BO,DA,DB,ALIGHT
      COMMON/B/ M,NODES
      COMMON/C/ L,LS,LS2,DT,DT2,LPS,P,L2
      COMMON/D/ DX,DTT
      COMMON/E/ N
      COMMON/F/ RK,NT
      REAL L,LS2,L2,LS,LPS
C
C       CALL SUBROUTINE RATE TO COMPUTE RATE CONSTANTS FOR THE VARIOUS LAYERS
C       OF LIQUID
C
      MP1=M+1
      DO 2 NN=1,MP1
      CALL RATE(M,BO,ALIGHT,RK)
    2 CONTINUE
C
C       CALL SUBROUTINES DIMEN,OXYGEN,VITAMIN TO COMPUTE CONCENTRATIONS
C       AT  NODES WITHIN THE ONE CENTIMETER LAYER
C
      DXX=1./FLOAT(M)
      DX=DXX/FLOAT(NODES)
      K=(M-1)*NODES+2
      NN=0
      DO 1 I=2,K,NODES
      J=I+NODES-1
      NN=NN+1
      CALL DIMEN(RK,NN,LS2,LS,DT2,DT,L,LPS,P,L2)
      CALL OXYGEN(I,J,AOLD,BOLD,BNEW,BNEWM,ANEW)
      CALL VITAMIN(I,J,AOLD,BOLD,BNEW,BNEWM,ANEW)
    1 CONTINUE
C
C       CALL SUBROUTINE DIMEN,OXYGEN,VITAMIN  TO COMPUTE CONCENTRATIONS
C       AT DEPTHS GREATER  THAN ONE CENTIMETER IN LIQUID
      NN=NN+1
```

```
      I=J+1
      J=NT-1
45    CALL DIMEN(RK,NN,LS2,LS,DT2,DT,L,LPS,P,L2)
      CALL OXYGEN(I,J,AOLD,BOLD,BNEW,BNEWM,ANEW)
      CALL VITAMIN(I,J,AOLD,BOLD,BNEW,BNEWM,ANEW)
      RETURN
      END
```

```
      SUBROUTINE RATE(M,BO,ALIGHT,RK)
C**************
C        THIS SUBROUTINE CALCULATES THE RATE CONSTANTS FOR EACH LAYER OF
C        LIQUID. THE SUBROUTINE IS WRITTEN FROM EXPERIMENTALLY OBTAINED
C        RATE CONSTANTS
C**************
      DIMENSION RK(10)
      IF(ALIGHT.GT.2142.) ALIGHT=2142.
      DXX=1./FLOAT(M)
      IF(BO.EQ.0.71) GO TO 1
      IF(BO.EQ.4.86) GO TO 2
      IF(BO.EQ.1.00) GO TO 3
    1 RDARK=.0001168
      RSLOPE=(.0018162-RDARK)*4.61/(2142.**.8)**.99
      GO TO 4
    2 RDARK=.0001267
      RSLOPE=(.0019178-RDARK)*4.61/(2142.**.8)**.99
      GO TO 4
    3 RDARK=.0001273
      RSLOPE=(.0013124-RDARK)*4.61/(2142.**.8)**.99
    4 CONTINUE
      X=0.
      DO 5 I=1,M
      RK(I)=(RDARK+RSLOPE*ALIGHT*EXP(-4.61*X))/3600.
      X=X+DXX
    5 CONTINUE
      RK(M+1)=RDARK/3600.
      RETURN
      END
```

```
      SUBROUTINE DIMEN(RK,NN,LS2,LS,DT2,DT,L,LPS,P,L2)
C**************
C        THIS SUBROUTINE COMPUTES THE DIMENSIONLESS VARIABLES
C**************
      DIMENSION RK(10)
      COMMON/A/ AC,RO,DA,DB,ALIGHT
      COMMON/D/ DX,DTI
      REAL L,LS2,L2,LS,LPS
      S=DA/DB
      DZ=((RK(NN)*AC/DB)**0.5)*DX
      DT=RK(NN)*AC*DTI
      L=DT/(DZ**2)
      P=AO/RO
      LPS=L*P*S
      DT2=DT/(2.*P)
      LS=L*S
      LS2=L*S/2.
      L2=L/2.
      RETURN
      END
```

```
      SUBROUTINE OXYGEN(MI,MF,AOLD,BOLD,BNEW,BNEWM,ANEW)
C***************
C        THIS SUBROUTINE COMPUTES THE OXYGEN CONCENTRATIONS AT THE
C        END OF TIME INCREMENT
C        ANEWM = DIMENSIONLESS VITAMIN CONCENTRATION AT THE END OF HALF TIME
C        BNEWM = DIMENSIONLESS OXYGEN CONCENTRATION AT THE END OF HALF TIME
C***************
      DIMENSION AOLD(100),BOLD(100),ANEW(100),BNEW(100)
      DIMENSION ANEWM(100),BNEWM(100)
      DIMENSION A(100),B(100),C(100),D(100)
      COMMON/C/ L,LS,LS2,DT,DT2,LPS,P,L2
      COMMON/E/ N
      REAL L,LS2,L2,LS,LPS
      DO 1 I=MI,MF
      ANEWM(I)=LS2*AOLD(I-1)-(LS-1.+DT2*BOLD(I))*AOLD(I)+LS2*AOLD(I+1)
    1 CONTINUE
C
C        SET COEFFICIENTS FOR ARRAYS A,B,C,D FOR SUBROUTINE TRIDAG AND
C        CALL TRIDAG TO SOLVE SIMULTANEOUS EQUATIONS
C
      DO 2 I=MI,MF
      A(I)=L
      B(I)=-(2.*(1.+L)+DT*ANEWM(I))
      C(I)=L
      D(I)=-L*BOLD(I-1)+(DT*ANEWM(I)*2.*(L-1.))*BOLD(I)-L*BOLD(I+1)
    2 CONTINUE
      D(MI)=D(MI)-L*BOLD(MI-1)
      D(MF)=D(MF)-L*BOLD(MF-1)
      CALL TRIDAG(MI,MF,A,B,C,D,BNEW)
      DO 3 I=MI,MF
      BNEWM(I)=(BNEW(I)+BOLD(I))/2.
    3 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE VITAMIN(MI,MF,AOLD,BOLD,BNEW,BNEWM,ANEW)
C*************
C        THIS SUBROUTINE COMPUTES THE VITAMIN CONCENTRATIONS AT THE
C        END OF TIME INCREMENT
C*************
      DIMENSION AOLD(100),BOLD(100),ANEW(100),BNEW(100)
      DIMENSION A(100),B(100),C(100),D(100)
      DIMENSION ANEWM(100),BNEWM(100)
      COMMON/C/ L,LS,LS2,DT,DT2,LPS,P,L2
      COMMON/E/ N
      REAL L,LS2,L2,LS,LPS
C
C        SET COEFFICIENTS FOR ARRAYS A,B,C,D FOR SUBROUTINE TRIDAG AND
C        CALL TRIDAG TO SOLVE SIMULTANEOUS EQUATIONS
C
      DO 2 I=MI,MF
      A(I)=LPS
      B(I)=-(2.+P*(1.+L3)+DT*BNEWM(I))
      C(I)=LPS
      D(I)=-LPS*AOLD(I-1)+(2.+P*(LS-1.)+DT*BNEWM(I))*AOLD(I)-LPS*AOLD(I+
     11)
    2 CONTINUE
      D(MI)=D(MI)-LPS*AOLD(MI-1)
      D(MF)=D(MF)-LPS*AOLD(MF-1)
      CALL TRIDAG(MI,MF,A,B,C,D,ANEW)
      RETURN
      END
```

```
      SUBROUTINE TRIDAG(IF,L,A,B,C,D,V)
C***************
C        THIS SUBROUTINE SOLVES THE SIMULTANEOUS EQUATIONS
C***************
      DIMENSION A(100),B(100),C(100),D(100)
      DIMENSION V(100),BETA(100),GAMMA(100)
      BETA(IF)=B(IF)
      GAMMA(IF)=D(IF)/BETA(IF)
      IFP1=IF+1
      DO 1 I=IFP1,L
      BETA(I)=B(I)-A(I)*C(I-1)/BETA(I-1)
    1 GAMMA(I)=(D(I)-A(I)*GAMMA(I-1))/BETA(I)
      V(L)=GAMMA(L)
      LAST=L-IF
      DO 2 K=1,LAST
      I=L-K
    2 V(I)=GAMMA(I)-C(I)*V(I+1)/BETA(I)
      RETURN
      END
```